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Ferroelectric Curie points at perovskite-type oxides

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The covalent bond energy of the A–O bonding and the enthalpy of formation for perovskite-type oxides ABO_3 were found to show high correlations with Curie points. Perovskite-type titanates with a lower covalent bond energy show higher Curie points, while those with low standard enthalpy of formation show low Curie points, or do not cause displacive transitions. The standard enthalpy of formation of perovskite oxides was inferred to be approximately equal to the sum of that of simple oxides.

1. Introduction

Ferroelectric materials, or piezoelectrics and pyroelectrics, are being used in an increasing variety of applications. Lead zirconate titanate (PZT) is one of the most widely utilized ferroelectrics at present. However, an increasing demand for high-temperature ferroelectric materials would limit the use of PZT which is not able to work above about 350° C. Ferroelectrics working at high temperatures must have high Curie points. In this sense, there are no theories capable of showing what kind of combination of elements would make ferroelectrics with high Curie points.

There are two types of phase transition at ferroelectric Curie points: displacive transition and order–disorder transition. The former is a first-order transition in most cases. The transition in almost all ferroelectric ceramics belongs to this type [1].

There have been two streams of development of the theory on displacive transition. One is Cochran's lattice dynamics. In his theory a mode of lattice vibration is connected with the displacement of atoms in crystals, which gives us some physical image, but does not make clear the reason for the displacement of atoms [2, 3]. The other is a series of works by Shukla and Sinha [4], Kristoffel and Konsin [5], and Bersuker [6]. They noted the TiO_6 octahedron in perovskite-type titanates $ATiO_3$, and presented a reason for the distortion of the octahedron. According to their theory, the distortion is caused by an interaction between phonons and electron bands, which is called the pseudo-Jahn–Teller effect. Curie points in connection with the distortion of octahedrons could be discussed to some degree using their theory. However, there are two problems. First, it is difficult to obtain the values of parameters in the theoretical equations. The calculation only for $BaTiO_3$ was reported [7]. Second, they consider only the Ti–O bond in perovskite-type titanates $ATiO_3$ and not the A–O bond. Consequently, even though their theory could explain qualitatively why the Curie point of $PbTiO_3$ is higher than that of $PbZrO_3$ [6], it is not able to explain why the Curie point of $PbTiO_3$ is higher than that of $BaTiO_3$.

The intention of the present study is to illustrate what kind of perovskite-type ferroelectrics show a high or low Curie point. For this purpose, various thermodynamic constants and other physical constants were surveyed to see if they had a high correlation with Curie points. It was found that the covalent bond energy of the A–O bonding in ABO_3 and the standard enthalpy of formation were the two quantities showing high correlations with Curie points.

It is well known that most perovskite-type ferroelectrics and antiferroelectrics change into a cubic system with rising temperature at the Curie points, and that some other perovskite oxides go through nonferroelectric transition, at which they change into a cubic system. These three sorts of perovskites were not discriminated and such transition temperatures are denoted by T_t in this paper. Although some perovskite oxides have more than one transition temperature, temperatures other than T_t were ignored.

2. Correlation between Curie points and covalent bond energy of titanates

Pauling [8] assumed that a heteronuclear bond energy would be the average of the two homonuclear bonds. He did not, however, discern a polar bond from a nonpolar one. Sanderson [9] made a correction and found that the length of any actual polar covalent bond tended to be smaller than the sum of the nonpolar covalent radii of the two atoms. This should increase the covalent energy, because shorter bonds are always stronger. According to Sanderson, the covalent bond energy of the A–O bonding in AO, which is either a crystal or a biatomic molecule, can be expressed as

$$E_{cov}\,(A\text{–}O) = \frac{(E_{A\text{-}A}E_{O\text{-}O})^{1/2}\,(r_{cA} + r_{cO})}{R(A\text{–}O)} \qquad (1)$$

where $E_{A\text{-}A}$ and $E_{O\text{-}O}$ are the covalent energies of nonpolar bonds A–A and O–O (single bond), r_c is the

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TABLE I Bond lengths, covalent radii of A-atoms and nonpolar covalent bond energies of A–A bonds

	Bond length R(A–O) (nm)	Covalent radius* r_c(A) (nm)	Nonpolar covalent bond energy* E_{A-A}(kJ mol^{-1})	Reference
$PbTiO_3$	0.281	0.154	85.8	[10]
$(K_{0.5}Bi_{0.5})TiO_3$	0.279	0.206, 0.152	55.2, 127.2	[11, 12]
$(Na_{0.5}Bi_{0.5})TiO_3$	0.275	0.157, 0.152	75.3, 127.2	[11]
$BaTiO_3$	0.284	0.198	104.2	[13, 14]
$SrTiO_3$	0.276	0.192	135.6	[2, 15]

$r_c(O) = 0.070$ nm, $E_{O-O} = 140.2\,\text{kJ mol}^{-1}$ for a single bond O–O.
*See [9].

covalent bond radius, R(A–O) is the actual bond length in the compound AO. If the electronegativities of A′ and O were equal, it would be

$$E_{\text{cov}}\,(A'\text{–}O) = (E_{A'\text{–}A'}E_{O\text{–}O})^{1/2} \qquad (2)$$

But in fact, different atoms have different electronegativities, and so in general heteronuclear bonds always involve polarity. The factor, $(r_{cA} + r_{cO})/R(A\text{–}O)$, in Equation 1 represents the deviation in covalent energy due to the polarity. Sanderson [9] applied the method to simple organic and binary inorganic compounds.

We have attempted to apply Sanderson's method to perovskite-type oxides which consist of more than three kinds of element. The A–O bonds in titanates $ATiO_3$ were examined. Table I shows parameters from which E_{cov} (A–O)s are obtained and the result of the calculation. The room-temperature forms of these perovskites, except $SrTiO_3$, are not cubic [10–15] and have A–O bonds with different lengths [16, 17]. R(A–O) was defined here as

$$R(A\text{–}O) = V^{1/3}\frac{1}{2^{1/2}} \qquad (3)$$

where V is a lattice volume (for $Z = 1$) at room-temperature. The form of $(Na_{0.5}Bi_{0.5})TiO_3$ is rhombohedral and the lattice parameter $\alpha \simeq 90°$ [11], so that $V \simeq a^3$. For $(K_{0.5}Bi_{0.5})TiO_3$ and $(Na_{0.5}Bi_{0.5})TiO_3$ the covalent bond energy was obtained by

$$E_{\text{cov}}\,(A\text{–}O) = \frac{(E_{A'\text{–}A'}E_{O\text{–}O})^{1/2}(r_{cA'} + r_{cO}) + (E_{A''\text{–}A''}E_{O\text{–}O})^{1/2}(r_{cA''} + r_{cO})}{2R(A\text{–}O)} \qquad (4)$$

Fig. 1 shows the covalent energy of the A–O bond as a function of the observed T_t. It is seen that there is a clear linear correlation between the covalent energy and T_t, and that titanates with smaller E_{cov} (A–O) show higher T_t.

As was mentioned in the previous section, the distortion of the unit cells of perovskite titanates is attributed to the pseudo-Jahn–Teller effect in the TiO_6 octahedron. It may occur independently of the effect of the A–O bond. On the other hand, Equation 1 does not reflect the effect of TiO_6 octahedra explicitly, so the influence of A–O bonds on ferroelectricity or on Curie point would be properly dealt with independently. One A atom is surrounded by twelve oxygens and occupies the position at the centre of the oxygen dodecahedron at temperatures above T_t, but the dodecahedron becomes distorted below T_t [2, 16, 17]. The good correlation in Fig. 1 suggests that the A–O covalent bonds contribute greatly to the stability of the dodecahedron, and hence the transition temperature.

3. Estimation of standard enthalpy of formation

In the next section standard enthalpy of formation of perovskite oxides is discussed. Although various compounds of perovskite structure were found, thermodynamic constants were obtained only for some of them. A method of estimating standard enthalpy of formation is discussed here and the results will be used in the next section.

Standard enthalpy of formation, ΔH_f°, for ABO_3-type oxides can be estimated as follows:

$$\Delta H_f^\circ(A^{I}B^{V}O_3) \simeq \tfrac{1}{2}\Delta H_f^\circ(A_2O) + \tfrac{1}{2}\Delta H_f^\circ(B_2O_5) \qquad (5)$$

$$\Delta H_f^\circ(A^{II}B^{IV}O_3) \simeq \Delta H_f^\circ(AO) + \Delta H_f^\circ(BO_2) \qquad (6)$$

$$\Delta H_f^\circ(A^{III}B^{III}O_3) \simeq \tfrac{1}{2}\Delta H_f^\circ(A_2O_3) + \tfrac{1}{2}\Delta H_f^\circ(B_2O_3) \qquad (7)$$

Standard enthalpy of formation for each component oxide has been well documented (e.g. [18]), and that for ABO_3 could be confirmed for some of the perovskite oxides for which observed values of ΔH_f° have been reported. Table II shows the observed and calculated values of ΔH_f° which may be judged to be

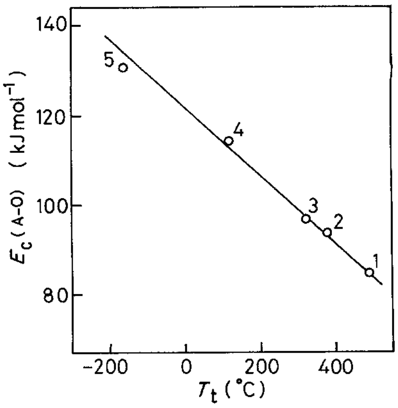

Figure 1 Covalent bond energies of A–O bonds plotted against Curie point (or transition temperatures to cubic) of perovskites ABO_3. 1, $PbTiO_3$; 2, $(K_{0.5}Bi_{0.5})TiO_3$; 3, $(Na_{0.5}Bi_{0.5})TiO_3$; 4, $BaTiO_3$; 5, $SrTiO_3$.

TABLE II Standard enthalpies of formation of ABO_3

	$\Delta H^{\circ}_{f,298\,K}$ (kJ mol^{-1})		
	Calculated	Observed [18]	Difference
Perovskite structure			
$PbTiO_3$	− 1160	− 1200	40
$BaTiO_3$	− 1500	− 1650	150
$BaZrO_3$	− 1650	− 1770	120
$BaHfO_3$	− 1670	− 1800	130
$SrTiO_3$	− 1540	− 1680	140
$SrZrO_3$	− 1690	− 1780	90
$SrHfO_3$	− 1700	− 1780	80
$CaTiO_3$	− 1580	− 1660	80
$CaZrO_3$	− 1730	− 1770	40
$CaHfO_3$	− 1760	− 1780	20
$CeAlO_3$	− 1750	− 1770	20
Ilmanite structure			
$MgTiO_3$	− 1530	− 1570	40
$FeTiO_3$	− 1200	− 1250	50
$CoTiO_3$	− 1180	− 1220	40
$MnTiO_3$	− 1320	− 1360	40

in good agreement. The difference between observed and calculated values is the enthalpy of reaction; $AO + BO_2 \rightarrow ABO_3$. Enthalpy of reaction is composed of the energy of dissociation and rearrangement of chemical bonds. In the case of the above reaction, A and B atoms are bound to oxygens both before and after the reaction and do not produce an A–B bond. This may be the reason why the enthalpy of reaction is small. Consequently, the present estimation would not be far from the truth and calculated standard enthalpies of formation are listed in Table III.

4. Correlation between phase transition temperature and standard enthalpy of formation

Another quantity which seems to correlate with Curie point is standard enthalpy of formation. This is shown in Fig. 2. The correlation here was not derived by a theory, but was searched out from a number of physical quantities. The compounds marked (F) and (A) are ferroelectric and antiferroelectric, respectively. For them T_t is a Curie point. Those marked (−) are other perovskite oxides which go through displacive transition. For them T_t is the transition temperature, at which their symmetry changes into cubic with increasing temperature.

TABLE III Estimated standard enthalpies of formation, $\Delta H_{f,298\,K}$ (kJ mol^{-1}) of perovskite-type paraelectrics, of which the B-ions have the electron configuration of rare gases [27, 28]

	$\Delta H_{f,298\,K}$		$\Delta H_{f,298\,K}$
Type $A^{1+}B^{5+}O_3$			
$KTaO_3$	− 1230		
Type $A^{2+}B^{4+}O_3$			
$CaTiO_3$	− 1580	$BaHfO_3$	− 1670
$CaZrO_3$	− 1730	$SrCeO_3$	− 1680
$SrZrO_3$	− 1690	$BaCeO_3$	− 1640
$BaZrO_3$	− 1650	$SrUO_3$	− 1150
$CaHfO_3$	− 1750	$BaUO_3$	− 1120
$SrHfO_3$	− 1700		
Type $A^{3+}B^{3+}O_3$			
$LaScO_3$	− 1850	$(Li_{0.5}Nd_{0.5})TiO_3$	− 1540
$CeScO_3$	− 1860	$(Na_{0.5}Nd_{0.5})TiO_3$	− 1500
$PrScO_3$	− 1860	$(K_{0.5}Nd_{0.5})TiO_3$	− 1490
$NdScO_3$	− 1860	$(Li_{0.5}Ce_{0.5})TiO_3$	− 1550
$SmScO_3$	− 1870	$(Na_{0.5}Ce_{0.5})TiO_3$	− 1500
$EuScO_3$	− 1810	$(K_{0.5}Ce_{0.5})TiO_3$	− 1490
$GdScO_3$	− 1860	$(Li_{0.5}La_{0.5})TiO_3$	− 1540
$DyScO_3$	− 1880	$(Na_{0.5}La_{0.5})TiO_3$	− 1500
$HoScO_3$	− 1890	$(K_{0.5}La_{0.5})TiO_3$	− 1480
$YScO_3$	− 1900	$(Rb_{0.5}La_{0.5})TiO_3$	− 1470
$YCeO_3$	− 1800		
$LaYO_3$	− 1850		

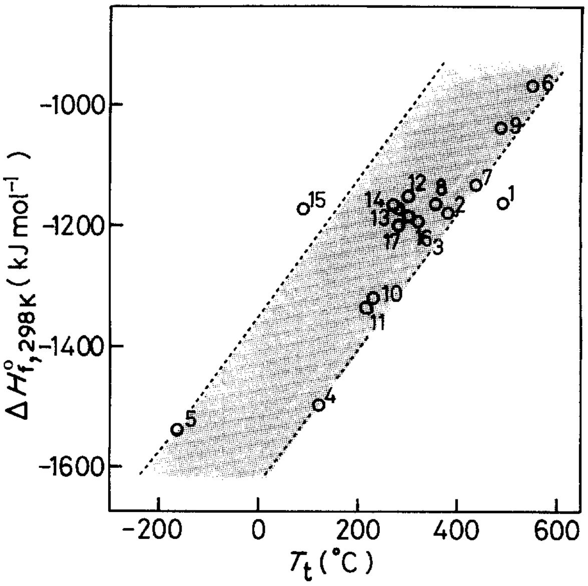

Figure 2 Standard enthalpies of formation plotted against Curie points (or transition temperatures to cubic) of perovskites ABO_3. 1, $PbTiO_3$ (F); 2, $(K_{0.5}Bi_{0.5})TiO_3$ (F); 3, $(Na_{0.5}Bi_{0.5})TiO_3$ (F); 4, $BaTiO_3$ (F); 5, $SrTiO_3$ (−); 6, $AgNbO_3$ (−); 7, $KNbO_3$ (F); 8, $NaNbO_3$ (A); 9, $AgTaO_3$ (−); 10, $PbZrO_3$ (A); 11, $PbHfO_3$ (A); 12, $Pb(Yb_{0.5}Nb_{0.5})O_3$ (A); 13, $Pb(Y_{0.5}Nb_{0.5})O_3$ (A); 14, $Pb(Lu_{0.5}Nb_{0.5})O_3$ (A); 15, $Pb(Sc_{0.5}Nb_{0.5})O_3$ (F); 16, $Pb(Yb_{0.5}Ta_{0.5})O_3$ (A); 17, $Pb(Lu_{0.5}Ta_{0.5})O_3$ (F).

The symmetry of $BaTiO_3$ is rhombohedral, orthorhombic, tetragonal and cubic in order of temperature. The change in symmetry from tetragonal to cubic occurs at the ferroelectric Curie point, 120° C [13, 14]. $(K_{0.5}B_{0.5})TiO_3$ transforms from a ferroelectric tetragonal phase to a paraelectric cubic phase, and $(Na_{0.5}Bi_{0.5})TiO_3$ from rhombohedral to cubic [11, 12]. $SrTiO_3$ is paraelectric at any temperature, but a phase transition from tetragonal to cubic occurs at − 163° C [2, 15]. $AgNbO_3$ becomes orthorhombic, tetragonal and cubic with increasing temperature. No evidence of ferroelectricity or antiferroelectricity has been reported. The temperature of its transition to cubic is 550° C [19]. $AgTaO_3$ also becomes orthorhombic, tetragonal and cubic with increasing temperature [19]. The behaviour of $NaNbO_3$ is more complicated, crystallizing in monoclinic, orthorhombic, pseudotetragonal, tetragonal and cubic forms. It has the antiferroelectric Curie point at 335° C at which it changes from one orthorhombic phase to another orthorhombic phase [20, 21]. The polymorphic transition behaviour of $KNbO_3$ is similar to that of $BaTiO_3$ [22]. $PbTiO_3$ [10], $PbHfO_3$ [23] and $Pb(Sc_{0.5}Nb_{0.5})O_3$ [24] become tetragonal and cubic. $Pb(Lu_{0.5}Nb_{0.5})O_3$, $Pb(Lu_{0.5}Ta_{0.5})O_3$, $Pb(Yb_{0.5}Nb_{0.5})O_3$ and $Pb(Yb_{0.5}Ta_{0.5})O_3$ transform from monoclinic to cubic at each Curie point [25].

Fig. 2 shows that there is a linear correlation between standard enthalpy of formation, $\Delta H^{\circ}_{f,298\,K}$ and

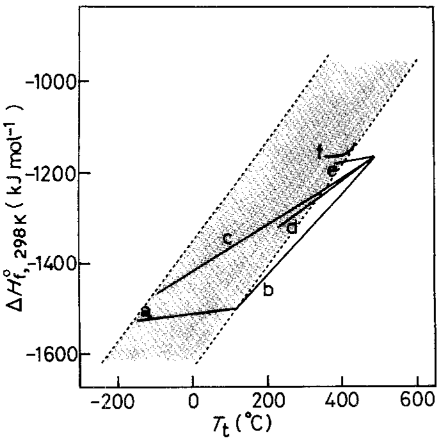

Figure 3 Standard enthalpy of formation plotted against Curie point of perovskite-type solid solutions. (a) $BaTiO_3$–$SrTiO_3$, (b) $BaTiO_3$–$PbTiO_3$, (c) $PbTiO_3$–$SrTiO_3$, (d) $PbTiO_3$–$PbZrO_3$, (e) $PbTiO_3$–$(K_{0.5}Bi_{0.5})TiO_3$, (f) $KNbO_3$–$NaNbO_3$. Data on Curie points: [28–33].

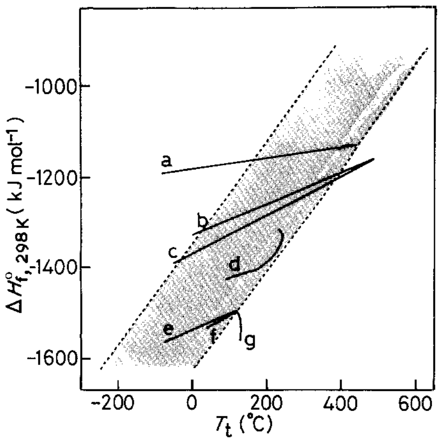

Figure 4 Standard enthalpy of formation plotted against Curie point of perovskite-type solid solutions. (a) $BaTiO_3$–$CaTiO_3$, (b) $PbTiO_3$–$(Li_{0.5}La_{0.5})TiO_3$, (c) $PbTiO_3$–$CaTiO_3$, (d) $PbZrO_3$–$SrZrO_3$, (e) $BaTiO_3$–$BaZrO_3$, (f) $BaTiO_3$–$BaZrO_3$. Data on Curie points: [28, 34–38].

T_t and the perovskites with low $H^\circ_{f,298K}$ have a low transition temperature.

Table III shows $\Delta H^\circ_{f,298K}$ (calculated) of perovskite oxides which do not show any phase transition below their melting points. Most of the compounds in Table III have lower $\Delta H^\circ_{f,298K}$ compared with $SrTiO_3$, which has the lowest $\Delta H^\circ_{f,298K}$ as shown in Fig. 2. Exceptions are only $KTaO_3$, $BaUO_3$ and $SrUO_3$.

Solid solutions of perovskite were also examined. When two kinds of perovskites ABO_3 and $A'B'O_3$ form a binary system $(A_{1-x}A'_x)(B_{1-x}B'_x)O_3$, the standard enthalpy of formation is estimated as

$$\Delta H^\circ_f\,(\text{solution}) = (1-x)\Delta H^\circ_f(ABO_3) + x\Delta H^\circ_f(A'B'O_3) \qquad (8)$$

where x is the mole fraction of $A'B'O_3$. Equation 8 may be valid, because the enthalpy of solution of isovalent perovskite oxides seems to be very small compared with the standard enthalpy of formation of their end members and also the entropy of mixing is small enough to be ignored. Thus, the ΔH°_f for solutions would vary linearly with x.

The binary systems in Fig. 3 include the perovskites, which are listed in Fig. 2, as end members which all show polymorphic transition. An isovalent solid solution has an intermediate Curie point between those of the end members in a number of cases [26]. The lines in Fig. 3 were drawn as x changed from 0 to 1 continuously. For all the systems except f, because both $\Delta H^\circ_{f,298K}$ and T_t vary linearly with x, the lines are straight. The broken lines in Fig. 3 are the same as the lines in Fig. 2. All the solid lines are seen to fall in the area between the broken lines.

Fig. 4 shows $\Delta H^\circ_{f,298K}$–T_t relations for the solid solutions formed between the compounds which show polymorphic transitions and those which show no phase transition. The lines in Fig. 4 are only for the composition ranges in which phase transition occurs and those lie in the same correlation zone.

Summing up, perovskite oxides of low $\Delta H^\circ_{f,298K}$ have low Curie points (or low transition temperatures to cubic systems), or do not transform.

5. Conclusions

1. In the present study two factors correlating with ferroelectric Curie points of perovskite-type oxides were found. (i) Curie point and covalent bond energy of the A–O bond of perovskite-type titanates $ATiO_3$ are in an exactly linear correlation. High Curie points belong to titanates with small covalent bond energy. (ii) Curie point and standard enthalpy of formation of perovskite-type oxides ABO_3 are also in high correlation. Perovskites with low enthalpy of formation have low Curie points, or no displacive transitions.

2. There are some perovskite oxides that are not ferroelectric or antiferroelectric but transform with rising temperature into cubic systems. The transition temperatures of these oxides were able to be included in the discussion along with the Curie points of ferroelectric and antiferroelectric oxides.

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