Sulfur Copolymers for Infrared Applications

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1.0 Abstract

A new process using excess elemental sulfur created as byproduct from other industrial processes has been developed which provides for the ability to create cheaper infrared lenses using safer materials and manufacturing methods while maintaining the industry standard of infrared (IR) transmission efficiency.

IR materials are often costly and many are created using toxic materials. Whereas organic polymers are easy to process, and have low cost manufacturing and materials associated with them, standard IR materials have a limited material supply resulting in higher cost and more difficulties in processing. Up to this point, processing of organic optical polymers has resulted in materials which absorb IR. Contrary to this, we present a process in which sulfur copolymers have been successfully used to create materials which are transmissive in the IR spectrum. The sulfur copolymer based materials have the potential to disrupt the IR market as a novel type of IR lens.

The general IR market is very strong and is expected to continue to grow in the foreseeable future as IR applications become an increasingly integral part of daily life due to the expansion of common capabilities such as automobile vision and the rise of the internet of things. Current drivers of the market such as military applications will also continue to persist as contributors to IR market progression. Nearly all of the components for IR devices have undergone major recent developments leading to advancements which allow for smaller, more inexpensive IR devices. IR lenses are the last major device component that hold the potential to be developed further to drastically reduce IR imaging device costs.

Although there are several areas that have market potential for sulfur copolymer lenses, the medical IR market was identified as an area which may have the most potential. If IR medical imaging can overcome the lack of medical community support, and strict guidelines in developed countries then there is a strong case for market success of sulfur copolymer lensed medical IR imagers for use in developed countries. Developing countries have a large need for the abilities that medical IR devices could provide, but lack the financial resources to make the market area appealing to investors. Philanthropic organizations may be a viable option to provide necessary funding for a developing countries medical IR device market. An organization such as the Gates Foundation could provide grant funding that would allow sulfur copolymer lensed medical IR devices to succeed in the market.

The following report explores the technical and market potential for sulfur copolymers as IR lenses including a financial evaluation of the processing and material costs. Further addressed in this report are industry expectations, general market outlook, and a competitor analysis.

2.0 Introduction

2.1 General Information on Infrared Materials

There are three infrared bands including the short-wave infrared (SWIR) ranging from 0.75 – 3.0 μm, mid-wave infrared (MWIR) ranging from 3 – 5 μm, and long-wave infrared (LWIR) ranging from 8 – 14 μm. A region in the SWIR band can be more specifically defined as the near-infrared (NIR) range from .8 – 1.6 μm creating a band range which is often referred to as a fourth IR band. The areas between these bands are not usable on terrestrial-based and low altitude systems due to absorption by molecules in the Earth's atmosphere[1].
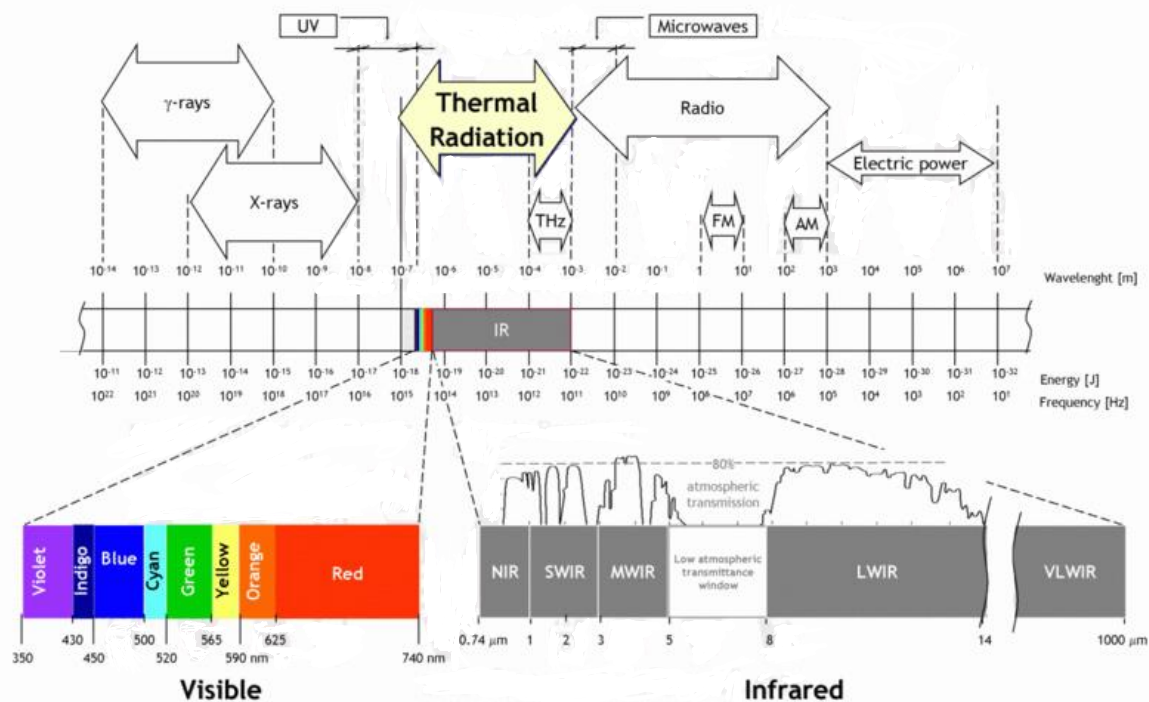
Figure 1. Chart of IR bands with wavelength[2].

Materials used in IR applications must possess a high refractive index as well as a high transparency in the IR spectrum; the high refractive index is required to maintain high quality imaging at long wavelengths. Current industry standard materials include inorganic semiconductors, halides and chalcogenide glasses with indices of refraction between 2.0-4.0 and low loss between 1-10μm. While the properties of these materials make them ideal for use in IR applications, the materials and methods used to create them can be expensive, toxic and more difficult to process when compared to organic polymeric materials[3].

2.2 Commonly Used Methods of IR Imaging

IR technologies are used in a wide variety of industries including, but not limited to, the civil, medical and military fields[3]. NIR devices can be used for night vision, gesture recognition in gaming, 3D range cameras, automotive, and surveillance applications[4]. NIR and SWIR imaging devices work similarly to visible cameras in that they use reflected light rather than thermal emissions to form a detected image. SWIR devices can be used for UAV based sensors, machine vision, solar cell fabrication, materials inspection and sorting, agricultural research, chemical process control, oil slick detection, counterfeit currency detection, and automotive imaging applications[5]. The MWIR region can be used for spectroscopic/biomedical imaging, materials characterization, explosives detection, microscopy, and non-destructive testing. Surveillance devices can use any range of NIR, SWIR, or MWIR depending on the specific application as well as the visual specification range. MWIR or LWIR can be used for environmental remote sensing[6], astronomy, building diagnostics, medical imaging, and thermal imaging[5]. MWIR is ideal for thermal imaging of hot objects with high resolution, while thermal LWIR is ideal for high performance capture of objects at ambient temperatures through mist and smoky conditions[7].

NIR	SWIR	MWIR	LWIR
• Night vision • Gaming • 3D range cameras • Automotive	• Machine vision • Solar cell fabrication • Materials inspection • Agricultural research • Chemical processes control • Counterfeit currency detection	• Thermal imaging (hot objects) • Spectroscopic imaging • Biomedical imaging • Materials characterization • Explosives detection	• Thermal imaging (ambient objects) • Medical imaging • Environmental remote sensing • Astronomy • Building diagnostics

**Table 1. Some of the possible infrared imaging applications used within each of the IR bands.**

3.0 Standard IR Industry Materials

3.1 A Brief History of IR Industry and Materials

While experimenting with temperature of the sun's spectrum through a prism, Frederick William Herschel discovered infrared light more than 200 years ago on February 11, 1800. By 1927 there were several published articles and patents on research and applications of selenium[8], a material used today in some chalcogenide glasses[9], which discovered in 1873 could be considered the first recognized IR transparent material.

The beginnings of modern IR technology originated during World War II, when German scientists created lead sulfide IR detectors and, subsequently, devices such as image intensifiers to aid in night vision were developed[7]. In later years other salt family materials were combined with lead to create similar detectors. Lead sulfides and similar compounds were used prominently in MWIR military-based IR sensors through the 1950s. During this time period, germanium and other materials were also introduced to the industry for creation of LWIR devices[8]. The first IR imaging seeker was developed in the 1950s for military smart weapons applications[7]. By the late 1950s narrow-band gap semiconductor alloys, such as HgCdTe, were in use as IR detector materials allowing for a more effective custom tailoring of a wide range of detectors across the entire IR spectrum. (Refer to Figure 2 for a timeline of detector materials.) HgCdTe remains the most widely used variable gap semiconductor IR detector material. The difficulty in growing these materials has lead to research and development of other materials which are less difficult to produce as alternatives. During the 1950s new IR detector materials were tested against HgCdTe including InGaAs which was found to perform as well as HgCdTe in the NIR region although its performance quickly deteriorates as the wavelengths increase towards the MWIR and LWIR due to defects caused by substrate lattice mismatch[8]. As detector materials developed, other IR devices were created including the first FLIR camera in the form of a linear scanner in the 1960s and the first space borne IR platform developed by NASA in 1967[7].
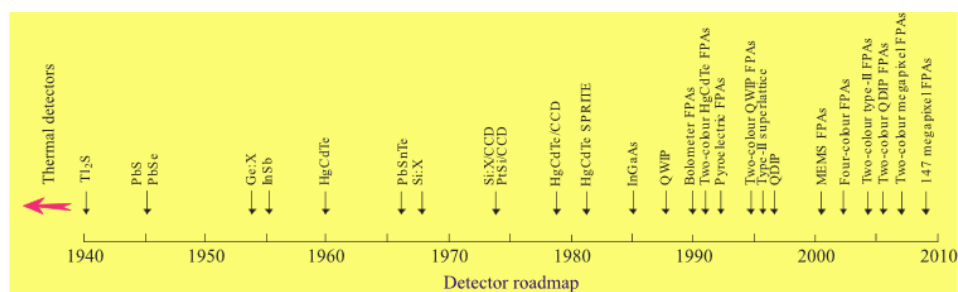
Figure 2. Timeline of materials used for infrared detectors and systems from 1940 to 2010[8].

With the development of a wider variety of IR applications across a larger range of the IR spectrum, IR transmissive lens materials which could function over a broader spectral range became a necessity. The most popular materials became germanium, silicon, fused silica, BK-7 glass, zinc selenide, and zinc sulfide[7].

While past decades saw the IR industry driven entirely by military needs and funding, the 1990s saw the emergence of commercial uses for IR applications in medical, industry, earth resources, and energy conservation fields. By the start of the 21st century, commercial industrial applications were beginning to become an integral part of the IR market with a share of 10%[7].

3.2 Current IR Materials

Current conventional IR materials include semiconductors, chalcogenides glasses, oxide based glasses (for use in the NIR), and halide metal compounds[10]. Current infrared materials are created using a number of processes including classic crystal growth, glass processing, plasma-enhanced chemical vapor deposition (coatings), and ion assisted deposition with electron beam sputtering (coatings)[1]. Table 2 shows the most commonly used IR lens materials under their respective category type.

Semiconductors	Chalcogenide Glasses	Oxide Based Glass	Halides
- Germanium (Ge) - Silicon (Si) - Gallium Arsenide (GaAs) - Cadmium Telluride (CdTe) - Zinc Selenide (ZnSe) - Sapphire (Al2O3) - Zinc Sulfide – Cleartran (ZnS)	- As_2S_3 - As_2Se_3 - As_2Te_3 - $Ge_{33}As_{12}Se_{55}$	- Fused Silica (SiO2)	- Barium Fluoride (BaF_2) - Calcium Fluoride (CaF_2) - Cesium Iodide (Csl) - Lithium Fluoride (LiF) - Magnesium Fluoride (MgF_2) - Cesium Bromide (CsBr) - Potassium Bromide (KBr) - Potassium Chloride (KCl) - Sodium Chloride (NaCl) - Thallium Bromoiodide (KRS-5)

Table 2. Table of commonly used IR materials by general category type [10].

3.3 Industry Expectations and Shortcomings of Current Common IR Materials

There are several characteristics that make for an ideal IR material; inexpensive raw materials and processing costs, high optical quality, a low dn/dT value, ability to be diamond turnable, minimal or absence of toxicity of materials, a high Knoop hardness value, water insolubility, a high index of refraction, and transmissivity over a wide range of wavelengths.

Cost is a large factor in the practicality and usability of an infrared material. There are two main cost factors involved with creation of infrared materials including the cost of the raw materials and the cost of the processes used to create the resultant lens. Additional processing costs are often attributed to a lack of other ideal IR characteristics such as water solubility and toxicity of materials. In some cases, the raw materials themselves can be very costly as many of the materials used are semi-rare elements. Some materials which are expensive or require expensive processing procedures include BaF2, CdTe, Ge, MgF2, ZnSe, Cleartran, and LiF.

The quality of optical properties is a major factor in the industry standard for IR materials. Current infrared materials range in transmissive efficiency from values greater than 70 percent, with many attaining an efficiency of greater than 90 percent[1]. See Figures 3 and 4 for the transmission properties of several common IR materials. Transmission efficiency values of any future IR materials would need to meet or exceed these industry standards. Sulfur copolymer lenses can currently attain a maximum transmission range between 2-6 microns, and are not yet transparent in LWIR. Some current IR

materials perform better than others in areas such as transmission efficiency and birefringence, refractive index which is dependent upon polarization. Whereas BaF_2 and CaF_2 are likely to display birefringence, KRS-5 displays a transmission efficiency of just 70% compared to most other common materials which display transmission efficiencies of at least 80%. Anti-reflection (AR) coatings can increase transmission efficiency percentage in some cases, but this additional process often expands overall production costs.
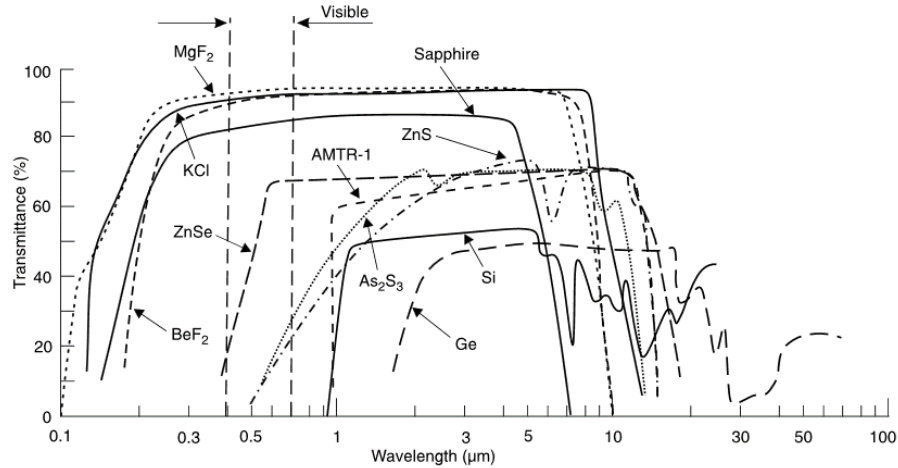

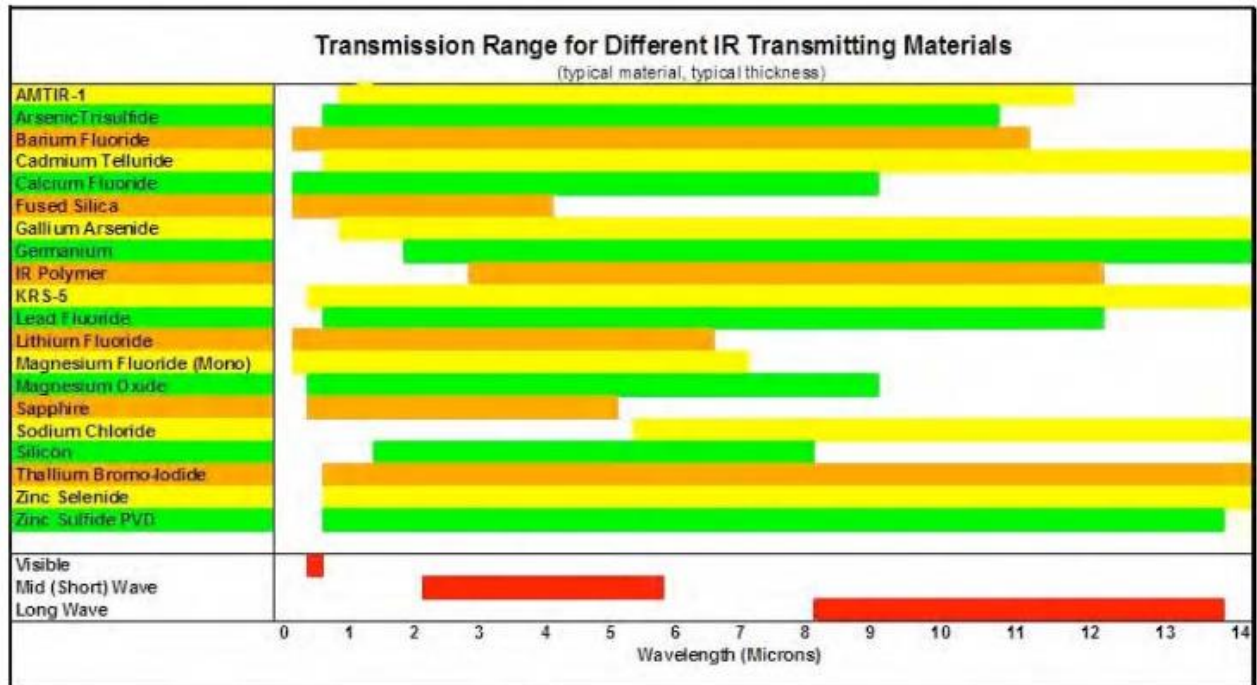**Figure 3. Transmission wavelength range of several common infrared lens materials[7].**

Figure 4. Chart of potential materials to be used as an IR window[11].

Several common IR materials are highly toxic, which can play a role in additional expenses for safety precautions required during manufacturing due to added special handling and safety procedures. There are some materials so toxic that few companies are willing to work with them which can also significantly drive up costs[12]. Current materials with the greatest toxicity include BaF2, CdTe, GaAs, KRS-5, and ZnSe.

The dn/dT of an infrared material is the thermo-optic coefficient, or the change in the index of refraction with temperature per degree. System defocus can occur when materials react to environmental thermal changes. This can be mitigated by athermalization at which point the optical system's properties are not altered with thermal changes. A low dn/dT is a desirable characteristic of infrared materials because it makes athermalization easier to attain[13]. Some of the common IR materials possess a high dn/dT value in comparison to other standard IR materials. Materials such as GaAs, Ge, Si, ZnSe, and some chalcogenide glasses are difficult to athermalize with because of their high dn/dT values.

Aspheric lens surfaces can help to eliminate and diminish certain types of optical aberrations. In order for a material to be molded into an aspheric surface at low cost a material must be compatible with diamond turning processes. While most common infrared materials are diamond turnable, allowing for low cost shaping of aspheric lens surfaces, there are a couple of common IR materials which are structurally too hard for this process including SiO_2 and Sapphire. It is most profitable to use a material which is diamond turnable to minimize production costs.

Several popular IR materials also have a small valued Knoop hardness, also known as a microhardness test value. Softer materials with a Knoop hardness of less than 100 kg/mm^2 such as CdTe, CsBr, CsI, KBr, KCl, NaCl, KRS-5 are fragile and can be more prone to breakage and scratching[14].

Some of the most common infrared materials are water soluble and require additional protective coatings for use under conditions in which moisture may be an environmental factor[1]. This in turn increases material and production costs. Several industry standard IR materials are water soluble including CsBr, CsI, KBr, KCl, and NaCl, i.e. essentially all of the salts. Materials which are water insoluble without added processing generally do not require the additional manufacturing costs of protective coatings and can be used in more versatile conditions.

In order for a material to be transmissive in the IR range it must have a low percentage of light atoms, such as hydrogen, which lead to high energy molecular vibrations. This is one of the primary reasons the polymers are typically poor IR transmitters. The preponderance of heavy atoms in IR materials directly leads to high indices of refraction (due to the high polarizability of some of these large atoms), which is a further benefit for IR imaging. Specifically, the indices of refraction of IR materials generally fall within the range of ~1.35-4.0[15]. IR materials which fall on the high end of that spectrum often require a special AR coating to improve transmission efficiency. A material such as germanium with an index of refraction of ~4.0 displays reflection losses of 53% without AR coating[16]. Other materials requiring AR coatings include KRS-5, Si, ZnSe, ZnS, GaAs, and CdTe. Not only is it important that the index of refraction fall within a specific range, but ideally a material should be characterized by a small change in

the index of refraction with respect to wavelength. Generally, a material's index of refraction decreases as wavelength increases causing some level of chromatic dispersion. If the level of chromatic dispersion is large then the spectral range over which imaging can occur will be limited[17].

Consumers of infrared devices often require the capability of imaging over a wide range of wavelengths. A material which is effectively transmissive across a wide range of the IR spectrum would be most beneficial for use in a single multi-wave range infrared device. An added benefit of an infrared material is transmissivity into the visible and UV bands, so they can be used in multi-sensor applications with visible and UV capabilities. All current popular IR materials are transmissive over a broad range of wavelengths to include at least two IR bands, and many extend far into the visible and UV bands.

In summary, all of the current industry materials are lacking in at least one important area as outlined in the color coded Table 3 chart with Table 4 color key.

Material	IR Transmission wave range	Transmission % in ideal IR wave range	dN/dT (10⁻⁵/°K)	Water soluble	Diamond turnable	Refractive index	Knoop Hardness (kg/mm²)
BaF2	NIR, SWIR, MWIR (.6 – 9.5 µm)	>90% from .25 to 9.5 µm	1.52	No	Yes	~1.46	82
CdTe	SWIR, MWIR, LWIR (1 – 25 µm)		5	No	Yes	~2.65	45
CaF2	NIR, MWIR	>90% from .25 to 7 µm	-1.1	No	Yes	~1.4	158
CsBr	NIR, SWIR, MWIR, LWIR	>80% from .35 to 32 µm	7.9	Yes	Yes	~1.6	19.5
CsI	NIR, SWIR, MWIR, LWIR	>80% from .42 to 40 µm	-9.9	Yes	Yes	~1.7	20
Chalcogenide Glasses	NIR, SWIR, MWIR, LWIR	8 to 12 µm	3.5 to 14.5	No	Yes	~2.5 – 2.8	106-143
SiO2	NIR, SWIR (.6 to 3.5 µm)		1	No	No	~1.45	461
GaAs	MWIR, LWIR (2 to 15 µm)		14.8	No	Yes	~3.3	750
Ge	MWIR, LWIR (2 to 14 µm)		39.6	No	Yes	~4	780
LiF	NIR, SWIR, MWIR (.6 to 8.5 µm)		-1.27	No	Yes	~1.35	102
MgF2	NIR, SWIR, MWIR (.6 to 7.5 µm)		0.17	No	Yes	~1.35	415
KBr	NIR, SWIR, MWIR, LWIR (.6 to 23 µm)	>80% from .26 to 23 µm	-4.08	Yes	Yes	~1.5	5.9
KCl	NIR, SWIR, MWIR, LWIR (.6 to 21 µm)	>80% from .3 to 21 µm	-3.32	Yes	Yes	~1.45	7.2
Sapphire	NIR, SWIR, MWIR (.6 to 5 µm)		1.3	No	No	~1.76	~2000
Si	NIR, SWIR, MWIR (1.2 to 7 µm)		16.0	No	Yes	~3.4	1150
NaCl	NIR, SWIR, MWIR, LWIR (.6 to 12 µm)	>80% from .23 to 12 µm	-3.6	Yes	Yes	~1.5	15.2
KRS-5	NIR, SWIR, MWIR, LWIR (.7 to 32 µm)	>70% from .7 to 32 µm	-23.5	No	Yes	~2.35	40
ZnSe	NIR, SWIR, MWIR, LWIR (.6 to 16 µm)		6.1 to 10.7	No	Yes	~2.4	110
Cleartran (ZnS)	NIR, SWIR, MWIR, LWIR (.6 to 12 µm)		3.85 to 5.43	No	Yes	~2.3	160

Table 3. Table of commonly used IR materials with basic material properties information and color codes (see Table 4 for Color Code Key)[1].

Color Code Key for Figure 7	
Expensive	🟥
Poor optical quality	⬜
Toxic	🟩
High dn/dT	🟦
Not diamond turnable	🟢
Soft – Knoop hardness value below 100	🟦
Water soluble	🟨
High index of refraction (requires AR coating)	🟪

Table 4. Color Code Key for Table 3.

4.0 Sulfur Copolymers

4.1 Background on Sulfur Copolymers

A global excess of elemental sulfur in the amount of 70 billion kilograms is created annually[10], largely as the by-product of petroleum refining in which a hydrodesulfurization method is used for the reduction of sulfur dioxide emissions from fossil fuel combustion. While some amount of elemental sulfur is used in the production of sulfuric acid, phosphates for fertilizers, synthetic rubbers, and cosmetics[18], a large remainder of 7 billion kilograms of elemental sulfur by-product goes unused annually[10]. Processes to create synthetic materials with a high sulfur concentration have not been widely explored. Beyond the above listed industries, applications for the use of elemental sulfur are limited[18].

Most organic polymers possess a small refractive index between 1.5-1.6 and high loss due to IR absorptions of vibrational modes for wavelengths ranging from 2µm to 20 µm. While creation of organic polymers displaying higher index of refraction properties of 1.6-1.8 have been explored for areas such as organic light emitting diodes (OLED), organic polymer materials with indices of refraction exceeding 1.8 without significant optical loss in the IR spectrum have yet to be achieved[3].

Combined research between the College of Optical Sciences and the Department of Chemistry and Biochemistry at the University of Arizona has created proof of concept optically IR transmissive high sulfur concentration polymeric materials with an index of refraction of ~2.0 which can be processed using melt or solution methods[3].

Recent testing has included altering the chemical composition with the addition of selenium to thereby increase the refractive index by 0.2 in the best case scenario reducing scattering affects and achieving the 2.0 index of refraction value. Further testing of this chemical alteration is expected to allow for a more compact form factor while maintaining the optical performance characteristics and potentially increasing the IR transmission efficiency. Longer term testing will include decreasing the number of hydrogen bonds with replacements of halogens such as chlorine and bromine in the chemical makeup allowing for increased optical quality in the LWIR band. The thermal performance has also been improved maintaining stability to a temperature of ~140°C.

4.2 Chemical Makeup

Elemental sulfur (S_8) takes the form of an 8 membered ring. It is characterized by limited solubility in most organic solvents except for aromatic media, carbon disulfide, and some ionic liquids. At 120-124°C S_8 will melt into a yellow liquid state. Increasing the temperature to 159°C and greater will transform S_8 into polymeric sulfur with a high molecular weight and a deep-red coloring[18].

In order to achieve transparency in the IR spectrum, heavy atoms must be used to reduce the vibrational frequency that is responsible for IR absorption caused by high energy molecular vibrations due to lightweight atoms.   Sulfur is an ideal element for this because it is heavier than the common organic elements such as fluorine, oxygen, nitrogen, carbon, and hydrogen. Sulfur also holds the characteristic of high atomic polarizability, which results in the greater index of refraction required for IR imaging performance[10].

The sulfur copolymers created contain S-S bonds composing between 50-80% of the total material weight with the remaining weight percentage being composed of 1,3 diisopropenylbenzene (DIB). Thin films could then be created with a controllable thickness between 1-60 µm[3].
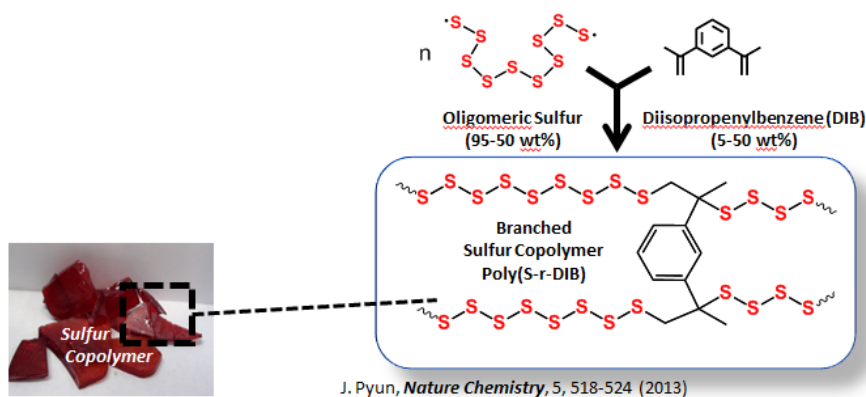
Figure 5. Chemical makeup of sulfur-based optical copolymers[10].

4.3 Inverse Vulcanization Method

Creation of sulfur-based copolymers requires only simple chemistry[10]. A conventional vulcanization method is used to create synthetic rubber by cross-linking polydienes with a small amount of sulfur. A new method, termed inverse vulcanization, is used to create synthetic polymers that are transparent not only in the near infrared spectrum, but also display transparency through the MWIR band[18]. Molten sulfur heated to 185°C is used as a solvent; the molten sulfur is copolymerized with 1,3 diisopropenylbenzene (DIB) resulting in a sulfur plastic that is both chemically stable and processable[3]. The inverse vulcanization method allows for the direct copolymerization of elemental sulfur with vinylic monomers yielding polymers with tunable thermomechanical properties[18], and allows for the ability to mold the copolymers using pre-polymer resins of low viscosity from the reaction mixture[3].

Several experimental procedures were used in creating various sulfur copolymer based optical materials. The following is an exhaustive list with detailed steps on the procedures used in creation of test sulfur copolymers[3], as practiced by the Pyun group in the Department of Chemistry and Biochemistry.

1) Preparation of poly(sulfur-random-(1,3-diisopropenylbenzene) (poly(S-r-DIB)) copolymers
    a. Varying wt% DIB values from 20 to 50% were obtained by using different amounts of S_8 in combination with amounts of DIB. Below are the amounts used for each scenario.
        - 20-wt% DIB: S_8 = 4.00 g, 15.6 mmol and DIB = 1.00 g, 6.32 mmol used resulting in a red solid of 4.98 g;
        - 30-wt% DIB: S_8 = 3.50 g, 13.7 mmol and DIB = 1.50 g, 9.48 mmol used resulting in a red solid of 5.00 g;
        - 40-wt% DIB: S_8 = 3.00 g, 11.7 mmol and DIB = 2.00 g, 12.6 mmol used resulting in a red solid of 4.97 g;
        - 50-wt% DIB: S_8 = 2.50 g, 9.69 mmol and DIB = 2.50g, 15.8 mmol used resulting in a reddish-brown solid of 4.99 g;
    b. The varying wt% DIB material amounts were each used in the below preparation of poly(S-r-DIB) copolymers:
        - add S_8 to a 24 mL glass vial with a magnetic stir bar;
        - in a thermostated bath, heat the glass and contents to T = 185° C until the contents become molten and display a clear orange color.
        - use a syringe to add the DIB and stir the mixture for 8-10 minutes at T = 185° C until vitrification occurs;
        - remove the magnetic stir bar and use a metal spatula to remove the vitrified product from the vial to allow for cooling at room temperature;
2) Thermomechanical forming of poly(S-r-DIB) copolymer powders to create free-standing films:
    a. poly(S-r-DIB) copolymer powder was placed between two pieces of Kapton film in heated platens of a hydraulic press;
    b. the platens were closed and the sample was heated without pressure for 1 minute at T = 150° C;
    c. the pressure was then increased to 50kN for 2 minutes;
    d. the pressure was additionally increased to 125kN for another minute;
    e. the sample was removed and cooled; the Kapton films were then peeled away.
3) Preparation of poly(S-r-DIB) copolymer lenses:
    a. Preparation of polydimethylsiloxane (PDMS) replica mold from glass master lenses.
        - silicone elastomer base and silicone elastomer curing agent (10:1 ratio) were combined by mixing in a 50 mL plastic beaker;
        - the solution was poured over the glass master lens and placed in a vacuum oven in which pressure was reduced thereby removing bubbles from the solution;
        - the mixture was placed in a heat oven at T = 80° C for 2 hours to cure;
        - following curing the replica lens could be removed from the master lens.

b. The varying wt% DIB material amounts referenced in 1) were each used in the below preparation of poly(S-r-DIB) copolymers:
   - add S_8 to a 24 mL glass vial with a magnetic stir bar;
   - in a thermostated bath heat the glass and contents to T = 185°C until the contents become molten and display a clear orange color;
   - use a syringe to add the DIB and stir the mixture for 8-10 minutes at T = 185°C until vitrification occurs;
   - the solution was then poured into the PDMS molds, measuring 15.0 mm Dia. X 75.0 mm FL, and covered with Teflon coated aluminum foil;
   - the covered sample was then vitrified in a heat oven at T = 185°C;
   - once completely cooled at room temperature, the now glassy sample can be removed from the PDMS.

4) Preparation of thin films onto glass substrates from poly(S-r-DIB) copolymer solutions:
   a. 11 mL glass vial with magnetic stir bar was used to mix 2.0 g of poly(S-r-DIB) copolymer powder and 2.0 mL of 1,2-dichlorobenzene;
   b. in a thermostated bath heat the glass and contents to T = 125°C until the contents become molten and display a deep red color;
   c. a two part spin protocol was used to spin-coat substrates with copolymer solutions;
      - 2000 rpm, acceleration rate of 266 rpm/sec for 15 seconds
      - 8500 rpm, acceleration rate of 665 rpm/sec for 15 seconds
   d. the films are placed in a heated vacuum for 10 minutes of curing at T = 185°C with reduced pressure of -28 in. Hg;
   e. the vacuum pressure is then released and the films are cured for another 10 minutes at T = 185°C before being allowed to cool at room temperature.

5) Spin elemental sulfur solutions onto glass substrates
   a. S_8 of 1.08 g, 4.21 mmol, 6.0 M was added to an 11 mL glass vial with magnetic stir bar, placed in a thermostated oil bath, and heated to T = 185°C until molten and clear orange colored;
   b. 1,2-dichlorobenzene (DCB) of 0.9 g, 0.70 mL was added to the molten sulfur at -T = 185° C using a syringe and stirred until homogenous;
   c. substrates heated to T = 150°C were spin coated with the homogenous sulfur based solution with a two part spin protocol.
      - 2000 rpm, acceleration rate of 266 rpm/second for 15 seconds
      - 8500 rpm, acceleration rate of 665 rpm/second for 15 seconds resulting in a crystalline film

6) Preparation of spin coated poly(S-r-DIB) copolymer films on NaCl plates
   a. poly(S-r-DIB) copolymer powder of 1.0 g and 1,2-dichlorobenzene of 2.0 mL were added to an 11 mL glass vial and heated to T = 125°C in a thermostated bath until the solution displayed a deep red color;
   b. a two spin protocol was used to spin-coat substrates with the copolymer solution;
      - 2000 rpm, acceleration rate of 266 rpm/second for 15 seconds

- 8500 rpm, acceleration rate of 665 rpm/second for 15 seconds

c. the films are placed in a heated vacuum oven for 10 minutes at T = 185°C with reduced pressure of -28 in. Hg;

d. the pressure is then released and the sample continues to heat at T = 185°C for an additional 10 minutes before being allowed to cool at room temperature.

7) Preparation of thick, supported poly(S-r-DIB) copolymer films

    a. Varying wt% DIB values from 20 to 50% were obtained by using different amounts of S_8 in combination with amounts of DIB as referenced in section 1) a. The varying wt% DIB material amounts were each used in the below preparation of poly(S-r-DIB) copolymers.

- add S_8 to an 11 mL glass vial with a magnetic stir bar.

- in a thermostated bath, heat the glass and contents to T = 185°C until the contents become molten and display a clear orange color;

- use a syringe to add the DIB and stir the mixture until the solution is deep cherry red in color;

- a two part spin protocol was then used to spin-coat substrates heated at T = 150°C with the sulfur solution;
  - 2000 rpm, acceleration rate of 266 rpm/second for 15 seconds
  - 8500 rpm, acceleration rate of 665 rpm/second for 15 seconds

- the films are placed in a heated vacuum oven for 10 minutes at T = 185°C with reduced pressure of -28 in. Hg;

- the pressure is then released and the sample continues to heat at T = 185°C for an additional 10 minutes before being allowed to cool at room temperature.
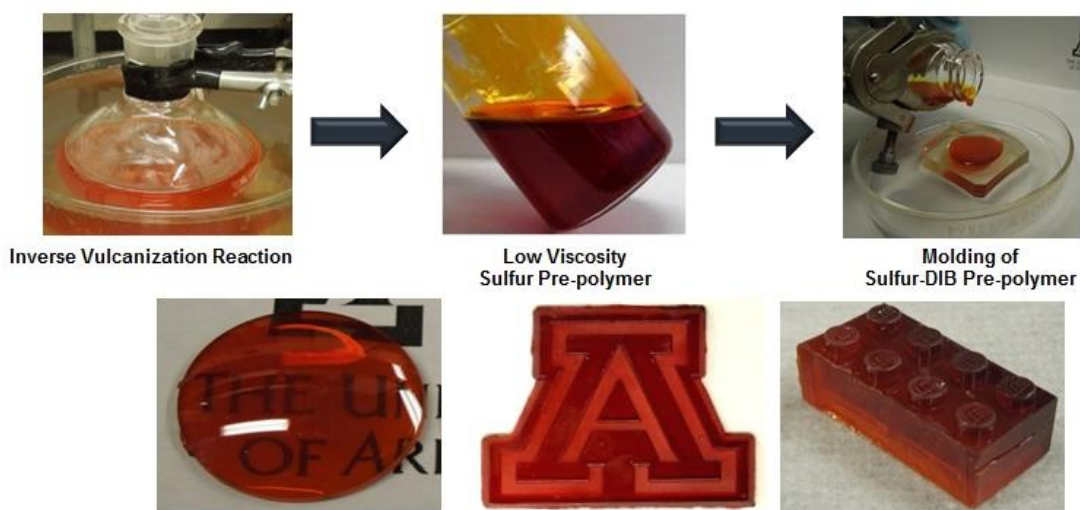
Figure 6. Steps of the inverse vulcanization process on the top row and examples of resultant molded optical materials on the bottom row[10].

4.4 Sulfur Copolymer Test Results

The sulfur copolymer lenses and films are colored based on the processing method used; faint yellow for solution-based, and deep red for melt-based. The coloration which occurs during the polymerization of S_8 to polymeric sulfur has been long observed by scientists, but its origin is still unclear. The materials were stored under ambient conditions for several months and remained chemically stable, maintaining their red coloring[18]. Coloration of the materials does not introduce any negative effects while imaging in the IR spectrum[3]. While the poly(S-r-DIB) copolymer lens is transmissive in the visible spectrum as well, the color would pose a problem within the visible, resulting in a discolored image[19]. Several other commonly used IR materials have various colorations which do not affect IR image quality. Figure 7 shows the colorations of a poly(S-r-DIB) 20-wt% DIB copolymer lens in comparison to commonly used IR materials germanium and KRS-5[3].
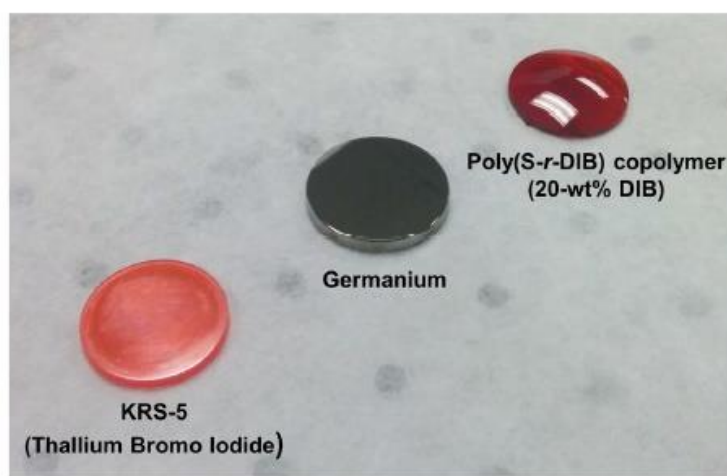
Figure 7. Coloration of poly(S-r-DIB) 20-wt% DIB copolymer, germanium and KRS-5 lenses[3].

Poly (sulfur-random-1,3-diisopropenylbenzene) (poly(S-r-DIB)) copolymers were evaluated for their refractive indices from ~600-1600 nm using a Metricon 2010 prism coupler. The thermoplastic copolymers possess a refractive index of ~1.8 in this region. Materials containing the highest percentage of S-S bonds of 80% also displayed the highest refractive indices from 1.865 to 1.845 across the wavelength range of 633-1554 nm. Materials with the lowest percentage of S-S bonds at 50% displayed refractive indices over the same spectral range from 1.765 to 1.745. The correlation of increased sulfur percentage to increased index of refraction was attributed to the large polarizability of sulfur electrons[3] (Table 5).

	633 nm	816 nm	1305 nm	1554 nm
80% S-S	1.877	1.852	1.832	1.829
70% S-S	1.837	1.813	1.796	1.792
60% S-S	1.795	1.773	1.757	1.754
50% S-S	1.757	1.737	1.723	1.72

Table 5. Indices of Refraction from 50-80% sulfur-doped copolymers over several wavelengths[10].

All of the materials displayed low birefringence within the tested spectrum of 633 to 1554nm. The table below shows that the refractive indices are similar in the perpendicular direction (TE) and the parallel direction (TM) to the film, which is an indication of low birefringence[3].

Wavelength (nm)	50-wt% DIB		60-wt% DIB		70-wt% DIB		80-wt% DIB	
	TE	TM	TE	TM	TE	TM	TE	TM
633	1.7564	1.7567	1.8390	1.8383	1.8561	1.8561	1.8720	1.8649
816	1.7369	1.7362	1.8138	1.8133	1.8318	1.8318	1.8487	1.8466
1030	1.7231	1.7226	1.7965	1.7966	1.8135	1.8134	1.8314	1.8319
1554	1.7193	1.7197	1.7929	1.7929	1.8096	1.8098	1.8293	1.8289

Table 6. Poly(S-r-DIB) copolymers of various wt%-DIB from 50 to 80% with measured refraction indices in the TE and TM directions across varying wavelengths[3].

Optical transparency using UV-VIS-IR absorption spectroscopy was evaluated from 500-20,000 nm. The sulfur copolymer materials displayed high transparency in the visible spectrum above 600nm and the NIR spectrum with comparable values to conventional IR materials. Along with high transparency the materials also displayed low optical scattering and high refractive index. The materials which contained 80% S-S bonds displayed a much higher transparency at wavelengths above 2000nm up through the MWIR region. The materials with 80% S-S bonds allowed for the capture of detailed images[3].
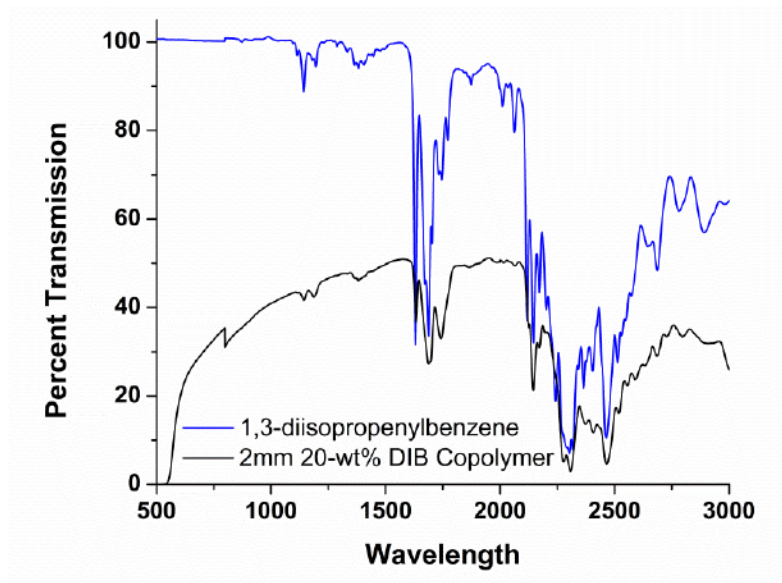
Figure 8. The transmission spectra from SWIR to LWIR for 200μm thick films of poly(S-r-DIB) copolymers of wt% DIB 20 and 50% using Fourier Transform Infrared (FTIR) spectroscopy measured with a Thermo Nicolet 4700 spectrometer[3].

It has been observed that when the materials thickness approaches that of near-IR wavelengths a spectrum with interference fringes is produced. This characteristic is generally indicative of a high quality optical film[3].
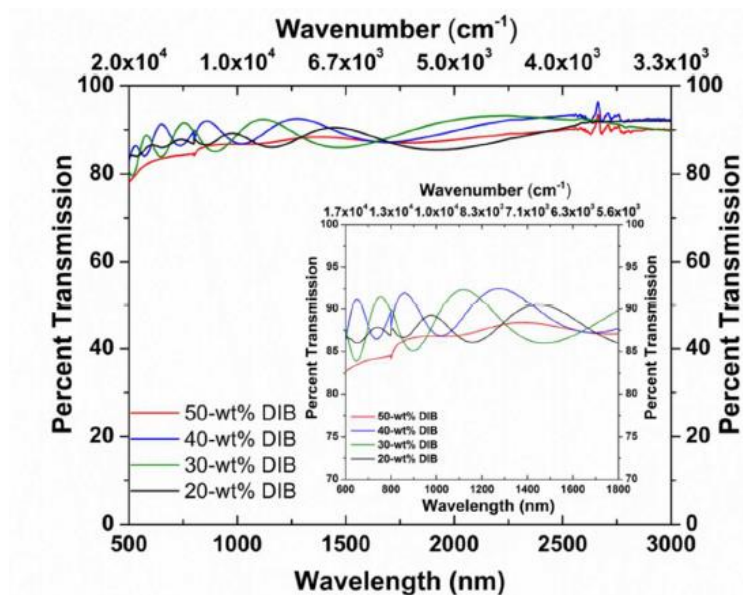
Figure 9. Transmission spectrum from UV-VIS to NIR of ~1μm thickness poly(S-r-DIB) copolymer films from wt% DIB range of 20 to 50% on NaCl plates[3].

IR imaging capabilities of poly(S-r-DIB) windows at NIR and mid-IR wavelengths of 1550nm and 3-5 μm were tested. When imaging with an MWIR camera through the sulfur based window, the resultant image displayed low loss and high detail.
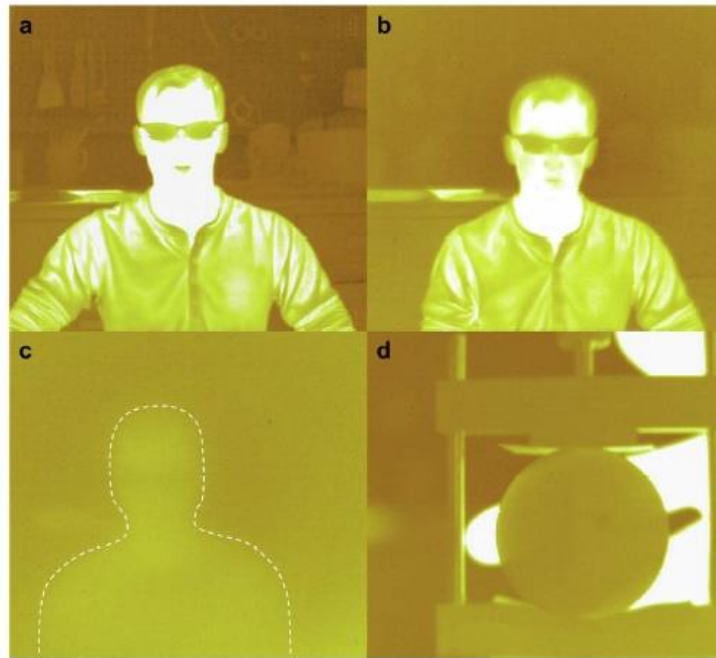
Figure 10. The above images were captured in the MWIR band between 3-5μm and false colored Sepia was applied: a) thermogram captured using a MWIR camera; b) thermogram captured using a MWIR camera through a poly(S-r-DIB) copolymer film (80-wt% S_8); c) thermogram captured using a MWIR camera through PMMA in which the dotted line shows where the individual in the image was present; and d) thermogram captured through a MWIR camera of a subject's hand placed behind a glass lens[3].

Lenses produced from sulfur copolymers displayed a reduced focal length in the NIR wavelength range in comparison to materials with lower indices of refraction including glass or PMMA. This characteristic suggests that the sulfur based polymers may be best fitted for use in compact NIR and SWIR optical systems[3].

	N-BK7 Glass	Poly(S-r-DIB) (50 wt% S_8)	Poly(S-r-DIB) (80 wt% S_8)	PMMA
Diameter (mm)	15.00	15.00	15.00	15.00
Measured Focal Length (mm)	–	55	47	–
Calculated Focal Length (mm)	75	53.6	47	81.8*
Refractive Index	1.52	1.723	1.832	1.474**

Table 7. Focal lengths in the NIR waveband using a 1310 nm laser for poly(S-r-DIB 50 wt% S_8) and poly(S-r-DIB 80 wt% S_8) in comparison to N-BK7 glass and PMMA. The refractive index of N-BK7, 50 wt% S_8, and 20 wt% S_8 were measured using a Metricon 2010 prism coupler. All lenses had a radius of curvature of 38.76mm. (*Calculated using the Lens Maker Equation, **Calculated refractive index) [3].

Below is a comparison of the transmission spectra of poly(S-r-DIB) 20-wt% DIB 2mm film and 5mm film of commonly used IR material, germanium[3].
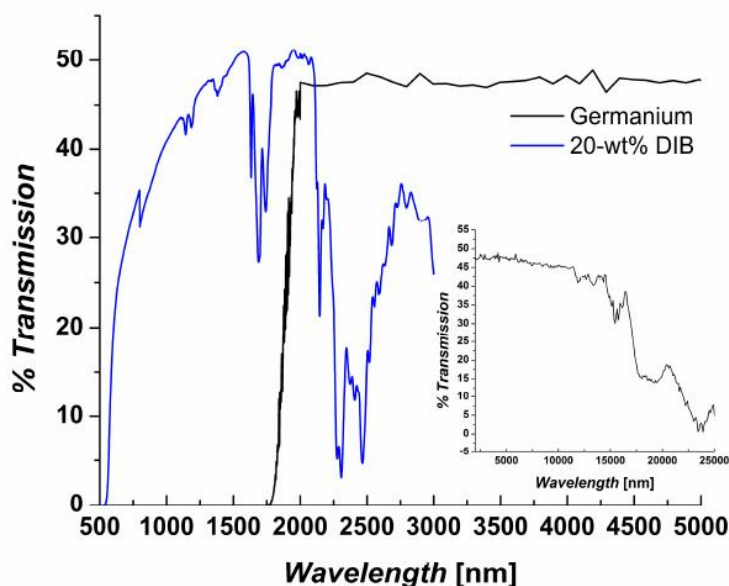
Figure 11. Transmission spectrum of poly(S-r-DIB) 20-wt% DIB 2mm film and germanium 5mm film measured using a Cary 5000[3].

5.0 Market Assessment

This section will detail the general IR market potential and trends, as well as a more detailed niche market application of medical imaging for developing countries, which was evaluated as holding the greatest potential for application of sulfur copolymer lenses. Other areas which may be worth considering, but are not covered in this report, are cell phone and personal night vision applications, law enforcement imagers, and the Internet of Things (IoT) applications.

5.1 General IR Market

5.1.1 Future of the IR Industry

Although the IR industry began in support of military applications, the market is increasingly moving towards commercial applications. There are several contributing factors that have made increased integration into commercial applications possible including technological advancements such as improved bolometer design, sizable price reductions in IR products which have been estimated to have already dropped by 60% from 2011 to 2015, and increased consumer demand leading to further commercial investment in R&D, design, and manufacturing[20]. Bolometer array technology continues to progress and become cheaper 82x62 uncooled silicon FPA from Robert Bosch GmbH for <$50[21]. The growth of several other industries has also had a positive effect on the IR market as IR imaging devices become an integral part of varying commercial industries. Some of these areas of increased interest include home automation products, and commercial surveillance. With the rise in demand for IR imaging products there has also been a rapid rise in the number of IR lens manufacturers and lens material options. Major optical lens manufacturer, Schott, introduced their first line of IR lenses in 2008 with just two material options: zinc sulfide and chalcogenide glass. Another primary optical lens retailer, Edmund Optics, provided fewer than 100 Commercial Off-The-Shelf (COTS) IR items in 2006, but has increased their selection to offer more than 525 IR items as of 2011[20].

Although commercial industry is contributing the most to the expansion of the IR market, defense still continues to play a vital role in overall market figures. Military spending budgets are declining across the world due to debt and austerity, which may negatively impact the global IR market. Although overall military budgets are decreasing, it is predicted that over the next few years through 2018 military applications are likely to dominate the market due to considerable military activity taking place in the Middle East and Asia Pacific. Night vision equipment relying on IR imagers has also become an integral and necessary part of military missions as many operations and surveillance often take place in darkness[22]. As of 2011, 80% of the IR market could be attributed to military applications with 2013 bringing in the largest defense applications contribution[20].

The two largest costs of IR vision enhancement systems have been identified as the bolometer senor array and the IR lens assembly. Bolometer array technology continues to progress and become cheaper. There has also been increased availability of IR lens materials such as germanium, zinc sulfide, zinc selenide, calcium fluoride, amorphous material, and chalcogenide glass[20].

Currently, the US is the largest regional contributor to the global IR market in part because the majority of IR manufacturers are physically located in the region, but with major economic growth and development taking place in Asia the IR market is expected to greatly expand for commercial application in that region. Military spending is also expected to grow through 2019 in regions of Asia such as India, Japan, and South Korea as those countries ramp up their military capabilities.

5.1.2 Global IR Market

The global IR market is predicted to expand and flourish in the coming years. Maxtech International, Inc. values the 2015 global general IR imaging market at $2.325B, and forecasts that by 2020 the market will grow to $4.227B. Based on collected and forecasted data from 2014 – 2920 , a CAGR of 12% is forecasted[21].

	2013	2014	2015	2016	2017	2018	2019	2020	CAGR
IR Uncooled (USD $B)	1.874	2.129	2.325	2.661	2.992	3.367	3.754	4.227	12%

Table 8. Five year market forecast for worldwide commercial and military IR imaging equipment[21].

Several industries are contributing to the growth of the global IR market. Below are a few of the industries that are predicted to contribute most to the market.

- Medical imaging
- Veterinary sciences
- Airport screening for epidemics
- Automotive industry for night vision and pedestrian recognition
- Smartphone cameras
- Maritime/aircraft inspection

5.1.3 NIR Market

The NIR market is increasingly becoming an integral part of several high demand commercial industries. In 2003 the European Commission enacted a law that all mid and high-level cars implement integrated pedestrian recognition systems in the vehicles by 2015. Most companies have integrated NIR into their vision systems, as NIR complements visible imagers to obtain daytime and nighttime imagery[20]. Not only is NIR being implemented into human operated vehicles, there has also been recent development in creating autonomous automobiles as well. Google's Autonomous Vehicle uses a LIDAR system in conjunction with video cameras, radar sensors, GPS, ultrasonic sensors, and odometry sensors to identify its location and surroundings. The LIDAR and the GPS are the most expensive components and have the most room for cost optimization. The current LIDAR system, developed by Velodyne, costs $8,000, which is too costly for the average consumer to afford[23].

Surveillance is also an ever growing industry in both commercial and military sectors. NIR is often used in combination with visible detectors in a single device to optimize collection under an increased lighting scenario range detecting up to a 1000nm range of wavelengths. Commercial gaming is another industry

which has closely incorporated NIR capabilities for uses such as gesture recognition for motion controlled gaming[4].

5.1.4 SWIR Market

While SWIR is the least developed of the IR markets, it has grown in recent years and is predicted to experience continued growth, driven mostly by military applications. As of 2011 the global SWIR market was estimated at $50M[24]. SWIR imaging devices have faced several challenges to growth over the years including a limited manufacturing base relative to other types of IR imaging devices, competition with less cooled MWIR devices, and general lack of knowledge of critical application purposes within the IR user community.

5.1.5 MWIR Market

The MWIR market was estimated to be $789M in 2012 and is predicted to steadily increase in the upcoming years. According to an October 2013 report by Winter Green Research, the MWIR market is expected to grow to $7B dollars by 2019. Uncooled MWIR used for thermal applications is expected to have the highest growth value within the thermal heat seeking market[24].

Growth factors include increased performance capabilities, significant cost decrease, and reduction of overall device size. AR coatings for lenses used in MWIR and LWIR can now bring transmission efficiency percentages up from as low as 40% without the use of AR coating to 95% after addition of coating greatly adding to the overall performance of MWIR devices. Costs are also expected to drastically decrease over the next few years in which a unit costing $3,000 in 2012 will cost just $300 by 2019. Sizes are also being minimized from bench sized to handheld and portable sized devices.

The biggest industry push for growth in this IR sub-category is the exploding interest in the Internet of things (IoT) market, which comprise a preponderance of MWIR imaging devices. Other industries which continue to grow and necessitate a need for MWIR devices are materials characterization, explosive detection, microscopy, non-destructive testing, and bio-medical imaging.

5.1.6 LWIR Market

LWIR imagers, more commonly known as thermal imagers, can be uncooled or cooled. Uncooled devices use a sensor that operates at ambient or near-ambient temperatures. Uncooled thermal imagers are generally less expensive and are able to be designed in a more portable form factor.

Much like the other IR categories, LWIR uncooled cameras have expanded beyond military applications and into the commercial industry which has become the major driving factor of growth. Devices incorporating micro bolometer detectors are the most highly produced type of IR array technology and hold the majority of the IR market share. Advances in bolometer technology have been very beneficial to the uncooled thermal market allowing for the creation of devices which do not require cooling equipment. While in 2014 the LWIR uncooled market was worth $2.1B, by 2016 it is expected that the uncooled LWIR FPA market will grow to $3.4B [24] with more than 1.1 million units being sold.   By 2020 the market is estimated to be at $3.7B. The growth is in large part due to commercial surveillance,

automotive, and thermography applications. Along with major growth, there will also be significant price reductions of 12-15% per year for the next 5 years. High quality thermal uncooled FPA imaging devices are already available for as little as $1,000 from companies such as FLIR making them more accessible to commercial consumers. The automotive industry is predicted to sell more than 500,000 units with integrated thermal imagers in 2016. Although commercial applications are helping to drive the market, military applications are still a very large contributor, with high demand for such applications as weapon sights, portable goggles, and vehicle vision[8]. See Figure 13 for a graphic of commercial versus military uncooled LWIR units sold and predicted to be sold from 2009 to 2016.
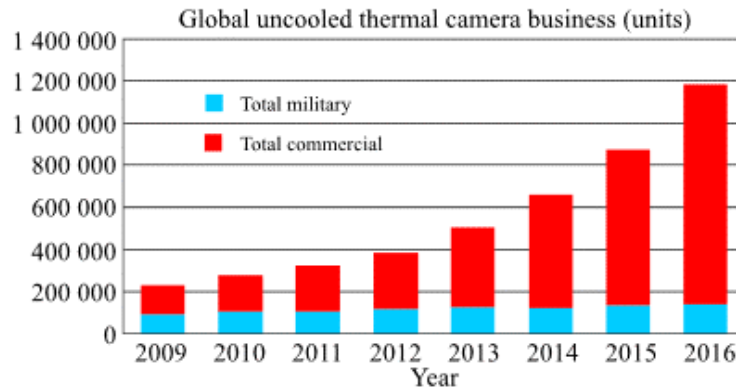
Figure 13. Uncooled focal plane array (FPA) thermal camera market distribution and growth between military and commercial industries from 2009 to 2016[8].

5.1.7 IR Lens and Window Materials Market

IR lens materials are generally much more expensive than their visible lens counterparts. A visible lens costing $100 is likely to cost $5,000 for a germanium IR lens equivalent[22]. The most commonly used IR material is germanium which made up 35% of the market in 2013. This material has been made popular by its favorable mechanical properties and its non-hygroscopic characteristic. One of the many providers of germanium, Vital Materials, produces 50 tons annually of the material alone[25].

Germanium production results as a byproduct of other processes including base metal refining of sphalerite zinc ores, copper ores, and fly ash coal from coal power plants. The extracted Germanium is purified using a chlorination and distillation process to produce germanium tetrachloride ($GECl_4$), hydrolyzed and dried to produce germanium dioxide ($Ge)_2$), then reduced with hydrogen to produce germanium metal powder. The metal powder is melted at a temperature of 938.25°C or greater and molded into bars upon cooling. The melting and cooling process, known as zone-refining, removes impurities in the germanium resulting in high purity germanium of 99.999%. The high purity germanium is then grown into crystals, which can be sliced thin into optical lenses. Germanium is similar to sulfur copolymer production in that it is largely created as a byproduct and undergoes a melting and cooling process in lens development. It differs in the fact that crystal growth is required prior to formation into IR lenses[26].

The other major materials used most commonly for IR lenses are silicon, zinc selenide, Cleartran and sapphire. Figure 14 shows the predicted sales of the industry's most popular IR lens materials from 2012 to 2020. Zinc selenide is predicted to grow at a rate which is greater than the global average over the next forecast period due to its integration into the medical imaging industry. Of the zinc selenide and Cleartran produced, ~25% of it goes towards navigation systems and heat sensing[25].

Global IR camera market by material, (USD Billion), 2012 – 2020
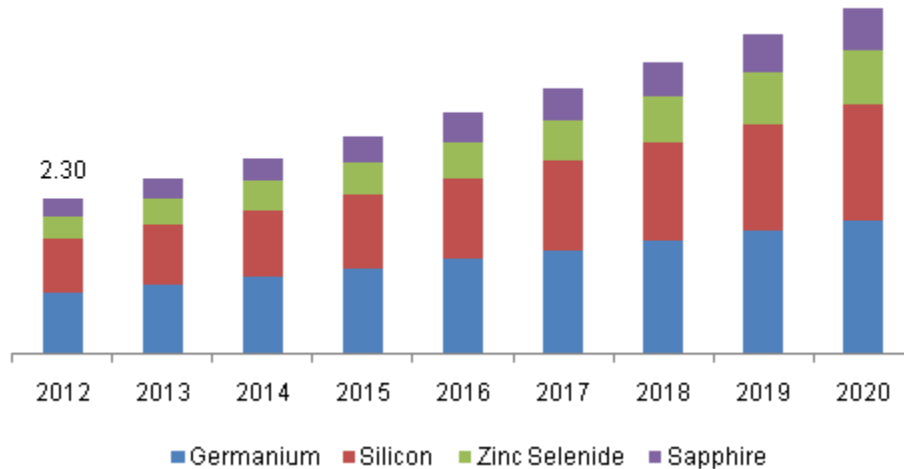
Figure 14. Global IR market sales as broken down into category by four of the most common IR materials[25].

5.1.8 Competitor Analysis

5.1.8.1 Primary Industry Competition

There are numerous companies in the IR materials development and manufacturing business. Below are brief summaries of some of the major competitor companies focused on IR materials and lenses. Several of the companies are privately held, therefore financial statistics are unavailable, but those companies that are public offer important insights into the lens market and show that IR lens companies are generally prospering within the IR materials market. Companies which provide customized IR products do not list pricing information without specific inquiry while pricing is generally provided for COTS lenses in most cases. Pricing information gathered shows a wide range of costs from tens to thousands of dollars based on the size, quality, and optical/mechanical characteristics of a specific lens. While a few of the major market players offer COTS lenses the majority of the companies specialize in customized lens designs. Those that do offer COTS products provide a selection of hundreds of lens options. All of the major companies offer lenses of expected crystalline IR materials including Ge, ZnSe, ZnS, CdTe, Si, CaF_2, BaF_2, GaAs, NaCl, KBr, and sapphire, as well as chalcogenide glasses. Less common materials offered include black diamond and glass ceramics. Many of the distinguished IR lens companies are US based, but most have additional international offices and facilities. While there are a few companies that were founded in the past few decades, many of the companies have been

established for a considerable amount of time. None of the major IR lens players are startups with the most recent evaluated company established in 1993. While information on the number of employees was not available for all companies, information that was available indicates that several of the companies have very large workforces or attachment to a sizable parent company.

Elcan Optical Technologies is a global provider of precision optics catering to the medical, defense and surveillance, industrial, commercial, and entertainment industries although they are best known for their combat optics. Founded in 1848, Elcan is a Canada-based privately held company and is now a subsidiary of Raytheon. Elcan specializes in IR lenses made from Ge although they also manufacture ZnS, ZnSe, sapphire, and fluoride-based customized lenses[27].

II-VI Infrared is the infrared focused business unit of optoelectronic component parent company II-VI Incorporated. Founded in 1971, the US based company specializes in synthetic crystal materials growth and optical fabrication. The company is known for its customized products and is capable of production ranging from prototypes to OEM. II-VI creates IR lenses using CdTe, ZnSe, ZnS, Ge, Si, CaF_2, and AMTIR (a chalcogenide glass) materials[28]. As of November 2016 II-VI Incorporated had a Market Capitalization of $1B[29]. Annual revenue increased from 2013 to 2014 by 22.4%[30] and the trend of increased revenue continued through 2016 with revenue of $827.22M[29].

Janos Technology is a US based precision IR optics company founded in 1970. The company caters to the security, commercial, and defense industries with a focus on manufacturing of thermal imaging lenses in the MWIR and LWIR ranges. Janos has a wide selection of COTS IR lens products with a focus on chalcogenide glasses. The company is privately held and is owned by parent company Fluke which specializes in creation of electronic test tools and manufactures a limited selection of Ge IR lenses[31].

Edmund Optics is a privately held US based supplier of optics and optical components founded in 1942. The company offers a wide selection of hundreds of COTS IR lens products ranging in price from $15 to $4,000 USD. Ge (210 COTS products), ZnSe (80 COTS products), sapphire (71 COTS products), Si (62 COTS products), and black diamond (40 COTS products) are the materials used for the majority of the lenses offered, but BaF_2, MgF_2, KBr, and NaCl are also used by the company in the manufacturing of IR lenses[32].

Schott AG develops, manufactures, and distributes customized special glass materials and components. Based in Germany, they were established in 1884 and now have several international locations. Schott manufactures sapphire, chalcogenide glass, and ceramic processed ZnS IR lenses. The company is privately held, but according to their 2013/2014 Annual Report their annual revenue was $1.87B euros. The company's income before tax was increased from $31M euros the prior year to $98M euros. The company has a reported 15,445 employees[33].

LightPath Technologies is an optical design, manufacturer, and distributor founded in 1985. The US-based company specializes in chalcogenide glasses for the MWIR and LWIR ranges. The company provides custom IR lens design taking a product through the full development chain from concept to volume production and global distribution[34]. As of November 2016, the company had a listed Market Capitalization of $22.23M. LightPath's 2016 annual revenue was $17.27M[35]. Although revenue has

remained fairly consistent over the past few years, the company has experienced loss of earnings due to its handling of non-production general and administrative costs[36].

ISP Optics is a privately held US-based company established in 1993. The company focuses on MWIR and LWIR products. ISP Optics offers customized lenses as well as hundreds of COTS lenses ranging in price from ~$100 to $2,000 USD. Materials used for production of IR lenses include BaF_2, CaF_2, Ge, Si, ZnSe, ZnS, GaAs, chalcogenide glasses (Amtir and GASIR), NaCl, and KBr[37].

While there are a large number of competitor companies there are also a large number of potential customer companies in the business of manufacture of full IR systems such as FLIR, DRS, Raytheon, and Fluke. Assessment of the competition indicates that there is much profit to be made in the IR lens industry with increasing profit trends and while the industry may be saturated with companies developing lenses with standard IR materials, our research has not uncovered any major companies adding to the market with novel IR materials comparable to sulfur copolymer technology.

5.1.8.2 Novel and Upcoming Infrared Materials

Following extensive research, to our knowledge no comparable development of organic copolymer based materials for creation of IR materials has been achieved. Recent additional progress and focus in optimization of IR transmissive materials stems from further development of glass ceramics, chalcogenide glasses and coatings for existing crystalline or glass lenses to improve optical and mechanical characteristics of materials in use by the industry today. The focus for most IR material researchers has been altering existing materials rather than creating brand new materials in contrast to our proposed sulfur copolymer process.

Development of glass ceramics as IR materials has been fairly recent occurring in the past decade and has already become a marketable product by big names lens suppliers such as Schott. Glass ceramics are polycrystalline materials created as a result of heat treatment of amorphous glass. The process uses traditional glass processes followed by slow cooling and heat treating which allows for the controlled growth of crystals. Glass ceramics are generally meant to be an alternative to LWIR material CVD processed ZnS, often used in the creation of IR windows and domes. Recent research has attempted to create glass ceramics with increased transparency, reduced cost, and mechanical stability in comparison to industry standard ZnS. Figure 15 shows the current level of transmission achieved by materials developed by Pacific Northwest National Laboratory (PNNL)[38].

In order to achieve characteristics comparable to CVD ZnS, a glass ceramic must have a small grain size to reduce optical scattering. As of 2013, according to researchers at PNNL, with the exceptions of Al_2O_3-Ln_2O_3-ZrO_2 with ~100nm grain size and Ba-Al-O with 500-5000nm grain size, ideal grain size for IR applications has rarely been achieved using glass ceramics. As a goal to replace ZnS, glass ceramics have become a viable option. Several additional materials were proposed and rejected following extensive studies. These ineffective replacement materials include:

- o diamond: Not acceptable for multispectral devices due to its MWIR absorption characteristics. High cost and production difficulties are additional negative attributes of the material.
- o CaLa$_2$S$_4$: A powder processed ceramic which displays poor thermal characteristics when compared to ZnS and other industry materials.
- o Coating improvements to ZnS: Added costs and risk to the already existing process.
- o ZnS powder composites with diamond or Ga$_2$S$_3$: Displays high optical scattering[38].
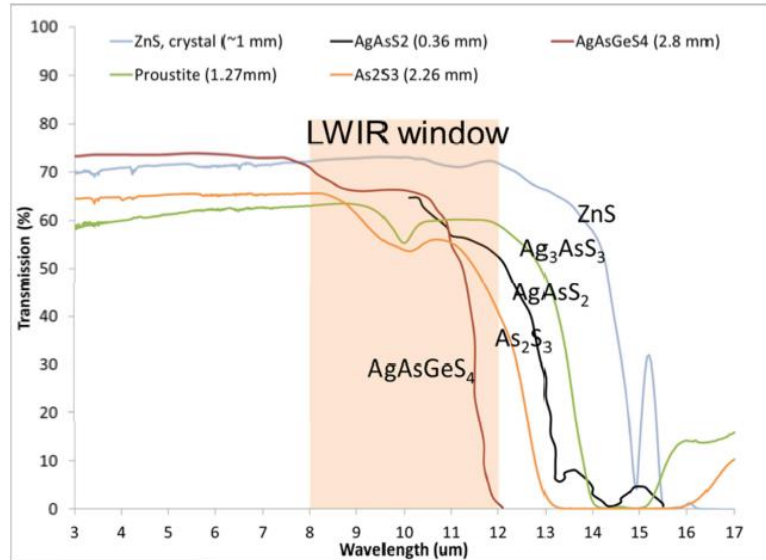
Figure 15. Transmission properties of several glass ceramics across the IR spectrum in comparison to popular industry material ZnS[38].

PNNL plans to substitute varying amounts of Se or Te for S into several ceramic glasses to test the potential increased LWIR transmission characteristics that researchers are expecting to result from the substitution. Below is a table showing several glass ceramics which PNNL has assessed and will perform upcoming Se and Te substation tests[38].

Glass Ceramic	Advantages	Disadvantages
Ga$_2$S$_3$	• Commercially available • Good LWIR characteristics in crystalline phases.	
GeS$_2$	• Production easier than Ga$_2$S$_3$ • Good LWIR characteristics	• Reduced mechanical properties
As$_2$S$_3$	• Excellent LWIR characteristics	• Slightly softer than ZnS
Chalcopyrite (ZnGeP$_2$)	• Good MWIR characteristics	• Unacceptable LWIR characteristics

Table 9. Table showing the materials analyzed and rejected by PNNL as a CVD ZnS replacement as part of their glass ceramics research[38].

Several other groups and corporations have achieved recent developments in various forms of glass ceramics such as Materials and Electrochemical Research Corporation's development of magnesium aluminum spinel for large MWIR domes and windows[39], and research performed by a team funded by a grant from the President of the Russian Federation to develop better NIR transmissive optical material, TiO_2-SiO_2[40].

IR lens coatings have also been an area of major interest to researchers recently. Although a variety of coatings are currently available commercially, advances in novel coating materials and methods, such as diamond-like carbon (DLC) coatings, continue to optimize optical and mechanical properties of lenses made from commonly used IR materials. Research performed in 2015 by the US-based company, Reynard Corporation, has led to the development of a new composite DLC coating. DLC is an amorphous form of carbon with nanoscale atoms arranged in tetrahedral or hexagonal bonding groups. Although DLC coatings are not a new concept, chemical tailoring of the DLC process has further optimized the performance level that a DLC coated lens is able to attain. Reynard Corporation's proprietary DLC method involving an intermediate dielectric index and a stress matching material placed between the substrate and the DLC layer allows for a 3-50% increase in transmission efficiency dependent on wavelength from visible to MWIR bands. The coating also allows for increased mechanical performance for use in high abrasion environments and reduced thickness in comparison to other DLC coated lenses. The coating is versatile and can be used with several high index IR materials including Ge, Si, ZnS, ZnSe, and chalcogenide glass[41]. Figure 16 shows the transmission efficiency improvements achieved using composite DLC as compared to traditional DLC.
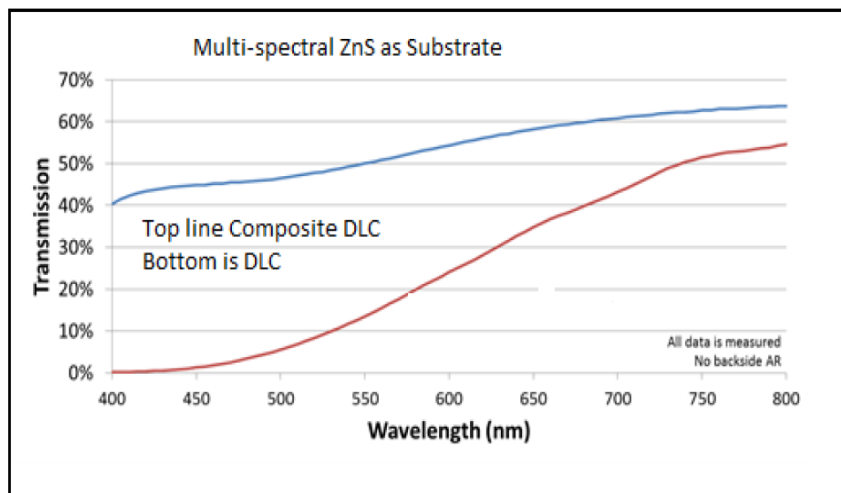
Figure 16. Transmission properties of a composite DLC coating in comparison to a pure DLC coating[41].

Umicore is another company which has recently made progress in the area of DLC coatings with their iDLC product specifically designed to be used with their chalcogenide glass product, GASIR, but also usable with additional IR materials such as other chalcogenide glasses, Ge, and ZnSe for transmission in the 1.4μm to 15 μm wave range. Much like Reynard Corporation's DLC development, Umicore's progress results in a coating allowing for increased environmental protection, transmission and spectral performance in comparison to standard DLC coatings. The iDLC is also able to be mass produced[42].

There have been several groups working on further development of chalcogenide glasses. Chalcogenide glasses have the advantage of being customized in their optical and physical properties by varying the amounts of Ge, As and Se as compared to crystalline optics which are limited by the physical properties of the crystal lattice[43]. Chalcogenides additionally hold many disadvantages including their toxicity, high expense, fragility, and large Fresnel optical loss due to high refractive index. Chalcogenides have received considerable attention by research groups over the past two decades [44] and are currently one of the main products in the IR lens industry with many of the most well-known companies offering chalcogenide selections. Although chalcogenides are not new, several research groups have selected them as the material of choice in attempts to advance IR lens material technology.

Under a DARPA contract in 2014, several new chalcogenide glasses were created from various combinations of As, Ge, Ga, Sb, S, Se and Te by co-molding of the layered preform. This has allowed for all of the benefits of standard chalcogenide glasses, but adds the advantage of reduction of size and weight of the optics. The glasses that they created are optically efficient from SWIR to LWIR bands in a range of 1.4 to 12.7μm[45].

In a joint research project by PNNL, IRradiance Glass, Inc. and several academic institutions, improvements to chalcogenide glasses were achieved by adding various levels of Ge and Se to AsSe. Both the refractive index and dn/dT were found to decrease when Ge or Se were increased. The team was able to show potential to achieve a dn/dT equal to 0[43].

Some companies, such as Sting Ray Optics, have developed their own proprietary high end optical lenses to tackle the inefficiencies of standard IR lenses. While the specific composition and manufacturing processes are unknown in these cases, none have been found to be similar to our proposed sulfur copolymer lenses. For example, Sting Ray's SuperBand optical lenses, first marketed in 2011, are able to cover a wide range of bands from the visible to LWIR with a single lens and a reduced size. They are composed of an achromatic material. Materials specifically investigated for use by Sting Ray Optics for IR lens creation include AH-OP5, AH-OD4, DI-OL3, AH-OF7, DI-OL1, and DI-O83 some of which may be included in their SuperBand lenses[17].

Based on considerable research, to our knowledge it appears that there is no other organic polymer process for creation of IR materials at this time. Furthermore, it appears that no open source research or commercial company has created any new IR materials, but rather have expanded on existing processes and materials for increased lens capabilities. As a result, the new processes under research are just as toxic and often equally expensive or more costly in comparison to current materials and methods. Although there are no new comparable materials being added to the industry, the developments taking place are addressing some of the same optical and material characteristics which sulfur copolymers must attain to compete against top of the line IR materials and therefore the above described developments can be considered viable competition to sulfur copolymers.

5.2 Medical IR Market
5.2.1   General Market
5.2.1.1 General Market Figures

In this section the term, 'medical devices', is defined as equipment used to treat, diagnose, or come in contact with a patient. The definition of medical devices used in these statistics is comparable to what the World Health Organization (WHO), and the US Food and Drug Administration (FDA) currently use. In 2016 the medical device market totaled $339.5B globally. The market is expected to grow in all areas of the world with increasing demand over the next several years[46]. According to a 2016 report released by the International Trade Administration's (ITA) Global Health Team, the medical device market is expected to grow significantly over the next 4 years increasing by nearly $100B globally from 2016 to 2020. In 2016 the market was estimated to be worth $339.5B, of which $93.3B is related to non-American (North and South continents), and Western European countries encompassing the majority of the regions containing developing countries while $246.2B is related to geographic regions in which the majority of developing countries are located. The medical device market in each world region is forecasted to continue to grow over the next 4 years through 2020 (Table 10) [46].

Region	2016	2017	2018	2019	2020
Americas	166.6	176.5	187.3	197.9	208.6
Asia/Pacific	68.7	72.6	77.6	82.9	88.6
Central/Eastern	14.6	15.7	17	18.1	19.1
Middle East/Africa	10	10.8	11.5	12.5	13.2
Western Europe	79.5	85.1	92.6	101.4	106.2
Total	339.5	360.8	386.1	412.8	435.8

Table 10. This chart shows the forecasted growth of the general medical devices market in USD billions. Infrared medical tools fall under the subgroup of surgical and medical instruments[46].

Medical device exports from the US were $45B in 2015. The largest subgroup of medical devices is surgical and medical instruments (including optical diagnostic apparatus) of which US exports grew by 27.5% from 2007 to 2012. In 2015 the US export of surgical and medical instruments totaled $12.6B, and in 2016 totaled $12.4B[46].

Approximately 90% of medical research investment goes towards the benefit of only the wealthiest 10% of the world's population. This precludes the 5 billion people considered to live in developing countries and regions many of which live in Africa, Asia and Latin America[47]. If this statistic is applied to US exports of surgical and medical equipment then it can be inferred that the market for developing countries is approximately $1.24B while the market for developed countries is $11.16B.

Global demand for medical devices will continue to increase due to the development of new hospitals and clinics, implementation of public healthcare in some regions, and an emphasis on better global health. Other factors which will contribute to the growth of the medical device market are the increase of lifestyle diseases, aging populations, and increased incomes in developing countries. Demand for

medical devices in some developing countries is rising by double digit percentages, which indicates that there will be significant expansion in this particular industry[46]. Developed countries will also see an increased demand due to a change in perspective of how and what medical procedures should be accomplishing. Whereas currently many medical procedures diagnose diseases, which may have already caused detrimental effects, and provide treatment, there is a shift in perspective that maintaining health and detecting deviations of this at the very first stage is ideal. To implement this idea newly designed medical devices will be required.

5.2.1.2 Potential Competition or Partnerships

Of US based medical device companies, 80% are small to mid-sized companies with less than 50 employees. Often times startups have little or no revenue and may heavily rely on partnerships in the form of mergers, or acquisition deals by larger companies. Geographically, the majority of medical device companies are based out of California, Florida, New York, Pennsylvania, Michigan, Massachusetts, Illinois, Minnesota, and Georgia. The following is a list of some of the major US based medical device companies: Baxter®, Beckman Coulter®, Becton Dickinson®, Boston Scientific®, GE Healthcare Technologies®, Johnson & Johnson®, Medtronic®, St. Jude® and Stryker Corporation®. Large medical device companies are expected to increase R&D budgets by ~3% while the rest of the medical device industry is expected to increase R&D budgets by more than 5% between 2013 to 2020[46].

Many foreign companies are also looking to establish a US-base for the innovation and productivity advantages held regionally. The US is the world leader in medical device manufacturing, but there is also strong competition from Germany, Japan, and the Netherlands on high end products, with secondary competition on lower end products from China, Brazil, Korea, Taiwan, Mexico, and India[46].

Germany is known to produce high quality medical equipment, specifically in the areas of medical diagnostics and optical technologies[46]. While there is no known existing competition to a proposed sulfur copolymer lensed IR device, a German-based company may have the potential to provide the other components necessary for an IR medical tool requiring sulfur copolymer lenses. Approximately 95% of the German medical device market is made up small to mid-size companies, and sub-groups of large companies. Larger companies in the market include Siemens, B. Braun, and Fresenius[46].

Medical device industry trade associations which are highly involved in the industry include: Advanced Medical Technology Association (AdvaMed), Dental Trade Alliance (DTA), Medical Device Manufacturers Association (MDMA), Medical Imaging Technology Association (MITA) and the International Association of Medical Equipment Remarketers & Servicers (IAMERS)[46].

Currently, there is no tool available on the market which meets the needs of an infrared medical diagnostic to be used in developing countries, therefore the sensor selected to be used with sulfur copolymer lenses would likely need to be custom developed.

Developed countries have limited medical IR devices all of which are relatively costly. Land vIRalert, Cantronic Systems FeverScan, Thermoteknix FevIR, and FLIR Systems A320 are FDA and CE approved products for fever detection. InfraReDx using NIR/SWIR spectroscopy is used in a handful of US

hospitals for open heart surgery. Spectron IR, MammoVision, and InfraMedic's ReguVision and FlexiVision are used for breast cancer thermography[21].

Introducing a new medical product to the US market can often times be very difficult due to strict regulations established by the Food and Drug Administration (FDA), Medicare, and Medicaid[46]. Although considerable research has been carried out in the area of infrared imaging for medical purposes and has proven to be effective in many cases [21], and with some procedures having already been approved by the FDA [48], the method has not been broadly adopted among the mainstream medical community, and such procedures are not always covered by US insurance. Within the US, most medical infrared tools are only approved for screening purposes rather than as diagnostic tools[21]. Exporting a medical product to a foreign market is often easier than entering the US market[46].

5.2.2   Developed Countries Market Potential

Developed countries have the luxury and the interest to change current medical processes of diagnosis and treatment to health identification and maintenance providing a market opportunity for medical IR, which often has the ability to detect first deviations from health earlier than traditional medical diagnostic methods. [49] Although IR imaging has the potential to meet this need, there has been a lack of acceptance by the mainstream medical community due to poor results from the 1970s and 1980s displaying many false positives and false negatives[21]. This is largely due to the first medical IR cameras using uncooled FPA microbolometers which lacked sufficient computer hardware and software, displayed significant noise, thermal drift and poor resolution, and used methodologies and protocols which were not consistent. There have been significant improvements since then with current microbolometer technology able to provide noise free, drift free, high resolution, high reproducibility, and high sensitivity of more than 30mK[49]. Despite trials from over two decades ago medical IR is widely considered a screening tool rather than a diagnostic tool in the US. High quality peer reviewed research will need to be performed in order to sway the opinion of the medical community[21].

Standards and regulations vary from country to country, but when marketing to the US a medical device must be FDA approved, while in Europe a device must be CE approved[50]. This can be very difficult to do as the laws are very strict. In the US many insurance companies do not currently cover IR diagnostics including Medicare, however, some private insurance companies do provide coverage.

It is estimated that 648,00 people develop infections annually from stays in US hospitals of which 75,000 die according to the Centers for Disease Control and Prevention (CDC). Infectious bacteria can live on surfaces for up to several days including the surfaces of medical equipment thus increasing the risk of being passed between people[51]. Sulfur copolymers have the ability to contribute to the reduction of infection risk. Since sulfur lenses are much lower cost than traditional IR lenses they can be treated as disposable. Many of the infectious bacteria in hospitals remains on surfaces for several days. By eliminating surface space which touches multiple patients using disposable exterior imaging lenses the risk of infection may be reduced.

Not only does the disposable property of sulfur copolymer lenses benefit reducing infection rate, it also reduces costs. These costs include overall device costs, ultimately lowering procedure costs, and

equipment damage related costs. Lenses can be replaced for minimal costs, or easily fixed using heating techniques. In addition to low cost sulfur copolymer lenses, the price of microbolometer technology has also significantly decreased to the scale of $10s or $100s for quality detectors[21] contributing to the relatively low cost of an overall IR medical device[49].

The US has a per capita income of $23,000, and the US government spends $1,300 per capita on healthcare. Many other developed countries have similar statistics[50]. Marketing to a developed country may be beneficial in the case of sulfur copolymer lenses since those areas provide the most funding for medical research. Hundreds of millions of dollars by several companies have been spent on research of medical IR imaging[21]. Additionally, there is generally enough wealth that a relatively large price markup could be placed on a finished product while still maintaining a low cost price to the consumer.

Currently there are a limited selection of medical IR devices available in the US and Europe such as Mammovision and InfraMedic infrared imaging systems which received CE approval in 2007. In Europe laws dictate that medical infrared imaging may only be used by trained physicians with a medical certificate from the German Society for Thermography and Regulation Medicine, the European Association of Thermology, or the University of Glamorgan, Wales. Other devices which do not have FDA or CE certification exist, but by law are limited to use as imagers without measurement or temperature reading functionalities[49]. The fact that IR medical devices already exist and are in use in some the US and Europe can be both a benefit and a challenge. The existing products may provide a platform for potential partnerships, or competition for a sulfur copolymer medical lens use case.

5.2.3   Developing Countries Market Potential

Developing countries and regions lack suitable equipment for medical purposes including visual diagnostic tools. In such areas, where the national income is low to mid-range, cost plays a major factor, and in many cases there is the additional factor of harsh environment which also has a significant influence over the availability and accessibility of usable medical equipment.

Currently, many developing countries receive their medical equipment via donations from wealthier countries. The donated medical equipment is almost always second-hand, and often times fails to function with approximately 50% of all donated equipment inoperable. Some of the inoperability is due to the environments in which the systems are required to be used. For example, power outages are a frequent issue in many developing countries. Many medical devices are not designed to withstand this sort of scenario since it is a very rare issue in first world countries. Developing countries also lack technical experts, which means that there is often no one with the knowledge to fix the donated machines when they break. Spare parts are also not generally available. These issues generate a need for new, re-designed medical systems which provide the same purposes with Conformité Européene (CE) and FDA approved standards, but are "context-aware" in design to meet the environmental and user challenges encountered in developing countries. This is a large hurdle since the CE and FDA do not take into account the conditions in the developing world when creating standards[52].

Infrared medical tools do not currently exist in any capacity in the developing world. This means that there is no existing market specific to this area [21], which presents additional challenges. As such, any product successfully filling this void would be disruptive to the market with little to no early competition. An infrared sensor using a sulfur copolymer lens could fulfill this need. Although sulfur copolymer lenses are not ruggedized they can be replaced at minimal cost if damaged. Infrared diagnostic methods also tend to be non-invasive or minimally invasive. This is optimal in developing areas where the infection rate is generally high and hygiene standards may be low, with every wound having the potential to become infected. In some places in Africa the hospital rate of infection reaches up to 25%[53].

Many developing countries only have a per capita income of $500 or less. The governments of such developing countries may spend as little as $4-5 per capita on health care. Much of the money contributed by the governments of the developing world go towards hospitals and medical schools located in the country's capital region rather than to rural communities. Much of the cost for healthcare provided to developing areas is taken on by the United Nations including such organizations as WHO, UNICEF, and the World Bank. Other contributors are foreign aid agencies from developed countries, church-sponsored missions, relief organizations, and volunteer-assisted health care groups[54].

Another option for funding of projects involving developing countries are grants from philanthropic organizations. One of the largest philanthropic organizations is the Gates Foundation of which a primary objective of the foundation is to improve the health of populations in developing countries. The Gates Foundation has supported work in over 100 countries globally (including developed and developing countries), and has provided global medical grants to projects focused on developing countries ranging from $1,000 to $1.55B. The grant amount offered is largely dependent on the scope of the project. A grant involving sulfur copolymer lensed IR medical devices may fall under the Global Health or Global Development label[55]. Other charitable philanthropic organizations that may have the ability to provide grant funding to a medical IR project for developing countries include AMB Foundation, BD Foundation, Bohemian Foundation, Brach Family Charitable Foundation, Chanel Foundation, Chrysalis Trust, David Weekley Family Foundation, ECOM Foundation, Green Family Foundation, Harold Simmons Foundation, Henry E. Niles Foundation, Jackman Family Foundation, Johnson & Johnson Family of Companies Foundation, Lacewing Foundation, Lawrence Foundation, Penwel Fund, Frank Pernell Foundation, Philip and Irene Toll Gage Foundation, Robertson Foundation, Satter Foundation, SC Johnson Giving, Stavros Niarchos Foundation, Vibrant Village Foundation, Violet Jabara Charitable Trust, and the Virginia Wellington Cabot Foundation[56].

Much like developed countries, developing countries have similar issues driving the need for medical devices, such as aging populations, lifestyle diseases, and more awareness of overall health especially in urban areas[46]. Each country holds different social taboos, cultural priorities, government budgets, medical approval processes, import tariffs, and demographics. Some developing areas are not necessarily countries, but rather specific areas within a country. For example, although China is considered a high-income country, 29% of its population is in developing regions within the country. There is often a significant difference in healthcare between rural and urban populations within a country [54], as there was in the U.S. in Appalachia during the 1960's and 70's. All developing countries

and regions are markets worth considering. Some of those countries include Mexico, Malaysia [46], Cambodia, Rwanda, and Haiti[47]. Several countries have been considered by WHO for assessment for Emergency and Essential Surgical Care coverage. The below figure charts several of the countries in need of basic medical equipment[57]. The colored areas can be considered to be some of the countries categorized as developing countries which lack accessibility to key medical equipment. Due to the fact that there are numerous areas in this category, the following paragraphs show a very small sub-sampling of potential markets based on the country of Nigeria.

Estimated coverage of Integrated Management for Emergency and Essential Surgical Care (IMEESC), 2010

Initial introduction
Scale-up training throughout country
Training of trainers
Utilization of IMEESC tools/adaptation
Data not available
Not applicable

The boundaries and names shown and the designations used on this map do not imply the expression of any opinion whatsoever on the part of the World Health Organization concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. Dotted lines on maps represent approximate border lines for which there may not yet be full agreement.

Data Source: World Health Organization
Map Production: Public Health Information and Geographic Information Systems (GIS)
World Health Organization

World Health Organization
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Figure 17. Countries considered by WHO to require some form of assistance with Emergency and Essential Surgical Care[57].

The Nigerian market has the potential for high medical device demand as the Nigerian healthcare system is significantly lacking in suitable equipment especially in rural areas. Nigeria has 54 federal tertiary hospitals, 22 federal medical centers, and 9,000 private health facilities of which 2,600 are hospitals and clinics. As of 2014 Nigeria estimated 134,000 available hospital beds, equivalent to 0.8 per every 1000 of the population. The number of available doctors has grown at a rate of 3.8% since 2009. Nigeria's medical industry relies heavily on imports of medical equipment, in particular, there is a large market opportunity to export to Nigeria in the areas of medical imaging diagnostics including MRI, CT, X-ray, ultrasound, and mammography. While there is a high demand for diagnostic equipment, the

budgets of small and mid-sized diagnostics center are small and the current strategy is to buy and use second hand medical equipment. The largest factors in a successful sale from the Nigerian perspective are cost and after sales support. In 2013, a law was passed by the Nigerian government in which there would be no tariff on imported medical equipment. This law has not yet been implemented and a 20-25% tariff is still in effect. The recommended way to break into the Nigerian medical market is to use the relationships set up by the Commercial Service between the US and Nigeria including agents and distributors with local companies. The Nigerian market continues to grow, but many individuals rely on self-medication due to high costs of medical treatment provided by hospitals. Wealthy individuals often seek treatment internationally. The Nigerian government intends to spend $26.7 billion in upcoming years over an undisclosed period of time on their healthcare system including diagnostic centers, medical equipment, and construction of hospitals. The budget proposal was introduced in 2010 with a completion goal of 2015, but that timeline was not achieved. A new timeline goal is unknown, but is speculated to be 2020 to coincide with the government's plan to cover 100% of its population with medical insurance thus increasing the population which has access to hospital treatments. Currently, the majority of the Nigerian population relies on health product distribution via independent drug stores. Competition in medical exports to Nigeria include European countries, who hold the majority of the market, and China and India, who deal in the area of low end devices. In order to enter the Nigerian market registration with The National Agency for Food and Drug Administration and Control (NAFDAC) must be completed, and the regulations of The Standard Organization of Nigeria (SON) must be met[46].

5.2.4 Challenges

Regulation is a significant factor in the global medical realm. Mandatory standards have been put in place by the Global Harmonization Task Force (GHTF), and were built upon further by the International Medical Device Regulators Forum (IMDRF). The IMDRF plays a large role in a company's success to breaking into the medical market in developing countries[46].

In the US there are several medical associations and academies competing with each other. In Europe there just two accredited medical associations: the German Society of Thermography and Regulation Medicine, and the European Association of Thermology. Rather than competing, these associations work in cooperation with each other[49].

If a product is already approved by the FDA for distribution in the US then that product can be exported anywhere internationally without additional approval from the US although approval of the importing country must be attained. If a product is not approved for use in the US by the FDA then the product must follow the export process of the Federal Food, Drug and Cosmetic (FD&C) Act. A trend in developing countries is to have regulations that exceed even those in place in developed countries. This can cause US companies additional time and costs for requirement research, additional clinical trials, and added fees[46].

A challenge to consider is that there is currently no standard process among funding agencies, manufacturers, distribution systems, and government regulatory agencies[47]. Obstacles exist in exporting medical technology from the US. To enable success for US-based companies, market access

barriers must be reduced in order for the US medical industry to grow and survive on a global scale. This issue is considered a key component to the success of US industry making medical technology a National Export Initiative Priority. The US government must also reduce or remove tariffs on medical devices, address countries whose regulatory processes are not consistent with international standards causing discrimination against the US medical device industry, provide education on how to comply with international regulations, and provide comparable assistance to the industry as that which foreign entities enjoy in their own countries. Certain regions such as India, parts of Latin America, and parts of Asia charge high tariffs on US medical device exports which reduce the overall net sale of a product[46].

Another challenge that US medical device companies face is lowered international reimbursements. Globally, countries are dealing with rising health care costs and are attempting to make up for it by creating price caps, demanding price reductions, or limiting funds for medical devices. This can cause the reimbursement price to be lower than the value of the product in some cases. This practice has specifically been reported when dealing with Germany, France, Japan, Taiwan, Korea, China, and Brazil. Many of the existing "low cost" medical devices have had millions of dollars spent on research and development prior to being funded by a grant which also does not help a company when trying to achieve a profit[52].

In developing countries, those addressing medical needs are not necessarily trained physicians. As a result, the need for simple, easy to use diagnostic tools is compelling. Other desirable factors for a new tool would be to make it reliable, low-cost, handheld, and innovative. Ruggedization is also important and wet, humid, or dusty conditions should be taken into consideration. Those that would use the devices would require some sort of training. The most beneficial diagnostic device would be one with point of care functionality, meaning that diagnostic results can be determined on location at the site of measurement rather than having to transport the measurement to a different location for further analysis[47].

A government's decision when allocating resources for health care is often based on cost-effectiveness of the overall treatment often taking into account disability-adjusted life year (DALY) data compared to average population lifespan. Certain diseases may be largely ignored by a developing country if the DALY percent is not high enough for the country's government to consider health care a priority[54].

Percentage of DALYs by age and cause

Disease	DALYs (percent)				
	0-4	5-14	15-44	45-59	60+
Respiratory infections	18.1	7.4	2.5	1.8	4.3
Diarrheal disease	16.0	6.5	1.7	0.7	-
Measles, DPT, Polio	10.7	8.3	-	-	-
Tuberculosis	0.5	4.9	7.6	7.9	3.0
HIV	0.5	-	7.9	0.5	-
Intestinal helminths	-	11.9	-	-	-
Sexually transmitted diseases *	0.5	-	5.1	-	-
Other infectious diseases	9.3	8.0	5.1	3.4	1.6
Total, infectious diseases	**55.6**	**47.0**	**29.9**	**14.3**	**8.9**
Perinatal	18.6	-	-	-	-
Pregnancy-related disease	-	-	8.9	-	-
Injuries	5.6	17.8	23.5	7.6	3.9
Cancer	-	2.3	4.4	16.7	12.5
Cardiovascular diseases	1.0	3.0	6.2	25.0	41.6
Chronic respiratory diseases	1.9	3.6	2.3	5.0	11.1
Neuropsychiatric diseases	1.1	8.4	11.9	8.0	6.9
Other diseases	9.6	16.8	12.9	22.5	15.1
Total	**100.0**	**100.0**	**100.0**	**100.0**	**100.0**

* excluding HIV

Table 11. The DALY percent, or the measure of number of years of life lost due to poor health, for several diseases based on age group. [58]

5.2.5 Mammography Screening

5.2.5.1 Background

Some of the medical applications that have been identified as potentially benefitting from disruptive infrared screening and diagnostic equipment include various cancers, general fever detection, UTI diagnostics, diabetes monitoring, and brain injury imaging. Due to the wide swath of medical topics which could implement infrared imaging, this market report will focus on breast cancer screenings, an area with considerable research performed and market figures which show great potential for sulfur copolymer lenses. It is worth noting that the other medical areas listed above in combination with developed countries, developing countries, or other markets such as emergency disaster scenarios, and international airports in regions of increased epidemic risk may be additional market opportunities to explore[21].

Due to the high prevalence of breast cancer occurrences globally, and the significant amount of R&D completed on IR mammography techniques, breast cancer detection is an ideal market area for medical IR.

According to WHO, as of 2015, cancer is the leading cause of death globally. 14 million new cancer cases, and 8.2 million deaths caused by cancer occurred in 2012 alone. These figures are expected to grow by 70% over the next 2 decades. The leading cancers among men are lung, prostate, colorectal, stomach, and liver cancer, while among women the leading cancers are breast, colorectal, lung, cervix,

and stomach cancer. More than 70% of cancer related deaths occur in Africa, Asia, Central America, and South America. Early detection is considered the most important factor in preventing cancer related deaths[59].
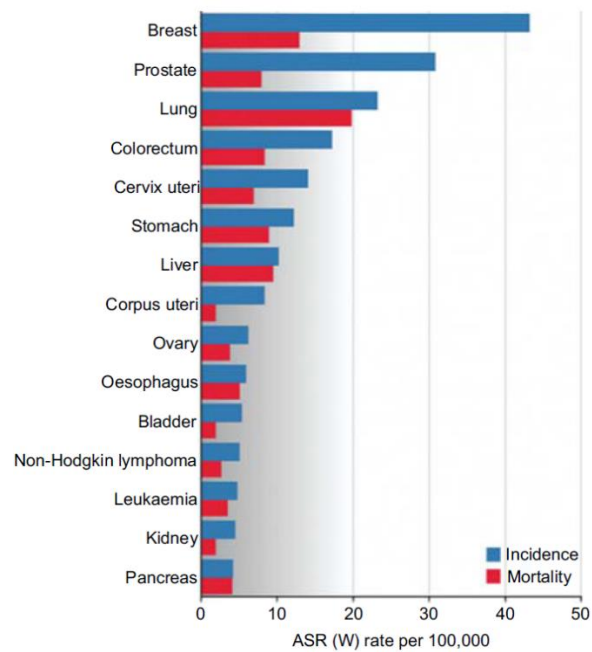
Figure 18. Incidence and mortality rates of various cancer types for the overall global population (combined male and female)[59].

Globally, breast cancer is the leading cause of death for women [60] with an estimated 521,000 deaths annually[59]. While the rate of incidence in low and middle income countries is generally lower than in high income countries, it still remains a leading cause of death with more than half of breast cancer incidences attributed to developing countries in which most cases are not discovered until late stage[60].

Region	Country and city	% Stage I/ localized	% Stage III-IV/ regional-metastatic	Year (s)	Source of data
Latin America	Mexico [4]	14	48	2002	Registry of the Mexican Social Security Institute
	Peru, Lima [5]	9	49	1985–1997	Instituto Nacional de Enfermedades Neoplasicas
	Brazil, [5]				
	Sao Paulo	10	67	1979–1989	Academic Hospital of the University of Sao Paulo
	Puerto Alegre	16	30	1975–1997	Academic Hospital of the Fed. University of Rio Grande do Sul
Asia	India: [6, 7]				
	Mumbai	8	35	1995	Tata Memorial Hospital Registry
	Trivandrum	4	53	1996	Hospital Cancer Registry Trivandrum
Middle East	Saudi Arabia [8]*	24	62	2004	National Cancer Registry
	Jordan, Amman [9]**	23	37	2008	Jordan Cancer Registry
	Egypt, Gharbia [7, 10]*	26	74	2000–2002	Tanta Cancer Registry
	Egypt, South [11]	11	50	2001–2008	South Egypt Cancer Institute
Africa	South Africa [12]				
	Blacks	5	78	1970–1987;	Grote Schuur, Cape town;
	Whites	31	31	1976–1997***	Provincial Hospitals of Port Elizabeth and East London, and Johannesburg General Hospital
North America	United States [13]	60	38	1999–2005	National cancer registry

*For these countries data were not provided by stage (I, II, III, IV) and were given only as localized versus regional or distant metastatic.
**The Jordan Cancer Registry for 2008 figures are 3% in-situ, 23% Stage I, 29% Stage II, 23% Stage III, 14% Stage IV, and 7.5% unknown.
***Data collected from 4 hospitals, three from the first-time period listed and the fourth from the second-time period listed.

Table 12. The table shows the stage of breast cancer at first diagnosis for a selection of low-income countries, middle-income countries, and the US[60].

Based on the decreasing mortality trend in the US, studies suggest that early detection and treatment of breast cancer could play a significant role in increasing the survival rate in countries of low and middle income. Currently, these countries often do not have affordable access to such options, or do not have the option at all[60].

TABLE 2: Mortality/incidence ratios for breast cancer in the USA between 1950 and 1975.

Year	Incidence/100,000	Mortality/100,000	Mortality/incidence ratio
1950	66·6	28	0·42
1955	64·9	29·8	0·46
1960	73	28·3	0·39
1965	82·9	28·5	0·34
1970	84·4	27·4	0·32
1975	119·2	31·6	0·27

Based on the Connecticut SEER database.

Table 13. As early breast cancer detection methods came into existence and expanded in the US from the 1950s-1970s, mortality to incidence ratio rates have decreased throughout the country[60].
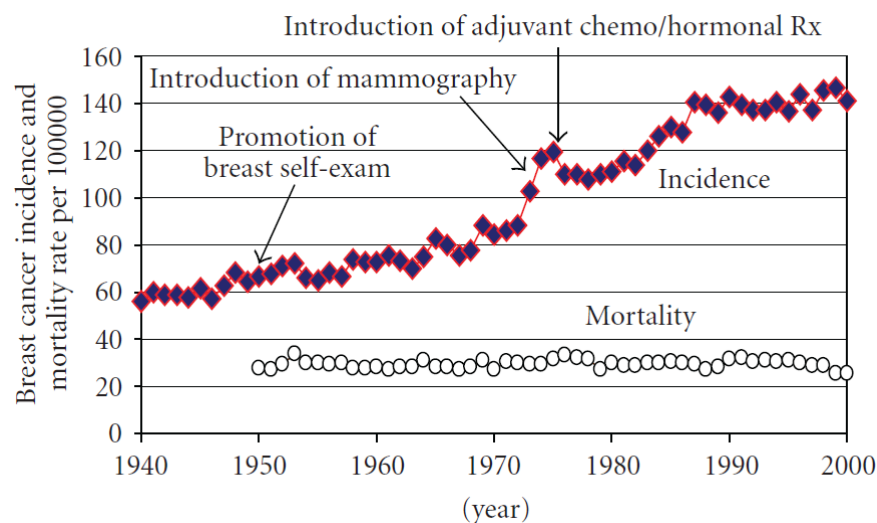
Figure 19. Breast cancer incidence and mortality in the US from 1940-2000. Although the incidence rate has significantly increased throughout the years, since the introduction of mammography the mortality to incidence rate has decreased[60].

Of all global breast cancer cases 52.9% occur in developing countries, and of all global breast cancer deaths 62.1% occur in developing countries. The mortality to incidence rate in developing countries is 37% compared to 20% in developed countries[61]. The rate of breast cancer incidences in developing countries is expected to increase quickly due to lifestyle changes in reproduction, a reduction of physical activity, and increased lifespan[60].

Care must be taken to ensure that the correct group is targeted, such as the right age demographic. If this is incorrectly identified then cost may significantly and unnecessarily increase due to more evaluations, and overloaded facilities[62]. A difference in the developing world is that the incidences tend to occur in younger women compared to developed countries[60]. The general age of onset of breast cancer varies based on lifestyle factors and genetics in a given region. For example, Chinese women develop breast cancer at a younger age than the global average[61].

| Country	Organizational level	Year implemented (nationwide)	Participation rate	Interval (years)	Screening age
LDCs					
Russia	Khanty-Mansiysky autonomous Region-Yugra	2007	67.50 %	2	>40
Brazil	State of Sao Paulo	2003	56.70 %	2	40–69
Mexico	Mexico City	2005	50 %	2	40–69
Uruguay	Nationwide	2006	Mandatory	2	40–59
Hungary	Nationwide	2002	56.30 %	2	45–65
Croatia	Nationwide	2006	60 %	2	50–69
Poland	Nationwide	2007	40 %	2	50–69
DCs					
Sweden	Nationwide	1986 (97)	81 %	1.5/2	40–74
UK	Nationwide	1988 (96)	76 %	3	50–64
Canada	Nationwide	1988	79 %	2/3	50–74
US	Nationwide	1991	83 %	1	$\geq$40
US-ACS				1	$\geq$40
US-ACR				1	$\geq$40
US-ACOG				1	$\geq$40
USPSTF				2	50–75

LDCs less developed countries, *DCs* developed countries, *ACS* American Cancer Society 2003, *ACR* American College of Radiology 2013, *ACOG* The American College of Obstetricians and Gynecologists 2011, *USPSTF* US Preventive Services Task Force (2009)

Table 14. Statistics on mammography screening programs for a selection of developing and developed countries[61].

In many locations throughout the world there are no options for mammography currently. These areas are beginning to rely on education and training to perform self-breast exams[60]. The discussion of breast cancer is mixed globally and varies from country to country due to differences in such issues as social stigmas. A single plan of action is not expected to work uniformly among all developing countries. While some countries consider implementing universal mammography screening programs, that is not a viable option for all countries. A more viable option for those countries which cannot afford or easily implement full mammography screening programs is a preventative screening mammography program in which only individuals who have been identified as high risk proceed to a full mammogram[61]. Most developing areas are a long way off from access to current mammogram technology available in developed countries. There has been little effort to create a low-cost technological mammography device alternative leaving that area of the breast cancer treatment chain wide open in regards to the market, but also nearly uncharted even in concept as most organizations are focusing on education and awareness rather than technological advances[60].
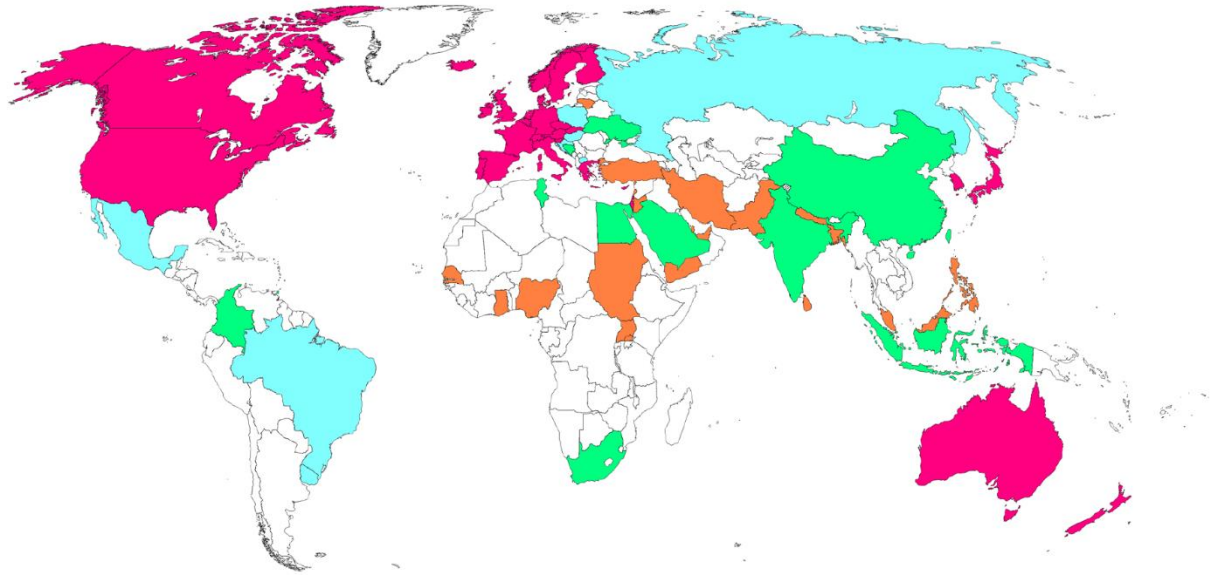
Figure 20. Mammography screenings globally. Red indicates developed countries. Blue indicates LDC with nationwide or localized mammography screening program. Green indicates LDC currently determining if a mammography screening program would be beneficial based on trials and studies of certain populations. Orange indicates LDCs which have surveys and questionnaires related to breast cancer awareness with some form of access to mammography. Uncolored countries do not have any mammography screening program or did not report any data[61].

Factors that a country's government may take into account when deciding if a mammography screening program is worth pursuing include target population, resources, ratio of cost to lives saved per year, per quality life year, per disability life year, among others. The specific factors that a country will take into account vary by country. A major factor that is likely to determine the demand for breast cancer diagnostic equipment by country will be based on the continued expansion of breast cancer awareness and education[61]. Each country has its own requirements for breaking into the medical market. For example, in Mexico, the Oportunidades program and Seguro Popular, and the Partners in Health program in rural Africa and Haiti, offer lessons to improve women's health and may have the potential to be used as an outreach source for new technology in those regional areas[60]. These organizations may have the potential to train community health care workers rather than nurses and physicians to carry out mammography diagnostics thus expanding the reach of mammograms to communities that are lacking in vital healthcare basics.

While breast cancer is becoming more prevalent in developing countries, it is still a major issue for developed countries as well. In the US among women, breast cancer death rates are higher than all other cancers, with the exception of lung cancer, and is the most diagnosed cancer, with the exception of skin cancer. 12% of women develop breast cancer in their lifetime with 40,450 deaths annually. There are 246,660 new cases of invasive and 61,000 non-invasive breast cancer in females discovered in 2016, and an additional 2,600 invasive breast cancer cases diagnosed in males in 2016[63].

41.2% of the US female population is 45 years of age and older equating to 64.4M individuals (according to the 2010 U.S. Census) in the age range recommended for mammography screening. As of December 2016, 39,251,908 mammography procedures were reported for a single year by 16,959 accredited locations[64].

Based on these numbers, ~61% of women in the target age range are getting mammography procedures leaving a large population of 39% of women who do not undergo a mammography procedure.

Figure 21. US female population by age in 2010. The target age range for mammography screening is 45 years and older[65].

5.2.5.2 Use Case

While there are several key components to early detection of breast cancer, including general education, mammography provides the best rate of early detection. In developing countries standard mammography often poses a problem due to the high cost of equipment, and lack of physical hospital space. Sulfur copolymer lenses have the potential to play a part as the lens component for a small, low-cost infrared mammography screening tool. Such a tool would provide greater access to mammograms to a much larger population of the women in developing countries.

This type of diagnostic tool could act as a preventative screening program which may be appealing to countries who want to improve healthcare, but minimize costs. A preventative screening program would be much cheaper to implement than a full scale mammography program. Another factor that may contribute to a country's willingness to accept a mammography screening program is its population's life expectancy to breast cancer patient rate. For example, Sudan has an average life expectancy rate that is 20 years less than that of a developed country therefore the lives saved through breast cancer screening

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do not benefit the overall country's population significantly making the issue less of a priority to that specific country[61].

When choosing ideal regions to implement a screening program, it is beneficial to consider that certain populations are genetically more receptive to traditional mammography screenings with respect to breast density. Traditionally mammography techniques are more effective in scanning less dense breast tissue. Asians have the densest breast tissue, while Africans have the least dense, with the density decreasing with age[61].

While populations in developed countries generally have wide access to mammography screening, figures show that a large percent of the population does not participate. This may be due to high costs of the procedures without insurance coverage, or a lack of willingness to be exposed to x-ray radiation levels on an annual basis, however minimal.

5.2.5.3 Existing Technology, Competition, and Potential Partnerships

No existing portable, robust breast cancer screening devices targeted for use in developing countries have been identified. This means that there is no existing apparent competition or potential partners. A large amount of research has been performed using infrared technologies that could be applied to development of such a device. Developed countries have limited successful thermal mammography devices in use including Spectron IR Thermography in the US, MammoVision in the EU, and ReguVision and FlexiVision by InfraMedic also in the EU. These companies could be considered for partnership in creating a brand new device catered for use in developing countries, or altered as is with low-cost replaceable lenses for developed countries potentially reducing the overall cost of medical procedures. Regardless of the infrared technology used, sulfur copolymer lenses will have little if any competition as a low cost disposable lens.

Approximately 5% of standard mammograms result in a positive reading. Of these, 80-93% are false positives. Standard mammography procedures also miss 10-15% of the positive cases that should be detected[48].

There are two proven methods of identifying abnormal breast tissue using infrared imaging; NIR spectroscopy, and thermography. An over diagnosis rate of 1-10% is generally accepted [61] and the effectiveness of a sulfur copolymer lensed IR device would need to meet or exceed these standards.

5.2.5.3.1 Near-Infrared Spectroscopy (NIRS)

NIRS has the ability to diagnose several types of cancer by analyzing a sample of cells, serum, saliva, or tissue. This technique identifies differences between endogenous chromophores for cancer and normal tissues. This process can use any combination of oxy-hemoglobin, deoxy-hemoglobin, lipid, and water bands. This technique can often be applied using non-invasive, or minimally invasive procedures. In the case of breast cancer the techniques are minimally invasive. Handheld near-infrared devices currently play a part in the military, fire and rescue services, law enforcement, environmental agencies, and food control. They do not currently have a role in cancer related services, but it is recognized that there is

much potential for this type of role. A challenge when miniaturizing a device for this purpose could include ensuring that the precision and performance of the technical capability is not degraded. Recent studies have proven that the same quality can be achieved with handheld devices as compared to larger benchtop devices. Based on research performed to this point by various institutions, NIRS is not yet fully developed and can be further optimized, but shows great potential for future use[59].

Spectroscopy of:	Cells	Serum	Saliva	Tissue
	Breast Cancer	Breast Cancer	Oral Cancer	Breast Cancer
	Prostate Cancer	Brain Cancer		Bladder Cancer
		Choroidal Cancer		Colorectal Cancer
		Prostate Cancer		Pancreas Cancer
				Skin Cancer

Table 15. Table showing the cancers diagnosable by NIRS and what type of sample is required for diagnostics[59].

Wavelength range (nm)	Measured parameters
630-900	Changes in oxy-haemoglobin and deoxyhaemoglobin status, quantification of total haemo-globin; concentration and tissue oxygen saturation
967,980,1154, 1195, 1402, 1444, 1888, 1944	water
1471,1911	DNA
2055, 2172,2347	Proteins
1111-1265 and 1666-1818	Lipids
650-1400	Tissue scattering differences

Table 16. Wavelength ranges used in the NIRS process for different types of cancer[59].

Sulfur copolymer lenses are transmissive in the NIR spectral range and would therefore be compatible as the lens component for NIRS technology. A couple of challenges with regards to this technology exist. One is that the procedure related to breast cancer detection techniques is minimally invasive. This opens the possibility for infection which can be a concern to both developing and developed countries. The other challenge with this type of technology is that it has not been fully developed yet, and needs to be further optimized. An advantage to NIRS is that there is potential for detection of several types of cancers which could significantly expand the market in which sulfur copolymer lenses could be used.

5.2.5.3.2 Thermography

Studies show that thermography can achieve an average specificity and sensitivity of 90% when testing for abnormal breast tissue by detecting increased blood flow caused by vascular proliferation from angiogenesis, which has a link to tumors[50]. This technique also relies on surface heat pattern symmetry to compare healthy to unhealthy areas[49].

In order to meet optical specifications required to image the skin profile of a human an infrared camera must have a minimum resolution of 320 x 240, and have a narrow temperature range, such as 20-40 °C to allow for more detail in temperature measurements, and a readout area no smaller than 8x8 pixels[50]. The device must have a thermal sensitivity better than 80mK, with high quality devices displaying a sensitivity of at least 50mK. Measurement readings must be reproducible with a change of no more than 2°K between identical readings at a temperature of 30°C, with high quality instruments displaying no more than a change of 1°K between readings[49].

Using a thermal imager requires very little effort on the user's end since the imager is doing all of the measurement. It is also non-invasive, requiring no direct physical contact to the patient's skin. The act of thermography holds no threats, and does not require any harmful radiation. Images can be captured and stored on the device for instant review or transferred to other locations for further review. Thermography as a technique of breast pathology has now been scientifically accepted. While at one point appropriate thermal imagers cost a minimum of $45,000, there are now capable imagers for less than $2,500 from Wahl. In addition to breast cancer, other issues commonly identified by thermography are muskoskeletal, and circulation problems[66].

A study performed on 100 women showed that thermal screening techniques were more accurate than their standard counterpart. When used in combination with standard mammography, thermal imagery increased the sensitivity of the procedure from 84% to 95%. The infrared technique was able to detect vascular and metabolic changes caused by tumors in earlier stages of breast cancer. Tumors develop a localized blood supply which is used to sustain their growth[48].

Thermography for breast cancer screening purposes is FDA-approved. In the US a mammogram would be recommended post thermography only if the thermogram measurements indicated abnormal results. This indicates that the technology could be used as a screening device for developing countries. The thermography procedure can be performed on a sitting or standing patient. Currently the results are forwarded to a professional who analyzes the images. Images can be compared between the two sides of the body and temperatures which vary by 1-3°C may be an indicator of abnormality. Keeping a

record of on a specific individual will also help in future analysis of thermogram results for comparison. In the US, insurance often does not cover the thermography procedure. The cost in the Mid-Atlantic region is $150 for breast thermography[48].

Spectron IR provides medical thermography systems to the US market. The lowest end system that they provide uses a 320x240 uncooled microbolometer FLIR camera, provides thermal sensitivity of <0.05^{O}C at 30°C, has a frame rate of 9Hz, and is sensitive over the spectral range of 7.5-13 microns[67].

Since thermal imaging is non-invasive there are fewer limits to the type of environment in which it can be applied. It does not require a sterile environment such as a hospital. Thermography is a well-researched technique and is already widely in use in several non-medical fields, and has also seen limited use for medical purposes. Since thermography is already FDA approved for the purpose of breast cancer screenings, it may be easier to distribute a device using the technique to the international market. A disadvantage to using a thermal technique is that the sulfur copolymer lenses will require further expansion of transmissivity into the LWIR wave range.

6.0 Financial Analysis

6.1 Sulfur Copolymer Material Costs

According to an October 2012 Hydrocarbon Engineering article, elemental sulfur has experienced large price fluctuations in the recent past, but currently stands as a moderately stable market and is expected to remain so in the near future. However, an upcoming excess of elemental sulfur supply with a relatively small market demand may once again cause price fluctuations and sulfur market instability of unknown levels[68]. Based on past market trends, price fluctuations have tended to drop below the normalized value more often than increase as overall demand is not high enough at this time to justify sustained price increases. Current trends point to reasonable and relatively low prices in the foreseeable future. While an increasing demand for sulfur is expected, demand should not exceed the large supply available at any point in the near future although environmental emission laws and regulations may limit supply to an extent.

In the recent past the price of elemental sulfur has seen large swings from an average high price per ton of $264.04 in 2008 to an average low price per ton of $1.73 in 2009[69]. At times within the annual price cycle, elemental sulfur had been reported to cost as much as $800 per ton during the 2008 recession. With global economic recovery from the 2008 recession as well as increased demand for elemental sulfur over a range of industries, over the past few years the sulfur market has been strong with relatively stable and fair prices[68]. Table 17 shows the recent historical average annual price of sulfur while Table 18 shows the forecasted price of sulfur into the near future.

	2010	2011	2012	2013	2014
Reported average value of elemental sulfur per ton in $USD	70.16	159.88	123.54	68.83	95.00

Table 17. Average value of elemental sulfur per ton as reported by the U.S. Geological Survey[70].

	2011	2012	2013	2014	2015	2016	2017
Vancouver ($/ton)	208	182	125	105	95	105	115

Table 18. Annual average price forecast created in 2012 by the National Iranian Gas Company[71].

Sulfur price instability over an annual cycle in recent years has been due to demand fluctuations; increases in prices, like those seen in 2014, have arisen from large regions like China, increasing their need for the element as development continues[70]. Figure 22 shows the consumption of sulfur by world region.

World Consumption of Sulfur—2014
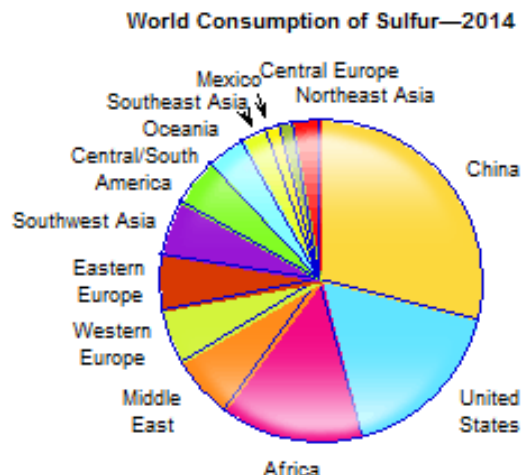
Figure 22. Global consumption of sulfur based on consuming country[72].

Elemental sulfur is largely created as an unwanted byproduct from processes such as the hydroprocessing of petroleum in which the unintended and poisonous byproduct hydrogen sulfide is created. Each year 600 billion tons of sulfur as byproduct are created from gypsum, coal, base metals, natural gas, and oil of which 5 billion tons are recoverable resources. In Europe and the US the removal of sulfur found in oil and gas has been mandatory by law since the 1980s as a way to reduce acid rain and forest degeneration caused by SO_2. Additional laws implemented within the past decade have established a reduction in gas and oil used by land based transportation (cars, trains, etc.) to contain 15ppm or less of sulfur[68].

The US ranks among the top producers of sulfur with 9 million tons per year produced, second after China's 12 million tons[70]. Closely following are Canada, Russia, and the combination of the Middle East, Saudi Arabia, Kuwait, Qatar and the UAE. The ample availability of sulfur in the US allows for low costs of attainment of sulfur for US based industries. The US alone creates 22,000 tons of sulfur per day from oil refineries and gas plants [68] and contains about one-fifth of the world's sulfur resources. In 2014, US consumption of elemental sulfur was largely supplied domestically at 63% while byproduct from acid made up 6% of the US market. The remaining 31% was imported from foreign countries[70]. The global consumption of sulfur is expected to increase by about 4% each year with a total of ~11% increase by 2019[72].

Although research shows that trends within the oil and gas industry indicate a declining interest in elemental sulfur as a profitable commodity, byproduct production will continue to create increasing amounts of sulfur as byproduct by many million tons. Oil and gas production from Saudi Arabia, UAE, Kuwait and Qatar has been predicted to grow significantly resulting in an increase of sulfur byproduct

from 7.1 million in 2012 to 15 million tons per year by 2016[68]. The oil sands of Alberta, Canada are also expected to significantly increase sulfur production in the near future[70]. As other industries continue to grow they too will increase the annual sulfur supply. Nickel and copper mining is expected to produce 2 million tons of sulfur per year as recycled material from the sulfuric acid used during the mining process[68]. In 2014 there was an increase of 5% in sulfur production from the petroleum and gas industry from the prior year. Sulfur is able to be extracted from petroleum and sulfide ores away from where original petroleum or sulfide ore processing takes place, therefore the US is able to process sulfur from foreign imports of petroleum and sulfide ore. US sulfur processing of Canadian bituminous crude is expected to increase. Elemental sulfur production from both gas and sulfuric acid byproduct is expected to remain relatively unchanged. According to USGS the global production of elemental sulfur has slightly increased from the past year and will continue with the trend in the future. The total global production of sulfur amounted to 72 million tons in 2014[70]. Large quantities of sulfur from Canada, the Middle East, and Eastern Europe are expected to go into inventory each year[72]. There exists a nearly limitless amount of sulfur globally creating a large surplus. Sulfur directly from or associated with the processing of evaporite, volcanic deposits, natural gas, petroleum, tar sands, and metal sulfides totals nearly 5 billion tons. Currently, processes to extract sulfur from such materials as coal, oil shale, and shale are very expensive, but could provide large amounts of sulfur totaling 600 billion tons. Expensive sulfur processing costs apply to gypsum and anhydrite, which can yield a nearly endless amount of sulfur[70].

Several other new or expanding industries will greatly increase the global sulfur demand for various processes. In the short term, as an expected temporary boost to the sulfur industry, drought in the US has caused an increased need for fertilizer to raise soil quality. Within the next decade an additional 4 million tons of sulfur are expected to be used for fertilizer production by China and India alone as their economies continue to mature and their middle classes grow. This is expected to continue as a long term trend with a 2 to 3% increase in fertilizer demand each year. Also in the near future, Africa has the potential to use 20 million tons of sulfur per year if new agricultural industry is developed there. The growing solar industry may also become an added player in the sulfur market as one of the most efficient solar energy collectors, polythiophene, requires sulfur with an estimated 0.5 tons required per rooftop with installed solar panels. The base metal mining industry is also expected to grow requiring an added demand for sulfuric acid. There are multiple potential uses for sulfur that are expected to catch on in the market gradually including usage as a concrete additive requiring 1 million tons of sulfur per year in the US, sulfur enhanced asphalt requiring 2 million tons of sulfur per year in the US, and sulfur enhanced fertilizer. These usage cases are expected to take up to a decade to attain substantial market status[68].

Although many sulfur compounds are highly toxic, such as sulfur dioxide, elemental sulfur is in fact non-toxic to humans with only minor irritations to the eyes, skin, and respiratory tract possible when interacting with it in its elemental form[28]. Sulfur in powder form is flammable, and caution is required to prevent any such situation as burning can cause the sulfur to decompose into highly toxic sulfur dioxide (SO_2). Since elemental sulfur is not toxic, no expensive handling or processing procedures are

required when creating lenses made from the primary component of sulfur. Basic lab equipment of goggles, rubber gloves, and a lab coat are enough to prevent potential irritation caused by sulfur[73].

All other materials required for the production of sulfur copolymer lenses are common, relatively low cost pieces of lab equipment and chemicals. Necessary lab equipment includes glass vials, a magnetic stir bar, thermostat bath with oil, syringe, metal spatula, kapton film, Teflon coated aluminum foil, plastic beakers, a hydraulic press, a vacuum oven, and a heat oven. Additional chemicals required include 1,3 diisopropenylbenzene (DIB), silicone elastomer base, silicone elastomer curing agent, polydimethylsiloxane (PDMS), and 1,2-dichlorobenzene (DCB). All chemicals used are considered non-toxic, with the exception of 1,2-dichlorobenzene.

6.2 Estimated Market Figures and Cost of Production

WHO estimates that 521,000 women die annually from breast cancer[59]. Nearly 50% of these cases and 58% of deaths occurred in developing countries. In most developing countries the incidence rate is below 40 for every 100,000 women. In Eastern Africa, also a developing region, the incidence rate is 19.3 per 100,000 women. The lowest incidence rates occur in Africa, but those figures are expected to increase. While survival rates in high-income countries are 80% or greater, in mid-income countries the rate is 60%, and just less than 40% in low-income countries. The lower rate of survival in low-income countries is largely attributed to the lack of early detection, lack of efficient diagnosis, and lack of treatment facilities[62].

There are an estimated 312,000 deaths attributed to breast cancer in LDCs annually, and an estimated 624,000 – 850,000 women in mid and low-income countries with breast cancer every year. This estimate is based on the low end statistic from WHO of 521,000 global breast cancer deaths that occur annually[6], and the high end statistic from the Susan G. Komen foundation that there were 1.7 million new cases of breast cancer diagnosed in 2012[74], along with the statistic that about 50% of these cases occur in developing countries[62]. The population of an older demographic is continuing to rise in developing countries as health standards continue to improve, positively affecting lifespan. Breast cancer is more likely to occur in older women, which would signify that the population affected by breast cancer will continue to grow. A general estimate based on figures from GeoHive is that there are approximately 381,010,735 women 45 years of age or older living in Africa, Central America, South Central Asia, and Southeast Asia. While this figure does not specifically encompass only developing countries, or all developing countries, it does focus on regions of the world in which the majority of developing countries are geographically located[75].

	45 – 64 years old	65+ years old	Total	Estimated Total Female Population
Africa	124,903,796	39,632,587	164,536,383	83,913,555
Central America	27,034,662	10,285,773	37,320,435	19,033,421
South Central Asia	300,446,591	92,203,339	392,649,930	200,251,464
Southeast Asia	116,539,983	36,033,145	152,573,128	77,812,295
Total	568,925,032	178,154,844	747,079,876	381,010,735

Table 19. Table showing the combined male and female populations, and the estimated female only population in general world regions containing majority LDCs[75].

In order to break down the figures into a country by county estimate, we will consider the case of Nigeria. In the case of Nigeria, one of the fastest growing countries in the world, the men to women ratio is 5:6[76]. Nigeria's rural population in 2015 was 103,411,000, and is predicted to grow to 107,758,000 by 2025. Based on the 5:6 ratio and the statistic that 15% of the population in Africa is 45 and older it can be estimated that 8,460,900 women at least 45 years of age lived in rural Nigeria in 2015, which will grow to 8,816,563 by 2025[77]. If one sulfur copolymer lens is able to be used to image 100 patients then it would require 84,609 lenses in 2015 and 88,165 lenses in 2025 to provide breast cancer screenings to the estimated 8,816,563 rural women of Nigeria. Table 20 provides cost estimates of all materials and equipment required to create sulfur copolymer lenses on a mass scale of the estimated 84,609 annual lens requirement for Nigeria. This number can also act as a reasonable estimate for initial market within the US. Since the US already has mammography capability, it is unlikely that all current techniques will be replaced immediately, therefore a very small percentage of the current 39M annual mammography screenings performed can for expected US market entry figures. In the US case, each exterior system lens is expected to be replaced between each patient[64].

Materials	Bulk Cost (USD)	Quantity Required per 84,609 devices (2 lenses per device)	Total Cost (USD)
Elemental Sulfur S8	115 /ton	19 tons	2,300
Selenium Disulfide	3.75 – 63 /lbs.	373 lbs.	23,498
1,3-diisopropenylbenzene (DIB)	900 /ton	2.66 tons	2,394
Methanol	800 /ton	1.046 tons	836
Tetrahydrofuran	6.28 /kg	21,152 kg	132,906
Injection Molding	0.44/lens	169,218 lenses	74,445
Total			236,379

Table 20. Table providing cost estimates of materials and equipment used for mass production of sulfur copolymers lenses[60, 78, 79, 80, 81, 82].

All core materials, as well as the processing method of injection molding are relatively low cost. The material which is most likely to fluctuate in price is selenium disulfide. The price of selenium has a direct inverse correlation to the mining of copper, copper and nickel, of which it is a byproduct. With only 25% of the world's copper refineries reporting selenium recovery, it is difficult to determine the selenium supply. In recent years the price of selenium has fluctuated between $3.75 - $63.00/lbs. Calculated lens manufacturing costs took the highest selenium price into account[83].

Based on production of 169,218 lenses it is estimated that the materials and manufacturing cost would be $236,379, equating to $1.39/lens. In order to determine a more accurate price for all materials a pilot scale production with raw material providers should be carried out.

It is worth noting that every country is different, and will thus have varying statistics leading to unique results. The exact ratio of men to women varies by country and more precise figures specific to each country can be gathered from United Nations statistics.

With their relatively low material cost, sulfur copolymer lenses have the potential to be a component in an IR medical device viable for use in developed, or developing countries when compared to statistics on similar current medical devices. The average life cycle for a medical device unit is 18 to 24 months[46], and the lowest end medical infrared system which Spectron IR offers to US costumers costs $375/month[67]. While sulfur copolymer lens life cycle is well below the average product life cycle duration, their low cost allows them to act as a disposable product achieving the functionality of other lenses. The potential for a significantly lower cost mammography device is promising when compared to current devices available in developed countries.

Regardless of which developing country is considered for a potential market, the overall device (lens, sensor, and software) cost should not exceed more than $4-5 per patient on the high end. This requires that the overall device cost not exceed $100. From a technical standpoint, the least developed piece of a medical IR setup is the software which may result in being the most expensive device component[49]. Developed countries can afford to spend more per capita, and therefore a higher mark up on products can be used.

Based on the expected market outlook, cost of materials, and cost of processing, an estimated financial perspective could be roughly calculated. Estimations include cost of sales, R&D expenses, capital expenditures, estimated net sales, and estimated operating margin. Table 21 shows the estimated figures for a developed country market, and Table 22 shows the estimated figures for a developing country market.

Market for Developed Countries	Estimated Costs (USD)
Cost of Sales	236,379
Capital expenditures	125,000
Net Sales	1,015,308
Operating Margin	64.4%

Table 21. Rough estimate of costs of initial developed country market of sulfur copolymer lens startup production.

Market for Developing Countries	Estimated Costs (USD)
Cost of Sales	236,379
Capital expenditures	125,000
Net Sales	758,096
Operating Margin	52.3%

Table 22. Rough estimate of costs of initial developing country market of sulfur copolymer lens startup production.

A proposed sales price of $6/lens for a developed country, and $4.48/lens for a developing country are proposed. The larger markup which a developed country can afford, allows the operating margin to be 12% larger in comparison to its developing country counterpart based on the first year value of a 5 year depreciation of capital expenditures.

7.0 Conclusion

Steady growth of the IR imaging device market lends an advantage to the potential for market success of sulfur copolymer based infrared lenses as the IR market will increasingly look to reduce costs to meet demand of everyday consumer devices geared towards the consumer.

Elemental sulfur is widely abundant and has a relatively small demand putting it at ideal prices for consumers of the raw material. Although at times unstable, past trends show that instability has usually been in favor of consumers of sulfur with temporary major price reductions. As the main building block for sulfur based copolymer lenses, elemental sulfur price trends and supply outlook are favorable as related to the supply needed in manufacturing of sulfur copolymer based IR lenses.

Currently, our proposed sulfur copolymer based lenses hold a great advantage over other IR materials in that they are non-toxic, and use inexpensive materials and manufacturing processes. Our sulfur copolymer lenses show much potential in the optical and mechanical characteristic areas necessary for success in the market such as a wide transmissive wavelength range into the MWIR band, water insolubility, easy processing procedures, and the positive optical qualities of relatively low chromatic dispersion and low birefringence. However, some of the material characteristics hold room for improvement. Upcoming research on sulfur copolymer optics should improve the areas in which the material is currently falling short of meeting ideal industry standards including the relatively low index of refraction, transmissive efficiency, and transmissive wavelength range expansion into the LWIR. If progress in these areas can be achieved then sulfur copolymer based lenses have the potential to break into the IR market as a novel, low cost IR lens option.

The US Air Force and the National Science Foundation have committed funding for further development and improvements to sulfur copolymer materials to optimize IR transmission properties. Phase I of the upcoming testing will include the substitution of selenium for a portion of the elemental sulfur. This is expected to improve the transmission efficiency of the sulfur copolymer lenses and raise their refractive indices. The use of selenium was not factored into the financial summary above. Phase II will include the reduction of hydrogen in the chemical makeup to expand transmission efficiency into the LWIR band. This process was also not factored into predicted costs.

The medical market is expected to expand globally due to a variety of factors including increased average lifespan, economic progress of developing countries, and shift in medical needs of developed countries. There is great potential for medical IR market success in both developed or developing countries, although the benefits and challenges differ depending on which market is explored. A challenge to the overall medical market is the lack of consistency of standards, rules, and regulations from country to country.

Developed countries hold the majority of the market share and provide a wealthier consumer base which will be able to handle a higher price mark up. This allows for greater profit. Additionally, newly designed sensor and software components are not necessarily required which may allow for a shorter timespan to bring a sulfur copolymer lensed medical device to market. Developed countries can benefit from the low cost of sulfur copolymer lenses, which may allow for medical procedure costs to be

reduced. This may in turn allow more of the population to be willing or able to partake in important medical procedures. Additionally, sulfur copolymers have the capability to provide additional health benefits. Not only may they help to reduce hospital stay infection with their disposable properties, overall medical IR procedure have shown to be more effective in diagnostics of disease at earlier stages in several cases when compared to standard non-IR medical techniques. Developed countries, however, do face very strict country dependent regulations and standards to bring a medical product to market. There is also a current lack of general medical community acceptance of IR medical techniques due to poorly performed decades old test trials. Based on more recent studies and trials resulting in favorable results, this perception should be nullified. In order to change the opinion of the medical community, further high quality peer-reviewed testing will be required costing time and money. Although the limited existing medical IR market within developed countries can be seen as beneficial from a potential partnership standpoint, it can also provide a challenge if those companies are unwilling to partner, or if a lack of need is seen for further improvements to the technology already in place.

Sulfur copolymer lenses may be ideal for use in medical IR products targeted toward developing countries. Many IR medical procedures which would use sulfur copolymers are non-invasive resulting in significantly decreased risk of infection from medical procedures. Unlike in developing countries in which one exterior lens could be used per patient, due to cost limitations it would be necessary for one exterior lens to be used on several patients. However, if a lens were to break during usage or transport, a lens could be easily replaced at minimal cost. Due to lack of space in hospitals within developing countries, and the need to be able to transport medical equipment to rural areas, sulfur copolymers with their reduced focal length would be ideal for a handheld or small system. Although the process to meet standards and regulations in developing countries may be rigorous, with processes varied from country to country, developing countries generally have less strict regulations in comparison to developed countries. Due to the lack of medical equipment in developing countries there is often limited or non-existent access to medical procedures. This means that if a viable solution were presented there would be great demand from developing countries. Currently there are few groups targeting medical products to combat the lack of healthcare in developing countries, and no known groups working on low cost IR imaging solutions. This signifies that there is no current competition in the medical IR market for developing countries, but there will also not be any current development to partner on tailored specifically to this use case. Exporting a medical product to a developing country can incur a tariff dependent on the country and their laws. This tariffs can often be quite expensive causing detrimental effect on profit.

The cost of manufacturing sulfur copolymer lenses on a large scale is very reasonable and much lower cost than current competition. The price of the main component, sulfur, is expected to remain low and relatively stable in upcoming years. The contributing material which may experience the largest price fluctuations is selenium which even at its expected maximum price is low cost enough to maintain the low price point of sulfur copolymer lenses. Based on the low cost of sulfur copolymers, there is a large profit potential in the developed countries market. While the developing countries market, with its economical limitations will be more difficult to achieve a profit, there is a promising opportunity for success via additional funding from philanthropic organizations.

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