



# Predictive method to assess chalcogenide glass properties: bonding, density and the impact on glass properties

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**Abstract:** This paper evaluates composition and property measurements for 267 chalcogenide glass compositions developed by researchers over the past several decades for potential use in infrared optical applications. It addresses the role and impact of chemical bonding as it relates to the physical properties for this class of materials, by applying a novel strategy to predict density, based on a new theory which assigns molecular bonding type and type contribution. This theory challenges decades of beliefs by pioneers in the field. The authors validated the models using a wealth of supportive measured density data from literature. The predictive algorithms developed in this paper are intended to aid the infrared optical engineer's understanding of the physics and properties of bulk glass components, planar thin films and fibers for imaging and sensing devices.

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## 1. Introduction

Researchers have always considered the relationship between glass properties and composition to be a key dataset for interpreting a new chalcogenide glass (ChG) family's molecular structure and physio-chemical behavior. Trends in these data allows the prediction of a multitude of properties that guide compositional choice for potential targeted applications, including glass choices for specific optical applications. A glass' density is often the most frequently measured property in this data set, since it is readily measured in the laboratory, even for small melt samples. As a result, dozens of new families and hundreds of new ChG compositional densities have been measured and reported by researchers and institutions in the field, supplying a wealth of data for theoretical modeling.

A comprehensive data review of this density research performed as part of our present study has enabled the authors to evaluate such trends and to specifically focus on the molecular bonding nature of chalcogenide glasses. In particular, we have collected density data from a broad range of literature references for 40 glass families and 267 ChG individual compositions, reported by many dozens of principal authors and institutions over the past 50 years.

Following a brief review of key literature that has defined much of this current thinking, we summarize our interpretation gleaned from analysis of experimentally determined density data. We provide two different but correlated methods, which can be applied to the vast majority of chalcogenide glass families to predict bulk glass density quite accurately, prior to actual fabrication. The first method uses effective atomic radius factors and compositional percentages. The second method uses elemental density factors and compositional weight percentages. We also provide a means to improve the accuracy of prediction for all families with regression analysis equations and an extended factor database.

## 2. Method

### 2.1. Background

In his comprehensive and highly-referenced 1989 paper on the subject of density and the nature of the chalcogenide glass bond, Tanaka presents Phillips theories on ChG topology and element coordination [1,2]. He presents and explains Zallen's theories on molecular dimensionality. Zallen advanced a dimensionality term ("D") by leveraging his belief that most, if not all, chalcogenide glasses possess medium-range order of about 20 Å. Tanaka incorporates both of his colleague's beliefs to theorize a model for ChGs, whereby increasing numbers of discrete elements and/or elemental 'coordination numbers' define the extent of network connectivity [3]. Coordination numbers are directly related to an element's place on the periodic table.

Furthermore, as a consequence of employing Zallen's "D" term, Tanaka's suggests a summation equation which biases the proportioning of covalency and van der Waals (vdW) forces heavily in favor of covalency. As will be shown below, our evaluation of density data collated in this study will challenge the bias toward covalency. Specifically, if the nature of the chalcogenide glass bond is predominately covalent, then calculations involving known density, atomic mass, covalent radii, atomic packing and random atomic distribution in an amorphous-based model should be all that are necessary to validate Tanaka's assertion. Therefore, to evaluate his theory fairly, we contend that one must ignore the bias of a dimensionality constant and consider the possibility of length scales of order less than 20 Å. This approach serves as a key premise in our study.

Covalent radii for elements are well-established, published values and typically do not vary by more than 1 picometer (pm) from one source to the next. This fact was confirmed after reviewing many sources and subsequently we developed a data table of covalent radii values to start our analysis. In an effort to explore Tanaka's summation equation using conventional mathematical methods, we calculated the approximate covalent radii bonded molar volumes for a small subset of the chalcogenide glass (ChG) compositions investigated during this study. Using these data in combination with the proportioned molar masses of each element and comparing the results against their respective published density data (*i.e.*, *density equals grams of element per mole divided by volume of element per mole*), we determined that covalent bonding could not explain the predominant atomic bonding nature of these glass formulations. Calculated densities using covalent radii were considerably higher and for the most part not within 60% of measured values, due to calculated atomic volumes being substantially smaller than would have been required (*even with a calculation biased with a packing factor consideration*). Hence, it was postulated that considerably larger-radiused, weaker atomic bonding forces must be physically employed. We determined that van der Waals (vdW) radii would be the most reasonable pathway to provide atomic volumes consistent with our density measurement data.

Sourcing van der Waals radii data from the 1981 Handbook of Physics and Chemistry and considering how best to apply these radii correctly in a molecular environment to calculate atomic volume, we evaluated, as a first approximation, the subset of ChG compositions for their molar and atomic volumes employing solely vdW radii. Based upon this data, all calculated densities were found to be in close agreement (*within ~5.5%*) of published measured density values. These early results were compelling and prompted a more thorough assessment of as many different ChG families and compositions as possible, mining published room temperature density data references for a multitude of ChG glass families.

In parallel, we queried the numerous sources for current data on van der Waals radii of the elements, which we could apply with some confidence to validate our theory. Our research indicated that vdW radii were originally determined empirically from the mechanical properties of gases, and more recently by using measurements of atomic spacing between pairs of unbonded atoms in crystals and most recently from measurements of electrical polarizability and/or optical

molar refractivity properties [4–6]. Even with advancements in measurement practices, the most recent techniques give values for the van der Waals radii of an element's atom which vary considerably from one source to the next. Importantly these data are similar but not identical, often differing by as much as  $\pm 0.30 \text{ \AA}$  ( $\pm 30 \text{ pm}$ ). Consequently, different tables often have different values for the vdW radius of an element, leading one research group of physicists to conclude that there is no justification for the van der Waals radius to be a fixed property of an atom in all settings and to expect that a vdW radii will vary with the atom's particular physio-chemical environment [7].

Recognizing that the atoms found within ChGs experience their own unique physio-chemical environment, we chose to re-evaluate our initial subset of ChG compositions by employing the most current vdW radii values from sources considered by our review and their reputation to be most reasonably accurate [8,9]. When applying vdW radii in a density volume equation, packing factor is not included in the calculation since we employ "effective atomic radii". Effective atomic volume is determined simply by calculating the equation for the volume of a sphere ( $4\pi r^3/3$ ) where  $r$  is the effective atomic radius (*equivalent to a distorted and compliant atomic field volume, elegantly managing the issue of packing factor*). To our amazement, the correlation of research measured ChG composition density values with those calculated using our forecast model using tabulated effective atomic radii resulted in substantially better agreement and in many cases values within  $\pm 1.5\%$ .

For the vast majority of glass data found in the present study, we neither made the melts, duplicated the melts nor made the measurements ourselves. Therefore, to a large extent, we were dependent on a particular researcher's measurement method, lab protocols and the fidelity of their annealed samples. We knew from our past research that a properly annealed sample is necessary to achieve the most representative room temperature density value attainable. We were aware that many lab sample researchers do not consider anneal quality an important protocol; sometimes choosing to use 'as quenched' glass for their density tests. For those who do consider it important, they often do not publish the parameters employed in their anneal thus raising questions as to the temperatures employed, the soak time and/or the  $\Delta T/\Delta t$  annealing rate. Moreover, many researchers sometimes do not have appropriate equipment, techniques or samples to measure density accurately to better than  $\pm 4\%$ , despite claims to the contrary. Armed with this understanding and background towards our interpretation of published data, we understood why fairly different density values were reported for identical glass compositions by different authors. In one notable case, this type of conflict was discovered in two publications by the same research team. Thus, it is probable that variations seen in our data are in part due to these types of random and systematic errors. However, we believe that these error contributions are small and do not diminish the reliability of the approach used in our models and our findings.

As presented below, it will be shown that our models allow researchers to predict glass densities based upon knowing the glass composition and applying a set of elemental factors [either (1) atomic masses and effective atomic radii or (2) density factors]. For the vast majority of common ChG glass compositions, we have found that a single fixed universal elemental 'factor-set' works very well. This evidence provides testimony to the nature of chalcogenide glass molecular bonding in general, with its weak atomic forces bonding most, if not all of the molecules in the network in a completely amorphous manner, with apparent 'short-range structural order' well below Zallen's  $20 \text{ \AA}$ .

For a significant subset of glass compositions, we have found that certain elements within the composition require factor adjustments, which allow for changes in the degree and extent of covalent bonding. It should be mentioned that only a few ChG elements show evidence of large amounts of covalent bonding. Glasses formed from these elements, which will be shown as exceptions to the general rule based on our evaluation, are none-the-less important in their own right and have been reported in this study. A comprehensive data review of this density research

performed as part of our present study has enabled the authors to evaluate such trends and to focus specifically on the molecular bonding nature of chalcogenide glasses. In particular, we have collected laboratory-measured density data from a broad range of literature references for 40 glass families, and 267 ChG individual compositions, which were reported in more than 30 peer-reviewed publications, for research made over the past 50 years [10–41].

## 2.2. Establishing element covalency and van der Waals percentages

To develop the forecast models below, we employed our own Reverse Monte Carlo approach and data regression techniques to mine available ChG compositions for their measured density data. Reverse Monte Carlo (RMC) modeling involves applying a theoretical algorithm to a large set of data, whereby a researcher continually adjusts the model until an endpoint is reached where the parameters of the experiment exhibit the greatest correlation with the data. Therefore, it is an iterative process. RMC is frequently used in nuclear physics to study atomic models based on a set of experimental data and modeling constraints. To establish elemental factor tables, we determined the average elemental effective atomic radius values for each glass composition. To determine these values, we assumed a perfect (*truly random*) amorphous distribution of each element (*which is the equilibrium network configuration for properly melted, homogenized and annealed ChG*).

We established definitions for bonding we coined as: “% covalency,” “% van der Waals,” and “% sub-covalency.” From scientific literature, we determined each element’s covalent radius value ( $R_{\text{cov}}$ ) and each element’s van der Waals radius value ( $R_{\text{vdW}}$ ). (*Note: Sourced covalent radii are typically in close agreement and vary less than  $\pm 1$  pm. Sourced vdW radii can vary as much as  $\pm 14\%$ , depending upon physio-chemical environment and measurement technique. To overcome this problem, our vdW values are averaged from the most recent electrical polarizability and optical molar refractivity data and seem to vary by less than  $\pm 8\%$ .)*) These data allowed us to define the actual chalcogenide glass composition’s elemental effective atomic radius values used ( $R_{\text{Used}}$ ) in terms of % covalency, % van der Waals or % sub-covalency bonding, depending on the following:

when  $R_{\text{cov}} \leq R_{\text{used}} \leq R_{\text{vdW}}$  :

$$R_{\text{used}} = (\% \text{ covalency}/100\%) \times R_{\text{cov}} + ((100\% - \% \text{ covalency})/100\%) \times R_{\text{vdW}}, \quad (1)$$

when  $R_{\text{used}} > R_{\text{vdW}}$  :

$$R_{\text{used}} = ((100\% + \% \text{ van der Waals})/100\%) \times R_{\text{vdW}}, \quad (2)$$

and

when  $R_{\text{used}} < R_{\text{cov}}$  :

$$R_{\text{used}} = (\% \text{ sub-covalency}/100\%) \times R_{\text{cov}}. \quad (3)$$

Table 1 provides the results of our RMC and data regression activities for 147 glass compositions (a subset of the 267 ChG formulations in our study) that were analyzed using a fixed set of bonding values. We refer to them as the Fixed Element Values (‘universal values’) for % covalency, % van der Waals and % sub-covalency.

Notice in Table 1 that the ChG elements, **As**, **Bi**, **Ga** and **Sb** have relatively low % covalency values, which we believe implies that these elements have radii that are closer to their assigned vdW radius values (*typical ChG environmentally averaged*) and behave in what we call a ‘normally expected manner.’ Similarly, notice that the elements **I**, **In**, **Pb**, **S**, **Se** and **Te** have % van der Waals values, implying that these elements normally have radii values which exceed the element’s vdW radius. The only elements that exhibited significant “near-covalent” radius values in our assessment are **Ag** and **Cu** (where the latter element is ‘exclusively’ in the sub-covalent category).

**Table 1. Tabulated Covalent and van der Waals Radii Bonding Data by Element<sup>a</sup>**

ChG Element	BASIC REFERENCE DATA FOR THE 16 ELEMENTS USED IN OUR STUDY			FIXED RESOLVED BONDING FACTORS*		
	Covalent Radius (pm)	vdW Radius (pm)	Radii Data Sources (Cov., vdW)	% Cov.(eq. (1))	% vdW (eq. (2))	% Sub-Cov. (eq. (3))
Ag	145	172	1,2 3	88.3	—	—
As	119	185	1,2 3	15.5	—	—
Bi	148	207	1,2 3	5.0	—	—
Cu	132	140	1,2 3	—	—	86.4
Ga	122	187	1,2 3	22.3	—	—
Ge	120	211	1,2 3	43.7	—	—
I	139	198	1,2 3	—	9.0	—
In	142	193	1,2 3	—	4.6	—
Pb	146	202	1,2 3	—	0.4	—
S	105	180	1,2 3	—	5.4	—
Sb	139	206	1,2 3	22.3	—	—
Se	120	190	1,2 3	—	2.2	—
Si	111	210	1,2 3	33.1	—	—
Sn	139	217	1,2 3	47.7	—	—
Te	138	206	1,2 3	—	1.9	—
Zn	122	239	1,2 2	42.4	—	—

<sup>a</sup>(\* NOTE: Only one of the three equations will apply per element and is determined via RMC analysis.)

<sup>a</sup>(Sources: {1} PeriodicTable.com, {2} WebElements.com, and {3} Wikipedia - van der Waals Radius.)

### 2.3. Chalcogenide glass families evaluated

The 40 ChG families that form the subject of this study are listed in Table 2. The elements employed in these compositions cover a wide spectrum of common elements used in laboratory and commercial melts.

**Table 2. Chalcogenide Glass Compositional Families Studied in the Present Effort<sup>a</sup>**

<b>Vitreous Se</b>	<b>Ge-As-Se-Bi</b>	<b>Ge-S-Ag</b>	<b>Ge-Te-I</b>
<b>As-S</b>	<b>Ge-As-Se-Pb</b>	<b>Ge-Sb-S</b>	<b>Ge-Te-Se</b>
<b>As-Sb-Se</b>	<b>Ge-Bi-S</b>	Ge-Sb-Se	<b>Ge-Zn-Se</b>
<b>As-Se</b>	<b>Ge-Ga-S</b>	Ge-Sb-In-Se	Ge-Zn-Se-Ag
<b>As-Se-Cu</b>	<b>Ge-Te</b>	<b>Ge-Sb-Te-S</b>	Si-As-Te
<b>As-Se-S</b>	<b>Ge-Ga-Sb-S</b>	Ge-Se	Si-As-Te-Ag
<b>As-Se-Te</b>	Ge-Ga-Se	<b>Ge-Sn-S</b>	Si-As-Te-Se-Ag
<b>As-Se-Te-Cu</b>	<b>Ge-In-Se</b>	Ge-Sn-Se	Te-Bi-Se
<b>Ga-As-Te-Se</b>	Ge-In-Te	<b>Ge-Te-Ag</b>	Te-Se
Ge-As-Se	Ge-S	<b>Ge-Te-Ag-I</b>	<b>Te-Sn-Se</b>

<sup>a</sup>(**BOLD TEXT** indicates a subset of 25 families associated with Figure 1.)

The 16 elements examined in our study are found in Table 3. We have included their Periodic Table coordination number values in parentheses (). When summed in combination with a

ChG's composition by atomic percentage they are used to determine the composition's Mean Coordination Number (MCN).

**Table 3. Coordination Numbers for Elements Evaluated in Our Investigation**

Ag (1)	Cu (2)	I (1)	S (2)	Si (4)	Te (2)
As (3)	Ga (3)	In (3)	Sb (3)	Sn (4)	Zn (2)
Bi (3)	Ge (4)	Pb (3)	Se (2)		

## 2.4. Forecast models to estimate density

### 2.4.1. Forecast model based upon elemental radii factors

After establishing the % covalency, % van der Waals or % sub-covalency bonding values for each element, we developed a forecast density model for each glass composition based upon the atom percentage of each element in the chalcogenide glass composition.

From the literature, we determined the average atomic weight (gm/mol) for each element very accurately. 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.

$$M = \sum_i (\text{atm}\%_i \times [\text{elemental gram/mole}]_i) \quad (4)$$

To calculate density, (*equal to molar mass divided by molar volume*), we needed to establish the molar volume associated with the specific elements in the ChG composition. We calculated the effective atomic radius ( $R_{\text{used}}$ ) values for each element from (eq. (1)), (eq. (2)) or (eq. (3)) using our RMC analysis algorithm and created Table 4 using the respective fixed % covalency, % van der Waals or % sub-covalency values from Table 1. (*We supply our RMC analysis resolved data in Tables 1 and 5. The reader is not expected to make direct use of equations (1) through (3).*)

This exercise enabled us to determine the molar volumes for the ChG compositions as follows:

$$V = \sum_i (\text{atm}\%_i \times [\text{elemental cm}^3/\text{mole}]_i) \quad (5)$$

The **elemental cm<sup>3</sup>/mole** for an element is determined by multiplying Avogadro's number ( $N_A$ ), (**6.0221e+23**) and the formula for spherical volume ( $V = 4/3 r^3$ ); where the effective atomic radius ( $r$ ) is  $R_{\text{used}}$  for the element as provided in Table 4.

Figure 1 shows the results of applying our forecast model 'blended' covalent and van der Waals radii values by element to a subset of the overall glass compositions we studied (The families applied are found **bolded** in Table 2). Our forecast model was compared to actual reported density measurements for the 147 glass compositions contained within these 25 families. We recognize that our data-mined measured values may not represent the highest possible value for the composition, as the best reported value is only achieved after careful annealing of the glass. We expect sample annealing error to contribute less than 2% density error, based on our own ChG melt work.

Notice that, for these ChG families, the predicted and measured values are in particularly good agreement. The range of densities involved goes from as low as 2.6 gm/cc to as high as 6.3 gm/cc. A measure of the accuracy of our forecast model is exhibited by the  $R^2$  value based upon a linear regression of the data equal to 0.9946 (*almost unity*) with a near zero offset. **It is important to mention** that the linear regression equation may be used as an additional adjustment tool to improve prediction reliability further for specific compositions being contemplated, prior to melt. Simply enter your particular '*calculated density value*' into this equation and the solution should

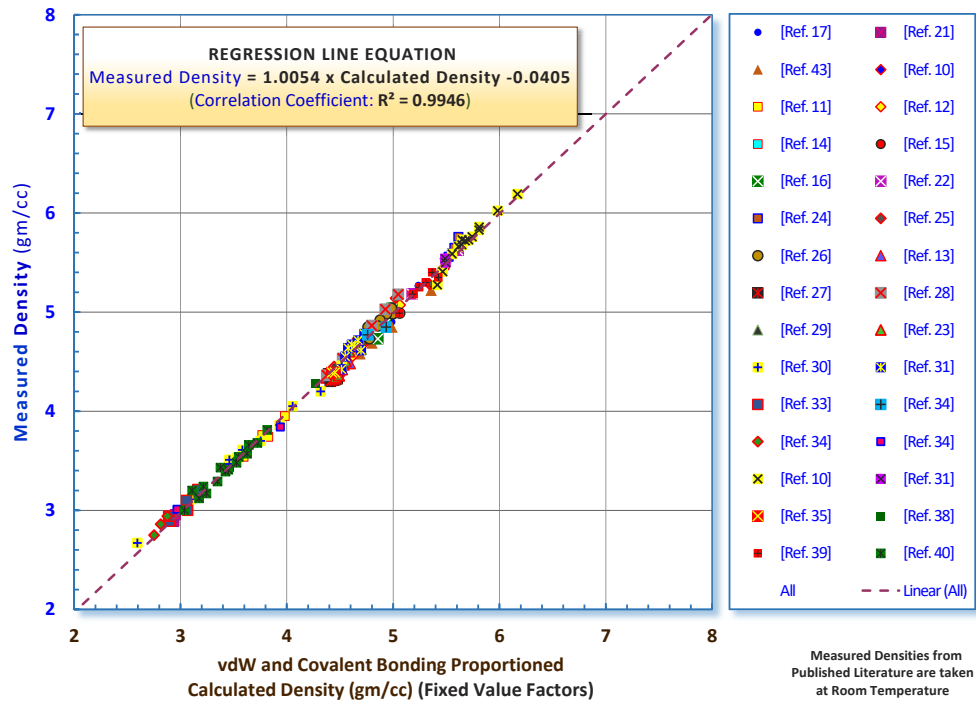
**Table 4. Fixed Radii for use with Figure 1 Density Prediction (Fixed vdW, Fixed Covalent Radii Forecast Model)**

Chalcogenide Glass Element	van der Waals Radius (pm)	Covalent Radius (pm)	Blended Radius Used (calculated $R_{used}$ ) (pm)
Ag	172	145	<b>148</b>
As	185	119	<b>175</b>
Bi	207	148	<b>204</b>
Cu	140	132	<b>114</b>
Ga	187	122	<b>173</b>
Ge	211	120	<b>171</b>
I	198	139	<b>216</b>
In	193	142	<b>202</b>
Pb	202	146	<b>203</b>
S	180	105	<b>190</b>
Sb	206	139	<b>191</b>
Se	190	120	<b>194</b>
Si	210	111	<b>177</b>
Sn	217	139	<b>180</b>
Te	206	138	<b>210</b>
Zn	239	122	<b>189</b>

**Table 5. Family Adjusted Elemental Values for Resolved Bonding Factors and Blended  $R_{used}$** 

ChG Family	Compositional Element(s) Adjusted	Bonding Factor Adjustment by Element (column 2, respectively)	Adjusted Blended $R_{used}$ by Element (pm)
Ge-As-Se	Ge, As	33.5%, 0.7% *	180, 186
Ge-Ga-Se	Ge, Se	33.5%, 2.9% *	180, 195
Ge-In-Te	In, Te	0.7% *, 3.9% *	194, 214
Ge-S	Ge, S	33.5%, 4.9% *	180, 189
Ge-S-Ag	Ag, S	87% #, 1.9% *	127, 184
Ge-Sb-In-Se	Ge, In, Sb, Se	40.4%, 9.5%, 33.8%, 2.0%	174, 188, 183, 189
Ge-Sb-Se	Ge, Sb	33.5%, 33.8%	180, 183
Ge-Se	Ge, Se	33.5%, 2.9% *	180, 196
Ge-Sn-Se	Ge, Sn	40.4%, 24.7% *	174, 271
Ge-Zn-Se-Ag	Ge, Ag	33.5%, 0.0%	180, 172
Si-As-Te	Si, As, Te	38.2%, 0.7% *, 3.9% *	172, 186, 214
Si-As-Te-Ag	Si, As, Te	38.2%, 0.7% *, 3.9% *	172, 186, 214
Si-As-Te-Se-Ag	Si, As, Te	38.2%, 0.7% *, 3.9% *	172, 186, 214
Te-Bi-Se	Se	4.7%	187
Te-Se	Se	4.7%	187

(NOTE: \* denotes % van der Waals factor and # denotes % sub-covalency factor adjustment.)



**Fig. 1.** Covalent and van der Waals Bonding Proportioned, Measured Density vs Calculated Density for 25 Families and 147 Chalcogenide Glass Compositions, with  $R_{Used}$  from Table 4.

provide a more representative density value.

Calculated Theoretical Density

$$= \sum_i (\text{atm}\%_i \times [\text{elemental gm/mole}]_i) / \sum_i \left( \text{atm}\%_i \times \left[ \text{elemental} \frac{\text{cm}^3}{\text{mole}} \right]_i \right)$$

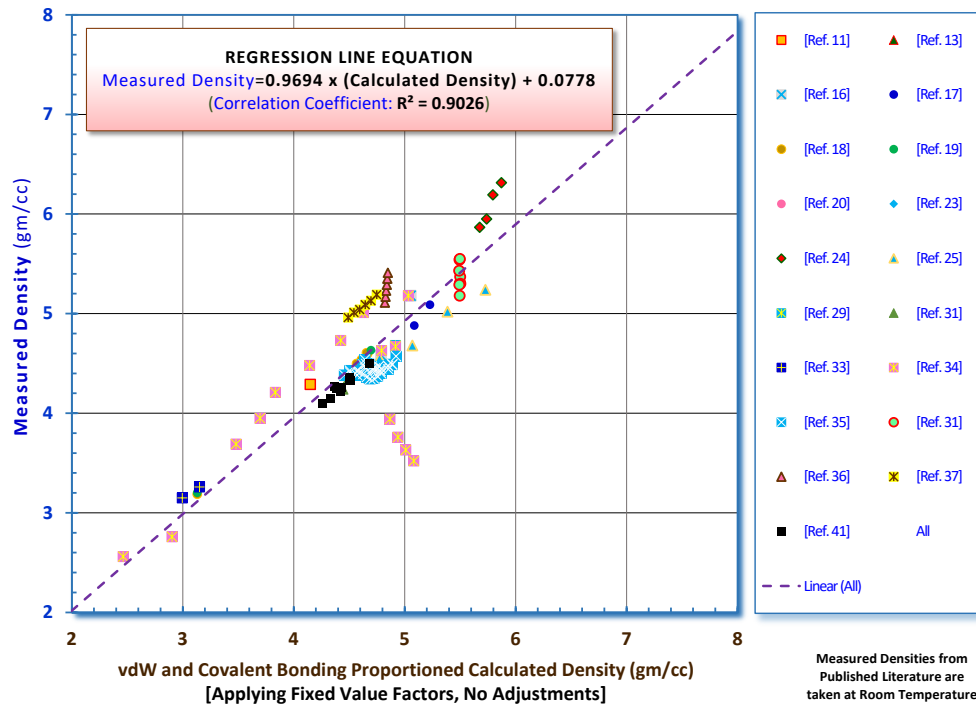
For the additional 15 ChG families and 120 ChG compositions studied, when applying our forecast model with fixed elemental radii values, we found that the density results exhibited varying degrees of unacceptable variability, as shown in Figure 2. We postulated that these glass families required adjustments to their elemental % covalency and/or % van der Waals and/or % sub-covalency factors to improve the prediction accuracy of our forecast model (*discussed later in this paper*).

We executed Reverse Monte Carlo simulations for each of these families and identified the elements that required varying degrees of adjustments. We created Table 5 from this data and improved density predictions vs measurements for these ChG formulations, as shown in Figure 3.

The regression fit for this adjusted forecast model for the 15 families plus the original fixed set results for the 25 families is particularly good with an overall  $R^2$  value equal to 0.9932. Once again, a final predicted density value can be improved by applying the linear regression equation to the calculated value.

In summary, the fixed radius set (Table 4) may be used to forecast the entire 40 families of glasses studied, if one is willing to accept density forecast differences between calculated and measured of about  $\pm 10\%$  (*with the exception of one family*). Over the range 2.6 gm/cc and 6.3 gm/cc, this is still a fair prediction tool ( $\pm 0.26$  gm/cc at the low end and  $\pm 0.63$  gm/cc at the high end). Contrast this situation against a **30% covalent radius** model with a **packing factor of 50%**, which by our calculations (*eq. (1)*) we find to predict densities which are at still at least





**Fig. 2.** Covalent and van der Waals Bonding Proportioned, Measured Density vs Calculated Density for the remaining 15 Families and 120 Chalcogenide Glass Compositions, using fixed effective radii found in Table 4, showing the need for additional adjustments.

**15% higher** than actual measured values. Even if the calculated densities were close to measured values at 30% covalency with a 50% pf, we couldn't consider this glass to be a predominantly covalently bonded material.

#### 2.4.2. Forecast model based upon elemental liquid density factors

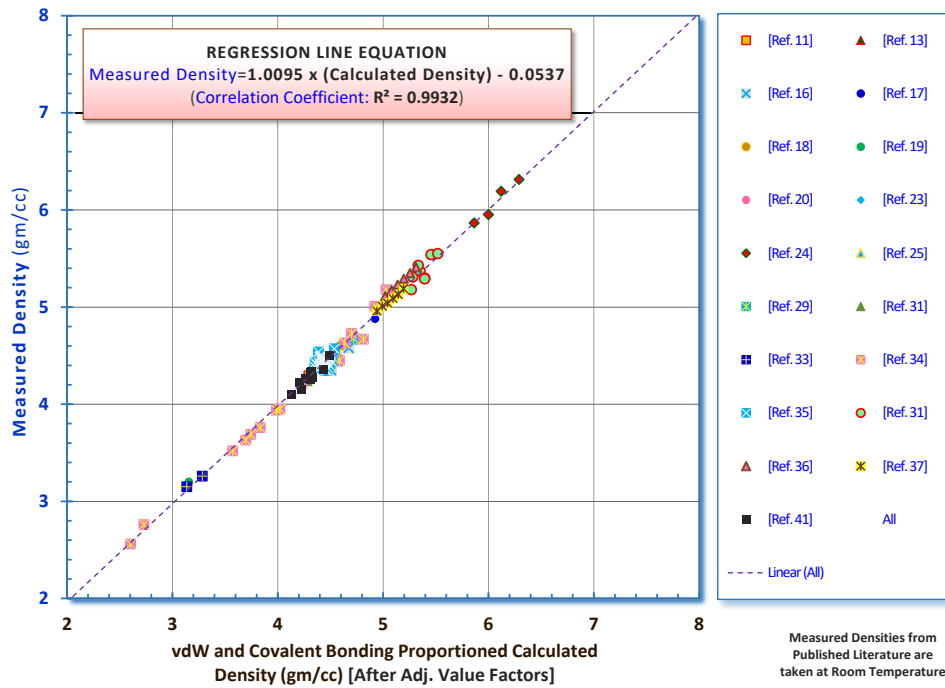
A second density forecast model has been developed based upon utilizing a set of what we refer to as elemental "Loretz Wt% Density Factors". We started examining this approach when we noticed that many ChG forming elements have densities at their melting temperatures which can be proportioned by their respective weight percentages to yield a composition density which is close to the measured density of that glass composition. Our work suggests that chalcogenide glasses are successfully formed when melted compositions are cooled in a manner which inhibits the reconstruction of covalent bonds in favor of the weaker van der Waals forces. Therefore, it makes sense that a glass' density would be similar to that found at the melting point; adjusted only by the thermal expansion characteristics.

The governing equation for determining the density of a composite mixture from each elemental density is:

$$\rho = 100\% / \sum_i (wt\%_i / \rho_i) \quad (6)$$

where [ wt%<sub>i</sub> ] is the weight percentage of element i in the glass composition and [ ρ<sub>i</sub> ] is the elemental liquid density factor associated with element i.

The weight percentage of each element in a ChG composition can be calculated knowing the atm% values for each element in the composition and the published average atomic weights of



**Fig. 3.** Covalent and van der Waals Bonding Proportioned, Measured Density vs Calculated Density for the additional 15 Families, 120 Chalcogenide Glass Compositions, using the Radii Adjustments of Table 5.

each element ( $M_i$ ).

$$\text{wt}\%_i = \text{atm}\%_i \times M_i / \sum_j (\text{atm}\%_j \times M_j) \quad (7)$$

In analogous manner to the forecast model and again based upon using elemental effective atomic radii, we employed reverse Monte Carlo and other regression techniques to establish a fixed set of elemental density values that can be used in (eq. (6)) to forecast ChG densities. The fixed set of density factors that were determined by our evaluations is shown in Table 6.

Figure 4 shows the results of our density forecast model for the 25 ChG families based upon a fixed set of density factors (see Table 6). (These are the same ChG compositions used in Figure 1.) The measured vs calculated density values show excellent agreement as evidenced by an overall  $R^2$  linear regression value of 0.9946.

Calculated Density

$$= 100\% / \sum_i (\text{wt}\%_i / [\text{elemental Loretz Wt}\% \text{ Density Factor (see Table 6)}]_i)$$

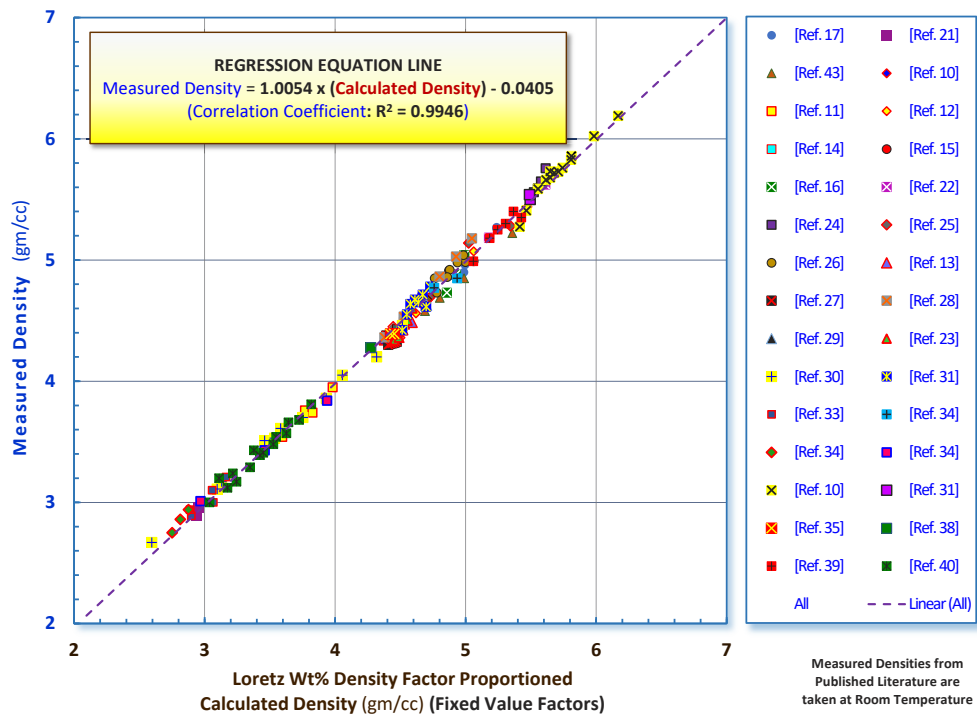
These results were not surprising to us, as they simply express that it is possible to determine the elemental Loretz weight percent density factors from the elemental molar masses (*atomic masses*) and the elemental molar volumes (*employing the  $R_{\text{used}}$  radius values*). The density of element 'i' is equal to gm/mol of element 'i' divided by the  $\text{cm}^3/\text{mol}$  of element 'i,' as discussed earlier in the paper.

### 2.5. Elements that require adjustments to their estimated density calculation

As shown in Table 5, we found that 15 glass families required adjustments to the elements: **Ag**, **As**, **Ge**, **In**, **S**, **Se**, **Sb**, **Si**, **Sn** and/or **Te** to yield good ChG density forecasts. The adjustments

**Table 6. Elemental Wt% Density Factors for use with Table 2 and Figure 4**

Chalcogenide Glass Element	Density @ Melting Pt. (gm/cc)	Melting Temperature (°C)	Loretz Wt% Density Factor (gm/cc)
Ag	9.32	962	<b>13.15</b>
As	5.10	615 (sub)	<b>5.56</b>
Bi	10.05	271	<b>9.75</b>
Cu	8.02	1085	<b>17.00</b>
Ga	6.10	30	<b>5.38</b>
Ge	5.59	938	<b>5.73</b>
I	4.93	114	<b>5.00</b>
In	7.02	157	<b>5.53</b>
Pb	10.66	327	<b>9.86</b>
S	1.82	115	<b>1.86</b>
Sb	6.53	631	<b>6.92</b>
Se	3.99	221	<b>4.27</b>
Si	2.57	1414	<b>2.00</b>
Sn	6.99	232	<b>8.10</b>
Te	5.17	450	<b>5.46</b>
Zn	6.57	420	<b>3.82</b>



**Fig. 4.** Loretz Wt% Density Factor calculated data for 147 Chalcogenide Glass Compositions and 25 ChG Families. Measured Density vs Calculated Density at RT. (using the fixed elemental wt% density factors of Table 6.)

needed by family appeared dependent on a combination of compositional makeup along with an element's individual proportions (*high or low*). As seen by comparing Table 4 to Table 5, many of the adjustments made in the factors for % *covalency*, % *van der Waals* or % *sub-covalency* are relatively small. Nonetheless, we see them as significant in our endeavor to predict accurate densities from compositional information. We believe that further research will help us to understand the various mechanisms which are responsible for these needed bonding adjustments.

It is possible to adjust the Loretz weight percent density factors in similar fashion to the vdW and covalent radii factors to create a subset which will satisfy the needs of all 40 glass families, in a manner similar to that presented for Figure 3.

### 3. Discussion

#### 3.1. Insight into our forecast model

Amorphous Selenium became an important data point during our early model development. Since it is a uniform amorphous network of 100% Se atoms, it allowed us to determine the elemental radii value and elemental liquid density factor values needed, directly for accurate glass density determination. Once this fixed value was established, all other elements could be determined more readily via our Reverse Monte Carlo algorithm analysis and other advanced mathematical regression techniques we developed specifically for the purpose.

It is important to note that the density data used in our forecast models was collected over a period of about 10 months. Most of the development of the elemental effective atomic radii values and elemental liquid density factors was based upon a very early, and small, subset of the data. Thus, we can say with all honesty that the additional glass compositions that came over time were more a test of our forecast models and elemental values than they were important data points for establishing the elemental effective atomic radii and elemental liquid density values.

As time progressed, minor adjustments were made to our existing database of factors and revised values were determined based upon either data-mining discovery of new compositional variations within an existing family, identical compositions being reported by additional authors or entirely new glass compositions being mined that had not been previously analyzed. The ability to predict densities accurately as we added measured values to our database increased our overall confidence in our models.

Databases of important values are easily managed and manipulated with the powerful spreadsheet features found within Microsoft EXCEL. We recognized that our models provided us the opportunity to calculate the average effective atomic radii associated with the atoms of each network "molecule" for each glass composition. We were curious to see the variations between glass families.

Table 7 was created by using our database of elemental effective atomic radii and ChG formulations to solve for the average effective atomic radii for each individual glass in a ChG family and subsequently solving the average for the entire family.

Astonishingly, for the 267 ChG compositions evaluated, the average effective atomic radius is about 191 pm with a standard deviation of about 6 pm. This is an important finding and provides a reliable value for chalcogenide glass's average network effective radius which can be used in other studies and models.

Note that we use the expression 'average effective atomic radii.' This is done for a specific reason. We recognize that the values being presented may be misinterpreted by some to suggest that we believe that *only* van der Waals radii are responsible for the molecular construction of a chalcogenide glass, as the magnitudes of the values are indeed consistent with those of typical vdW radii. What we are stating is that these are 'blended' radii, consisting of van der Waals *and covalent* contributions. We are presenting radii values that can be used effectively with the equation of a sphere, to provide a molecular volume which inherently contains a packing factor for a '*homogeneously amorphous*' chalcogenide glass. Our approach eliminates controversy

Table 7. Average Effective Atomic Radii Values by ChG Family

ChG Family	Average Eff. Atomic Radius (pm)	ChG Family	Average Eff. Atomic Radius (pm)	ChG Family	Average Eff. Atomic Radius (pm)
Se (vit)	194	Ge-In-Se	192	Ge-Ga-S	186
As-S	184	Ge-In-Te	205	Ge-Ga-Se	190
As-Se	191	Ge-Sb-S	186	As-Se-Te-Cu	188
Ge-S	183	Ge-Sb-Se	190	Ga-As-Te-Se	192
Ge-Se	191	Ge-Sn-S	186	Ge-As-Se-Bi	190
Ge-Te	204	Ge-Sn-Se	201	Ge-As-Se-Pb	188
Te-Se	191	Ge-Te-Ag	201	Ge-Sb-Te-S	188
As-Sb-Se	189	Ge-Te-I	204	Ge-Sb-In-Se	187
As-Se-S	187	Ge-Te-Se	196	Ge-Te-Ag-I	200
As-Si-Te	192	Ge-Zn-Se	189	Ge-Zn-Se-Ag	188
As-Se-Cu	184	Te-Bi-Se	191	Ge-Ga-Sb-S	185
Ge-As-Se	190	Te-Sn-Se	195	Si-As-Te-Se-Ag	190
Ge-S-Ag	174	Ge-Bi-S	188	Si-As-Te-Ag	193

Statistical Average for the 267 glasses found within all families: **191 ±6 pm**

associated with dimensionality, short-term covalent bonding structure and the need for associated packing factor considerations.

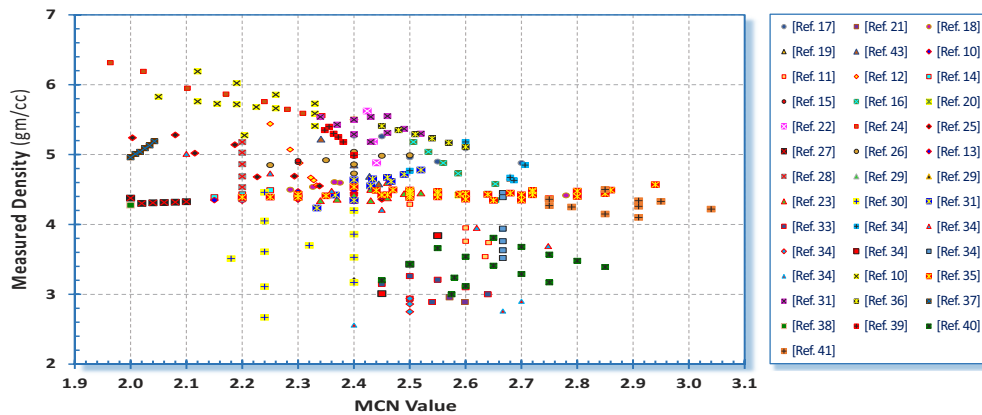
We suggest that the magnitude of the average effective atomic radii values presented lend credence to our belief that ChGs are predominantly (*not exclusively*) constructed by the weaker forces in physics. Calculated radii values for most elements studied are very similar. When one considers their vdW bonding weighting, it leads one to believe that chalcogenide glasses provide a unique physio-chemical environment, consistent with the beliefs of physicists who study vdW radii and the nature of atomic bonds. Covalency is most certainly involved in aspects of bonding. However, we believe that the percentage of covalent bonds, as well as their specific nature, coordination and strength are considerably less than typically promoted in the literature.

### 3.2. Glass formulation density versus mean coordination number (MCN) value

Although not directly a part of our forecast model development, we feel it necessary to mention our evaluation of density and mean coordination number (MCN) value behavior for the studied glass families and glass compositions. As we explained earlier in this paper, MCN theory is based on dimensionality theory, which in turn is based on a dominance of covalent bonds. We have seen attempts by some researchers to correlate density variations in glass families with the MCN values associated with the individual glass compositions.

During the course of compiling our ChG database for our forecast model development, we determined MCN values for each ChG composition studied, using Phillips and Tanaka's approach and the elemental coordination values in Table 3. As an exercise, we decided to plot the measured densities against the MCN values by ChG family and composition for the purpose of evaluating any general macroscopic trends. Figure 5 illustrates the results of this evaluation.

As clearly seen, there is no obvious macroscopic trend of density with respect to MCN value. Within a glass family, some ChG densities decrease with increase in MCN, while for other families, densities increase. Some families show little change in density despite exceptionally large changes in MCN. Other families show large changes in densities despite little change in MCN values. Based on this knowledge, we believe that we are justified to exclude any MCN



**Fig. 5.** Measured Density vs Mean Coordination Number Value for the 267 ChGs studied, illustrating the complete absence of consistent correlation between density of a ChG and the MCN of its compositional makeup.

functionality or contribution to our macroscopic forecast models. We include this information and commentary in support of our decision to exclude Zallen's dimensionality terms and Tanaka's summation equation from our models.

We do not discount the importance of the research effort nor the significance of MCN theory. We have found MCN theory valuable during our development of high temperature viscosity behavior of chalcogenide glasses. It does seem to provide a means to determine the schema associated with a composition's average molecular structure at melt temperature. We believe that it accurately predicts the manner in which all available atoms statistically orientate and align themselves in preparation for forming covalently bonded species. But its usefulness ends there, as the physio-chemical environment is van der Waals in nature and the vast majority of the atoms involved do not attain covalent bonding.

Simply stated, at their effective melt temperature, the atoms of a typical ChG composition lose all sense of covalent bond identity. In practice, they are randomized (amorphous) and adrift in a viscous soup of weakly-bonded, composite atoms. While at the effective melt temperature and as a result of entropy and the nature of atomic bonding, they *position* themselves in a manner which could lead to substantial covalent molecular bonding (*like coordination, but not quite the same*). However, as a consequence of a dramatic change in physio-chemical environment, predominantly van der Waals '*biased*' molecular bonding is favored during subsequent rapid quenching. Nonetheless, dependent upon family and specific composition, some atoms do favor covalency to a greater extent. As our studies show, the magnitude to which they do depends upon many factors. We have attempted to provide insight, where possible.

#### 4. Conclusions

The applicability of non-oxide, chalcogenide glasses in optical systems for the infrared continues to expand. Hence, an understanding of composition-structure-property relationships in systems that can be modeled based on their bonding characteristics, enables the glass researcher to predict performance more accurately in the desired material's environment of use.

This study has examined published data for 267 ChG formulations which comprise 40 different ChG families on the most well reported glass property, density, to illustrate how bonding type influences glass network structure and resulting property predictions. We propose two models which can be used to predict a ChG's density very accurately, based solely on composition. One model makes use of elemental effective atomic radii data in conjunction with the atomic

percentages of the composition and the other model makes use of weight percentages of the composition and density factors. Both models reinforce our theory that the amorphous blend of elements that comprise the chalcogenide glass chemical environment are defined by individual atoms predominantly bonded by weak atomic forces associated with van der Waals radii. They are not bonded exclusively or even principally by forces associated with covalently bonded molecules, as generally expressed historically by our community. While in many cases, there is measurable covalent bonding present, this has been found to be based on the specific elemental makeup and proportions. However, for the vast majority of ChG families and compositions, covalent bonding was not found to be the primary bonding mechanism.

Our review of the density data generated with our model has shown that an average effective atomic radius exists for all chalcogenide glass compositions. It is about 191 pm, with a standard deviation of about 6 pm. This deviation is well within the  $\pm 30$  pm variance associated with atomic environment theory and van der Waals radii assignment and therefore we feel that this deviation is not particularly significant. In fact, these results lend credence to physicists who theorize that van der Waals forces bonded materials can exhibit elemental effective atomic radii which vary, depending on specific chemical compositional environment.

We have found that elements in certain ChG molecules seem to have effective atomic radii that are consistently somewhat smaller than the average assigned ChG van der Waals radii, as resolved in our study. In similar but opposite fashion, we have also found that a subset of elements has effective atomic radii that are consistently somewhat larger than their assigned van der Waals radii.

Lastly, without dismissing MCN theory out of hand, we have provided ample evidence to support our decision not to employ MCN theory and its various contributions in our macroscopic forecast models for ChG density prediction.

**Disclosures.** The authors declare no conflicts of interest.

**Data availability.** Data underlying the results presented in this paper, other than those which are referenced explicitly in Tables and Figures, are not publicly available at this time but may be obtained from the authors upon reasonable request.

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