



RESEARCH ARTICLE

Composition-Dependent Density Modeling of Chalcogenide Glasses: Empirical Evidence for Influential van der Waals Interactions and the Central Role of Lone-Pair Electrons

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Abstract: We present an expanded empirical framework for predicting the density of chalcogenide glasses (ChGs) and use it to examine atomic bonding interpretations across a broad compositional landscape. Building on our earlier methodology and dataset work, we compile 468 measured densities spanning 60 elemental families and 19 constituent elements. Using an iterative nonlinear optimization to determine element-specific high- and low-concentration empirical coefficients, combined with a Sigmoid interpolation for concentration dependence, the model predicts density directly from composition with high accuracy (majority of predictions within $\pm 2.5\%$ of measured values; nearly all within $\pm 5\%$). Beyond predictive performance, we analyze systematic trends in the fitted coefficients and show that the results may possibly be explained by a network landscape noticeably influenced by weak, non-shared-electron interactions that are well described by van der Waals radii and volumetric packing considerations, rather than exclusively by covalent electron sharing, as conventional theory promotes as untested fact. To account for the nonstructural anomalies of low-temperature aging, we introduce a conceptual framework rooted in electromagnetic interactions, establishing a testable hypothesis to be fully formalized in a forthcoming companion work. The primary contribution is a reproducible, data-driven density model that both serves as a practical design tool and motivates a testable physical interpretation of bonding and polarizability in ChGs.

Keywords: chalcogenide glass aging, chalcogenide glass density, lone-pair electrons, element-based estimator algorithms, two-photon absorption (2 PA)

1. Introduction

Chalcogenide glasses (ChGs) are central to infrared optics, photonics, and phase-change devices because of their unique optical and electronic properties [1–7]. Understanding how composition influences the physical properties of ChGs remains central to the design of infrared optical materials. The structural theories of Tanaka [8], Zallen [9], and Phillips [10] define ChG systems and are well known in our community. They have remained unopposed for more than 50 years. We suggest that the results presented in this paper should challenge these researchers' conclusions on the importance of covalent bonding in ChG structural makeup—conclusions which have been accepted for all these years by the ChG community, without peer review challenges or requests for testing verification [11–16].

Among the many measurable properties, density is one of the most widely reported because it can be obtained reliably even from small laboratory-size melt volumes. Density is a fundamental, widely reported property that reflects atomic packing and

indirectly encodes information about local bonding and structural motifs. The ChG literature contains several decades of density measurements across numerous glass families, providing a rich dataset for empirical modeling and compositional trend analysis. Our team has mined and harvested this data to develop our bonding strategies and algorithms. Recent machine learning [17–19] efforts have begun to leverage these datasets, but most approaches rely on fixed assumptions about bonding or structural motifs that are most likely incorrect and do not generalize across diverse chemistries. Loretz et al. [20] introduced an empirical composition-based density model and demonstrated its utility across several glass families. That study established a compact set of elemental parameters that, when combined with mixture rules, reproduced measured densities with useful accuracy.

Here we extend that approach with a substantially enlarged dataset (468 measured densities) and an improved interpolation and fitting strategy [21–23]. Our goals are twofold: (1) to provide a robust, reproducible empirical tool for predicting density from composition across diverse ChG chemistries and (2) to examine whether systematic trends in the empirical parameters can aid in the determination of a physically meaningful

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interpretation of bonding in ChGs. We evaluate the hypothesis that weak, non-shared-electron interactions (van der Waals (vdW)-type) may heavily influence the volumetric and polarizability behavior of many ChGs and that lone-pair electrons on chalcogen atoms are central to polarizability and device-relevant electronic behavior.

We emphasize that the model parameters are empirical fit quantities used for prediction. Nevertheless, when combined with independent knowledge of atomic radii, polarizability, and electronic structure, the parameter trends can motivate physically testable interpretations. We present the model, the fitting procedure, representative validations, and a focused discussion arguing for the vdW-dominant interpretation and the role of lone-pair electrons, together with proposed validation experiments.

To extract consistent elemental contributions from this dataset, we employ a similar methodology to the Reverse Monte Carlo (RMC) analysis employed in our abovementioned prior work that determines high- and low-concentration empirical coefficients for each element based upon a subset of the glass compositions. Essentially, our analysis is an iterative nonlinear optimization (INO) procedure (a variation of conventional RMC analysis used in nuclear physics to determine structural models of materials by iteratively fitting simulated data like neutron or X-ray scattering to experimental measurements). These coefficients are not interpreted as physical bonding descriptors; rather, they serve as model parameters that enable accurate density prediction across a wide compositional space. Building on this foundation, we introduce a composition-dependent interpolation scheme based on a Sigmoid functional form. This interpolation improves predictive accuracy by smoothly transitioning each element's contribution between its low- and high-concentration limits without requiring *ad hoc* adjustments for specific glass families.

Our goal is to provide a transparent, reproducible, and broadly applicable empirical method for predicting ChG density directly from chemical composition. Beyond this goal, we examine systematic trends in the fitted parameters and hypothesize about structural or bonding environments. Therefore, while we focus on the development, validation, and application of a unified density-prediction model supported by a large experimental dataset, we also attempt to add a framework to network bonding. The resulting framework offers practical utility for materials selection, compositional screening, and the early-stage design of infrared optical glasses.

2. Methods: Iterative Nonlinear Optimization of Elemental Coefficients

2.1. Dataset

The dataset comprises 468 measured densities collected from the literature and internal laboratory measurements, covering 60 elemental families and 19 constituent elements. It is formalized in Table 1. The dataset includes binary through senary glasses across S-, Se-, and Te-rich systems and containing network modifiers (e.g., Ag, Pb, Bi, halides.) Please see Table S1, which can be found in the Supplementary Materials.)

2.2. Empirical mixture framework

We model glass density (ρ_{mix}) from composition using an element-wise mixture rule. Two equivalent formulations are used in practice: (1) weight fraction-based density factors and (2) molar volume-based effective radii. The *weight-fraction form* mixture rule is:

$$\rho_{\text{mix}} = \frac{1}{\sum_i \left(\frac{w_i}{\rho_{\text{eff}}^{(i)}} \right)} \quad (1)$$

where w_i is the weight fraction of element i and $\rho_{\text{eff}}^{(i)}$ is the *element's effective density coefficient* in the given composition.

In the molar-volume/radius formulation, each element contributes a *molar volume* determined by an *effective atomic radius*, $R_{\text{eff}}^{(i)}$ using Equation (5), and the mixture molar volume is the sum of elemental molar volumes. The two formulations are algebraically consistent when the effective coefficients are chosen appropriately. To calculate the molar mass for a ChG composition, we can weight each element's atomic weight by its atomic percentage (atm%) in the glass as shown in Equation (2). The predicted density is determined by evaluating the molar mass divided by the molar volume.

$$M = \sum_i (\text{atm}\%_i \times [\text{elemental gram/mole}]_i) \quad (2)$$

2.3. Concentration-dependent interpolation

To capture concentration dependence of elemental contributions, we interpolate between empirically determined low- and high-concentration endpoints for each element using a Sigmoid

Table 1
Updated chalcogenide glass families in our database

Elemental family							
Vitreous Se	S-Se	Ge-As-Se	Ge-Bi-S	Se-S-Zn	Ge-As-Se-Te	Ge-Sb-Te-S	Ge-Ga-S-Cd-I
As-S	Te-Se	Ge-As-S	Ge-Sn-S	Te-Sn-Se	Ge-As-Se-Bi	Ge-Te-Ag-I	Ge-Sb-S-Cs-Cl
As-Se	As-Se-Te	Ge-Ga-Se	Ge-Sn-Se	Te-Bi-Se	Ge-Bi-Se-Cd	Ge-Zn-Se-Ag	Si-As-Te-Se-Ag
Ge-S	As-Se-Cu	Ge-Ga-S	Ge-S-Ag	As-Se-Te-Cu	Ge-Ga-Sb-S	Si-As-Te-Ag	Ge-Sb-Se-Te-Pb
Ge-Se	As-Se-S	Ge-Sb-Se	Ge-Te-Ag	Ga-As-Te-Se	Ge-Sb-In-Se	Ge-Ga-Se-S-Cs	
Ge-Te	As-Si-Te	Ge-Sb-S	Ge-Te-I	Ga-Ge-Se-In	Ge-Sb-Se-Te	Ge-Ga-Se-Cs-Cl	
Se-I	As-Sb-Se	Ge-In-Te	Ge-Te-Se	Ga-Ge-Se-Pb	Ge-Sb-Se-Ag	Ge-Ga-S-Cs-Cl	
Se-Zn	As-Sb-S	Ge-In-Se	Ge-Zn-Se	Ge-As-Se-Pb	Ge-Sb-Se-Cd	Ge-Ga-S-Cd-Cl	

Note: Bold texts are the 20 new elemental glass families analyzed (see Loretz et. al. [20]).

function of atomic fraction (x). The authors furthered development of this method while researching ChG elastic moduli estimator algorithms [24].

$$\text{Sigmoid}(x) = 2 \left[\frac{1}{1 + e^{(-7.5788x)}} - \frac{1}{2} \right] \quad (3)$$

The $\text{Sigmoid}(x)$ function, Equation (3), is chosen for smoothness and reproducibility. It is an empirically derived, numerical interpolation tool, not a physical law. Solutions of $\text{Sigmoid}(x)$ for various atom fractions (*atomic percentage divided by 100*) are provided in Table 2.

$$\rho_{\text{eff}}^{(i)} = \rho_{\text{low}}^{(i)} + \text{Sigmoid}(x_i) [\rho_{\text{high}}^{(i)} - \rho_{\text{low}}^{(i)}] \quad (4)$$

For the purposes of this study, we assume that the Sigmoid functional form is the same for every element, as shown in Equation (4). A future extension may be to explore elemental dependencies of the Sigmoid function's exponent. Equation (5) calculates $R_{\text{eff}}^{(i)}$ for the radius-based formulation using the same $\text{Sigmoid}(x)$ function:

$$R_{\text{eff}}^{(i)} = \left\{ \left[\frac{1}{(R_{\text{low}}^{(i)})^3} \right] + \text{Sigmoid}(x_i) \left[\frac{1}{(R_{\text{high}}^{(i)})^3} - \frac{1}{(R_{\text{low}}^{(i)})^3} \right] \right\}^{-1/3} \quad (5)$$

2.4. Iterative nonlinear optimization of endpoints

We determine $\rho_{\text{low}}^{(i)}$, $\rho_{\text{high}}^{(i)}$ (or $R_{\text{low}}^{(i)}$, $R_{\text{high}}^{(i)}$) by minimizing the discrepancy between calculated and measured densities across the dataset. For each element (i), we define an element-specific least-squares objective in Equation (6):

$$\chi_i^2 = \frac{1}{K_i - 1} \sum_{k_i=1}^{K_i} [\mathcal{Q}_{\text{calc}, k_i} - \mathcal{Q}_{\text{meas}, k_i}]^2 \quad (6)$$

where K_i is the number of compositions containing element i and $\mathcal{Q}$ denotes density.

The global dataset is overlapping across elements; we therefore use a stochastic coordinate-descent optimization:

1. Randomly select an element (i), and decide whether to perturb its low or high endpoint.
2. Propose a small perturbation ($\pm\Delta$).
3. Accept the perturbation if it reduces (χ_i^2) ; otherwise, reject it and propose a new ($\pm\Delta$).

4. Enforce positivity and physically reasonable bounds on parameters with a rigorous set of unbending rules.
5. Repeat until convergence thresholds for all (χ_i^2) meet this set of rules.

We use various limited data sets to determine the elemental density parameters. We can state that the parameters remain relatively stable, as further discussed in Section 4.5. It is neither our intention to claim that the set of parameters is unique nor that uniqueness is a requirement. Our concern is that the resulting predicted overall densities remain in close agreement with measured density values using the elemental set of density parameters established.

2.5. Special cases and constraints

For selenium, the high-concentration limit is fixed to the value corresponding to vitreous Se, and only the low-concentration coefficient is optimized. This constraint reflects the availability of reliable reference data for the pure element. All other elements are treated symmetrically, with both high- and low-concentration coefficients allowed to vary within bounded ranges.

2.6. Output of the optimization

The final optimized coefficients for all 19 elements are presented in Table 3. These values are *empirical fit parameters* derived from our iterative optimization procedure. They should not be interpreted as direct measures of bond strength, covalency, or vdW character but as numerical inputs to the interpolation model that enable accurate density prediction by composition.

3. Results

3.1. Predictive performance graphical illustration

Figure 1 displays the results of the measured vs. calculated regression analysis for the 468 glass compositions (60 glass families) studied in this research paper. The legend data on the right side are associated with measured and calculated density values harvested by the authors for unique families of glasses. All glass compositional data and density values used to create this figure are available in Table S1 of the Supplementary Materials.

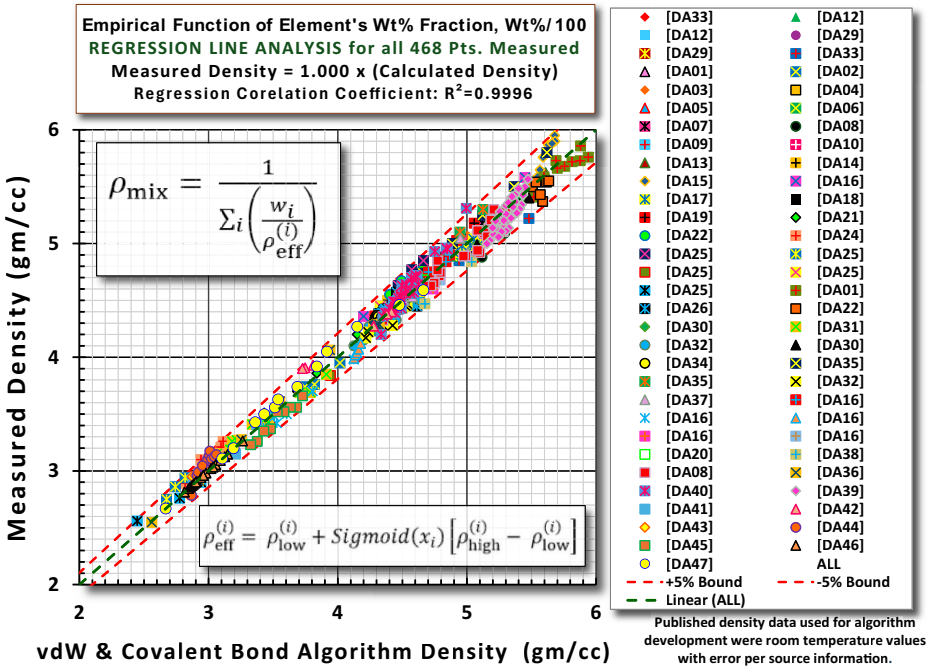
Table 2
Sigmoid values versus elemental atom fractional values

Atom fraction	Sigmoid value	Atom fraction	Sigmoid value	Atom fraction	Sigmoid value	Atom fraction	Sigmoid value	Atom fraction	Sigmoid value	Atom fraction	Sigmoid value
0.00	0.000	0.16	0.542	0.32	0.837	0.50	0.956	0.66	0.987	0.84	0.997
0.02	0.076	0.18	0.593	0.34	0.859	0.52	0.962	0.68	0.989	0.85	0.998
0.04	0.150	0.20	0.640	0.36	0.877	0.54	0.967	0.70	0.990	0.86	0.999
0.06	0.224	0.22	0.682	0.40	0.908	0.56	0.972	0.72	0.992	0.87	
0.08	0.294	0.24	0.721	0.42	0.920	0.58	0.976	0.74	0.993		
0.10	0.362	0.26	0.755	0.44	0.931	0.60	0.979	0.76	0.994	to	1.000
0.12	0.426	0.28	0.786	0.46	0.941	0.62	0.982	0.80	0.995		
0.14	0.486	0.30	0.813	0.48	0.949	0.64	0.984	0.82	0.996	1.00	

Table 3
Elemental bonding percentages by our algorithm applied to empirical radii and Loretz density factors

ChG element	Empirical Concentration Level Dependent Values							
	Covalency for high (100%) (%)	Covalency for low (0%) (%)	vander Waals for high (100%) (%)	vander Waals for low (0%) (%)	Radius for high (100%) (pm)	Radius for low (0%) (pm)	Loretz density factor for high (100%) (gm/cm ³)	Loretz density factor for low (0%) (gm/cm ³)
Ga	30.0			0.0	167.5	187.0	5.88	4.23
In		0.0	2.5		197.8	193.0	5.88	6.33
Si	27.4	25.0			182.9	185.3	1.82	1.75
Ge	27.5	26.0			186.0	187.3	4.48	4.38
Sn	60.0	5.0			170.2	213.1	9.54	4.86
Pb	74.0	0.0			160.6	202.0	19.84	9.97
As	15.0	1.9			175.1	183.7	5.33	4.79
Sb	50.0	5.0			172.5	202.7	9.40	5.80
Bi	0.0	30.0			207.0	189.3	9.34	12.21
S			3.7	24.0	186.7	223.2	1.95	1.14
Se			2.2	6.6	194.2	202.5	4.28	3.77
Te			0.5	0.0	207.0	206.0	5.70	5.79
Zn	95.0			65.0	127.9	394.4	12.40	0.42
Ag	110.0	150.0			142.3	131.5	14.84	18.80
I	15.0			7.0	189.2	211.9	7.43	5.29
Cu	300.0	325			116.0	114.0	16.14	17.00
Cd	40.0	110.0			222.6	130.9	4.04	19.87
Cl	68.0	73.0			123.3	119.5	7.49	8.23
Cs	65.0	73.0			272.8	264.2	2.60	2.86

Figure 1
Calculated (predicted) versus measured density, 60 glass families, 19 elements, and 468 discrete compositions



Note: Red dashed lines at +/- 5 % of the trendline and data in this figure are derived from Equation (1), Equation (4), and Table 3.

3.2. Representative examples

Using the optimized empirical endpoints and Sigmoid interpolation, the model predicts densities across the 468-composition dataset with strong accuracy: >59% of predictions fall within $\pm 2.5\%$ of measured values and >98% within $\pm 5\%$ (Figure 1). Residuals show no large systematic bias across composition families; errors are modestly larger in compositions containing heavy halides or high modifier content, where local packing and ionic contributions are more complex. The level of accuracy for measured values is dependent on laboratory measuring protocols, skills, and techniques.

Based on our team's exposure and direct involvement with commercial, government, and university laboratory glassmaking facilities, we note that the accuracy for commercially manufactured glass density data is very good. We suggest $\pm 0.5\%$, as these materials see rigorous annealing protocols and the technicians are typically well-skilled. For government laboratories, we suggest about $\pm 1.5\%$ accuracy, where our experience indicates that these labs cool more rapidly than might be advisable during annealing. The remaining sources rarely anneal samples, and when they do, the technicians (typically students) are not well-trained in annealing procedures. We suggest that this last group contributes data with mathematical inaccuracies of about $\pm 5\%$. With these unconfirmed assumptions in mind, cross-validation is performed by withholding subsets of compositions and verifying predictive stability. Solution of the regression equation for all data yields a slope of 1.000 for the measured versus calculated values, indicating a very tight correlation.

To illustrate the use of the empirical coefficients in Table 3 and the Sigmoid interpolation values in Table 2, we present several representative examples spanning binary, ternary, and quaternary glass compositions. These examples demonstrate the application of the model and highlight its predictive accuracy across diverse chemistries. All calculations follow directly from the solution of the applicable Sigmoids from Equation (3), the interpolation scheme of Equation (4), and the mixture rule in Equation (1). Table 4, Table 5, and Table 6 provide the raw empirically derived data for each glass composition's density determination.

3.2.1. Example 1: GeTe_4

This binary telluride glass provides a straightforward demonstration of the interpolation procedure. Using the atomic fractions, weight fractions, Sigmoid values, and high/low empirical coefficients (*Loretz density factors*) for Ge and Te, the interpolated elemental density factors are computed in Table 4. A ternary and quaternary ChG will be solved in Examples (2) and (3).

Interpolating between low- and high-concentration endpoints for each element's effective density using Equation (3) yields:

$$\rho_{eff}^{Ge} = 4.38 + 0.640 * (4.48 - 4.38) = 4.44$$

$$\rho_{eff}^{Te} = 5.79 + 0.995 * (5.70 - 5.79) = 5.70$$

Table 4
Summary of data needed to solve Equation (4) and Equation (1) for density of GeTe_4

Periodic element	Atom fraction	Atomic mass	Weight fraction	Sigmoid value	Loretz density factor (low concentration)	Loretz density factor (high concentration)
Ge	0.20	72.63	0.1246	0.640	4.38	4.48
Te	0.80	127.6	0.8754	0.995	5.79	5.70

Table 5
Summary of data needed to solve Equation (4) and Equation (1) for density of $\text{Ge}_{30}\text{As}_{20}\text{Se}_{50}$

Periodic element	Atom fraction	Atomic mass	Weight fraction	Sigmoid value	Loretz density factor (low concentration)	Loretz density factor (high concentration)
Ge	0.30	72.63	0.2857	0.813	4.38	4.48
As	0.20	74.92	0.1964	0.640	4.79	5.53
Se	0.50	78.97	0.5179	0.956	3.77	4.28

Table 6
Summary of data needed to solve equation (4) and Equation (1) for density of $(\text{GeTe}_4)_{0.9} - (\text{AgI})_{0.1}$

Periodic element	Atom fraction	Atomic mass	Weight fraction	Sigmoid value	Loretz density factor (low concentration)	Loretz density factor (high concentration)
Ge	0.18	72.63	0.1120	0.593	4.38	4.48
Te	0.72	127.6	0.7873	0.992	5.79	5.70
Ag	0.05	107.9	0.0463	0.187	18.80	14.84
I	0.05	126.9	0.0544	0.187	5.29	7.43

Applying the mixture rule of Equation (1) yields a predicted density of:

$$\rho_{GeTe_4} = \frac{1}{\left(\left(\frac{0.1246}{4.44}\right) + \left(\frac{0.8754}{5.70}\right)\right)} = 5.505 \text{ g/cm}^3$$

The measured density is 5.499 g/cm³, an error of approximately 0.11%, demonstrating excellent agreement. This level of agreement for a binary ChG composition is better than the mean value for binaries, which is approximately 1.4%.

3.2.2. Example 2: $Ge_{30}As_{20}Se_{50}$

This ternary composition illustrates the model's ability to manage systems with three chemically distinct contributors. Using the interpolated coefficients in the same manner as above yields: Interpolating between low- and high-concentration endpoints for each element's effective density using Equation (3) yields:

$$\rho_{effective}^{Ge} = 4.38 + 0.813 * (4.48 - 4.38) = 4.46$$

$$\rho_{effective}^{As} = 4.79 + 0.640 * (5.53 - 4.79) = 5.26$$

$$\rho_{effective}^{Se} = 3.77 + 0.956 * (4.28 - 3.77) = 4.26$$

Applying the mixture rule of Equation (1) yields a predicted density of:

$$\rho_{Ge_{30}As_{20}Se_{50}} = \frac{1}{\left(\left(\frac{0.2857}{4.46}\right) + \left(\frac{0.1964}{5.26}\right) + \left(\frac{0.5719}{4.26}\right)\right)} = 4.485 \text{ g/cm}^3$$

Applying Equation (1), the predicted density is 4.485 g/cm³. The measured value is 4.478 g/cm³, an error of approximately 0.16%. Small discrepancies of this magnitude may arise from differences in thermal history, as rapid quenching will produce somewhat lower densities than fully annealed samples. Such effects are well known in ChG processing but are not explicitly modeled here. Our research shows that typical measured versus predicted values for unannealed ternary glass composition samples of unknown post-quench thermal history have a mean value of approximately 2.3%.

3.2.3. Example 3: $(GeTe_4)_{0.9} - (AgI)_{0.1}$

This quaternary system includes both heavy chalcogenide constituents and halide modifiers, providing a stringent test of the model. The interpolated coefficients are:

$$\rho_{effective}^{Ge} = 4.38 + 0.593 * (4.48 - 4.38) = 4.44$$

$$\rho_{effective}^{Te} = 5.79 + 0.992 * (5.70 - 5.79) = 5.70$$

$$\rho_{effective}^{Ag} = 18.80 + 0.187 * (14.84 - 18.80) = 18.06$$

$$\rho_{effective}^I = 5.29 + 0.187 * (7.43 - 5.29) = 5.69$$

$$\rho_{(GeTe_4)_{0.9} - (AgI)_{0.1}} = \frac{1}{\left(\left(\frac{0.1120}{4.44}\right) + \left(\frac{0.7873}{5.70}\right) + \left(\frac{0.0463}{18.06}\right) + \left(\frac{0.0544}{5.69}\right)\right)} = 5.70 \text{ g/cm}^3$$

Applying Equation (1), the predicted density is 5.70 g/cm³. The measured value is 5.662 g/cm³, corresponding to an error of approximately 0.67%. Given the high density and compositional complexity of this system, this level of agreement demonstrates the robustness of our model. Our research shows that typical measured versus predicted values for unannealed quaternary glass composition samples of unknown post-quench thermal history have a mean value of approximately 3.7%. Notwithstanding, this particular composition was chosen intentionally because of its popularity in the community as a photonic material. Moreover, it was also chosen by the authors because of its algorithm-weighting importance during our INO of endpoints (Section 2.4).

3.3. Systematic trends in fitted endpoints

The fitted low/high endpoints reveal consistent trends (Figure 2):

1. **Chalcogens (Se, S, and Te):** relatively small difference between low and high endpoints, indicating consistent volumetric contribution across concentrations.
2. **Group IV/V network formers (Ge, As, Sb):** moderate increase in effective density/radius with concentration.
3. **Heavy modifiers (Pb, Bi, Cd):** higher low-concentration endpoints that decrease with concentration, consistent with isolated heavy-atom inclusion at low fractions.
4. **Halides and Ag:** large effective density factors reflecting high atomic mass and compact packing when present.

These trends are robust throughout cross-validation evaluations.

4. Discussion: Interpreting the Empirical Trends – vdW Dominance and Lone-Pair Role

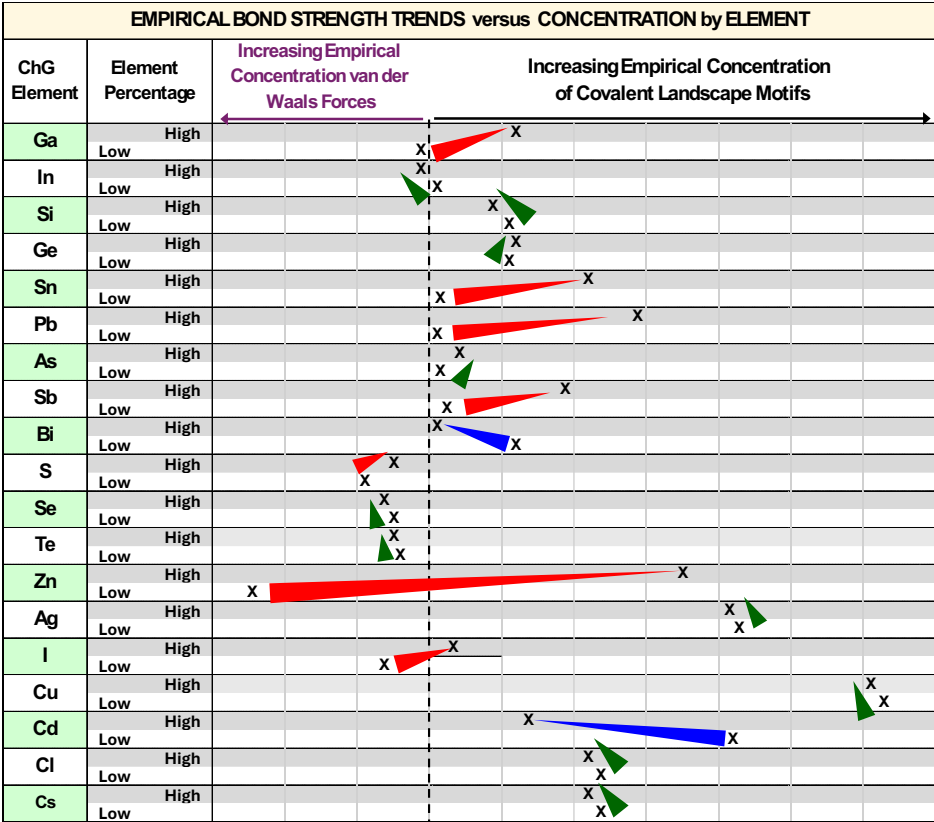
The empirical model is, by construction, a predictive tool. Even so, the consistency of the fitted endpoints with known atomic vdW radii, the volumetric nature of the mixture rule, and the observed concentration dependence together lend credence to a physically coherent interpretation. We conclude that for most ChG compositions, the volumetric interactions are influenced to some extent by weak, non-shared-electron forces that are well approximated by vdW-type bonding and packing, rather than exclusively by covalent electron sharing that would require large, composition-dependent changes in molar volume inconsistent with the dataset.

Below, we summarize the lines of evidence and the conceptual argument.

4.1. Volumetric evidence consistent with empirical vdW-type interactions

1. **Endpoint magnitudes align with vdW radii trends.** When the optimized effective radii are compared qualitatively to established vdW radii [25–27], the ordering and magnitudes are consistent: heavier chalcogens and heavy modifiers occupy larger volumetric contributions consistent with vdW packing rather than with covalent contraction or expansion.

Figure 2
Empirical trends in element bond strength determined by increasing and decreasing effective atomic radius by element and composition



Note: Red arrows move empirically toward greater covalency, blue arrows toward greater vdW forces, and green arrows show only minor movement.

2. **Weak concentration dependence for chalcogens.** Se, S, and Te show small endpoint shifts with concentration, consistent with their role as network formers whose local coordination and lone-pair occupancy produce volumetric contributions dominated by atomic size and polarizability rather than by strong directional covalent bonding changes.
3. **Mixture-rule success.** The mixture rule based on effective volumetric contributions reproduces densities across diverse chemistries without invoking explicit bond-counting or coordination changes. This parsimony suggests that volumetric packing and non-shared-electron interactions are critical determinants of bulk density.

4.2. Lone-pair electrons and polarizability

Lone-pair electrons on chalcogen atoms (Se, Te, S) occupy the highest occupied valence states and contribute strongly to local polarizability. We propose the following roles for lone pairs:

1. **Enable high polarizability.** Non-bonding electron density increases local polarizability, which in turn enhances vdW-type dispersion interactions and contributes to refractive index and dielectric response.
2. **Facilitate defect formation and trapping.** Lone pairs create electronic environments that can stabilize localized defect states or trapped charges when processing introduces structural imperfections.

3. **Permit rapid electronic/optical switching.** In phase-change and PC-RAM materials, the presence of lone pairs and the associated polarizability enable rapid changes in electronic structure under external stimuli.

These roles are consistent with first-principles studies that identify lone-pair character in chalcogenide electronic structure [19, 22, 23] and with experimental observations of high refractive indices and strong optical nonlinearities in ChGs.

4.3. Reconciling covalency and vdW contributions

In our model, we do not deny that covalent bonding exists in ChGs; rather, we propose that covalent electron sharing defines local connectivity and short-range structural motifs. However, our empirical dataset suggests that these covalent contractions are not the sole determinants of bulk volumetric packing across diverse composition landscapes. Instead, we propose a coexistent structural framework where localized, rigid covalent units are embedded within a surrounding network that is significantly influenced by vdW-type dispersion interactions and lone-pair electron distributions.

This coexistent framework provides a holistic perspective on the sub- $T_g(0)$ aging phenomena observed in ChGs. Traditional glassy models attribute aging exclusively to structural relaxation, where atoms mechanically rearrange to optimize bond angles and distances. While we agree that such atomic-scale adjustments can occur concurrently, we also recognize that the extremely high viscosity of these networks at deep sub-strain point

temperatures implies that purely mechanical relaxation timescales are remarkably prolonged. We hypothesize that electronic degrees of freedom, such as the slow, quantum electrodynamic (QED)-mediated relaxation and reconfiguration of the highly deformable lone-pair electron cloud, coexist alongside traditional structural relaxation. Under this view, electronic relaxation offers a complementary pathway that explains the observed macroscopic shifts in refractive index and optical polarizability over time, even when macroscopic structural density remains practically unchanged. We note that this electronic mechanism is presented only as a testable hypothesis. It needs to be evaluated alongside established structural relaxation paradigms, rather than considered as an exclusive or mutually restrictive explanation.

4.4. Processing, defects, and trapped charges

Our dataset and model indicate that deviations from predicted density often correlate with processing history. We have witnessed these deviations in our own laboratory and commercial melting facilities, where specific melting methodology, quench technique, quench rate, and annealing protocols can all influence the final material properties. We interpret this as possible evidence that processing-induced defects and trapped charges—which are enabled by lone-pair environments—“modulate” local packing and polarizability. This provides a pathway to reconcile device-level metastability and aging with the volumetric, vdW-dominated picture: processing controls defect density, which in turn affects polarizability and electronic trapping without fundamentally altering the vdW-dominated volumetric baseline.

4.5. Testable predictions and validation experiments

While the proposed coexistent vdW and QED electronic frameworks offer a physically coherent narrative to explain the systematic patterns in our elemental coefficients, we explicitly acknowledge that an empirical density model cannot independently prove a microscopic physical mechanism. The parameter endpoints (ρ_{low} , ρ_{high} , R_{low} , and R_{high}) are primarily numerical inputs optimized for predictive utility. To establish the physical interpretability and scientific reliability of these parameters beyond simple dataset fitting, rigorous validation is required. To verify the suitability, robustness, and general applicability of the fitted parameters, we conducted standard cross-validation and sensitivity analyses. Systematically withholding random subsets (ranging from 10% to 50%) of the 468-composition dataset during optimization revealed high parameter stability, with out-of-sample density predictions maintaining an accuracy of $> 95\%$ within a $\pm 5\%$ error bound. Furthermore, parameter identifiability was confirmed by performing localized perturbation analyses on the elemental endpoints; the objective function exhibited well-defined global minima for key network formers, demonstrating that the optimized parameters are distinct mathematical solutions rather than arbitrary artifacts of overfitting.

We have strong evidence to support our model for heavy vdW influence in ChG amorphous networks. We discovered that the bulk densities of As_2S_3 and As_2Se_3 glass compositions may be calculated very accurately using only vdW atomic radii dimensions as found in newer periodic tables and reference literature (not our empirical radii dimensions, which were discussed earlier within this paper). The vdW radii are $\text{As} = 185$ pm, $\text{S} = 180$ pm, and $\text{Se} = 190$ pm. Their “mass densities” are 74.92, 32.06, and 78.97 g/mol, respectively. Applying real physics, we proportioned compositional mass contributions by their atomic

fractions and divided this mass value by a calculated volume value: $V_{\text{AVG}} = (4/3)\pi(N_0)[(\alpha_{\text{E}_1} r_{\text{E}_1}^3) + (\alpha_{\text{E}_2} r_{\text{E}_2}^3)]$, where N_0 is Avogadro’s number (atoms/mol) and the atomic packing consideration for a vdW-bonded network, which is defined by the geometry of a conforming sphere, $(4\pi r^3/3)$. These calculations yielded density values for As_2S_3 of 3.234 and for As_2Se_3 of 4.612 g/cc. The reported room temperature values of Schott Technologies, Inc. for these glasses are $\text{As}_2\text{S}_3 = 3.202$ and $\text{As}_2\text{Se}_3 = 4.633$ g/cc ($\pm 0.5\%$). With differences of less than 1% from measured values, we believe that any researcher in the field should view this as real evidence for vdW network contribution. More importantly, applying even modest percentages of respective covalent radii to the proper model equations yields density values which quickly exceed 20% of the measured values. (See reference [20] for additional information on this mathematical analysis.)

To move our proposed electronic relaxation and vdW influence concepts from speculative hypotheses to validated theories and to measure the extent of covalent bonding for the first time in the history of ChG science, targeted independent experiments and computational modeling are required. We propose the following focused validation agenda for the ChG scientific community:

1. **High-resolution pair distribution function:** Utilizing neutron and X-ray scattering data to map intermediate-range order and directly compare measured experimental atomic distances against the model’s effective vdW radii endpoints.
2. **Dispersion-corrected Density Functional Theory (DFT) calculations:** Employing first-principles quantum chemical modeling to isolate the specific energy contributions of London dispersion forces versus covalent sharing across representative binary and ternary glass families.
3. **Electron Paramagnetic Resonance (EPR) and deep-level transient spectroscopy:** Evaluating processing-induced defects and trapped charges to assess definitively whether localized electronic relaxation correlates with the magnitude of optical aging.
4. **Dielectric mapping:** Tracking changes in high-frequency dielectric response during controlled thermal annealing to isolate electronic polarizability shifts from structural volume changes.

The outcome of these experiments will provide evidence for interpretation of network bonding interactions and may also provide knowledge about lone-pair polarizability, both of which are central to ChG volumetric and optical behavior.

5. Discussion and Conclusions

This study presents an expanded empirical framework for predicting the density of ChGs across a broad and diverse compositional landscape. Our empirical density model is robust and reproducible. Across the full dataset, more than half of all predictions fall within $\pm 2.5\%$ of measured values, and nearly all fall within $\pm 5\%$. This level of accuracy demonstrates the practical utility of the model for compositional screening, materials selection, and early-stage design of infrared optical glasses. The framework is transparent, reproducible, and easily extensible to new compositions as additional experimental data become available.

Analysis of the fitted empirical radii values and their concentration dependence motivates a physically coherent interpretation that bulk volumetric behavior in ChGs appears may be heavily influenced by vdW-type, non-shared-electron interactions, and lone-pair electrons on chalcogen atoms may provide the polarizability and electronic environment that govern optical and defect-related phenomena. This observation is more easily

understood by comparing an element's vdW-bond radius value with its covalent counterpart. Covalent radii are typically 57% to 68% the size of corresponding vdW dimensions. When cubed, these covalent radii lead to significantly smaller atomic volumes and much higher ChG-calculated material densities than are actually measured and reported.

Covalent bonding remains important locally for connectivity and electronic structure, but it is not likely the sole volumetric determinant across the broad compositional field studied. As with any amorphous material, increases in the number of covalently bonded species quickly lead to nucleation and crystallization of the fragile network. ChGs are no different in this regard, and we would suggest, perhaps, even far more susceptible. We propose that ChGs develop and maintain their amorphous nature because they are not inclined to nucleate or crystallize after successful initial quenching. We interpret this to mean that the number of covalent bodies has been minimized during the rapid cooling process of a well-homogenized chemical mixture. Moreover, we justify our reasoning by explaining that the resultant glass formed after quenching has achieved a viscosity that precludes formation of new covalent bodies or development of existing covalent bodies (such as $AsSe_3$ tetrahedra).

The empirical model itself is a practical tool for materials design and compositional screening. We reiterate and emphasize that these trends cannot be interpreted as direct indicators of bonding type or strength. Rather, they suggest compositional regions where structural or spectroscopic studies may yield new insights. We outline specific experimental and computational validations that can confirm or refute the vdW-dominant picture and clarify the role of lone pairs.

It is well known that a ChG's supercooled amorphous state is "metastable" and that the vast majority of measurable properties can exist for a duration with little change, when not "disturbed" [28–30]. However, over extended time (*or under external stimuli such as acoustic modulation, or elevated thermal exposure still well below the glass composition's strain point temperature*), many ChG systems transition ("*age*") toward an ultimate stability state. One of the signatures of this final state is remarkably higher polarizability, which translates directly to increased refractive index dispersion. In mission-critical applications, where an optical system may be inventoried under brutal temperature conditions for a lengthy period of time, this aging problem will most likely result in failure of the system when put in the field.

We conclude that ChG aging well below the glass Strain Point ($\log_{10} \eta \sim 13.5$ Pa.s) is not the product of a molecular relaxation event where relaxation times (τ) exceed many years per step. It cannot possibly be explained as the consequence of covalently bonded species attempting to achieve more amenable bond angles or distances. Aging manifests in temperature domains where amorphous viscosities prohibit any type of molecular rearrangement from taking place in reasonable periods of time. Hence, it occurs despite the fact that structural relaxation time constants exceed hundreds to thousands of years and compels us to consider the physics of QEDs. Any application of QED theory requires carefully designed and controlled experiments to be performed before any conclusions can be made one way or the other.

At its core, QED describes how charged particles—especially electrons—interact through the exchange of virtual photons. In ChGs, this framework would be important if the dominant interactions governing structure and aging are found to be electromagnetic and not mechanical.

Our research leads us to hypothesize that aging is directly linked to "*induced metastability*" of vdW-motifs and lone-pair electrons; the amount and nature of which are dependent upon specific glass fabrication protocols. We believe that this induced metastability is vulnerable and can be eliminated. Theoretically, in a vdW-biased glass composition, the electron clouds of lone-pair-rich chalcogen atoms would be highly deformable. Therefore, from a provisional QED perspective, the instantaneous dipoles responsible for vdW attraction would originate from vacuum fluctuation-driven charge density oscillations. Such oscillations couple through virtual photons, producing the familiar London dispersion forces [31–33]. Cooling a chalcogenide melt extremely slowly would permit the electron clouds time to relax into a lower energy, more correlated configuration, maximizing polarizability. This in turn would increase the infrared refractive indices. Conversely, faster cooling traps the system in a higher energy electronic configuration with reduced dipole–dipole correlation, lowering polarizability and decreasing refractive indices.

To model these purely electronic shifts without violating our static volumetric density baseline, we will be using our rate-independent "true" glass transition temperature, $T_g(0)$, at isothermal equilibrium, to provide a unified mathematical framework linking microscopic intermolecular potential energy surfaces to macroscopic property drift [34]. A rigorous, first-principles mathematical derivation of this local-field micro-cavity model is reserved for a forthcoming companion paper. Its qualitative implications provide immediate clarity to the density and aging paradox observed here.

Two-photon absorption (2 PA) in ChGs provides us with an additional and powerful window into the electronic structure of these materials [35–43]. Because 2 PA is a nonlinear optical process that depends on electron cloud deformability and virtual state coupling, its magnitude and spectral characteristics offer independent, corroborating evidence for the importance of vdW interactions and the soft electronic behavior implied by our density model parameters. The strong 2 PA response observed experimentally in ChG literature aligns naturally with a model in which lone-pair electrons, not rigid covalent bonds, dictate the optical and aging behavior of the network.

2 PA occurs when two sub-bandgap photons are absorbed simultaneously, promoting an electron to a higher energy state that neither photon could reach alone [38, 39]. This second-order process requires (1) large electronic polarizability, (2) highly deformable electron clouds, (3) strong dipole–dipole coupling pathways, and (4) accessible virtual intermediate states. These conditions are characteristic of vdW-biased chalcogenide networks, where lone-pair electrons are loosely correlated and easily perturbed. In contrast, rigid covalent networks (*e.g., silica*) exhibit weak 2 PA because their electrons are tightly bound and less responsive to external fields. Thus, the strength of 2 PA in chalcogenides is itself evidence of a soft, polarizable electronic environment enriched by vdW interactions.

2 PA spectra in ChGs typically show broad absorption tails, sub-bandgap transitions, strong sensitivity to local electronic disorder, and enhanced response in Se-rich and As-rich compositions [35, 36]. These features are difficult to reconcile with a rigid covalent network but are fully consistent with a soft, polarizable electronic landscape shaped by vdW interactions and lone-pair electron distributions.

We express again that we don't dismiss covalent bonds in our framework. Covalent units within our model's network function

as rigid, low polarizability islands. In our model, they suppress 2 PA locally, reduce electronic deformability, create internal electric field gradients, and partition the network into vdW-rich domains. This mixed environment enhances nonlinear optical response by producing regions of high electronic softness adjacent to rigid covalent anchors, increasing local field intensification and contributing to the observed 2 PA strength.

When we step back and analyze the landscape we've created, we draw our most important testable conclusion. The transition dynamics depend on composition, bonding, and the distance from equilibrium imposed by an *"imperfect manufacturing process."* Our framework provides insight into the "aging" or stability problems observed in many ChG compositions, which are important to the electro-optics and photonics community. In our model, trapped electrons are not created as an intrinsic property of ChG compositional physics but are introduced as a consequence of ineffective manufacturing protocols [44]. While certain compositions may be more vulnerable to these defects, our working theory suggests that correct processing can eliminate these outcomes across all systems. We are collecting data that suggest that processing a ChG composition in a manner that greatly reduces or mitigates trapped-electron formation will yield a material that is essentially free of deleterious aging effects and completely suitable for sub-Strain Point temperature applications. As such, it will provide maximum polarizability (*hence, maximum and stable refractive index dispersion behavior*) and superior stability for all "bulk" physical properties. These attributes are critical for infrared electro-optic and photonic materials. We will provide further information about these findings and detailed processing protocols in a future article.

The physical interpretation of our empirical results provides a focused research agenda to deepen our scientific community's understanding of ChG structure–property relationships. We understand and agree that our approach to examining and predicting properties based on bonding and bond stability over time warrants further study, including revisiting prior efforts to examine time-dependent variation in optical and physical properties across different glass forms (i.e., bulk, thin film, and fiber). Our framework provides a unifying lens through which these observations can be interpreted.

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Ethical Statement

This study does not contain any studies with human or animal subjects performed by any of the authors.

Conflicts of Interest

The authors declare that they have no conflicts of interest to this work.

Data Availability Statement

The data that support the findings of this study are openly available in the Supplementary Materials (Table S1). The legend in Figure 1 reflects these data and provides a simple means for cross-referencing to Table S1 in the Supplementary Materials.

Author Contribution Statement

Thomas J. Loretz: Conceptualization, Validation, Investigation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project Administration. **Richard A. Loretz:** Conceptualization, Methodology, Software, Validation, Formal Analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing.

Supplementary Materials

The supplementary materials are available from the article webpage at <https://doi.org/10.47852/bonviewJOPR62029989>.

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