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Correlations between transition temperature, tolerance factor and cohesive energy in 2+:4+ perovskites

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Abstract

Cohesive energies were calculated *ab initio* for a range of simple 2+:4+ perovskites ($A^{2+}B^{4+}O_3$). Correlations were sought between the sets of lattice parameters, cohesive energies, cubic transition temperatures and Goldschmidt tolerance factors for these compounds. There is a noticeable correlation ($R = -0.60$) between the transition temperatures and the tolerance factors, but only weak relationships between the cohesive energy and the other parameters. However, for more than half the set of compounds, there is a strong correlation ($R = 0.989$), in the form of a simple linear trend between the tolerance factor and the ratio of cubic transition temperature to cohesive energy density. The remaining compounds form two distinct clusters and either retain cubicity down to 0 K or undergo transitions to lower symmetry at substantially lower temperatures than might be expected from the trend.

1. Introduction

The term ‘perovskite’ is used to denote a category of inorganic crystalline solids with the general formula ABX_3 , where A and B are cations and X is an anion. In the ideal case, the structure consists of a cubic network of corner-sharing BX_6 octahedra with the A cation occupying the cuboctahedral interstice [1], as shown in figure 1. This cubic structure can transform into a number of distorted polymorphs. Their precise geometry depends on chemical composition, temperature, pressure and, in some cases, electric field [2]. As a rule, with rising temperature, perovskites tend to undergo a series of transitions to progressively higher symmetry, culminating in the cubic structure where experimentally accessible [3].

Oxide perovskites (ABO_3) exhibit a variety of interesting electronic [4, 5], electromechanical [6–8] and conductive [9, 10] properties, which are the basis for many existing and potential applications. Such properties are often symmetry dependent. This is, by definition, true of ferroelectric materials [8], which form a large subset of industrially useful perovskites. One of the fundamental parameters for any ferroelectric material is the Curie temperature (T_C), the temperature at which the transition between the paraelectric and

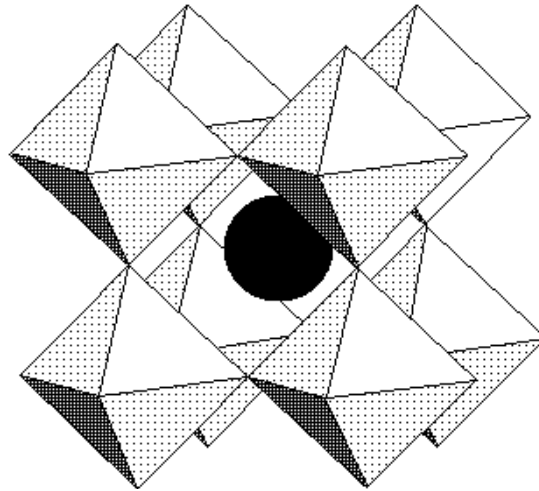


Figure 1. The ideal ABX_3 perovskite structure: a cubic network of BX_6 octahedra with the A cation (black sphere) in the body-centre interstice.

ferroelectric (or antiferroelectric) polymorphs occurs. The ability to predict if and when such a transition might occur in as yet unsynthesized materials would clearly be of value to both scientists and technologists alike.

There have been several attempts to identify methods of correlating T_C with other characteristics of structure and/or perovskite composition. For example, Abrahams, Kurtz and Jamieson proposed a simple relationship between the ferroelectric or antiferroelectric transition temperature (T_C) and the magnitude of displacement (Δz) of the ‘homopolar’ cation [11]. They assumed that the B–O bond behaves as a Hooke’s law spring, and that the amount of thermal energy required to ‘lift’ the cation out of the potential well is proportional to the square of its original displacement. Hence

$$2k_B T_C = K(\Delta z)^2, \quad (1)$$

where k_B is the Boltzmann constant and K is an empirical spring constant. However, the results are far from satisfactory (see figure 1 of [11]). The spread of data points is such that the relationship is far from clear; in fact, in the case of $PbTiO_3$, the relationship gives a prediction over 1000°C above the experimentally observed transition temperature. As the authors point out themselves, the assumption that the B cation is the main ferroelectrically active ion is not always a safe one; for example, it does not hold in the case of $PbTiO_3$.

More recently, Eitel *et al* [12] conducted a survey of $PbTiO_3$ -based solid solutions based on the Goldschmidt tolerance factor (t) [13], a widely used ionic radius ratio, of the form

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}, \quad (2)$$

where r_A , r_B and r_O are the ionic radii of the respective ions. They found a correlation between the tolerance factor of the non- $PbTiO_3$ end member and T_C at the morphotropic phase boundary (MPB) (see figure 1 of [12]). Whilst these findings suggest that ionic size mismatch is a strong determinant of T_C , the correlation is hidden in the wider picture. Indeed, the construction of similar plots for all Pb-based ferroelectric compounds (not solid solutions) shows a much reduced correlation; the same plot for all perovskite ferroelectrics shows practically zero correlation. A simplistic explanation is that T_C is a function of both the ionic size mismatch

(t) and the nature of electronic structure or bonding. In the case of the PbTiO_3 -based solid solutions the bonding is dominated by the lone-pair characteristic of PbTiO_3 . If this factor is held constant, as in Eitel's data set [12], then a correlation between T_C and tolerance factor becomes apparent.

In recent years, quantum-chemical calculations have become more widely accessible. Attempts have been made to employ them to parameterize lattice-dynamical models of phase transitions in perovskites [14–19]. Two approaches in particular have come to prominence: shell-model molecular dynamics and the effective Hamiltonian. In the former, certain assumptions are made about the polarizabilities of individual atoms and the character of pairwise interactions between them [19]. In the case of the effective Hamiltonian approach, assumptions are made about the way the energetics of a whole crystal vary in response to particular types of deformation [15]. Both approaches allow us to follow the response of a structure to variations in the vibrational energy by tracing its behaviour over a series of time steps. In both cases, the assumptions are made on the basis of quantum-chemical calculations. Using BaTiO_3 as a representative case, Tinte *et al* recently carried out a systematic study of the errors generated by such methods [16]. They found that both schemes reproduced the correct sequence of phases, but can be quite inaccurate in predicting the transition temperatures, typically overestimating T_C by more than 100 K. The authors isolated two main sources of error: the approximations inherent in the simulations (failure to account for cross-mode coupling and thermal expansion effects) and shortcomings of the quantum-chemical algorithms (particularly the exchange–correlation algorithms).

In summary, the simpler predictive rules lack precision and universality and can be hard to rationalize; however, the more theoretically rigorous approaches, which rely on atomistic calculations, can still result in errors of the order of ± 100 K.

In this paper, we investigate whether there are general correlations that can be made between transition temperature and a selection of simple structural and energetic characteristics, an approach that falls between the two extremes described above. We have attempted to limit the degrees of crystallographic and compositional complexity to a minimum, working with the larger set of all cubic transitions rather than only the ferroelectric subset. We define cubic transitions in perovskites as all those to and from the highest possible symmetry ($Pm\bar{3}m$). The symmetry of the higher-temperature phase presents a well-defined crystallographic motif that is, in theory, common to all perovskites. To limit the degree of chemical complexity, we chose to concentrate solely on simple perovskites (i.e. those in which there is no compositional variation from one unit cell to the next) belonging to the $\text{A}^{2+}\text{B}^{4+}\text{O}_3$ category. This allows us to disregard any potential thermodynamic consequences of local inhomogeneity, as might be seen in solid solutions (e.g. $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$) or complex perovskites (e.g. $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$). The 2+:4+ valence category was chosen because of the availability of a large volume of pertinent experimental data in the literature.

2. Methods

Cohesive energy (E_c) can be considered as a measure of a structure's overall chemical stability [20]. It is defined as the difference between a structure's total electronic energy and the sum of the electronic energies of its constituent atoms at infinite separation:

$$E_c = E_t - \sum E_a, \quad (3)$$

where E_t is the total energy of the structure in question, and the E_a are the energies of the corresponding non-interacting atoms. E_t and E_a were obtained from plane-wave pseudopotential density-functional theory (DFT) calculations with the aid of CASTEP [21]. In

the E_t calculations, the cut-off energy ($E_{\text{cut-off}}$) was generally set at 380 eV; the one exception was BaCeO₃, for which $E_{\text{cut-off}}$ was raised to 700 eV to achieve satisfactory convergence. In the case of E_a , $E_{\text{cut-off}}$ varied between 260 and 700 eV. In the majority of cases, $E_{\text{cut-off}}$ was set at 1.1 times the value of $E_{\text{cut-off}}$ required to achieve a 0.1 eV/atom convergence in a single-atom calculation. In several cases, where there were problems with slow or irregular convergence (e.g. BaCeO₃), $E_{\text{cut-off}}$ was raised further. The distance between sampling points in reciprocal space (k -point mesh) was set to 0.04 \AA^{-1} . The density of the fast Fourier transform (FFT) grid was varied between 85% and 100% of that required for zero aliasing. Generally, higher densities were used in cases of poor convergence. Ultrasoft pseudopotentials [22] and generalized gradient approximation (GGA) exchange–correlation functionals, following the Perdew–Burke–Erzenof (PBE) scheme [23], were used throughout. GGA functionals were preferred to the local density approximation (LDA) due to the latter’s tendency to underestimate the lattice constant in perovskites by as much as 2% [24]. The PBE scheme provided sufficiently rapid convergence of the calculations without the risk of introducing some of the known shortcomings of later revisions when employed for ionic crystals [25]. The set of pseudopotentials optimized for the PBE scheme within CASTEP were employed throughout.

Values of E_t were obtained for the highest-symmetry ($Pm\bar{3}m$) phases using a simple five-atom unit cell. Two sets of E_t were obtained: one using a static unit cell with the dimensions fixed at literature values (a) and another with the unit cell length relaxed so as to achieve theoretical minimum-energy unit cell dimensions (within the constraints of $Pm\bar{3}m$ symmetry). The minimum-energy volume was found by repeating the single-point calculations for a set of slightly different unit cell length and fitting to a quadratic curve. This simple and transparent procedure turned out to be remarkably reliable and the results closely corresponded to those obtained by the much more sophisticated but inefficient Broyden–Fletcher–Goldfarb–Shannon geometry optimization procedure [21].

The E_a were calculated using a single-atom simple-cubic unit cell with an 8–10 Å unit cell length. This separation was deemed sufficient to approximate zero interaction. (Convergence tests showed an energy difference between 9 and 10 Å unit cells of less than 0.01 eV.) The tolerance factors (t) were calculated from the ionic radii tabulated by Shannon [26]. Temperatures of the cubic transition (hereafter referred to as T_C) were taken from the literature (see table 1 for references).

3. Results and discussion

The values of the calculated unit cell parameters are plotted against the literature values in figure 2. There is generally good agreement between the two data sets which provides part verification of the methodology for the calculation of lattice energies. The largest discrepancies are seen for the hafnium compounds, suggesting that the pseudopotential for Hf⁴⁺ might be improved. The calculated cell size for BaPbO₃ is also a little larger than that measured experimentally. The corresponding cohesive energies (i.e. those corresponding to the relaxed cell versus those calculated from the literature values of the lattice parameters) are plotted in figure 3. The relative deviations are less significant than those for the cell sizes, which confirms the important observation that variations in cohesive energy due to composition changes are much greater than those due to changes in the unit cell size. All the correlations reported below employ the experimental lattice parameter data set and the corresponding cohesive energies. Given the good agreement between the calculated and experimental data sets, the conclusions drawn below are virtually independent of the set used.

Some interesting trends were found to emerge among E_c , a , t and T_C . Figures 4 and 5 show the cohesive energy per unit cell (E_c) and the cohesive energy density (G_c , the cohesive

Table 1. Tolerance factor (t), lattice parameter (a), cohesive energy (E_c) and transition sequences of the simple 2:4 perovskites in this study. The bold Roman numeral or 'tricit.' label refers to the order of the transition (first order, second order or tricritical). Question marks indicate uncertainty.

	BaCeO ₃	SrZrO ₃	SrHfO ₃	PbZrO ₃	CaTiO ₃	PbHfO ₃	PbSnO ₃	BaPbO ₃	SrRuO ₃	SrTiO ₃	BaZrO ₃	BaHfO ₃	PbTiO ₃	BaTiO ₃
t	0.9428	0.9531	0.9577	0.9701	0.9730	0.9748	0.9844	0.9850	1.0014	1.0091	1.0111	1.0160	1.0272	1.0706
a (Å)	4.44	4.15	4.11	4.16	3.89	4.15	4.07	4.29	3.97	3.91	4.20	4.17	3.97	4.02
E_c (eV)	-36.35	-40.09	-37.63	-37.37	-38.75	-35.47	-29.80	-27.92	-34.05	-38.73	-40.57	-38.42	-36.13	-38.78
Ref.	[42]	[43]	[44]	[34, 40]	[45]	[32, 33]	[36]	[46]	[47]	[48]	[49]	[50]	[6]	[6]
Transition sequence														
	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)	$Pm\bar{3}m$ ($a^0a^0a^0$)
	1200 K	1380 K	1380 K	~520 K	1634 K	~484 K	~400 K	723 K	950 K	105 K			763 K	393 K
	↔	↔	↔	↔	↔	↔	↔	↔	↔	↔			↔	↔
	II	tricit.	II	?	tricit.	?	?	tricit.	II (?)	II			I	I
	$R\bar{3}c$ ($a^-a^-a^-$)	$I4/mcm$ ($a^0a^0c^-$)	$I4/mcm$ ($a^0a^0c^-$)	?	$I4/mcm$ ($a^0a^0c^-$)	Tetrag.(?)	Mono.(?)	$I4/mcm$ ($a^0a^0c^-$)	$I4/mcm$ ($a^0a^0c^-$)	$I4/mcm$ ($a^0a^0c^-$)			$P4mm$ ($a^0a^0a^0$)	$P4mm$ ($a^0a^0a^0$)
	673 K	1113 K	1113 K	?	1500 K	435 K		548 K	825 K					273 K
	↔	↔	↔	↔	↔	↔		↔	↔					↔
	I	I	II	?	I	?		I	I					I
	$Imma$ ($a^0b^-b^-$)	$Imma$ ($a^0b^-b^-$)	$Cmcm$ ($a^0b^+c^-$)	$Pbam$ ($a^0b^-b^-$)	$Cmcm$ ($a^0b^+c^-$)	$Pbam$ ($a^0b^-b^-$)		$Imma$ ($a^0b^-b^-$)	$Imma$ ($a^0b^-b^-$)					$Amm2$ ($a^0a^0a^0$)
	573 K	1023 K	1023 K		1380 K			?	685 K					183 K
	↔	↔	↔		↔			↔	↔					↔
	II	II	I		I			II (?)	II (?)					I
	$Pnma$ ($a^+b^-b^-$)	$Pnma$ ($a^+b^-b^-$)	$Pnma$ ($a^+b^-b^-$)		$Pnma$ ($a^+b^-b^-$)			$Pnma$ (?)	$Pnma$ ($a^+b^-b^-$)					$R3m$ ($a^0a^0a^0$)

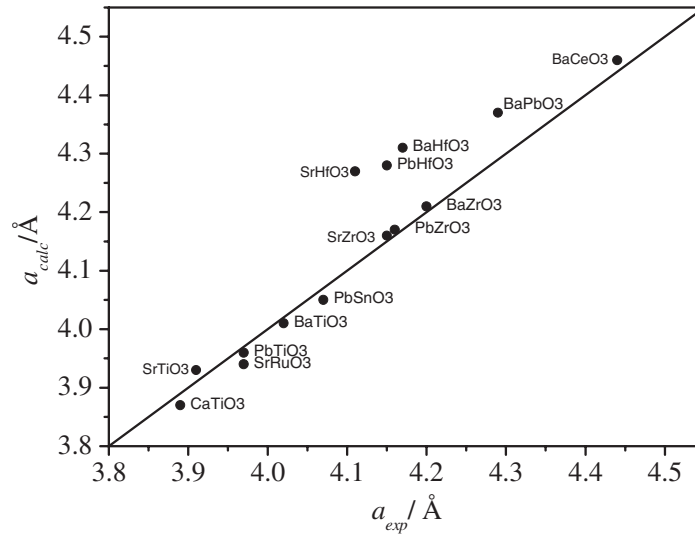


Figure 2. The set of lattice parameters calculated from the minimum energy condition, a_{calc} , plotted against the set of literature values, a_{exp} (see table 1 for references). The line represents $a_{calc} = a_{exp}$.

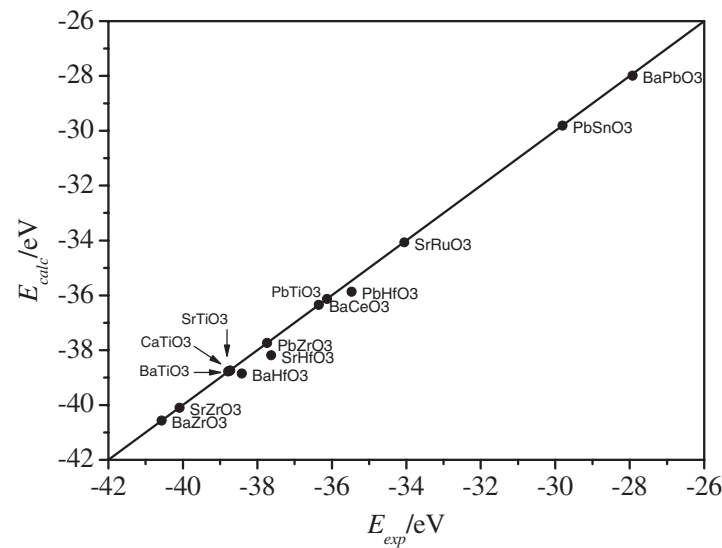


Figure 3. The set of cohesive energies calculated for the relaxed unit cell, E_{calc} , plotted against the set calculated from the literature value lattice parameters, E_{exp} . The line represents $E_{calc} = E_{exp}$. The points for SrTiO₃, CaTiO₃ and BaTiO₃ are virtually coincident.

energy per unit volume = E_c/a^3) as a function of lattice parameter. Although there is no obvious correlation between E_c and a , the data are rather well grouped, with the majority of lattice parameters falling between 3.9 and 4.3 Å, with energies in the range -34 to -41 eV per formula unit. The notable outliers are PbSnO₃ and BaPbO₃, with cohesive energies of -30 and -28 eV respectively, and BaCeO₃, which has the largest unit cell due to the relatively large Ce⁴⁺ ion. The apparently good correlation between G_c and a ($R = 0.797$) only confirms the

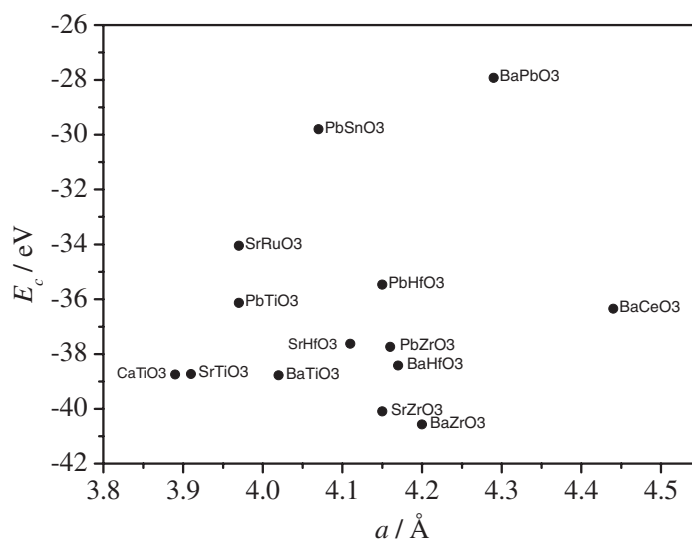


Figure 4. Calculated cohesive energies plotted against lattice parameters.

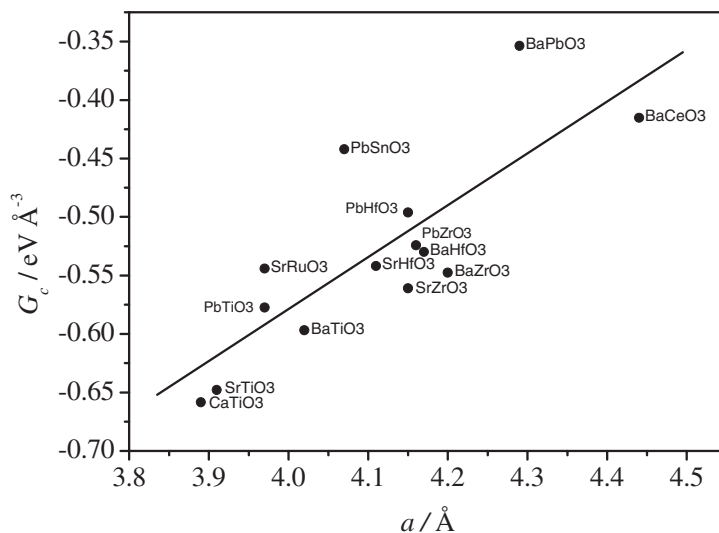


Figure 5. Calculated cohesive energy densities plotted against lattice parameters. The line represents a least squares fit to the data.

implicit relationship between the two. However, the figure confirms that the titanates have the largest cohesive energy densities whilst PbSnO₃, BaPbO₃ and BaCeO₃ have the lowest, with the zirconates and hafnates being grouped in between.

Figure 6 shows the cohesive energy as a function of the ionic size mismatch, or tolerance factor, t . Unsurprisingly, BaCeO₃ has the lowest tolerance factor whilst BaTiO₃ has the highest. It is notable that the two compounds with the lowest cohesive energy have tolerance factors close to 1. This suggests that the greater the degree of ion-size match, the less tightly bound the structure needs to be in order to stay together. However, the scatter in the full data set does

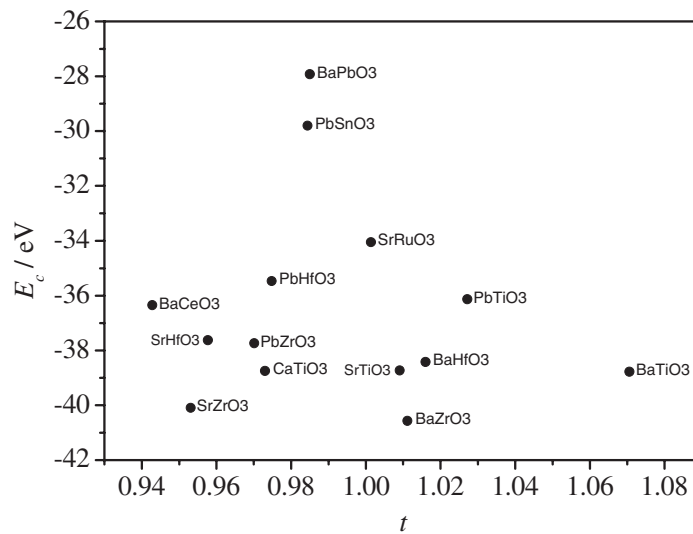


Figure 6. Cohesive energy as a function of tolerance factor.

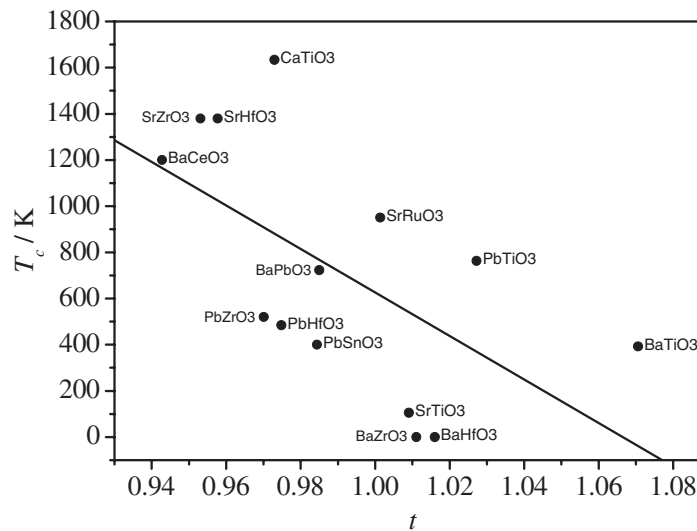


Figure 7. Cubic transition temperature plotted against tolerance factor. The line is a least squares fit to the data.

not imply the converse (greater size mismatch required greater cohesive energy) and seems to contradict Navrotsky and co-workers' idea that the closer a perovskite is to ideal geometry the more stable it is likely to be [27–30].

Figure 7 shows that, at least for this data set, T_c does generally tend to rise with decreasing t , but the correlation ($R = -0.60$) is not sufficient to have any real predictive value. Figure 8 is a plot of T_c versus E_c . Above 800 K there appears to be a systematically receding field boundary, suggesting that strong bonding is necessary to retain the distorted geometry at high temperatures.

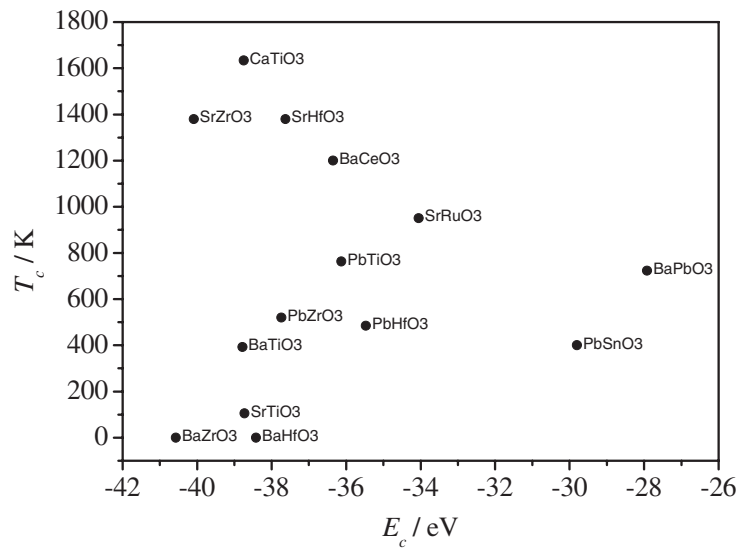


Figure 8. Cubic transition temperature plotted against calculated cohesive energy.

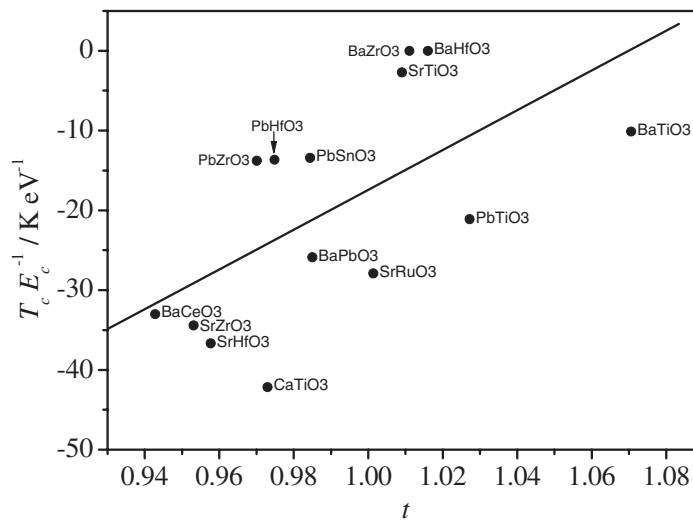


Figure 9. T_C/E_c plotted against tolerance factor. The line is a least squares fit to the data.

Considering the significant scatter in the correlation between T_C and t and the weak indications from the remaining plots of some connection between cubic stability and tolerance factor, combinations of the three parameters (E_c , T_C and t) were explored. Figure 9 is an attempt to determine whether the scatter in T_C versus t is associated with the variations in cohesive energy, through a plot of T_C/E_c versus t . The observed trend is actually no better than that of T_C versus t , having a similar correlation coefficient ($R = 0.60$). However, the plot of T_C/G_c versus t (figure 10) is rather surprising. More than half the data points appear to follow

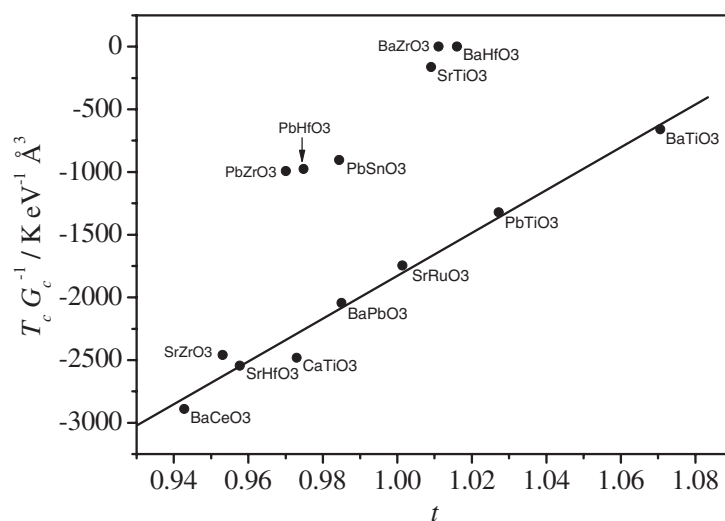


Figure 10. T_c/G_c plotted against tolerance factor. The line is a least squares fit to the subset of data that lies close to the line.

a linear trend with remarkable fidelity ($R = 0.9895$), implying a relationship of the form

$$\frac{T_c}{G_c} = mt + c, \quad (4)$$

where m and c are constants equal to 1.71×10^5 and $-1.89 \times 10^5 \text{ K eV}^{-1} \text{ \AA}^3$ respectively, and implying that $T_c = 0$ for $t \geq 1.105$. The remaining data points form two distinct clusters: (i) all compounds with lead on the A site, except PbTiO_3 (i.e. PbZrO_3 , PbHfO_3 , PbSnO_3), and (ii) compounds where $t \approx 1$ and $T_c \ll 273 \text{ K}$ (i.e. SrTiO_3 , BaZrO_3 , BaHfO_3).

The linear trend unites phase transitions irrespective of their order; some transitions are first order, some are second order, and some are tricritical (table 1). Moreover, the trend unites qualitatively different transitions: there are six octahedral tilt transitions ($Pm\bar{3}m \leftrightarrow I4/mcm$) and two octahedral distortion transitions ($Pm\bar{3}m \leftrightarrow P4mm$). The trend also unites compounds with a variety of A and B cation valence shell configurations. Out of the eight perovskites in the group, seven contain alkaline earth A cations with formally empty valence shells. The exception is PbTiO_3 , where the Pb^{2+} ion carries a stereoactive lone pair. Similarly, six out of the eight compounds in question have d^0 cations on the B site, the two exceptions being SrRuO_3 and BaPbO_3 with, respectively, $\text{Ru}^{4+}(d^4)$ and $\text{Pb}^{4+}(d^{10})$.

Surprisingly, perhaps, there is no discontinuity in the linear trend at or near $t = 1$, where the match of ion sizes approaches perfection, leaving progressively less room for distortion. There is a logic in the expectation that, close to $t = 1$, T_c should be close to zero. However, the existing data points are relatively widely spaced. It is possible that in the immediate vicinity of $t = 1$ there is a localized spike of which the $\text{SrTiO}_3/\text{BaZrO}_3/\text{BaHfO}_3$ cluster forms the tip.

Notwithstanding the possibility of a local deviation close to $t = 1$, should the apparent trend be regarded as meaningful, or simply a rather improbable coincidence? In the absence of an immediate explanation for the linear trend, the question may be approached by initially accepting the trend as ‘normal’ behaviour and then asking whether there are logical reasons for the observed exceptions.

The three lead compounds with $t < 1$ (PbZrO_3 , PbHfO_3 and PbSnO_3) form one of the clusters. At ambient temperature, PbZrO_3 and PbHfO_3 adopt the $Pbam$ geometry. Both

undergo an almost direct transition to cubic at around 500 K. However, recent research suggests a gradual reorganization of cation shifts with rising temperature, giving rise to a small region of an intermediate phase close to the cubic transition [31–33]. The $Pbam$ symmetry is not common among tilted perovskites. In terms of the Glazer notation [35], it corresponds to a basic $a^0b^-b^-$ tilt pattern overlaid with other types of distortion, most notably the substantial displacement of the Pb^{2+} cation from the centre of its ideal coordination polyhedron, which allows it to adopt a heavily distorted ‘umbrella’ coordination (a trigonal bipyramid with the lone pair taking up one of the apices). The fact that these perovskites appear to retain the $a^0b^-b^-$ arrangement down to 0 K, rather than undergo a further transition to $a^+b^-b^-$, which is the normal ground state for tilted perovskites, suggests that the Pb lone pair, again, has a very marked stabilizing effect. Similarly, the short stability interval and complicated symmetry of the intermediate phases between $Pbam$ and $Pm\bar{3}m$ suggests that the two tilt arrangements commonly found above $a^0b^-b^-$ ($a^0a^0c^-$ and $a^-a^-a^-$) are not adopted, because neither one allows a special position for the Pb lone pair [31–33]. This difficulty in finding a sterically acceptable intermediate step between $Pm\bar{3}m$ and $Pbam$ could account for the lowering of T_C relative to the linear trend. The ambient-temperature structure of $PbSnO_3$ is not known and has only been reported as unspecified ‘monoclinic’, which undergoes a transition to cubic at 400 K, but it is reasonable to expect that similar considerations might come into play [37]. In $PbTiO_3$ ($t = 1.027$) the smaller B site allows Pb^{2+} to adopt its preferred coordination, and the cubic transition is dominated by octahedral distortion.

The second group of exceptions are those already discussed with $t \approx 1$. The simplest explanation for this group is to accept that indeed the trend is not linear in this region and that there is a sharp deviation towards $T_C = 0$. If this is the case, then it is perhaps $SrRuO_3$ which is the exception; should this compound not also remain cubic down towards 0 K? Woodward [37] has shown that the stability of the cubic structure with respect to tilt transitions varies continuously but nonlinearly with the number of d electrons, the greatest stability being observed for d^1 and d^2 configurations. He explains this behaviour in terms of the interaction between the shifts in the width and position of the weakly anti-bonding t_{2g}^* band and its population. The instability of the cubic geometry in $SrRuO_3$ with respect to octahedral tilt transitions is accounted for by the four d electrons of Ru^{4+} populating the t_{2g}^* band. This weakens the B–O $p(\pi)$ – $d(\pi)$ bonding framework, which ordinarily opposes tilting deformation. This is possibly a reason why the transition occurs at, or close to, the highest possible temperature (the linear trend). If the d band were less populated, one would have expected a somewhat depressed transition temperature, because of the proximity to $t = 1$.

Whilst the above arguments do provide some justification for the exceptions to the observed linear trend, they do little to help us understand the trend itself. For this we must attempt to integrate the observation with existing theories of phase transitions, notably the soft mode approach [38, 39]. Following this treatment, the frequency ω_T of the transverse phonon mode in a simple diatomic crystal is given by the difference of two terms

$$\omega_T^2 = \frac{1}{\mu} \left(R_0 - \frac{AZ^2}{V} \right), \quad (5)$$

where A is a constant, μ is the reduced atomic mass, V is the unit cell volume, R_0 is a term representing short range forces, and Z is a term representing Coulomb forces due to cooperative charge displacements. This leads to the basic finding of the soft mode theory:

$$\omega_T^2 = B(T - T_C), \quad (6)$$

and that the transition occurs at the temperature at which the two terms in equation (5) cancel each other. Attempting to prove some equivalence between equation (5) and the observed linear trend in T_C (equation (4)) goes beyond the scope of this paper. Nevertheless, it can be pointed

out that there may be some commonalities between the two relationships. The magnitude of the cohesive energy is likely to figure in determining the local force constants in the unit cell, whilst the tolerance factor may be correlated with the maximum displacement amplitudes of transverse modes and the resulting Coulomb forces. However, it is also clear that the two relationships are not directly equivalent. In the soft mode approach it is the temperature dependence of the cell volume term that is often considered to be responsible for the softness of the transverse mode, whereas the terms in equation (4) are considered here independent of any temperature dependence, having been determined at either room temperature or, in the case of the cohesive energy, calculated at 0 K.

Given that there are significant doubts whether the observed trend is physically meaningful, further critical experimental evidence should be sought. An obvious approach is to carry out similar calculations for the other perovskite valence combinations (+:5+; 3+:3+). Secondly, the current data set could be tested by considering the behaviour of solid solutions. A notable case should be (Ba, Ca)TiO₃, the two end members of which lie at opposite extremes of the linear trend. However, this material is difficult to prepare with confidence that the all Ca²⁺ ions remain on the A site, leading to difficulties in identifying the correct tolerance factor and transition temperature. Perhaps more instructive would be the case of (Ba, Zr)TiO₃, which is known to exhibit an almost linear decrease in T_C as a function of Zr concentration [6]. Careful comparison of calculations with experimental data could confirm the locus of the tie line between the two end members in figure 10; does it follow the shortest path, or does it initially follow the linear trend away from BaTiO₃? A similar set of experiments for Sr(Ti, Zr)O₃ would also be useful.

Finally, we should ask whether the observed relationship serves any practical purpose. As virtually all 2+:4+ perovskites have already been synthesized, there is clearly no predictive utility to be gained. The same could be said of the set of 1+:5+ and 3+:3+ oxide perovskites. However, if the relationship is shown to be more widely applicable, it may be of useful use in helping predict the properties of solid solutions or complex perovskites, or perhaps more significantly could be used as a guide in studies of the fluoride perovskites which may yield some novel functional materials.

4. Conclusions

Correlations between cohesive energy, lattice geometry and the temperatures of the cubic transition in simple 2:4 oxide perovskites have been sought. Cohesive energies were obtained for a range of these materials via DFT plane-wave pseudopotential calculations [21]. Goldschmidt tolerance factors, taken as a measure of deviation from ideal ‘hard-sphere’ geometry, were calculated from Shannon’s ionic radii [24]. Temperatures of the cubic transition were taken from the literature [2, 9, 32, 34, 36, 40, 41].

A limited correlation ($R = -0.60$) was found between tolerance factor and transition temperature. However, for a significant subset of the simple 2:4 perovskites, a more pronounced correlation ($R = 0.989$) was found between the temperatures of the cubic transition, the cohesive energy, the tolerance factor and the unit cell volume, taking the form of a simple linear relationship. Two sets of exceptions from this behaviour can be explained by (i) the tendency of compounds with $t \approx 1$ to remain cubic down to 0 K, and (ii) the suppression of the normal sequence of oxygen octahedral tilt transitions by the need to accommodate the lone pair in the set of Pb A-site compounds other than PbTiO₃.

Further studies are required to determine whether the observed linear trend is physically meaningful and transferable to other systems.

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