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PARTICLE SIZE EFFECT ON THE NEW PHASE TRANSITION IN A TRIDYMITE COMPOUND, $CsCoPO_4$

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A new phase transition (III–IV) was found at 311 K in $CsCoPO_4$ by DSC measurements. The crystal structure of all the phases, I–IV, in $CsCoPO_4$ was studied by synchrotron-radiation X-ray powder diffraction. The diffractometry revealed that $CsCoPO_4$ had the same crystal structure as that of corresponding phases in $CsZnPO_4$. An extremely large particle size effect was found on III–IV phase transition in $CsCoPO_4$; the phase transition enthalpy decreases with decreasing the particle size around 0.1 mm. Such large particle size effects had been also observed in $CsZnPO_4$. However, no III–IV phase transition was observed in the particle smaller than 0.1 mm of $CsZnPO_4$, while such a critical size was not found in $CsCoPO_4$.

Keywords: *crystal structure, $CsCoPO_4$, DSC, giant size effect, phase transition*

Introduction

So-called fine particle size effect on the phase transition in ferroelectric crystals, such as $BaTiO_3$ and $PbTiO_3$, has been studied extensively, because of their practical application for miniaturization of electronic devices and production of ferroelectric thin films, and so on [1–6]. The high-temperature paraelectric phase is supercooled below the ferroelectric transition temperature in the crystals smaller than a critical size of about several nm. The reason should be a surface energy due to the surface structure and the gradient term; non-uniform distribution of the order parameter near the surface. Such fine size effects on solid-state phase transition have been widely observed in various nano-size crystalline particles and now are considered as a universal feature in nano-size crystalline particles [7–9]. However, recently we have found abnormally large size effect on the phase transition in $BaZnGeO_4$ [10, 11] and $CsZnPO_4$ (CZP) [12, 13].

CZP is a trydimite-type phosphate with general formula $A^+B^{2+}PO_4$ (A^+ and B^{2+} denote monovalent and divalent cation, respectively) [14], and the crystal has successive phase transitions at 220, 533 and 583 K due to the phase sequence of IV–III–II–I [15–17]. We found abnormally large thermal hysteresis and martensitic behavior [12], and the giant size effect on III–IV phase transition [13]. The sample with the crystal size of *d*>0.25 mm showed the heat capacity anomaly due to III–IV phase transition, and no heat capacity anomaly was detected for the sample of *d*<0.03 mm. The results indicate that III–IV phase transition is strongly influenced by such abnormally large crystal size. Since this critical size is 1000–10000 times larger than that of $BaTiO_3$ and $PbTiO_3$, we called that 'giant size effect' [13].

As the ionic radius of Zn^{2+} is almost the same as that of Co^{2+}, the substation of Zn^{2+} by Co^{2+} affects little on the structure and the phase transition sequence in the compounds, $A^+_2B^{2+}X_4$. In fact, $CsCoPO_4$ (CCP), which is the substitution compound of CZP, has a similar trydimite-type structure [18]. It has been reported that the successive phase transitions are at 481 and 512 K due to the phase sequence of III–II–I [18]. However, the space group of CCP is only reported for the room temperature phase as $P2_1$, which is the same as that of IV phase of CZP [19]. Although the crystal structure of higher-temperature phases has not been reported, I–II phase transition in CCP is thought to be a ferroelectric phase transition like CZP. As the reported crystal structure and the phase transition sequence of CCP were similar to CZP, we started the investigation of the detailed phase transition behavior of CCP. From the present systematic study, we found a new phase transition corresponding to the III–IV phase transition in CZP and the giant size effect on III–IV phase transition in CCP.

Experimental

The single crystal of $CsCoPO_4$ (CCP) was synthesized by a self-flux method similar to that used for CZP [12]. The starting materials, Cs_2CO_3 (99.99%),

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P_2O_5 (99.99%) and CoO (99.9%) were purchased from Rare Metallic Co., Ltd. They were weighed in the stoichiometric ratio and mixed in an agate mortar. Because of the high reactivity of P_2O_5 with water, the procedure was done in a dry box. The mixture was put into a platinum crucible, and heated up to 1373 K in an electric furnace and then it was held for 24 h. After that, it was cooled down to 1115 K with cooling rate of 1 K h^{-1}, and finally it was cooled down to room temperature with cooling rate of 1 K min^{-1}. The product was put into water, and the flux $Cs_4P_2O_7$ included in the product was dissolved.

For the X-ray powder diffraction with synchrotron radiation, a small amount of sample was ground in an agate mortar into fine powder of about 10 μm. The fine powder was put in a silica glass capillary of 0.3 mm inside diameter. The powder diffraction experiments were carried out with a large Debye–Sherrer camera [20] installed at BL02B2 in the synchrotron radiation facility SPring-8, Japan. A high-energy X-ray with wavelength 0.5 Å was used as the incident X-ray. The wavelength of the incident X-ray was confirmed using standard CeO_2 sample (SRM674a). The diffraction patterns of the sample were recorded on an imaging plate in transmission geometry. The measurements were carried out at 530, 495, 350 and 250 K, for phases I–IV, respectively. The diffraction data were analyzed by the Rietveld method with the program RIETAN-2000 [21].

The differential scanning calorimetry (DSC) was carried out using Q100 (TA Instruments). The DSC measurements were made for the single crystals and the fine powder samples in the temperature range from 300 to 673 K with a scanning rate of 10 K min^{-1}. The powder sample was prepared by grinding the synthesized sample, and then annealed at 1223 K for 3 h to remove some possible mechanical effects caused by the grind. The powder samples of different particle sizes were separated by using meshes. The amount of sample loaded in the aluminum pan was about 15 mg. To obtain quantitative data from the DSC measurements, the calibration was performed with the melting point of indium and zinc. Below room temperature, the heat capacity measurement on a single crystal of 7.958 mg was performed using a relaxation type calorimeter (PPMS, Quantum Design).

Results and discussion

The X-ray diffraction data of phase I obtained at 530 K were analyzed by the Rietveld method, where the structure parameters with isotropic atomic displacement reported for CZP [22] were used as the initial structure. Table 1 shows the results of the Rietveld analysis of phase I. The resultant reliability factors, the weighed profile, Bragg intensity, and goodness-of-fit indicator 15, are R_{wp}=5.96%, R_I=4.03% and S=1.77, respectively. These values indicate that phase I of CCP has a similar structure to phase I of CZP, space group Pnma. The abnormally large thermal displacement parameters are observed for oxygen atoms, which were also reported in CZP. The results of the Rietveld analysis for phase II are tabulated in Table 2. The reliability factors of R_{wp}=6.12%, R_I=3.59% and S=1.80, indicate that phase II of CCP is of the same structure as that of CZP, space group $Pn2_1a$.

Table 1 Results of the Rietveld analysis of phase I at 530 K of $CsCoPO_4$. Pnma, a=9.1572(2) Å, b=5.4973(1) Å, c=9.4360(2) Å

Site	$g(\sigma)$	Atom	x	y	z	$B/Å^2$
4c	1.0	Cs	0.0023(2)	1/4	0.19865(8)	2.93(3)
4c	1.0	Co	0.1730(2)	1/4	0.5866(3)	1.82(5)
4c	1.0	P	–0.1965(4)	1/4	–0.4184(6)	1.75(9)
4c	1.0	O1	–0.029(1)	1/4	–0.3999(9)	7.8(3)
4c	1.0	O2	–0.281(2)	1/4	–0.261(2)	10.8(4)
8d	1.0	O3	–0.251(5)	–0.502(2)	–0.477(10)	4.6(2)

Table 2 Results of the Rietveld analysis of phase II at 495 K of $CsCoPO_4$. $Pn2_1a$, a=9.2027(2) Å, b=5.4763(1) Å, c=9.4007(2) Å

Site	$g(\sigma)$	Atom	x	y	z	$B/Å^2$
4c	1.0	Cs	0.0027(1)	0.242(1)	0.19884(8)	2.73(2)
4c	1.0	Co	0.1736(2)	0.244(2)	0.5848(3)	1.42(4)
4c	1.0	P	–0.1940(4)	0.238(3)	–0.4127(5)	1.79(9)
4c	1.0	O1	–0.029(1)	0.239(10)	–0.3990(9)	7.1(3)
4c	1.0	O2	–0.272(1)	0.161(2)	–0.267(1)	3.9(4)
4c	1.0	O3	0.256(2)	0.004(3)	0.452(1)	2.9(4)
4c	1.0	O4	–0.243(2)	0.047(2)	–0.524(1)	2.8(4)

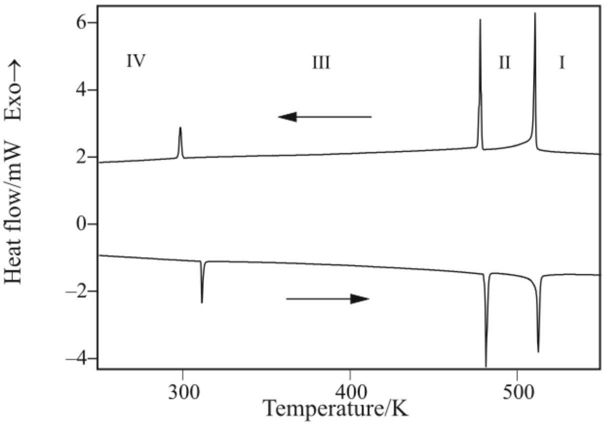


Fig. 1 DSC traces of CCP single crystal (17.125 mg) of heating and cooling runs with a scanning rate of ±10 K min^{-1}

The DSC traces are shown in Fig. 1, where three anomalies are clearly seen both in heating and cooling runs. In the heating run, three endothermic peaks are observed at 311, 481 and 512 K. The two peaks at higher temperatures are consistent with II–III and I–II phase transitions reported previously [18]. However, the peak at 311 K had not been reported previously. We name this phase transition as III–IV phase transition. Thus, the new phase which is stable between 311 and 481 K is phase III, and that below 311 K is phase IV. As the III–IV phase transition is substantially supercooled, it should be the first order phase transition, which is the same as that of III–IV phase transition in CZP [12]. The transition enthalpies are 140, 370 and 510 J mol^{-1}, for III–IV, II–III and I–II phase transition, respectively. The heat capacity below 300 K measured by a relaxation method on a single crystal is shown in Fig. 2, where no anomaly due to phase transition is seen below room temperature.

We analyzed the crystal structures of just below and above the newly found III–IV phase transition temperature of CCP. The results of the Rietveld analysis for phase III measured at 350 K and for phase IV measured at 250 K are tabulated in Tables 3 and 4, respectively. The crystal structure of phases III and IV are shown in Fig. 3. The reliability factors are R_{wp}=6.60%, R_I=2.85% and S=2.17 for phase III, and R_{wp}=7.21%, R_I=1.84% and S=2.38 for phase IV, which indicate that phases III and IV have the same crystal structure as those of CZP. Thus the space group of phases III and IV of CCP is $P2_1/a$ and $P2_1$, respectively.

Since the space group of phases III and IV of CCP is the same as that of CZP, the similar giant particle size effect on III–IV phase transition in CCP may be expected. Figure 4 shows the DSC traces near III–IV phase transition in the heating direction after

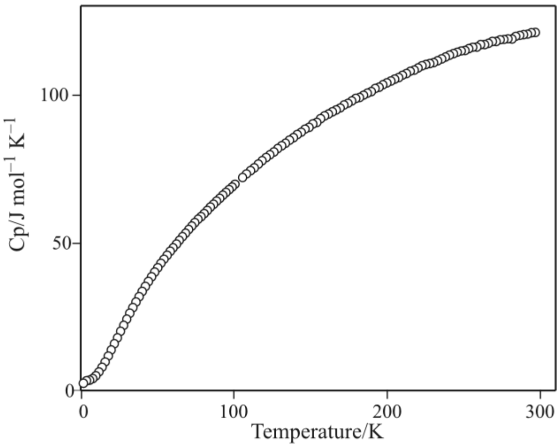


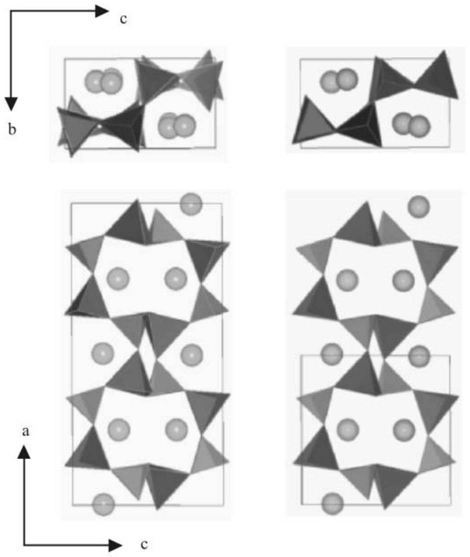
Fig. 2 Low temperature heat capacity of $CsCoPO_4$ single crystal (7.985 mg) measured by a relaxation method

Table 3 Results of the Rietveld analysis of phase III at 350 K of $CsCoPO_4$. $P2_1/a$, a=18.4403(3) Å, b=5.47502(8) Å, c=9.3231(2) Å, β=90.315(1)°

Site	$g(\sigma)$	Atom	x	y	z	B/Å^2
4c	1.0	Cs1	0.0030(1)	0.2435(8)	0.2047(2)	1.76(5)
4c	1.0	Cs2	0.2500(1)	0.7274(5)	0.6916(2)	1.71(5)
4c	1.0	Co1	0.0879(2)	0.260(1)	0.5831(4)	0.91(8)
4c	1.0	Co2	0.1659(2)	0.721(1)	0.0890(4)	0.78(8)
4c	1.0	P1	0.0979(4)	0.757(2)	0.4180(8)	1.0(1)
4c	1.0	P2	0.3465(4)	0.738(2)	0.0900(8)	1.0(1)
4c	1.0	O1	–0.0162(8)	0.249(6)	0.561(2)	2.1(1)
4c	1.0	O2	0.8813(10)	0.1749(2)	0.750(2)	=O1
4c	1.0	O3	0.861(1)	0.042(4)	0.489(2)	=O1
4c	1.0	O4	0.373(1)	–0.008(4)	0.535(2)	=O1
4c	1.0	O5	0.2670(8)	0.760(4)	0.142(1)	=O1
4c	1.0	O6	0.6051(9)	0.208(4)	0.784(2)	=O1
4c	1.0	O7	0.3560(10)	0.902(3)	0.960(2)	=O1
4c	1.0	O8	0.370(1)	0.465(4)	0.051(2)	=O1

Table 4 Results of the Rietveld analysis of phase IV at 250 K of $CsCoPO_4$. $P2_1$, a=9.2063(2) Å, b=5.4734(1) Å, c=9.2738(2) Å, β=90.394(1)°

Site	$g(\sigma)$	Atom	x	y	z	B/Å^2
4c	1.0	Cs1	1.006(2)	1.258(1)	0.2056(2)	1.29(6)
4c	1.0	Cs2	0.4994(2)	0.726(1)	0.6897(2)	1.27(7)
4c	1.0	Co1	0.8229(4)	0.759(2)	0.4185(4)	0.70(9)
4c	1.0	Co2	0.3325(4)	0.724(2)	0.0890(4)	0.74(9)
4c	1.0	P1	0.8069(6)	0.256(3)	0.5822(7)	0.3(1)
4c	1.0	P2	0.6910(7)	0.728(3)	0.0937(7)	0.5(1)
4c	1.0	O1	0.538(2)	0.755(5)	0.151(1)	1.5(1)
4c	1.0	O2	0.790(2)	0.808(4)	0.215(2)	=O1
4c	1.0	O3	0.727(2)	0.451(4)	0.059(2)	=O1
4c	1.0	O4	0.713(2)	0.900(3)	-0.033(2)	=O1
4c	1.0	O5	0.967(2)	0.235(5)	0.554(1)	=O1
4c	1.0	O6	0.740(3)	0.9890(4)	0.543(2)	=O1
4c	1.0	O7	0.728(3)	0.467(4)	0.494(2)	=O1
4c	1.0	O8	0.770(2)	0.319(4)	0.748(2)	=O1



A B

Fig. 3 Crystal structure of phases III and IV of $CsCoPO_4$ determined by Rietveld analysis; A – phase III and B – phase IV. The circle, light tetragon and dark tetragon denote Cs, PO_4 and ZnO_4, respectively. Solid line denotes the unit cell

cooling down to 183 K. The endothermic peak decreases with decreasing the particle size of CCP crystal, and the values of the transition enthalpy are tabulated in Table 5, together with those of II–III and I–II phase transitions. Although the transition enthalpy of II–III and I–II phase transitions is independent from the particle size, that of III–IV phase transition decreases drastically with decreasing the particle size. This behavior indicates the giant particle size effect as observed in CZP. In this case, however, III–IV phase transition is observed even in smaller particles of d<0.03 mm. In the case of CZP, III–IV phase transition was not observed in the particles smaller than a critical size that was 0.1 mm. The room-temperature phase III is easily supercooled below the III–IV phase

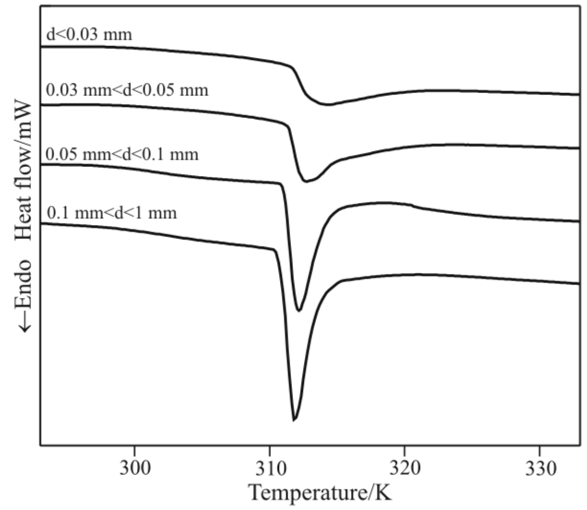


Fig. 4 Thermal anomaly due to III–IV phase transition in the powder samples of different crystal sizes of $CsCoPO_4$

Table 5 Enthalpy of transitions of $CsCoPO_4$ determined by DSC

Crystal size/mm	$\Delta H_{IV–III}$/ J mol^{-1}	$\Delta H_{III–II}$/ J mol^{-1}	$\Delta H_{II–I}$/ J mol^{-1}
d<0.03	53	365	585
0.03<d<0.05	109	360	584
0.05<d<0.1	123	363	594
0.1<d<1	139	370	589

transition temperature, and the metastable phase III transforms to the stable phase IV very slowly below the III–IV phase transition temperature. As III–IV phase transition is of the first order, the transition mechanism should be governed by the kinetic effects such as the nucleation and growth process. The previous study showed that the heterogeneous nucleation process should play an important role for III–IV phase transition. The kinetic effects generally depend on the thermal activation process and thus the temperature should play an important role for the phenomena, that is, the phase transition should progress more rapidly at higher temperatures. The III–IV phase transition temperature of CCP (311 K) is much higher than that of CZP (220 K), and the heterogeneous nucleation process may progress more rapidly in CCP than CZP. Therefore, III–IV phase transition is observed even in smaller particles, and thus no critical size is in CCP.

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