Understanding the Crystallographic Phase Relations in Alkali-Trihalogeno-Germananates in Terms of Ferroelectric or Antiferroelectric Arrangements of the Tetrahedral GeX₃ Units

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The alkali-trihalogeno-germananates AGeX₃ with A: Rb or Cs and X a halogen (I, Br, Cl) along with the corresponding stannates (ASnX₃) and plumbates (APbX₃) exhibit a large variety of crystal structures, some of which are of the perovskite type. These materials, better known as “halide perovskites” have recently gained worldwide attention as promising photovoltaic and more broadly opto-electronic materials. However, their stability problems relative to the non-perovskite phases are a major issue. It is shown that some of the phase relations in these materials can be understood in terms of the relative orientation of the GeX₃ tetrahedral units, which is ferroelectric (FE) in the perovskite phase but antiferroelectric (AFE) in the competing monoclinic phase. Electrostatic dipole interactions favor the AFE phase and the additional bond formation favors the FE phase. The change in phase is accompanied by a large change in band gap.

1. Introduction

The hybrid halide perovskites have become a major new class of photovoltaic materials with record efficiencies being established in a very short development time.[1,2] At the same time these materials have generated a large interest from the scientific community to understand what underlies their success as solar cell materials. In the process it has become evident that these materials show a rather unusual combination of ionic properties, such as large Born effective charges, and large \( \varepsilon_\infty \) with (typical for covalent materials) small band gaps and exciton binding energy and a flexible inorganic network with interesting dynamics.[3,4]

Most of these favorable properties for opto-electronics rely on the electronic band structure, which shows direct gaps close to the optimum range (1.2–1.8 eV) for single or tandem solar cells and relatively small carrier effective masses, in particular for holes.[3] However, a main difficulty with these materials is their thermodynamic stability, not only under environmental effects such as humidity or light exposure but intrinsically due to the existence of other competing phases which do not share these favorable features in the band structures. In fact, these other phases may well be an intermediate step in the decomposition process of the material to the AX and (Ge,Sn,Pb)X₂ reaction products. It is thus important to understand the relative stability and relations between these crystallographic phases, how they influence the band structures, and how their trends depend on the chemical substitution space.

Some of the relations within the perovskite type of structures are already well understood. Specifically, we have recently shown that both the Sn and Pb based compounds in this family primarily undergo octahedron rotations related to the Goldschmidt tolerance factor \( t < 1 \) while the Ge and Si based ones show a ferroelectric off-centering of the central IV-atom leading to a rhombohedrally distorted perovskite.[5] The rotational distortions in CsSnX₃ were studied both experimentally[6] and computationally[7] and are well known from oxide perovskites. Similar rotated octahedron phases also occur for the plumbates but are further complicated in the hybrid organic ones by the symmetry breaking of the organic ion. However, the relation between the perovskite and the non-perovskite phases such as the yellow phase[8] in CsSnI₃ or the monoclinic phase[9] of CsSnCl₃ are not yet understood. These phases are usually described in terms of edge-sharing rather than corner-sharing octahedra.

Because in the stannates the yellow phase has a higher density and the rotations also are clearly driven by the need to make the space for the alkali ion tighter, we proposed in previous work that to avoid the non-perovskite phases one needs to make the size of the IV-X network smaller relative to the A filler cation. First this already explains why larger organic ions are preferred to Cs in the plumbates but also guides the way to how to develop lead-free alternatives. This naturally led us to explore the Ge and Si based materials.[10–12] In fact, the CsGeX₃ family is found not to exhibit octahedron rotational distortions but a ferroelectric rhombohedral phase (R)[13] at low temperature and a cubic perovskite phase at high temperature and was shown to have a band structure maintaining the favorable features of the perovskite structure. However the situation is different for...
RbGeX₃, where the RbGeCl₃ shows a monoclinic P2₁/m phase (M)\[^{14}\] while RbGeBr₃\[^{15}\] and RbGeI₃\[^{16}\] show a low temperature orthorhombic Pn2₁/a phase, and in the case of RbGeI₃ another orthorhombic P2₁2₁2₁, besides the rhombohedral R3̅m and cubic Pm3m phases.

In this paper we show that the relation between these phases can be better understood in terms GeX₃ tetrahedral units. We focus on the relation and relative stability between the M and R phase. Even within the R phase, the Ge off-centering in its octahedron results naturally in Ge making stronger bonds with three of its six halogen neighbors. This results from the lone-pair chemistry of divalent Ge(II)\[^{5}\] and makes GeX₃ a natural motif in terms of which to describe the structures. These units clearly carry an electric dipole and as we will show below the monoclinic phase is then simply an antiferroelectric (AFE) arrangement of these dipoles while the rhombohedral one is a ferroelectric (FE) one. We show using first-principles calculations that the M phase is favored for the RbGeX₃ while the R one is favored for the CsGeX₃. We introduce an effective spin-model to explain why the electrostatic dipole interactions favor the antiferroelectric alignment while the ferroelectric alignment is stabilized by the additional bond formation. The trends in the total energy differences in the family can be understood on the basis of that model. The idea of using molecular motifs in analyzing crystal structures is obviously not new and has for instance been used recently to design novel improper ferroelectric phases using group theoretical analysis.\[^{17}\] Finally, we address how these different structures affect the electronic band structure.

2. Results

In Figure 1 we show the M and the R crystal structures of RbGeCl₃ viewed either with octahedral coordination of Ge or tetrahedral coordination. The perovskite structure is shown in a doubled cell for easy comparison to the monoclinic structure. We can see that while in the perovskite structure, the octahedra are corner-sharing and form a 3D network, in the M structure, the octahedra form 1D chains with edge-sharing octahedra. The octahedra are severely distorted and include three bonds of 2.35 Å, one of 3.56 Å and two of 4.06 Å. In the perovskite phase, the three short bonds are 2.43 Å and the three long ones are 2.90 Å. It is clear that the GeX₃ tetrahedral units are pointing in opposite directions in the M structure, while they point in the same direction in the R structure. In the Supporting Information, we show in more detail that one can simply rotate one of the GeX₃ units of the M structure around the b-axis about its center and hence arrive at the R structure after letting the structure relax by straightening out the network of connected Ge–Cl bonds and letting the Rb find its optimum position. The Ge atoms form a simple cubic lattice connected via Cl in cubic perovskite and this same lattice persists in the R and M structures in a distorted form but with the same topology.

Next, we examine the results of first-principle calculations of the relative total energies of these two structures. Both structures were fully relaxed and the details of the calculations, the crystal structure and Wyckoff positions are given in the Supporting Information. The M structure is seen to be the lower energy one for all Rb cases while the R structure has lower energy for the Cs compounds. The volume per formula unit (f.u.) is always larger in the M structure than in the R structure for the same compound. However the volume ratio is systematically larger for the Rb cases than the Cs cases.

To gain understanding of the reasons behind the relative stability of the two structures, we first consider the dipole electrostatic interactions. In a simple cubic lattice the net interaction energy of dipoles pointing in the [111] (or [T T T]) directions beyond nearest neighbors is significantly smaller than that of the nearest neighbors. Thus, we can map the electrostatic problem to that of dipoles or classical up-down spins in a fixed direction on a simple cubic lattice and with nearest neighbor interactions only. The key point, however, is that the spins have an anisotropic interaction. Writing the dipole part of the Hamiltonian as

\[ H_{dp} = J_1 \sum_{\langle \langle \rangle \rangle} S_{i\langle \langle \rangle \rangle} S_{\perp\beta\gamma} + J_\perp \sum_{\langle \rangle} S_{i\parallel} \cdot S_{\perp} \]

with the sums over nearest neighbor pairs, and \( S_{i\parallel\perp} \) means a spin on a pair of sites with connection vector parallel to the spin and \( S_{i\parallel\perp} \) spins on sites with connection vector perpendicular to the spin. Taking \( J_1 = V_{1\parallel} - V_{1\perp} \) and \( J_\perp = V_{2\parallel} - V_{2\perp} \), with \( V_{\parallel} = \frac{\langle p_r \cdot p_{\parallel} - 3(p_r \cdot r_{\parallel})(p_r \cdot r_{\parallel}) \rangle}{r_{\parallel}^3} \) the classical dipole interaction we obtain

\[ J_1 = -4 \frac{q^2 a^3}{d^3}, \quad J_\perp = 2 \frac{q^2 a^3}{d^3} \]

which will favor parallel alignment for neighbors in the direction parallel to the spin and anti-parallel alignment for neighbors in the direction perpendicular to the direction of the spin. Here \( d \) is the distance between the X₃ plane and the Ge in the GeX₃ tetrahedron and \( q \) the effective charge of the dipole in this molecule and \( a \) is the cubic lattice constant.

Spin and dipole interactions on a simple cubic lattice were studied by Luttinger et al.\[^{18,19}\] and the anisotropic exchange case was discussed by Belorizky et al.\[^{20}\]. These studies show that the preferred arrangement of spins is essentially the one observed in the M structure, namely, neighboring spins are

![Figure 1. a,b) Monoclinic and c,d) Rhombohedral structure viewed either as octahedral coordination (a,c) or tetrahedral (b,d) coordination of Ge.](image-url)
parallel in the direction in which the dipole points and antiparallel in the perpendicular directions. All we need to favor this arrangement is $J_1 < 0$ and $J_2 > 0$ which is obeyed by Equation (2). The conclusion from this is that the electrostatics of dipoles by itself would always favor the antiferroelectric alignment. In order to explain the possible stability of the ferroelectric alignment we then need to take into account that for this arrangement of the GeX$_3$ additional bonds can be formed by the Ge with the slightly further away halogens in the neighboring GeX$_3$ units, thereby in fact restoring the 3D corner-sharing octahedral environment. This could be described by adding a term to the spin Hamiltonian of the form $H_{\text{bond}} = -U \sum_{ij} \Theta(S_i \cdot S_j)$ with $\Theta$ the step function.

The key point is that the dipole energy $H_{\text{dip}}$ and the bond energy $H_{\text{bond}}$ must be of similar magnitude to have a meaningful competition. This is apparently the case from our first-principles results. To further illustrate this we calculated the energy difference between the two structures for RbGeCl$_3$ while artificially changing the dipole strength. We can do this by shortening the distance $d$ between the Ge and the halogen plane in the GeX$_3$ unit by $\delta d$, which reduces the dipole moment and hence makes the electrostatic term smaller. We can see in Figure 2 that for $\delta d > \delta d_{\text{crit}} \approx 0.006$ the perovskite phase becomes favored.

Furthermore, this model can now be used qualitatively to explain the trends in the total energy results. The larger Cs atom leads to an overall larger lattice constant a and hence a reduction of the dipole term compared to the Rb case. Because the bond formation energy depends less strongly on this term than the electrostatic energy this explains the basic finding why the CsGeX$_3$ favor the RbGeX$_3$ prefer the M structure. Within the Cs family the dipole term becomes stronger as we go from less ionic I to more ionic Br and Cl. Indeed we see that for the Cs cases, the $\delta E = E_{\text{rhombo}} - E_{\text{mono}}$ in Table 1 is less negative for Cl than Br than I, indicating the increasing importance of the electrostatic dipole stabilization term. For the Rb cases, also the highest $\delta E > 0$ occurs for the most ionic Cl case. The $\delta E$ however is lower for the Br than the I case. In fact, in the Br case, the reported low-temperature ($T < 93^\circ$ C) structure is not monoclinic but another (layered) antiferroelectric arrangement of the GeX$_3$ dipoles which already corresponds to a 3D network of corner-sharing octahedra but which now combines octahedral rotations with Ge off-centered distorted octahedra (see the Supporting Information) and was calculated to have a 5.5 meV per f.u. lower energy than the M structure. The $P2_12_12_1$ structure of RbGeI$_3$ (for $T < 181^\circ$C) on the other hand shows 10.6 meV per f.u. lower energy than the M structure. The key point is that these other structures are intermediate between the M and R structures in that the molecular GeX$_3$ unit form a different AFE pattern with intermediate relative orientations of the corresponding dipoles.

In a future paper we plan to present a more elaborate model in which we explore the energy landscape as function of fully rotating the rigid GeX$_3$ tetrahedra in all possible directions combined with an energy term that counts the number of Ge-X bonds being formed as the units rotate. This model indeed suggests that other (metastable) structures with intermediate relative orientations of the GeX$_3$ relative to each other exist. However, a full exploration which would allow to explain the stability of the above mentioned orthorhombic phases requires larger cells than we have treated until now. Such a model would also allow us to estimate the energy barrier between the AFE and FE phases but still would not provide sufficient information to address the phase transitions because that would require to also include the relaxation of other degrees of freedom, such as the counter positive ion Cs or Rb positions and the strains modifying the shape and volume of the unit cell that are coupled to these internal degrees of freedom.

The model presented here in principle also applies to the stannates and plumbates although the lone-pair related distortion in these cases is less pronounced and the $s^2$ electrons behave more as an inert-pair.[21] Nonetheless, for CsSnCl$_3$, a model in terms of SnCl$_3$ dipole carrying units applies and the higher ionicity/stronger electrostatic interactions compared to CsI$_3$ leads to a lowest energy monoclinic phase.[20] Even in CsSnI$_3$ the lowest energy phase may be the $Pnma$ phase.[21]

![Figure 2. Total energy difference between monoclinic and perovskite as function of the dipole strength varied by changing $\delta d$ in the GeCl$_3$ molecular unit. The inset show the definition of $d$ and $\delta d$ is the amount by which $d$ is shortened.](image)

| Crystal       | Stable Structure | $V_{\text{max}}$ | $\delta E$ [eV] |
|---------------|-----------------|-----------------|-----------------|
| RbGeCl$_3$   | Monoclinic      | 1.133           | 0.095           |
| CsGeCl$_3$   | Rhombohedral    | 1.094           | −0.034          |
| RbGeBr$_3$   | Monoclinic      | 1.131           | 0.043           |
| CsGeBr$_3$   | Rhombohedral    | 1.097           | −0.105          |
| RbGeI$_3$    | Monoclinic      | 1.149           | 0.054           |
| CsGeI$_3$    | Rhombohedral    | 1.093           | −0.169          |

Table 1. Relative structural stability of monoclinic vs. rhombohedral structure for CsGeX$_3$ and RbGeX$_3$. $V_{\text{max}} = V_{\text{mono}}/2V_{\text{rhombo}}$ is the volume ratio of the respective volumes per formula-unit, $\delta E = E_{\text{rhombo}} - E_{\text{mono}}$ the total energy difference per formula unit.
which corresponds to an intermediate orientation of the SnI$_3$ units between FE and AFE.

Finally, we consider the changes in band structure resulting from the different structural arrangements. In Figure 3 we show the band structure of the R and M phases along equivalent $\mathbf{k}$-directions. We can see that while in both cases bonding–antibonding interactions between the Ge-$s$ and the Cl-$p$ orbitals determine the band edges of the valence band (VB), the antibonding bands become separated in the M case and the overall band width is significantly reduced. This reflects the disruption of the 3D corner sharing network of Ge-$s$ and X-$p$ orbitals. Also, the Ge-$p$ orbitals which form the conduction band (CB) minimum become much flatter. This is because in the highly symmetric perovskite structure, these Ge-$p$ states at the Brillouin zone corner have no interactions with other orbitals.[3] The lower symmetry of the M structure allows more antibonding interactions between Ge-$p$ and I raising this band at $R2$ and flattening out the lowest CB. The splitting between the center of gravity of the non-bonding X-$p$ bands and the Ge-$p$ remains more or less constant because this is determined by the atomic energy levels. The net result of the narrowing of the VB and the flattening out of the lowest CB leads to a significant increase in the gap. The flatter bands in the M case reflect the molecular crystal like structure of disconnected units compared to a continuous network.

3. Conclusion

In summary, we have shown that the relative stability of the M to the R structure in AGeX$_3$ can be understood by viewing the structure in terms of GeX$_3$ dipole carrying units. The antiferroelectric arrangement of the dipoles in the M structure is favored by electrostatics while the additional bond formation for the ferroelectric arrangement stabilizes the R structure. It is the competition between these two effects which determines the crystal structure. The different connectivity of the basic units was shown to lead to drastic changes in band structure.

As an outlook toward future work, the fact that electrostatics plays a key role suggests that the ferroelectric alignment could possibly be enforced by means of an applied electric field. Phase transitions between AFE and FE phases are known in other systems and can occur both as function of temperature and electric field. A number of phase transitions in the present family of materials as function of temperature have already been reported but investigations as function of electric field have not been studied to the best of our knowledge. Calculating the critical electric field would require determining the energy barrier along the transition path between the two structures in the presence of a finite electric field and is beyond the scope of the present paper.

4. Experimental Section

The total energy calculations were performed using the all-electron full-potential linearized muffin-tin orbital method[22,23] as implemented in the questaal-suite[24] and within the Perdew–Burke–Ernzerhof (PBE)[25] generalized gradient approximation (GGA) to density functional theory (DFT). The band structures were calculated in the quasiparticle self-consistent (QS)GW approximation[26,27] where $G$ is the one-particle Greens' function and $W$ the screened Coulomb interaction (details in Supporting Information) in order to overcome the shortcomings of semilocal density functionals for predicting band gaps.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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