

Compounds based on Group 14 elements: building blocks for advanced insulator dielectrics design

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Abstract Being in the group with the most diverse set of properties among all in the periodic table, the Group 14 elements (C, Si, Ge, Sn, and Pb) are particularly interesting candidates for structure–property investigation. Motivated by the need to create new insulators for energy storage and electronics applications, we study a few compounds based on Group 14 elements in this work, namely the dihydrides, dichlorides, and difluorides. Using density functional theory (DFT) calculations, we establish patterns in their properties, including favored coordination chemistry, stability, electronic structure, and dielectric behavior. While a coordination number (CN) of 4 is commonly associated with Group 14 elements, there is a significant deviation from it down the group, with CNs as high as 7 and 8 common in Pb. Further, there is an increase in the relative stability of the +2 oxidation state as opposed to +4 when we go from C to Pb, a direct consequence of which is the existence of the di-compounds of C and Si as polymers, whereas the compounds of Ge, Sn, and Pb are strictly 3D crystalline solids. The coordination chemistries are further linked with the band gaps and dielectric constants (divided into two components: the electronic part and the ionic part) of these compounds. We also see that the more stable difluorides and dichlorides have large band gaps and small electronic dielectric constants, and most of the Ge and Sn compounds have remarkably large ionic dielectric constants by virtue of having polar and more flexible bonds. The staggering variation in properties displayed by these parent compounds offers opportunities for designing

derivative materials with a desired combination of properties.

Introduction

The chemical trends captured by the periodic table are seldom more interesting than in Group 14. With their impeccable placement, right between the metals on the left and nonmetals on the right [1, 2], the Group 14 elements are known to map the whole gamut of metallicity themselves, going from nonmetallic C (when in the diamond form) to the metallic Pb [2]. A valence of 4 is characteristic of this group; yet, divalent oxidation states are just as common as tetravalent. The tendency of $p\pi$ multiple bond formation decreases on going down the group [2]. These and many other factors contribute to the significant differences seen in the chemistry of the Group 14 elements: in bond strength, polarizability of bonds, and coordination geometry.

This is a study partly driven by curiosity, and partly powered by the need to identify insulating materials that can surpass ‘standard’ materials used in present-day energy storage and electronics applications. Toward that end, we explore the compounds of Group 14 elements (C, Si, Ge, Sn, Pb) in terms of their crystal structures, chemical coordination, electronic and dielectric properties [3–5] (which would be a fair measure of the electronic and dipolar polarizability of the system). Structure–property investigations were conducted for a number of compounds with the formula unit XY_2 , where X is one of the Group 14 elements and Y is either H or a halogen (Cl, F). It should be noted that Group 14 elements form XY_4 type molecules as well with varying stabilities, but the di-Y formula unit gives us the opportunity to consider solids and thus look at

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properties originating from the crystalline nature of the material.

We performed first principles computations on all the XY_2 compounds in five previously known prototypical structures to obtain the stable structural conformations, the XY_2 formation and cohesive energies, the band gaps, and the dielectric constants. The results obtained showed that the 15 systems adopt a backbone coordination number (CN) ranging from 4 to 8. The energetics showed an increasing stability down the group of the purely 3D crystalline solid as opposed to chain-like motifs, while the electronic and dielectric properties showed an interesting pattern of variation with X or Y. We attempt to capture all these observations and explain them in the coming sections.

Computational details

Density functional theory (DFT) [6, 7], as implemented in the Vienna ab initio software package (VASP) [8–11], was applied to determine the electronic structure and properties of the 15 XY_2 compounds. The Perdew, Burke and Ernzerhof (PBE) [12] functional was used with projector-augmented wave (PAW) [13] pseudopotentials. All calculations were carried out with a tight convergence criterion of 10^{-8} eV and an energy cut-off of 600 eV. Since the traditional PBE functionals are unable to capture van der Waals (vdW) interactions correctly, we incorporated the DFT-DF vdW correction [14, 15] into our calculations.

Further, it is known that PBE calculations underestimate band gap values, and this deficiency is overcome (to a large extent) by the use of Heyd–Scuseria–Ernzerhof (HSE) [16] functionals instead. The relaxed geometries of the structures that we obtained were used as input for the density functional perturbation theory (DFPT) [17, 18] calculations, which provided us with the dielectric constant tensors that included the electronic components as well as the ionic components. The reported dielectric constant values are obtained by averaging the diagonal elements of the tensors.

Results and discussions

Structures and coordination chemistries

Each XY_2 compound is known to exist in one of five different crystal structures shown in Fig. 1. While we could have, in principle, considered other crystal structures for each of the XY_2 compounds (or predicted the structures using a structure search algorithm), we have restricted our attention to just the five known structural prototypes in this

study. We believe that despite this restriction, we are able to effectively unearth trends in preferred structural motifs, and other properties determined largely by chemistry. We refer to the five structural prototypes considered here as Types A to E and describe them in detail in the following.

The specific case of CH_2 is nothing but polyethylene (PE) that occurs in structure Type-A, in which individual PE chains can be discerned characteristic of typical polymers. All the compounds were considered in a number of starting geometries. It turns out that all the dihydrides (of which CH_2 is the only one experimentally known [19]) as well as the difluorides and dichlorides of C and Si adopt structure Type-A, and are thus polymers isostructural with PE. The difluorides and dichlorides of Ge, Sn, and Pb are not polymers but closely packed 3D crystals, and are found to exist in the other four structures (Type-B to Type-E) shown in Fig. 1. We shall now explain the different structure types in more detail.

The PE structure [19, 20] consists of an orthorhombic unit cell with every C atom at the center of a tetrahedron whose 4 corners are formed by the 2 H atoms and 2 C atoms it is connected to. C is in a fourfold coordination and we see long chains of connected CH_2 units that are arranged in a crystal with weak interactions between adjoining chains [15]. This is a strictly polymeric structure, and the stability of the long chains lends PE some of its most vital properties. Replacing the H in PE by F or Cl does not change the CN or crystal structure (Type-A) at all, as we can expect from C being a stubborn CN 4 element [2]. SiH_2 , SiF_2 , and $SiCl_2$ are also seen to crystallize as polymers in the same Type-A structure with Si in a clear fourfold coordination. It is interesting that all the C- and Si-based systems here are polymers; this comes from both elements favoring the tetravalent (IV) state to divalence (II), as well as from the stability of C–C and Si–Si bonds.

Down the group, the divalent state increases in stability, meaning Ge(II), Sn(II), and Pb(II) are very common. That said, GeH_2 , SnH_2 , and PbH_2 all prefer structure Type-A again. These hydrides are not experimentally known and it stands to reason that if the Group 14 elements are forming dihydrides at all, they are going to be polymers isostructural to PE. It is when we go to the respective difluorides and dichlorides that we finally see something different. Although Ge, Sn, and Pb are in an overall +2 oxidation state, it is known from the works of Cotton [2], Trotter et al. [21], and Denes et al. [23] that more electrons than the 4 present in the valence band are actually involved in bonding which leads to a higher CN and to 3D crystal structures with little or no ‘polymeric’ behavior.

Both GeF_2 and $GeCl_2$ crystallize in orthorhombic structure Type-B [21, 22], where GeY_2 units ($Y = F, Cl$) are successively linked to each other via a bridge Y atom. Ge is strongly bonded to 3 Y atoms, but has one other Y

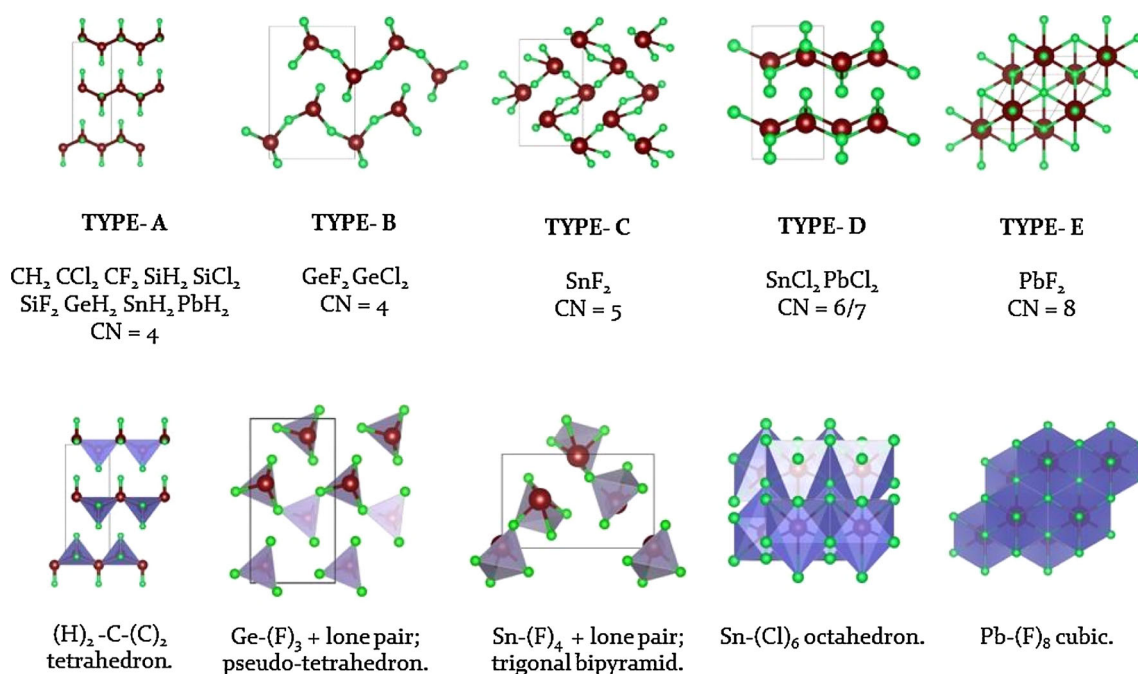


Fig. 1 Structure Types A to E along with the respective CNs and the example systems. Note that as many as 9 systems adopt structure Type-A: all C and Si-based systems, and dihydrides of Ge, Sn, and Pb

atom as its neighbor that it weakly bonds to, which means that although we see stacking of chains, there is stronger bonding between them than seen in PE. As previously explained by Doll et al. [22], the 3 F atoms around Ge along with the lone pair of electrons on it result in a pseudo-tetrahedral geometry (a CN of 4). It should be noted that structure Type-B is a metastable state for SiF_2 and SiCl_2 , and Si(II) may indeed be the preferred state at higher temperatures.

The difluorides and dichlorides of Sn and Pb deviate a fair bit from the structures seen so far. Unlike structure Types A and B, clear 3D networks are seen here which results in an increase in coordination around the X atom. SnF_2 adopts the Type-C structure, with a tetragonal unit cell where each SnF_2 unit is linked to two other SnF_2 units via terminal F atoms [23, 24]. Every Sn atom makes strong bonds with four F atoms and there is a lone pair of electrons on it, resulting in a trigonal bipyramidal geometry and thus, a CN of 5. The Type-C structure is in excellent agreement with the stable γ - SnF_2 polymorph that has been experimentally studied [25]. The dichlorides of Sn and Pb both adopt crystal structure Type-D, where an orthogonal unit cell contains chains of XCl_2 units ($X = \text{Sn}, \text{Pb}$) linked to each other through a bridging Cl atom. These chains are interconnected by means of 3 weaker X–Cl bonds [27] (4 in case of Pb [28]), resulting in little or no polymeric behavior and a CN of 6 and 7 for SnCl_2 and PbCl_2 , respectively. The last remaining compound is PbF_2 , which adopts structure Type-E that is isostructural with the

fluorite structure [26] (seen in compounds like CaF_2 and ZrO_2). There is a conspicuous absence of any kinds of 1D chains of connected XY_2 units here, and the system is a pure crystalline solid. A cubic unit cell contains the Pb atoms in FCC positions and the F atoms in tetrahedral voids [29, 30]. This has been shown with the rhombohedral primitive cell in Fig. 1 to better exhibit the eightfold coordination adopted by Pb here—the highest we have encountered among the XY_2 systems.

Shown in Fig. 2a are the CNs for all the XY_2 compounds in their most stable structures, clearly seen to be increasing from C to Pb. The lattice parameters of the 15 compounds we studied are listed in Table 1. The experimentally reported values are shown as well and generally seen to be in good agreement with the DFT-DF results. Table 2 lists the X–Y bond length comparisons of DFT values with experimental values for a few of the XY_2 compounds, with encouraging agreement once again.

It is interesting to see that while both X–X and X–Y bonds are present in structure Type-A, only X–Y bonds are there in the other four structure types. This is because of the reduced tendency for catenation as we go from C to Pb [2]. While C–C and Si–Si have very high bond strengths, Ge, Sn, and Pb are more likely to form bonds with other electronegative elements than with themselves. All the Type-A structures have X in an oxidation state of +4, whereas in the other four structures, X is in a +2 state owing to the lack of polymeric chain linkages. It is noted

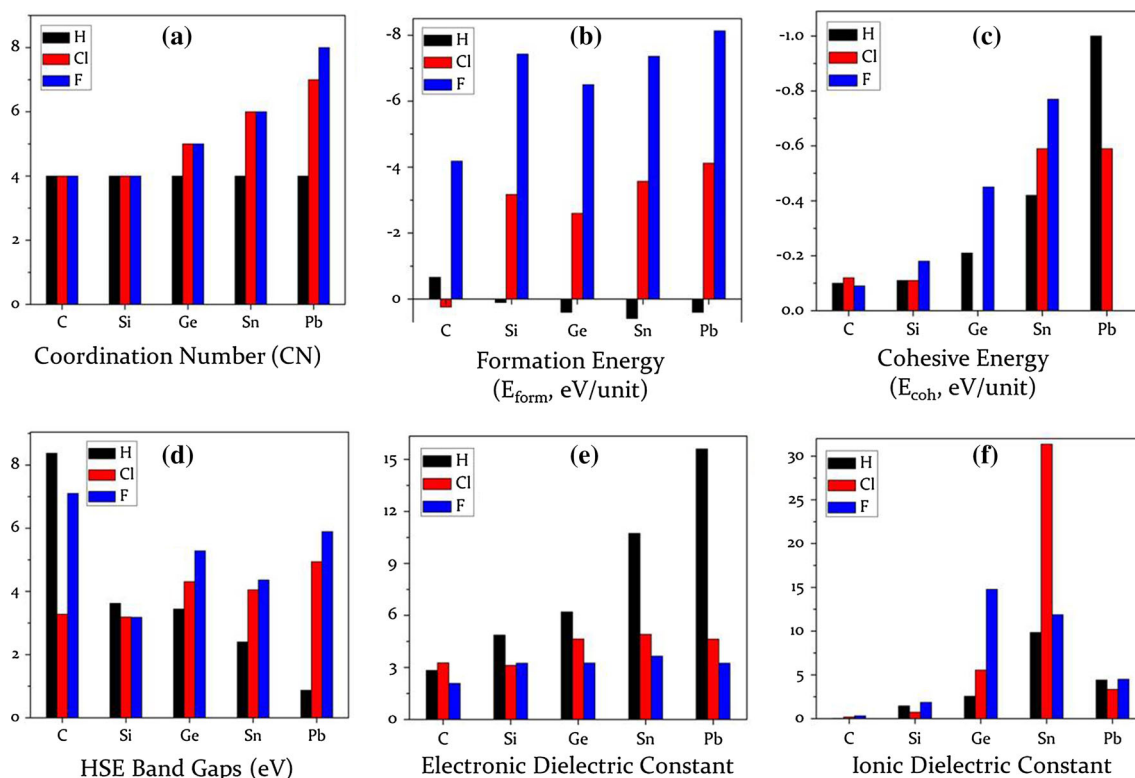


Fig. 2 Plots showing the following features of the 15 compounds: **a** coordination number (CNs), **b** formation energy (E_{form}), **c** cohesive energy (E_{coh}), **d** electronic dielectric constant (ϵ_{elec}), **e** ionic dielectric constant (ϵ_{ionic}), and **f** HSE Band Gaps

Table 1 Lattice Constants (in Å) of each XY_2 system occurring in the structural prototype shown in Fig. 1, calculated using DFT-PBE and DFT-DF functionals

		H			Cl			F		
		a	b	c	a	b	c	a	b	c
C	DFT-PBE	7.25	4.95	2.56	11.26	7.61	3.03	8.57	5.98	2.66
	DFT-DF	6.97	4.81	2.57	10.38	7.11	3.04	8.18	5.72	2.65
	Expt.	7.12	4.85	2.55	–	–	–	8.73	5.69	2.62
Si	DFT-PBE	8.89	5.37	3.92	12.07	8.39	4.03	9.56	4.89	4.17
	DFT-DF	8.72	4.89	3.95	11.13	7.8	3.98	9.05	4.65	4.21
	Expt.	–	–	–	13.35	6.78	4.06	–	–	–
Ge	DFT-PBE	8.87	5.25	4.1	12.25	8.45	4.36	4.29	9.21	4.79
	DFT-DF	8.8	4.92	4.16	11.39	7.86	4.33	4.49	9.13	4.71
	Expt.	–	–	–	–	–	–	4.68	8.31	5.18
Sn	DFT-PBE	9.24	4.92	4.8	10.19	8.13	4.32	5.14	8.43	5.14
	DFT-DF	9.06	4.86	4.85	9.43	7.94	4.44	5.12	8.37	5.12
	Expt.	–	–	–	–	–	–	4.98	8.48	5.14
Pb	DFT-PBE	9.03	4.85	5.09	4.56	7.76	9.42	4.19	4.19	4.19
	DFT-DF	8.99	4.82	5.17	4.59	7.71	9.22	4.21	4.21	4.21
	Expt.	–	–	–	–	–	–	4.24	4.24	4.24

Every X (C, Si, Ge, Sn, Pb) is listed vertically, while Y (H, Cl, F) is on the horizontal. Available experimental values are also listed

that there is an increased contribution of inner shell electrons to the bonding as we go from C-based compounds to Pb-based compounds, and the increase in CN down the group makes sense.

Energetics

Next, we explore the energetics of the XY_2 crystal structures relative to the elements in their standard states, as

Table 2 The average X–Y bond lengths (in Å) of each XY₂ system occurring in the structural prototype shown in Fig. 1

		H	Cl	F
C	DFT-DF	1.1	1.78	1.37
	Expt.	1.09	–	1.32
Si	DFT-DF	1.49	2.07	1.62
	Expt.	–	2.06	–
Ge	DFT-DF	1.56	2.17	2.09
	Expt.	–	–	2.09
Sn	DFT-DF	1.74	2.94	2.36
	Expt.	–	3.14	2.29
	DFT-DF	1.83	2.99	2.54
Pb	Expt.	–	3.04	2.57

Available experimental values are also listed

well as relative to isolated XY₂ chains. The latter is an attempt to quantify the tendency of these systems to exist as polymers with distinct 1D chains. We thus estimated two kinds of energies: the formation energy E_{form} and the cohesive energy E_{coh} , defined as

$$E_{\text{form}} = E(\text{XY}_2 \text{ crystal}) - (E(\text{X}) + E(\text{Y}_2)), \quad (1)$$

$$E_{\text{coh}} = E(\text{XY}_2 \text{ crystal}) - E(\text{XY}_2 \text{ chain}). \quad (2)$$

$E(\text{XY}_2 \text{ crystal})$ and $E(\text{XY}_2 \text{ chain})$ are the respective DFT energies (per XY₂ unit) of the XY₂ crystal and the XY₂ chain [4], while $E(\text{X})$ is the DFT energy of X in its elemental standard state and $E(\text{Y}_2)$ is the DFT energy of a Y₂ molecule. For elemental standard states, the diamond structure was considered for C, Si, Ge, and Sn, while Pb was considered in an FCC structure [1]. The XY₂ chain being considered here for each system consists of isolated chains of repeating XY₂ units very similar to a PE chain, in the possible assumption that this is how a hypothetical polymer chain of said XY₂ system would exist.

Figure 2b, c captures the calculated values of E_{form} and E_{coh} , respectively. The formation energies are mostly large negative numbers, which means X and Y₂ would rather form the XY₂ crystal than not, except, as can be seen from the small positive values, the dihydrides of Si, Ge, Sn, and Pb. As mentioned earlier, these dihydride polymers are not experimentally known, which could explain their possible instability. E_{form} is seen to become less negative as we go from the F containing to Cl containing to H containing compounds, which means that relative to elemental states, the difluorides are more stable than the dichlorides, which are more stable than the dihydrides.

Meanwhile, the values of E_{coh} seem to become more negative on going from the C-based systems to the Pb-based systems. This actually follows from our discussion in the previous section: the systems that adopt Type-A structure essentially contain 1D motifs arranged together

through weak interactions in a crystal, and will thus have stabilities close to that of isolated chains. The 3D crystalline structures of the difluorides and dichlorides of Ge, Sn, and Pb will have much lower stabilities for 1D motifs and thus, much lower cohesive energies. The Type-A crystal structures are all polymeric and thus close in energy with the individual chain energies, while the other structure types are not. Note that E_{coh} has not been mentioned for GeCl₂ and PbF₂, as the chains for these systems could not be isolated at all.

Electronic properties

The electronic band gap values, shown in Fig. 2d, are seen to go from the lows of around 2 eV to the highs of 8 eV, with the exception of PbH₂ that shows an unusually low band gap of less than 1 eV. Most of the compounds lie approximately in the 3–5.5 eV range which puts them somewhere in the semiconductor to insulator category. The C-based compounds have the highest band gaps, which come from the low polarizability of C–Y bonds. Increased polar nature of the bonds causes more dispersion of charge and thus lower band gaps in the remaining compounds; however, the band gaps are generally both high and relatively low in Si-, Ge-, Sn-, and Pb-based systems.

The dihydrides follow the simplest of trends here. The band gaps successively go down from CH₂ to PbH₂. An explanation for this can be drawn from the stability arguments in the previous section: the stability of the compound goes down from CH₂ to PbH₂, resulting in decreased X–H bond strength [2] and more free electrons, which reduces the band gap. Further, for any given X, all the XF₂ compounds show a higher band gap value than the corresponding XCl₂ compounds, which again relates to the higher stabilities of the difluorides as compared to the dichlorides. The bond strengths are higher for the X–F bonds than for the X–Cl bonds [2], leading to less free electrons in XF₂ compounds than in XCl₂. It can also be seen among the difluorides and dichlorides that moving toward a higher CN and increased 3D nature of the structure seems to cause an increase in the band gap. Of course, the more rigid a crystal structure is, the more immobile would be the electrons of the constituent atoms, and thus, the band gaps would be higher. It can be seen that the difluorides and dichlorides of Ge, Sn, and Pb all have high band gaps because of being very stable crystalline compounds.

Dielectric properties

To further understand the implications of the bonding and chemical coordination, and keeping in mind possible applications, dielectric constants were determined for the

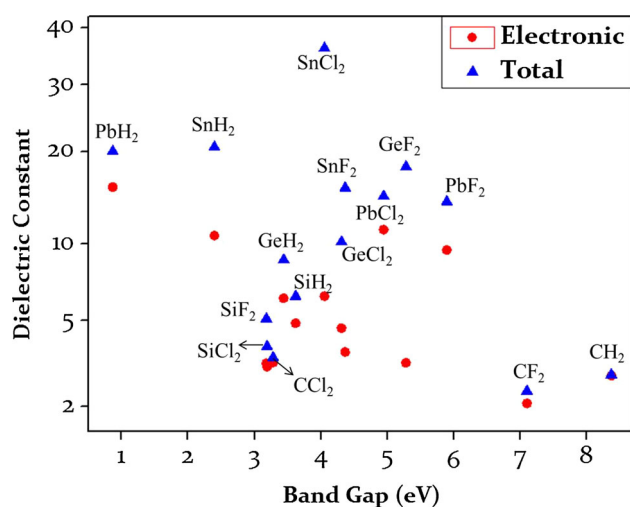


Fig. 3 Dielectric constant versus band gap for the 15 systems. The electronic component is seen to correlate inversely with the band gap. The total dielectric constant goes very high in cases with large ionic components

15 XY_2 compounds. DFPT calculations give as output the total dielectric constant tensor divided into two component tensors: the electronic part and the ionic part. While the electronic part of the dielectric constant (ϵ_{elec}) is a function of the polarizabilities and vdW volumes of all the atoms [4, 5], the ionic part (ϵ_{ionic}) depends on the strength and flexibility of the X–Y dipoles [4, 5].

It can be seen from Fig. 2e that ϵ_{elec} is increasing for the dihydrides from C to Pb, while for any given Group 14 element, it generally decreases from the dihydrides to the dichlorides to the difluorides. These observations can be deconstructed in the following manner: in the presence of an external electric field, there will be an induced dipole moment in the system, the strength of which depends on the ease of distortion of the electron cloud around an atom. This distortion becomes successively easier on moving to lower stability systems, leading to higher values of ϵ_{elec} ; thus, the gradual decrease in stability of the dihydrides going from C to Pb and the increased stabilities of the difluorides and dichlorides explain the aforementioned trends. Further, we could easily correlate the pattern of variation in ϵ_{elec} with what we saw with the band gap values, which in general were decreasing for the dihydrides down the group and increasing for the difluorides and dichlorides. Higher polarizabilities lead to lower band gaps [31], which may be understood by realizing that the polarizability of a bulk system can be written as a sum over electronic transitions from the valence to conduction band manifolds with the corresponding transition energies appearing in the denominator [20]. Thus, there can be said to exist an inverse relationship between the electronic dielectric constant and the band gap. In Fig. 3, we plot ϵ_{elec} as well as the total dielectric constant ϵ_{total} ($= \epsilon_{\text{elec}} + \epsilon_{\text{ionic}}$) against the band

gap values for the 15 systems, and it was seen that ϵ_{elec} does indeed correlate inversely with the band gap.

ϵ_{ionic} follows quite a different kind of trend. The values for C- and Si-based compounds are pretty low, whereas Ge- and Sn-based compounds are much higher, and Pb-based compounds—surprisingly—are low. We can try to understand this with some bond strength and dipole moment arguments. The contribution to ϵ_{ionic} comes from the presence of structural units having high dipole moments, and how easily the realignment of these dipoles takes place in the presence of external electric field [5]. For any X–Y bond, the dipole moment is known to increase with the bond length and the electronegativity difference between X and Y. Since the Group 14 elements (bar C) all have similar electronegativities (~ 2), the respective X–Y electronegativity differences can be said to be more or less equivalent for any Y (Y = H, Cl, F), meaning we only have to look at the bond lengths to determine which dipole moments are higher. It can be seen from Fig. 2f that for any given Y, ϵ_{ionic} is increasing from C to Si to Ge to Sn, and then decreasing again for Pb. The X–Y bond lengths increase as X goes from C to Pb (Tables 1, 2), resulting in increased dipole moments and thus higher ϵ_{ionic} values. It can be argued that Ge–Y and Sn–Y bonds are more susceptible to stretching/wagging than the bonds in the heavier Pb compounds, which leads to the drop in ϵ_{ionic} in PbY_2 .

Concluding thoughts

In this study, we have studied a variety of compounds (hydrides, fluorides, and chlorides) containing the Group 14 elements C, Si, Ge, Sn, and Pb. We have seen that from the C-based compounds to the Pb-based compounds, there is a general increase in the preferred CN as well as in the tendency for close 3D packing. The crystal structure changes from Type-A, a strictly polymeric structure with the backbone atom having a CN of 4, to Type-E, an extremely rigid 3D crystal with the backbone atom in a CN of 8. The intermediate structures have varying proportions of 1D/2D/3D characteristics in them, and CNs between 4 and 8. Even though they have not been considered in this work, we could anticipate that the structures and CNs of some other Group 14 elements-based compounds (like dibromides, diiodides) would have similar structures as well. Indeed, $GeBr_2$, $SnBr_2$, and $PbBr_2$ [32, 33] are, respectively, isostructural with $GeCl_2$, $SnCl_2$, and $PbCl_2$, while PbI_2 is isostructural with PbF_2 but with a lower CN of Pb.

From this study of the different XY_2 compounds, it is quite clear the oxidation states and electronegativities of X, the strength of the X–Y bonds, as well as the role of lone pair electrons have a major influence on the coordination geometries and stable conformations, and subsequently, the

properties. The trends make no secret of the intriguing nature of Group 14 that we talked about in the Introduction: from nonmetallic C to metallic Pb, we see what is very much a logical transition in the structures and properties. The electronic and dielectric properties, especially, reveal interesting trends that can be utilized in a number of ways. For instance, structural units containing Group 14 elements can be introduced into existing structures in order to tune the overall band gaps or dielectric constants, useful in applications like capacitors, organic-electronics, photonics and photovoltaics. Units like GeF_2 , SnF_2 , and SnCl_2 could be useful in applications requiring high dielectric constant and band gap. In fact, there has already been some amount of success [4, 5] with this sort of a strategy, and a deeper analysis of the different structures and properties of polymers containing such units is underway.

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