

Characterization of candidate bonding glasses for composite IR window structures

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ABSTRACT

Although there are several materials which have properties that make them attractive as IR window materials for electro-optical systems operating in the 8-12 μm range, no single material possesses the superior mechanical, optical, and thermal properties required for current supersonic window applications. Hence, composite structures have been examined for use in airborne window systems to maximize erosion resistance, provide high optical quality and maintain thermal stability. This paper reports the identification of a suitably robust bonding glass possessing the needed thermal, mechanical and optical properties for use in a ZnSe/glass/diamond composite structure. Recent results of our property characterization studies on candidate glasses are reported.

Keywords: composite window, chalcogenide glass, infrared, ZnSe, diamond

1. INTRODUCTION

IR windows for supersonic aircraft are subjected to extreme conditions that require them to be extremely durable. Although there are materials available that meet the IR transmission requirements in the 8-12 μm region, materials that possess good optical properties usually do not have the optimal mechanical properties to withstand the environmental effects of flight.¹ Composite structures have been developed to address these requirements for more than a decade, using various materials and methods.²⁻⁴

Preliminary experiments on composite hot-pressed ZnSe/chalcogenide glass/diamond layered structures have been performed.⁵ Structures prepared to date exhibited moderate rain erosion resistance; however, the glass bonding layer (referred to as chalcogenide A), critical to the thermal and mechanical integrity of the composite, possessed a high thermal expansion (46.8 $\mu\text{m}/\text{m}\cdot^\circ\text{C}$), low glass transition temperature ($T_g = 116^\circ\text{C}$), low hardness (37.2 kg/mm^2), and a slightly lower refractive index (2.135) compared to the adjacent ZnSe and diamond materials ($n_{\text{diamond}} = 2.376$ and $n_{\text{ZnSe}} = 2.41$ in the 8-10 μm region). Bonding-glass samples were useful, but optically, mechanically and thermally substandard for the desired application.

To improve the erosion resistance, thermal stability, and stress distribution within the composite associated with expansion mismatch, the present study focused on optimization of the chalcogenide bonding glass. The specific goals of the current study have been to engineer a glass that exhibited the following properties: (1) a refractive index closer to 2.41 to match the indices of the cladding and substrate in the 8-12 μm window, (2) a harder, tougher glass to improve erosion resistance,⁶ (3) a glass with a T_g near 200 °C to expand the thermal range over which the composite could usefully function, and (4) a glass with a lower thermal expansion coefficient to reduce stress due to thermal expansion mismatch between each of the composite layers.

Previous work examining ZnSe/glass/diamond and ZnSe/glass/ZnS composites used a bonding glass in the As-S-Se system.^{2,5} This glass system was chosen as a starting point for our experiments because of its broad glass forming region and well-studied composition dependence on physical properties.⁶⁻⁸ The results of the physical property evaluation of several new glass compositions are reported.

2. EXPERIMENTAL PROCEDURE

2.1 Glass processing

Ternary glasses were melted containing varying As-S-Se ratios. The glasses (typically 10 g melts) were batched in an inert nitrogen atmosphere glove box in silica ampoules. Glasses were batched using 99.99% purity or better elemental starting materials. The ampoules were then sealed with an oxy-methane torch under vacuum. The glasses were melted in either a Thermolyne 21100 rocking furnace or in a Thermolyne 1300 furnace. Depending on composition, samples were taken to a temperature of about 700-900 °C and gently rocked for 10-30 minutes. The glasses were removed from the furnace after 20 hours and allowed to air-quench. Samples were broken out of ampoules and formed as necessary for subsequent analysis.

2.2 Mechanical analysis

Disk samples of glass (typically 2-3 mm thick) were prepared for examination of Vicker's microhardness. Hardness testing was performed on a Shimadzu DUH-202 Microhardness tester. A static load of 10 mN (10 g) was used for the experiments, and the reported hardness value obtained is the average of 5 tests. Errors for hardness values are typically +/- 5%. However, errors of 10-15 % were encountered on some samples due to lack of parallelism.

2.3 Thermal analysis

Thermal analysis experiments to determine the glass transition temperature (T_g) and evidence of crystallization were carried out on a TA Instruments SDT 2960 simultaneous DTA-TGA (Differential Thermal Analyzer-Thermal Gravimetric Analyzer). Glass samples of 15-30 mg were placed in aluminum sample pans and were heated under a nitrogen purge of 100 mL/min at a ramp rate of 10 °C/min. T_g was determined by the intercept method (the point of intersection of tangents from the baseline and the

midpoint of the initial decrease of the endothermic transition). The sensitivities of the balance and DTA temperature were 0.1 μg and 0.001 $^{\circ}\text{C}$ respectively. No crystallization was noted in the compositions investigated in this study.

Disk samples prepared above were used for coefficient of thermal expansion (CTE) measurements. Experiments were performed on a TA Instruments TMA 2940 Thermomechanical Analyzer, using a heating rate of 5 $^{\circ}\text{C}/\text{min}$ and a load of 0.05 N. The slope (Δ thickness / Δ temperature) was determined from the linear portion of the expansion curve, and the upper temperature was typically 70-90% of T_g . The sensitivity of the Δ thickness measurement was 100 nm.

2.4 Optical analysis for refractive index

Refractive index values were calculated from measured transmission and reflectance on thin layers of glasses using spectrophotometric techniques in the 8-10 μm range.⁹ Experiments were carried out on a Vomem MB-110 FTIR. Two calculated values for the index on each material were obtained by attributing losses to either scatter or absorption. The average of these values was used for our study.

3. RESULTS

The results of the thermal, mechanical, and optical property measurements are summarized in Table 1. Glasses are listed in the table based on their arsenic content. Complete compositional information of samples shown is not available at this time.

Table 1. Experimental results of chalcogenide property measurements

Chalcogenide ID	As-S-Se glass (mole % As)	average coordination number	T_g ($^{\circ}\text{C}$)	CTE ($\times 10^{-6} \cdot ^{\circ}\text{C}^{-1}$)	temp range for CTE ($^{\circ}\text{C}$)	Vicker's hardness (kg/mm^2)	refractive index (8-10 μm)
A	18	2.18	116	46.8	40-80	37.2	2.135
B	35	2.35	182	31.0	58-160	-	2.420
C	4.3	2.04	49	92.1	30-34	27.2	2.291
D	24	2.24	121	37.6	40-95	84.2	2.318
E	36	2.36	167	26.6	25-140	103.6	2.384
F	35	2.35	174	26.3	40-140	128.4	2.398
G	40	2.40	195	25.1	50-170	103.6	2.470
I	40	2.40	196	26.9	40-155	100.2	2.389
K	32	2.32	173	41.6	40-134	95.5	2.353

4. DISCUSSION

Compositions A-E had been utilized in previous bonding experiments and were evaluated for their physical properties. Although none of these glasses had the optimum properties to meet system performance requirements, these compositions spanned the ternary phase diagram and gave indication of benchmark material properties. Additional glasses (F, G, I, and K) were made to complete the series. For all glasses, physical properties with respect to arsenic content were examined. As arsenic has a coordination of 3 in most chalcogenide glasses, with sulfur and selenium primarily 2-coordinated,¹⁰ increased arsenic content in the glasses should therefore increase coordination. The term average coordination number, also given in Table 1 for each composition, is used in describing the cross-linking in a glass. It is defined as the atom-averaged covalent coordination of the constituents. Of the thermal properties examined, it was expected that increased coordination of the glass structure should increase T_g and decrease thermal expansion.^{6,11} Figure 1 illustrates the dependence of T_g on increased arsenic content (mol %), and Figure 2 shows the relationship between coefficient of thermal expansion (CTE) and mol % arsenic. Both figures exhibit the expected monotonic increase and decrease, respectively, with As content.

CTE is critical to the construction of a layered composite in that it will influence residual stresses remaining in the structure following assembly at elevated temperatures. Structures in this study consisted of a diamond cladding (few 100 μm), bonding glass layer (10-20 μm), and a ZnSe substrate (1-2 cm). The stress due to expansion mismatch (25 °C to 200 °C) in the glass layer is calculated using the equation¹²

$$\sigma_{gl} = E_{gl} (T_o - T)(\alpha_{gl} - \alpha_{ZnSe})(1-3j+6j^2) \quad (1)$$

where σ_{gl} is the stress in the glass layer, E_{gl} is the Young's modulus of the glass, T_o is the initial stress-free temperature, T is the final temperature, and j is a ratio of the glaze-to-body thickness. If chalcogenide A is used in the calculation, stress in the glass layer between the ZnSe/glass interface is ~16 MPa. A similar value is obtained for the stress between glass/diamond interface. If the same calculation is performed assuming chalcogenide I is used as the bonding glass, the stress between the ZnSe/glass is ~15 MPa, and the value for glass/diamond interface is ~13 MPa.

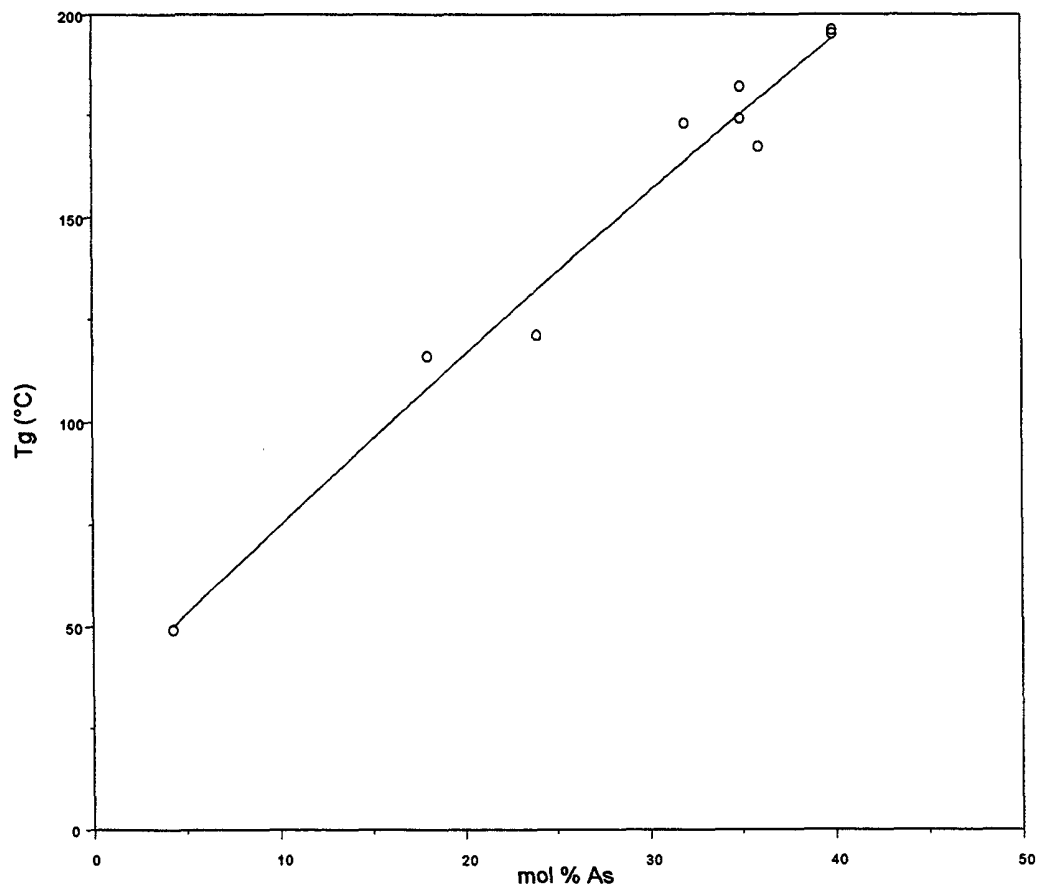


Figure 1. T_g as a function of arsenic content in glass

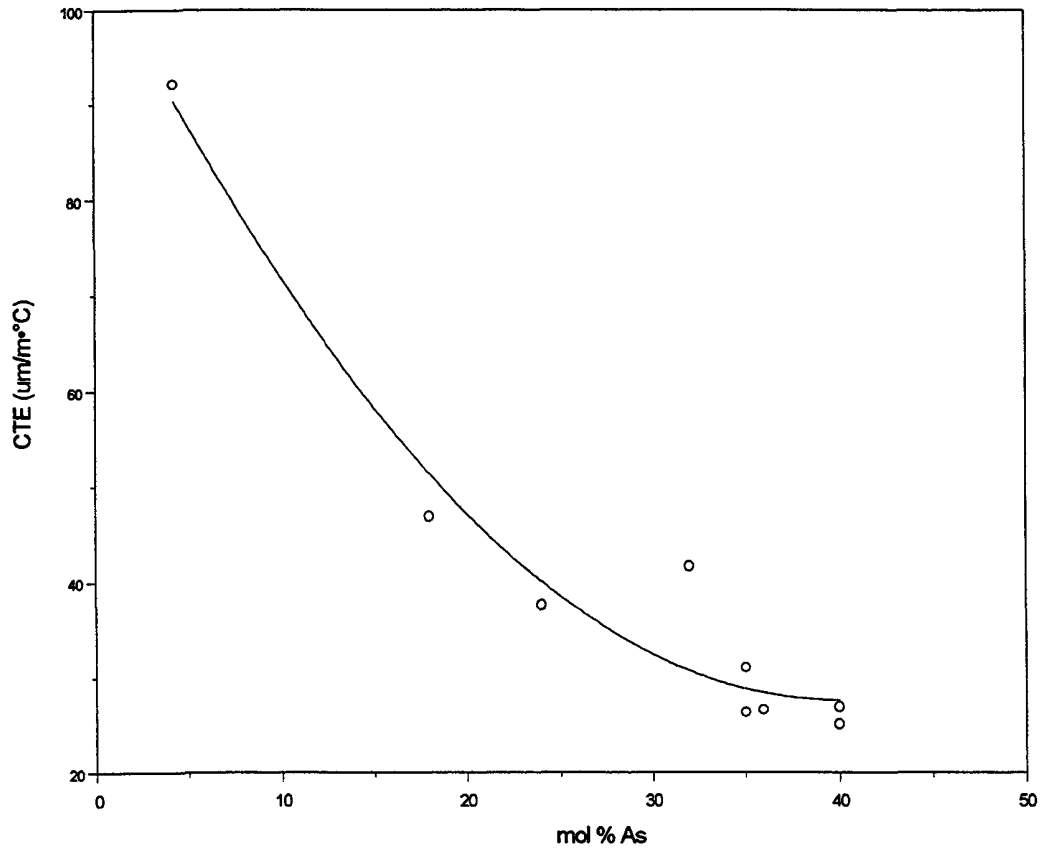


Figure 2. Variation in thermal expansion coefficient (CTE) with respect to arsenic content

Like thermal properties, mechanical properties of this glass system should also display a similar compositional dependence.¹³ Figure 3 shows the average hardness values measured for each of the examined glasses plotted as a function of mol % As. Error bars represent the standard deviation for the 5 tests on each sample. The large error bars for compositions F and K are due to the asymmetry in the observed indentation which resulted from wedge in the polished disk.

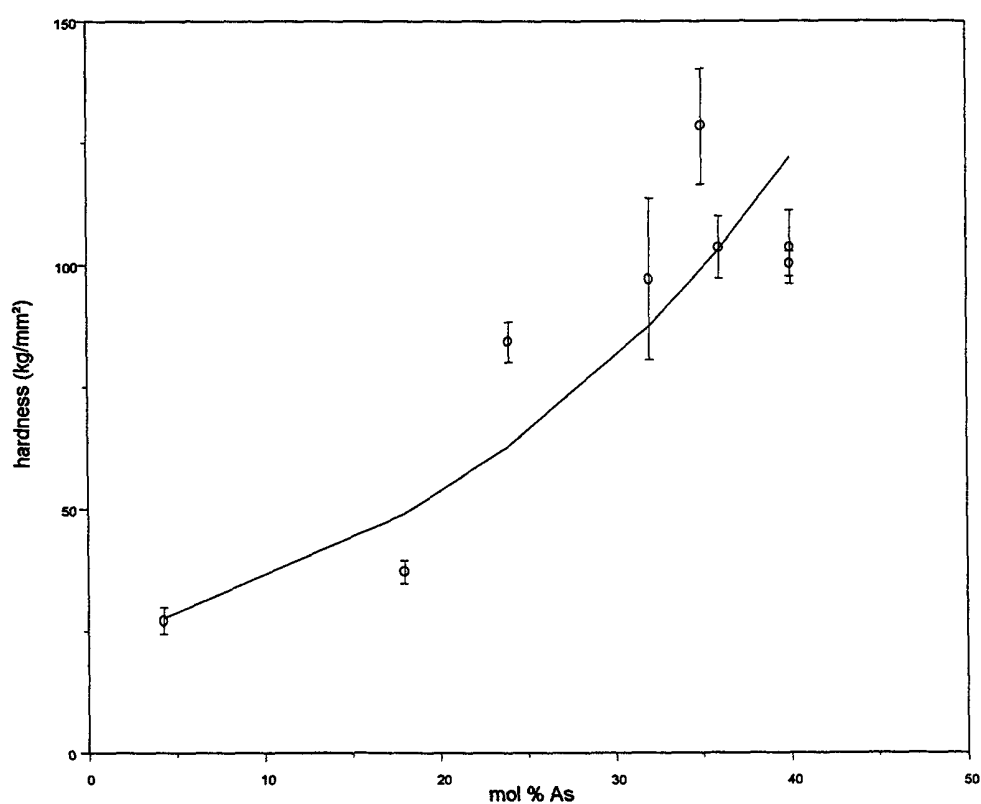


Figure 3. Graph of measured hardness values with respect to arsenic content

Finally, increased coordination should also lead to increased density, which generally results in an increase in the refractive index.¹⁴ Results from refractive index calculations are shown in Figure 4 as the average value, and error bars represent the standard deviation of the values. Index measurements on selected glasses, which contained a fairly constant mole percentage of sulfur (~30-40 mol % S), suggested that the refractive index followed an isokom across the ternary, spanning the As-rich to Se-rich compositions. The minimum value seen in Figure 4 is for chalcogenide A, which strayed from the isokom into a S-rich region (>50 mol %) of the ternary.

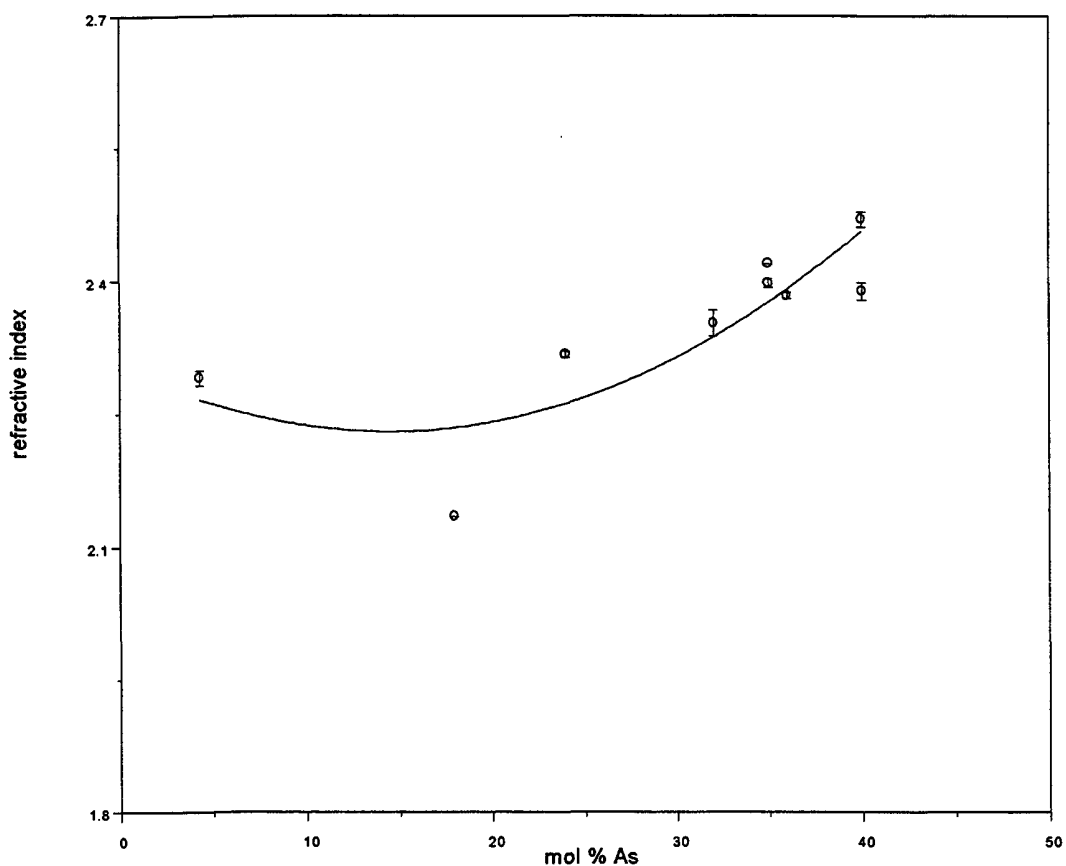


Figure 4. Refractive index (8-10 μm) versus arsenic content in glass samples

5. CONCLUSIONS

We have used an investigation of structure-property relationships to optimize the candidate glasses used in a ZnSe/glass/diamond composite structure. We have shown that increased coordination of the glass will improve the thermal and mechanical properties of the bonding glass. For the new glasses (F,G,I, and K) that were made following initial composition-property investigations, T_g values were just under 200 °C--close to the established goal for T_g. Thermal expansion coefficients for new glass compositions were lower than chalcogenide A. However, CTE remained high as compared to the expansion coefficients of the substrate (ZnSe) and cladding (diamond), and the expected tensile stresses resulting during cooling remain appreciable. Additionally, the optical properties of the latter glasses are closer to the refractive index goals and should prove suitable for specified optical performance goals. It is expected that the improved properties of the glass as described here should translate to an improved composite structure and a corresponding improvement in performance.

6. ACKNOWLEDGMENTS

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7. REFERENCES

- ¹ A.R. Hilton, *J. Electron. Mater.*, **2**, 221, 1973.
- ² R.H. Hopkins, W.E. Kramer, G.B. Brandt, J.S. Schruben, R.A. Hoffman, K.B. Steinbruegge, T.L. Peterson, "Fabrication and evaluation of erosion-resistant multispectral optical windows," *J. Appl. Phys.*, **49**, pp. 3133-3139, June 1978.
- ³ L.A. Xue, D.S. Farquar, T.W. Noh, A.J. Sievers, R.Raj, "Optical and mechanical properties of zinc sulphide diamond composites," *Acta Metall. Mater.*, **38**, pp. 1743-1752, Sept. 1990.
- ⁴ D.R. Gibson, E.M. Waddell, J.W. Kerr, A.D. Wilson, K.L. Lewis, "Ultra-durable phosphide based anti-reflection coating for sand and rain erosion protection," *SPIE Proc.* Vol 1760, in *Window and Dome Technologies and Materials III*, pp. 178-187, 1992.
- ⁵ W.D. Partlow, R.E. Witkowski, J.P. McHugh, "CVD diamond coatings for the infrared by optical brazing," in *Applications of Diamond Films and Related Materials*, Y. Tzeng, M. Yoshikawa, M. Murkawa, A. Feldman, Eds., Elsevier Science Publishers, 1991.
- ⁶ A.R. Hilton, D.J. Hayes, "The interdependence of physical parameters for infrared transmitting glasses," *J. of Non-Crystalline Sols.*, **17**, pp. 339-348, 1975.
- ⁷ M.F. Kotkata, "Trends in microhardness of monocomponent and multicomponent chalcogenide glasses," *J. Mater. Science*, **26**, pp. 4869-4877, 1991.
- ⁸ S S. Flaschen, A.D. Pearson, W.A. Nothover, "Low-melting inorganic glasses with high melt fluidities below 400 °C," *J. Amer. Ceram. Soc.*, **42**, p. 450, 1959.
- ⁹ S. Qian, "Deposition and characterization of glassy thin films for optical applications," *M. Sc. Thesis*, University of Central Florida, 1993.
- ¹⁰ K. Cerqua-Richardson, "Time-dependent defect processes in low-T_g chalcogenide glasses," *Doctoral Thesis*, Alfred University, 1992.

¹¹ A.N. Sreeram, D.R. Swiler, A.K. Varshneya, "Gibbs-DiMarzio equation to describe the glass transition temperature trends in multi-component chalcogenide glasses," *J. of Non-Crystalline Sols.*, **127**, pp. 287-297, 1991.

¹² W.D Kingery, H.K. Bowen, D.R. Uhlmann, *Introduction to Ceramics*, New York: John Wiley and Sons, 1976.

¹³ D.R. Swiler, A.K. Varshneya, R.M. Callahan, "Microhardness, surface toughness and average coordination number in chalcogenide glasses," *J. Non-Crystalline Sols.*, **125**, pp. 250-257, 1990.

¹⁴ A.R. Hilton, C.E. Jones, M. Brau, "Non-oxide IVA-VA-VIA chalcogenide glasses. Part 1. Glass-forming regions and variations in physical properties," *Phys. Chem. Glasses*, **7**, pp. 105-115, 1966.