Ti-isotope effect on ferroelectric phase transition of PbTiO$_3$ studied by heat capacity measurement

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Abstract

The heat capacity of perovskite lead titanate PbTiO$_3$ was measured by differential scanning calorimetry in order to investigate the isotope effect on ferroelectric phase transition. The transition temperature and the shape of the anomaly in the heat capacity curve due to phase transition changed by the Ti-isotope substitution. The phase-transition temperature of ^{46}Ti-enriched PbTiO$_3$ was about 8.8 K higher than that of ^{49}Ti-enriched PbTiO$_3$. The shape of the anomaly in the heat capacity curve became broad with increasing the mean mass of Ti. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: PbTiO$_3$; Ferroelectric phase transition; Isotope effect

1. Introduction

The study of nonhydrogen isotope effects on structural phase transitions in dielectric materials is very important to clarify the mechanisms of the transitions in relation to the phonon dynamics. Hidaka et al. have reported nonhydrogen isotope effects on various types of phase transitions in dielectric materials and the isotope effects on ferroelectric or antiferroelectric phase transitions for BaTiO$_3$ and PbZrO$_3$ have been observed [1–3]. In BaTiO$_3$, the temperature T_C rose markedly by the exchange of heavier isotopes (^{50}Ti or ^{138}Ba) with lighter isotopes (^{46}Ti or ^{134}Ba); the transition temperatures of ^{138}Ba^{50}TiO$_3$ and ^{138}Ba^{46}TiO$_3$ were 384 and 405 K, respectively [1]. In PbZrO$_3$, the temperature T_C rose slightly by the exchange of

heavier isotopes (^{94}Zr) with lighter isotopes (^{90}Zr); the transition temperature of Pb^{94}ZrO$_3$ and Pb^{90}ZrO$_3$ were 503 and 507 K, respectively [2]. Although the materials with heavy isotopes should have higher transition temperature than those with light isotopes from the viewpoint of classical theory, the experimental results were completely opposite to the expectation. Hidaka has explained this non-classical phenomenon by a quantum-mechanical electron–phonon interaction model [4]. It is, therefore, expected for other perovskite ABO$_3$ crystals that the transition temperature T_C becomes higher by increasing the abundance of lighter isotope.

The perovskite lead titanate, PbTiO$_3$ has a transition from cubic high-temperature phase (space group $Pm3m$) to ferroelectric tetragonal phase ($P4mm$), in which the type of the phase transition is the first-order one [6,7]. This is the same structural change with BaTiO$_3$, but both the unit cell and the relative atomic displacements display a larger tetragonal distortion for PbTiO$_3$ than for BaTiO$_3$.

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In our previous paper [5], we reported the change of T_C in PbTiO$_3$ by the exchange of ^{46}Ti with ^{48}Ti isotopes supplied by ISOTEC. The transition temperature of ^{46}Ti-enriched PbTiO$_3$ was found to be 7.6 K higher than that of ^{48}Ti-enriched PbTiO$_3$. The contents of chemical impurities such as Ba, Ca, Sr, Zr and Sn in the enriched PbO and TiO$_2$ used in our previous study were less than 0.01%. The amounts of these chemical impurities is thought to be negligibly small to compete with the isotope effects on the phase transition of PbTiO$_3$, considering the impurity dependence of the transition temperature [8–12]. In the present paper Ti-isotope effect on the phase transition of PbTiO$_3$ was studied in more detail using ^{46}Ti-, ^{48}Ti- and ^{49}Ti-enriched TiO$_2$ supplied by two different suppliers in order to clarify the non-sample dependence and of non-supplier dependence on the phase transition.

2. Experimental

For the investigation of Ti-isotope effect, the following samples of PbTiO$_3$ were prepared by the solid-state reaction method using natural PbO powder (99.99%; The Rare Metallic) and ^{46}Ti- and ^{48}Ti-enriched TiO$_2$ powder (ISOTEC) as starting materials: ^{46}Ti-enriched PbTiO$_3$ (PT(46.51^{ISO})O, mean mass of PbTiO$_3$ 301.72) and ^{48}Ti-enriched PbTiO$_3$ (PT(47.95^{ISO})O, 303.16), or natural PbO powder (99.99%; The Rare Metallic) and ^{46}Ti-, ^{48}Ti- and ^{49}Ti-enriched TiO$_2$ powder (Euriso-top) as starting materials: ^{46}Ti-enriched PbTiO$_3$ (PT(46.50^{ERU})O, 301.72 a.u.), ^{48}Ti-enriched PbTiO$_3$ (PT(47.95^{ERU})O, 303.16 a.u.) and ^{49}Ti-enriched PbTiO$_3$ (PT(48.66^{ERU})O, 303.87 a.u.). Table 1 shows the isotope

contents for TiO$_2$. Furthermore, different types of samples were prepared from the mixture of two different powders ^{46}Ti- and ^{48}Ti-enriched TiO$_2$ (ISOTEC): PT(46.87^{ISO})O (with 75% ^{46}Ti-enriched TiO$_2$ and 25% ^{48}Ti-enriched TiO$_2$, mean mass of PbTiO$_3$ 302.08 a.u.), PT(47.23^{ISO})O (with 50% ^{46}Ti -enriched TiO$_2$ and 50% ^{48}Ti-enriched TiO$_2$, 302.44 a.u.) and PT(47.59^{ISO})O (with 25% ^{46}Ti-enriched TiO$_2$ and 75% ^{48}Ti-enriched TiO$_2$, 303.16 a.u.).

PbO and TiO$_2$ powders were weighted and mixed so as to be in stoichiometric composition, then pressed into pellets under a pressure of 570 kg/cm^2. These samples were calcined in air at 1070 K for 12 h, and cooled to room temperature, reground in an agate mortar, followed by mixing and pelletization. These samples were sintered in air at 1270 K for 12 h. Identification of the phase was carried out by the use of an automatic two-circle X-ray diffractometer (Rigaku Rint Ultima$^+$ system) with graphite-mono-chromated Mo Kα radiation. The X-ray diffraction data were analyzed using the Rietveld technique [13]. All samples were homogeneous and contained only tetragonal perovskite phase (space group *P4mm*).

Heat capacities were measured to determine the transition temperature T_C of PbTiO$_3$ with a differential scanning calorimeter (Seiko Instruments, Japan) between 550 and 825 K. The sample weight was about 30 mg. The temperature was increased or decreased at a rate of 10 K/min. Heat capacity of empty calorimeter was calibrated by the use of sapphire as a standard sample. The error in the temperature measurement by DSC was within ±1.0 K. We repeated the DSC measurements three times to determine the transition temperature T_C and good reproducibility was obtained for all respective materials (see Fig. 1).

Table 1
Isotope contents of ^{46}Ti-, ^{48}Ti- and ^{49}Ti-enriched TiO$_2$

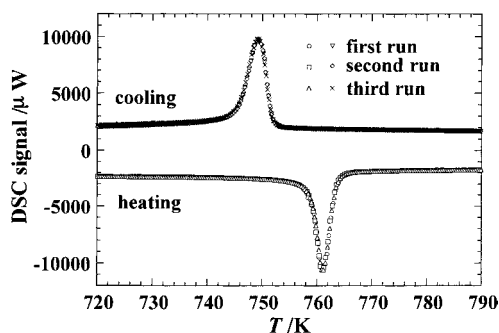| Isotope	^{46}Ti-enriched		^{48}Ti-enriched		^{49}Ti-enriched Euriso-top
	ISOTEC	Euriso-top	ISOTEC	Euriso-top	
^{46}Ti	73.26	73.80	0.15	0.04	1.70
^{47}Ti	2.78	2.60	0.30	0.05	1.90
^{48}Ti	20.65	20.10	99.23	99.80	22.60
^{49}Ti	1.64	1.70	0.21	0.08	71.50
^{50}Ti	1.67	1.80	0.11	0.03	2.30
Mean mass	46.508	46.502	47.946	47.948	48.656

Fig. 1. DSC signal for PT(46.51[ISO])O on heating and cooling. Good reproducibility was obtained.

3. Results and discussion

A typical DSC signal for PT(46.51[ISO])O is shown in Fig. 1. Each result exhibits an anomaly which corresponds to the ferroelectric phase transition. The observed thermal hysthersis confirms the first-order character assigned to this phase transition.The heat capacity values of some PbTiO$_3$ samples in the temperature range 730–770 K on heating are shown as a function of temperature in Fig. 2. The shape of the anomaly in the heat capacity curve becomes broad with increasing the mean mass of Ti. One of the reason for this tendency may be the isotopic disorder, since the shape of the anomaly in an isotopically disordered crystal becomes broad because of the interaction among different isotopes.

Figs. 3 and 4 show the relation between the mean mass of Ti and the transition temperature T_C and the relation between the mean mass of Ti and the transi-
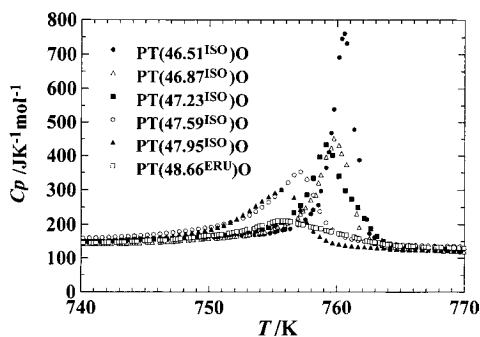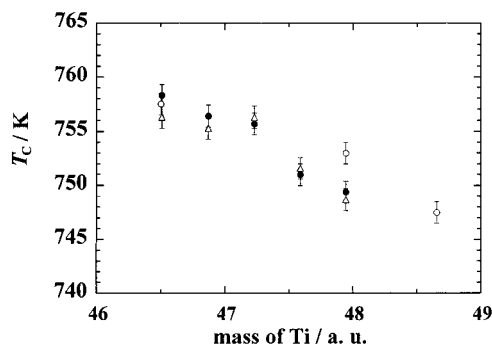

Fig. 3. The relation between the mean mass of Ti and the transition temperature T_C. Closed circles and open circles represent the results for PbTiO$_3$ using TiO$_2$ powder supplied by ISOTEC and Euriso-top, respectively. Open triangles indicate T_C given in our previous results [5].

tion entropy ΔS, respectively. As the mean mass increases, both the temperature T_C and the entropy ΔS decrease. This isotope-mass dependency of the temperature T_C in a series of PbTiO$_3$ samples prepared using [46]Ti- or [48]Ti-enriched TiO$_2$ powder supplied by ISOTEC is similar to that of T_C in a series of PbTiO$_3$ samples prepared using [46]Ti-, [48]Ti- or [49]Ti-enriched TiO$_2$ powder supplied by Euriso-top. The isotope-mean mass dependency of the temperature T_C, the shape of the anomaly in the heat capacity and the entropy ΔS in PbTiO$_3$ observed in this study is similar to that of T_C in BaTiO$_3$ reported by Hidaka et al. [1]. The Ti-isotope-mass dependence of T_C in PbTiO$_3$ was somewhat weaker than that of T_C in BaTiO$_3$, although
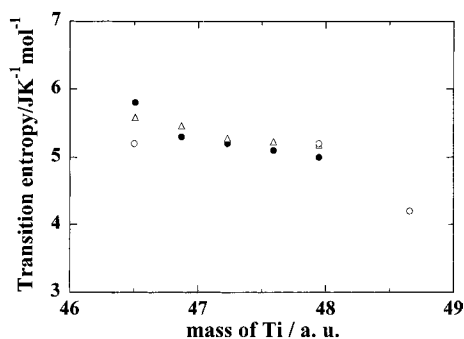

Fig. 4. The relation between the mean mass of Ti and the transition entropy ΔS. Closed circles and open circles represent the results for PbTiO$_3$ using TiO$_2$ powder supplied by ISOTEC and Euriso-top, respectively. Open triangles indicate T_C given in our previous results [5].

Fig. 2. Heat capacity of PbTiO$_3$ with various Ti-isotopes between 740 and 770 K.

the positional change shift of Pb or Ti atom at the phase transition in $PbTiO_3$ was larger than that of Ba or Ti in $BaTiO_3$.

Furthermore, the difference of the full width at half maximum of Bragg reflections and the difference of the lattice parameters among Ti-enriched samples were not observed within experimental error by powder X-ray diffraction.

In conclusion, the similar Ti-isotope effect to that in $BaTiO_3$ was observed in $PbTiO_3$ using several Ti-enriched TiO_2 supplied by different companies. The Ti-isotope mass dependence of T_C in $PbTiO_3$ and $BaTiO_3$ was larger than the Zr-isotope mass dependence of T_C in $PbZrO_3$ because the magnitudes of the ratio $\Delta T_C/(\Delta M/M)$ for Ti-isotope in $PbTiO_3$ obtained in this study and $BaTiO_3$ [1] were 223 and 405, respectively, and were larger than the value, 92, for Zr-isotope in $PbZrO_3$ [2], where M is the atomic mass of Ti or Zr, ΔM is the change in the atomic weight and ΔT_C is the shift of transition temperature. The used parameters are as follows: $^{138}Ba^{50}TiO_3$ (^{50}Ti-enriched Ti 49.10 a.u., T_C=384 K), $^{138}Ba^{46}TiO_3$ (^{46}Ti-enriched Ti 46.62 a.u., 405 K), $Pb^{94}ZrO_3$ (^{94}Zr-enriched Zr 93.87 a.u., 503 K) and $Pb^{90}ZrO_3$ (^{90}Zr-enriched Zr 89.91 a.u., 507 K). Therefore, O-isotope effect on structural phase transition in $PbTiO_3$ as well as Ti-isotope effect will be expected because the $\Delta M_O/M_O$ value among the three isotopes

^{16}O, ^{17}O and ^{18}O is large. The O-isotope effect in $PbTiO_3$ will be carried in our laboratory.

References

[1] T. Hidaka, K. Oka, Phys. Rev., B 35 (1987) 8502.
[2] T. Hidaka, K. Oka, Phys. Rev., B 42 (1990) 8295.
[3] T. Hidaka, Phys. Rev., B 45 (1992) 440.
[4] T. Hidaka, Phys. Rev., B 48 (1993) 9313.
[5] H. Shigematsu, T. Futatsugi, T. Matsui, Ferroelectrics 217 (1998) 189.
[6] G. Shirane, S. Hoshino, J. Phys. Soc. Jpn. 6 (1951) 265.
[7] G. Shirane, R. Pepinsky, B.C. Frazer, Acta Cryst. 9 (1956) 161.
[8] G. Shirane, F. Jond, R. Pepinsky, Proc. IRE. 42 (1955) 1738.
[9] G. Shirane, H. Danner, A. Pavlovic, R. Pepinsky, Phys. Rev. 93 (1954) 672.
[10] S. Nomura, S. Sawada, J. Phys. Soc. Jpn. 6 (1951) 36.
[11] S. Nomura, S. Sawada, J. Phys. Soc. Jpn. 10 (1955) 108.
[12] H.A. Sauer, S.S. Flaschen, D.C. Hoersterey, J. Am. Ceram. Soc. 42 (1959) 363.
[13] R.A. Young, The Rietveld Method, Oxford University Press, Oxford, 1995.