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Curie point of perovskite-type oxides containing bivalent ions of the 4th period in the B-site

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The effects of different B-site elements on the Curie points of the $PbTiO_3$–$Pb(M_{1/3}Nb_{2/3})O_3$ and $0.99BaTiO_3$–$0.01Ba(M_{1/3}Nb_{2/3})O_3$ series (M = Ca, Mn, Fe, Co, Ni, Cu, Zn), were examined. The Curie point was high when M was copper, while it was low when M was nickel. This was caused by the Jahn–Teller effect in the CuO_6 octahedron keeping the Curie point high. For the $0.99BaTiO_3$–$0.01Ba(M_{1/3}Nb_{2/3})O_3$ systems, the Curie points were correlated with axial ratio *c/a*.

1. Introduction

There are two factors which determine the ferroelectric Curie point: the variety of the element in the substance and the existence of lattice defects. A great number of studies [1] have been reported on dielectric properties of perovskite-type ferroelectrics to which various elements were added. Those solid solutions included lattice defects. Consequently, their Curie points were influenced by the above two factors. On the other hand, a number of combinations of solid solutions whose end members were both perovskite-type oxides, were also investigated (compensated valence substitution) [2]. They showed no structural imperfection, so their Curie points depended only on the elements contained. The present work is concerned with a study along the latter lines.

Igarashi *et al.* [3, 4] found that there was a correlation between Curie points and covalent bond energy in perovskite-type oxides. For example, $PbTiO_3$, whose covalent energy of the Ti–O bond is smaller, has a higher Curie point than $PbZrO_3$, whose Zr–O bond energy is larger. However, as far as perovskite-type oxides containing bivalent or trivalent transition metal ions are concerned, such a correlation does not exist. As shown in Table I, for a series of $Pb(M_{1/3}Nb_{2/3})O_3$ compounds, there is no correlation between the covalent energy of M–O bonds and the Curie points. The authors expect to find some factors which determined the Curie points of this kind of compound. However, there are insufficient data with which to discuss it.

The purpose of the present work was to supplement the data on the Curie points of perovskite-type oxides containing transition ions in the B-site. Here, the ions were confined to bivalent ones of the 4th period in the Periodic Table. Compounds with the composition $Pb(M_{1/3}Nb_{2/3})O_3$ or $Ba(M_{1/3}Nb_{2/3})O_3$ are not necessarily easy to synthesize, so perovskite-type titanates which were partially substituted by those ions were used to investigate the effect of those ions.

2. Experimental methods

TiO_2, Nb_2O_5, bivalent metal oxides and carbonates of barium or lead (purities 99.9%) were mixed with ethanol in an agate mortar, then dried with silica gel. The powder was pressed to cylindrical pellets, which were then put on a zirconia board. For pellets not containing lead, the zirconia board was placed in an alumina boat; for those which did contain lead, the zirconia was placed in a pair of boats in the way illustrated in Fig. 1. The pair of boats, the top edges of which were polished flat, were placed one on top of the other with the polished edges together in order to retain PbO gas. Two pellets of a mixture of $PbZrO_3$ and PbO powder were placed beside the starting material pellets so that a PbO atmosphere could be made. The alumina boats were placed in a mullite tube, through which air or reducing gas flowed, and were heated. Starting materials containing oxides of manganese, iron or cobalt were sintered in a reducing atmosphere to preserve the bivalency of those metal ions. Samples were made by sintering once.

Curie points were measured by differential thermal

TABLE I Covalent bond energy of the bond between bivalent ion and oxygen ion, E_{cov}(M–O), Curie point T_c, Curie–Weiss temperature, T_0

	$E_{cov}(M^{II}–O)$ (kJ mol^{-1})	T_c* (°C)	T_0* (°C)
$Pb(Cd_{1/3}Nb_{2/3})O_3$	144	270	?
$Pb(Zn_{1/3}Nb_{2/3})O_3$	158	140	135
$Pb(Mg_{1/3}Nb_{2/3})O_3$	146	−10	−10
$Pb(Co_{1/3}Nb_{2/3})O_3$	141	−98	?
$Pb(Ni_{1/3}Nb_{2/3})O_3$	165	−120	−130

M^{II} = Cd, Zn, Mg, Co, Ni.
*[11].

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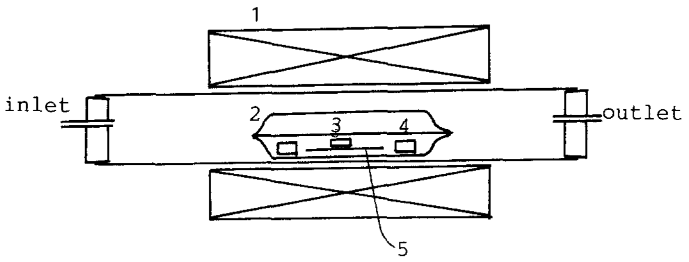

Figure 1 Illustration of apparatus for sintering of lead-containing compounds 1, Furnace; 2, alumina boat; 3, pellet of starting material; 4, pellet of $PbZnO_3$ + PbO; 5, zirconia board.

analysis (DTA) using a heating rate of 10° C min. Lattice constants were measured by X-ray diffraction (XRD) of powder specimens, with silicon powder as an internal standard.

3. Results and discussion

3.1. Features of each specimen

The conditions of sintering and the colours of the sintered samples are shown in Table II. For the $(1-x)PbTiO_3$–$xPb(Mn_{1/3}Nb_{2/3})O_3$ system, when the reducibility of the flowing gas was weak, the manganese ion was oxidized to trivalent and the colour of the sintered specimen became brown. When the reducibility was too strong, lead oxide was reduced to metallic lead. Only when x was less than 0.5, did the sintered samples become olive, the colour which is evidence of the bivalent manganese ion. Fig. 2 is the apparent phase diagram of the $(1-x)PbTiO_3$–$xPb(Ni_{1/3}Nb_{2/3})O_3$ system. $Pb(Ni_{1/3}Nb_{2/3})O_3$ is a well-known ferroelectric material whose structure is perovskite and its Curie point is – 120° C. When x was 0.65 to 0.97, three phases, i.e. perovskite, pyrochlore and NiO phases coexisted according to XRD.

In $(1-x)PbTiO_3$–$xPb(Fe_{1/3}Nb_{2/3})O_3$, only the perovskite phase existed in the region $x < 0.08$ as found by XRD. Perovskite and pyrochlore phases coexisted in the other regions. Phases of this and the $(1-x)PbTiO_3$–$xPb(Cu_{1/3}Nb_{2/3})O_3$ systems are shown in Fig. 3. The pyrochlore in the above systems was all $Pb_3Nb_4O_{13}$.

For the $(1-x)BaTiO_3$–$xBa(M_{1/3}Nb_{2/3})O_3$ systems, only samples of $x = 0.01$ were examined. The phase transition of $x > 0.02$ was diffuse. According to observation by SEM, the grain particle sizes of these systems were about $2\,\mu$m on average. Their relative densities were all less than 70%. The result shows that grain growth and sintering in barium titanate were inhibited by substitution of titanium with $(M_{1/3}Nb_{2/3})$. On the other hand, sintering of $PbTiO_3$ was promoted by substitution of titanium. (As is well-known, pure $PbTiO_3$ does not sinter.) The average grain particle size of $0.75PbTiO_3$–$0.25Pb(Ni_{1/3}Nb_{2/3})O_3$ was $8\,\mu$m, and that of $0.95PbTiO_3$–$0.05Pb(Ni_{1/3}Nb_{2/3})O_3$ was $3\,\mu$m. Only the $(1-x)PbTiO_3$–$xPb(Fe_{1/3}Nb_{2/3})O_3$ system was exceptionally hard to sinter. The average grain size was about $2\,\mu$m.

3.2. Comparison of Curie points

Curie points of perovskites containing different elements in the B-site are compared in this section. If synthesis of $Pb(M_{1/3}Nb_{2/3})O_3$ and $Ba(M_{1/3}Nb_{2/3})O_3$ for any bivalent ion M was possible, the Curie points would be easy to compare. In fact, only a few of them are possible. Thus partially substituted lead titanate and barium titanate are discussed.

Fig. 4 shows the Curie points of these compounds plotted against the number of d-electrons of the substituted ion in the B-site. The order of the Curie points of the barium compounds was not the same as that of the lead compounds. However, there was a similar tendency in that it was high when M = Cu, and it was low when M = Ni. For copper, the higher Curie point seems to be due to the Jahn–Teller effect, i.e. the CuO_6 octahedron is more stable when it is elongated along a diagonal axis than when it is regular. The distortion of the octahedron also promotes the ferroelectric distortion of the whole crystal. The stronger the tendency to ferroelectric distortion, the wider the range of temperature over which the crystal exhibits ferroelectricity. The relationship between the Jahn–

TABLE II Sintering conditions and colour of specimens investigated

Substitute ion	x	Sintering conditions			Colour
		Temp. (° C)	Time (h)	Flowing gas	
$PbTiO_3$					
$(Mn_{1/3}Nb_{2/3})$	0–1	1200	12	Ar, 1% H_2	olive
$(Fe_{1/3}Nb_{2/3})$	0–1	1200	12	Ar, 0.1% H_2	dark green
$(Ni_{1/3}Nb_{2/3})$	0–1	1250	14	air	yellow–green
$(Cu_{1/3}Nb_{2/3})$	0–1	1180*	12	air	light brown
$BaTiO_3$					
$(Ca_{1/3}Nb_{2/3})$	0.01	1350	14	air	white
$(Mn_{1/3}Nb_{2/3})$	0.01	1350	14	Ar, 1% H_2	pale green
$(Fe_{1/3}Nb_{2/3})$	0.01	1350	15	Ar, 0.1% H_2	brown
$(Co_{1/3}Nb_{2/3})$	0.01	1350	14	N_2	light brown
$(Ni_{1/3}Nb_{2/3})$	0.01	1350	14	air	yellow
$(Cu_{1/3}Nb_{2/3})$	0.01	1350*	14	O_2	pale yellow
$(Zn_{1/3}Nb_{2/3})$	0.01	1350	14	air	white

*Annealed in oxygen at 800° C for 8 h after sintering.

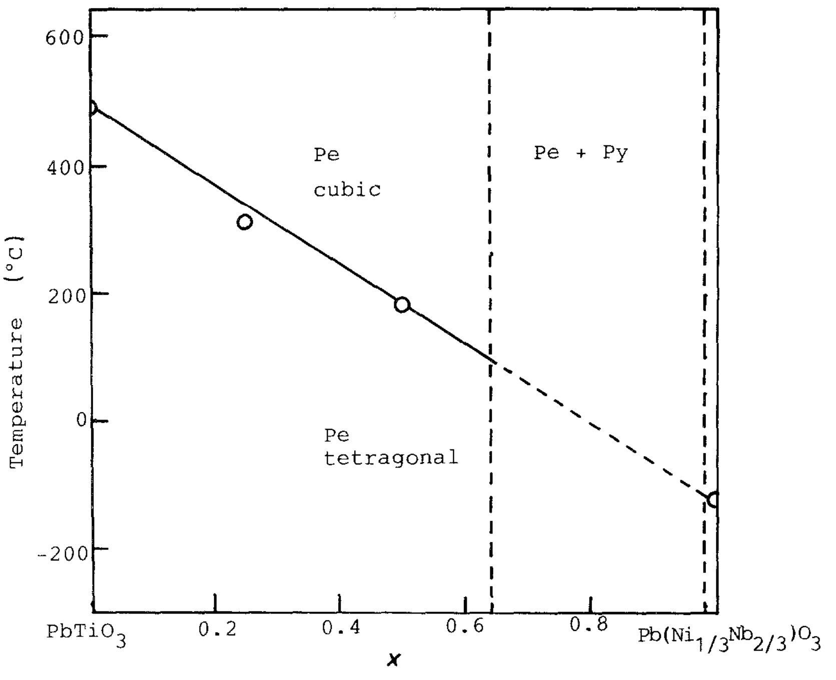

Figure 2 Curie points of (1 − x)PbTiO$_3$-xPb(Ni$_{1/3}$Nb$_{2/3}$)O$_3$.

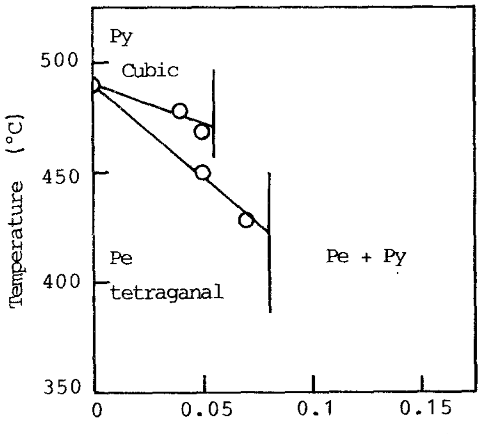

Figure 3 Curie points of (1 − x)PbTiO$_3$-xPb(M$_{1/3}$Nb$_{2/3}$)O$_3$ where M is Cu, Fe.

Teller effect and the Curie point has already been inferred by Sakudo [5]. For the other compounds, no relationship was found between the Curie points and the number of d-electrons.

In Fig. 4 the value of 0.95PbTiO$_3$-0.05Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$ is taken from Nomura *et al.* [6] and that of 0.95PbTiO$_3$-0.05Pb(Co$_{1/3}$Nb$_{2/3}$)O$_3$ is obtained by interpolation from the Curie points of PbTiO$_3$ and Pb(Co$_{1/3}$Nb$_{2/3}$)O$_3$.

Fig. 5 shows lattice constants a, c of 0.99BaTiO$_3$-0.01Ba(M$_{1/3}$Nb$_{2/3}$)O$_3$. These values showed no particular tendency. Fig. 6 shows plots of Curie point, T_c, against axial ratio c/a. T_c and c/a are in a high correlation. This tendency might be general for perovskite-type ferroelectrics, because c/a is large in PbTiO$_3$ and is small in BaTiO$_3$.

3.3. Comment on Baxter *et al.*'s study

Baxter *et al.* [7] synthesized the (Ba$_{1-x}$M$_x$)TiO$_3$ series (M = Mn, Fe, Co, Ni, Zn) and measured their dielec-

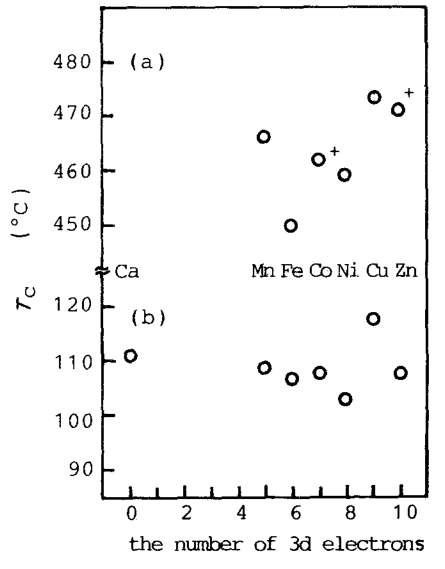

Figure 4 Curie points of (a) 0.95PbTiO$_3$-0.05Pb(M$_{1/3}$Nb$_{2/3}$)O$_3$, (b) 0.99BaTiO$_3$-0.01Ba(M$_{1/3}$Nb$_{2/3}$)O$_3$, where Ms are bivalent metal ions [2, 5].

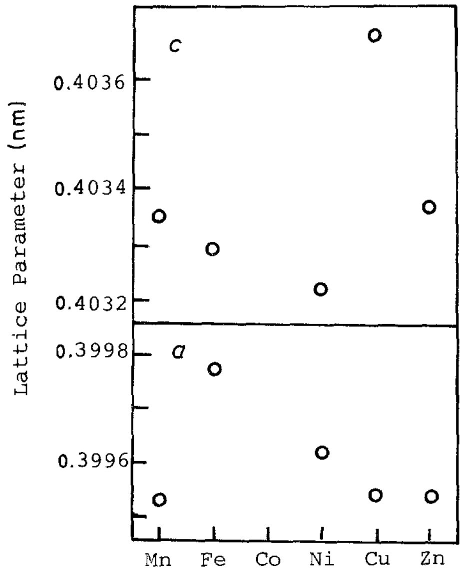

Figure 5 Lattice constants of 0.99BaTiO$_3$-0.01Ba(M$_{1/3}$Nb$_{2/3}$)O$_3$, M = Mn, Fe, Ni, Cu, Zn.

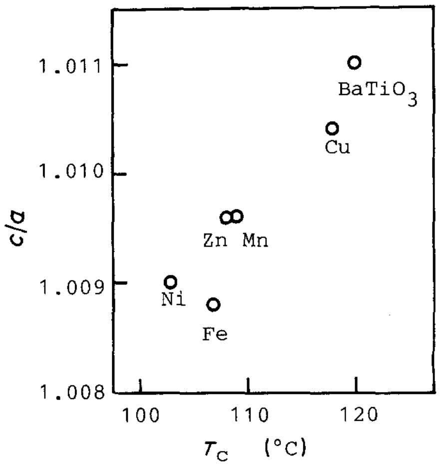

Figure 6 Plots of axial ratios of $0.99BaTiO_3$–$0.01(M_{1/3}Nb_{2/3})O_3$ and $BaTiO_3$ against Curie points.

tric properties. They considered that these M ions were positioned at the A-site. However, ions other than manganese and zinc have properties in favour of a coordination number of six, due to their crystal field stabilized energy (CFSE) which favours octahedron coordination, according to crystal field theory. Thus in fact, they quite properly take a structure like $(Ba_xTi_{1-x})(Ti_xM_{1-x})O_3$. One piece of evidence included in their paper is that the curve of the measured Curie point, T_c, of their system $(1 - x)BaTiO_3$–$xNiTiO_3$, when plotted against x had a minimum. If nickel were in the A-site, T_c should change linearly with x. This is because, as Jaffe *et al.* [8] pointed out, generally the Curie point changes linearly with composition when the perovskite-type binary systems have a common cation ($(AA')\underline{B}O_3$ or $\underline{A}(BB')O_3$), but changes accompanied by a minimum point when they do not [9, 10].

4. Conclusion

For perovskite-type ferroelectrics ABO_3, the difference in Curie point was discussed in relation to the different B-ions. The results are as follows.

1. Solid solutions of $(1 - x)PbTiO_3$–$Pb(M_{1/3}Nb_{2/3})O_3$ (M = Mn, Fe, Ni, Cu) were synthesized by solid-phase reaction of powder. Single phases of perovskites were obtained in the range $x < 0.05$, $x < 0.08$, $x < 0.06$ for Mn, Fe and Cu, respectively, and $x < 0.65$ and $0.97 < x < 1$ for Ni. Perovskite and pyrochlore-type $Pb_3Nb_4O_{13}$ phases coexisted in the other ranges.

2. Solid solutions of $0.99BaTiO_3$–$0.01Ba(M_{1/3}Nb_{2/3})O_3$ (M = Ca, Mn, Fe, Co, Ni, Cu, Zn) were synthesized by the solid phase reaction of powders. They were not sintered to high density, and their relative density was 65 to 70%.

3. For the $PbTiO_3$–$Pb(M_{1/3}Nb_{2/3})O_3$ and $BaTiO_3$–$Ba(M_{1/3}Nb_{2/3})O_3$ systems, the Curie points were high when M = Cu. This is thought to be due to the Jahn–Teller effect in CuO_6 octahedron. The Curie point was low when M = Ni.

4. There was a correlation between Curie points and axial ratio c/a for $0.99BaTiO_3$–$0.01Ba(M_{1/3}Nb_{2/3})O_3$ compounds.

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