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High-temperature X-ray structural, thermal and dielectric characteristics of ferroelectric $Bi_2VO_{5.5}$

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The X-ray powder diffraction, dielectric and thermal studies of bismuth vanadate ($Bi_2VO_{5.5}$) ceramic have been carried out as a function of temperature (300–900 K). The high-temperature X-ray studies, supported by differential scanning calorimetry, clearly demonstrate that $Bi_2VO_{5.5}$ undergoes two major phase transitions at $\sim$730 and $\sim$835 K. It was found that the one at 730 K is associated with both the ferroelectric and the crystallographic transition, while at 835 K, $Bi_2VO_{5.5}$ undergoes only the crystallographic transition. Anomalies in both the dielectric constant and specific heat curves have been observed at $\sim$ 730 and $\sim$ 835 K. The total heat, ΔQ, and entropy, ΔS, associated with the transition at 730 K were found to be higher than those at 835 K.

1. Introduction

Bismuth vanadate ($Bi_2VO_{5.5}$) is one of the interesting ferroelectric compounds found in the large group of ferroelectrics with layer-type structure, belonging to a family of the $[Bi_2O_2]^{2+}[A_{n-1}B_nO_{3n+1}]^{2-}$ series [1–4]. This compound has attracted the attention of several researchers from the point of view of its high ionic conductivity at elevated temperatures [5–8]. It is also fascinating from the point of view of its high-temperature phase transitions. Although the electrical transport properties of this compound have been studied as a function of temperature in detail, the phase transition studies need to be critically examined. We have been investigating $Bi_2VO_{5.5}$ from the thermal, dielectric, pyroelectric and ferroelectric properties point of view for quite some time. During the course of these investigations, we found that this compound undergoes two major phase transitions at high temperatures. We thought that it was worth establishing the nature of these transitions in order to understand any physical property studied as a function of temperature. In this paper, we report the results obtained on the high-temperature structural, dielectric and thermal studies carried out on $Bi_2VO_{5.5}$ ceramics.

2. Experimental procedure

The polycrystalline powder of $Bi_2VO_{5.5}$ (BiV) was prepared by heating a mixture of stoichiometric ratio of reactor-grade Bi_2O_3 and V_2O_5 in a platinum crucible initially up to 770 K for 8 h and finally at 1070 K for 24 h in air with intermediate grinding operations. The formation of the compound was confirmed at room temperature by X-ray powder diffraction (XRD) technique using a Phillips (PW-1050/70) X-ray powder diffractometer (CuK_α radiation). The prereacted powder was cold pressed into pellets of 12 mm diameter and 2 mm thick using a hydraulic press, at a pressure of $\sim$ 4.4 kbar, and were sintered at 1070 K for 36 h.

The differential scanning calorimetric (DSC) studies were carried out using a Perkin–Elmer DSC-2 differential scanning calorimeter. The sample was heated uniformly in a gold cup at a rate of 20 K min^{-1} from 320–900 K to identify the phase transition temperatures, while on cooling almost the same rate was maintained. The specific heat measurements were also performed using the same instrument. For this, the sample was heated at a rate of 10 K min^{-1} (320–900 K) by using sapphire as a standard.

The high-temperature X-ray powder diffraction studies were carried out using a high-temperature attachment (PW-1158) associated with the Phillips X-ray diffractometer (PW 1050/70). The tantalum boat containing the sample was inserted into a small cylindrical resistive furnace. A Cr–Al thermocouple was kept very close to the sample to monitor the temperature. The temperature of the sample was controlled with an accuracy of $\pm$ 2 °C by a proportional, integral and differential (PID) temperature controller. The XRD data were collected as a function of temperature (300–860 K) in the 2θ range of 20–62°, at a scanning rate of 0.5° min^{-1}.

The sintered ceramic samples were gold electroded and subsequently silvered for dielectric constant measurements. The capacitance and the dielectric loss, tan δ, were monitored as a function of frequency (100 Hz–10 MHz) using an HP 4194A impedance/gain phase analyser at a signal strength of 0.5 Vrms. The temperature variation (300–900 K) of the capacitance and the loss tangent were monitored using a HP 4274A multifrequency LCR meter at 100 kHz with the same signal strength. The samples were heated (or cooled) at the rate of 1–1.5 K min^{-1}.

3. Results and discussion

The differential scanning calorimetry (DSC) of BiV ceramic on heating, revealed two clear endothermic transitions at 730 and 835 K which are shown in Fig. 1. The first one is sharp, while the second one is rather broad and small in magnitude. These transitions are found to be reversible by cooling the sample. The first transition exhibits a large thermal hysteresis of about 95 K while the second one exhibits only 30 K. The variation of specific heat, C_p, of BiV as a function of temperature is shown in Fig. 2. The specific heat increases gradually with increasing temperature and was found to exhibit two anomalies at 730 and 835 K.

The total heat, ΔQ_1 and the entropy, ΔS_1, associated with the first transition at 730 K are

$$\Delta Q_1 = \int_{680\ \mathrm{K}}^{760\ \mathrm{K}} C_p\, \mathrm{d}T = 6.05\ \mathrm{kJ\,mol^{-1}} \qquad (1)$$

and

$$\Delta S_1 = \int_{680\ \mathrm{K}}^{760\ \mathrm{K}} \left(\frac{C_p}{T}\right) \mathrm{d}T = 8.14\ \mathrm{J\,mol^{-1}\,K^{-1}} \qquad (2)$$

The total heat, ΔQ_2, and the entropy, ΔS_2, associated with the second transition at 835 K are

$$\Delta Q_2 = \int_{760\ \mathrm{K}}^{860\ \mathrm{K}} C_p\, \mathrm{d}T = 2.07\ \mathrm{kJ\,mol^{-1}} \qquad (3)$$

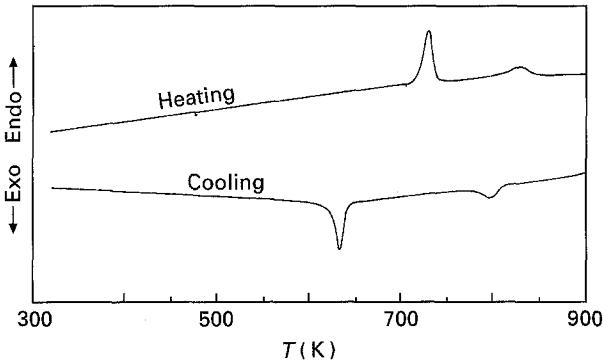

Figure 1 Differential scanning calorimetric curves of $Bi_2VO_{5.5}$ ceramic.

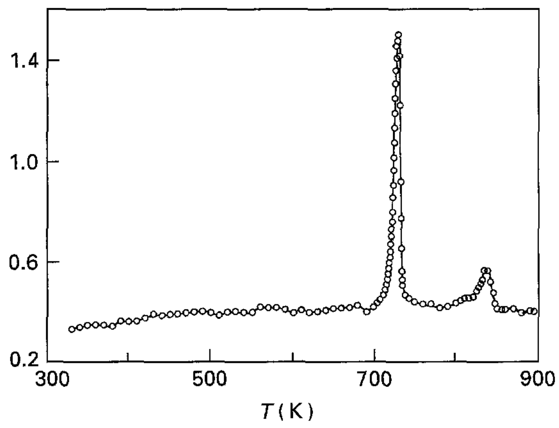

Figure 2 The variation of specific heat of $Bi_2VO_{5.5}$ ceramic as a function of temperature.

and

$$\Delta S_2 = \int_{760\ \mathrm{K}}^{860\ \mathrm{K}} \left(\frac{C_p}{T}\right) \mathrm{d}T = 2.28\ \mathrm{J\,mol^{-1}\,K^{-1}} \qquad (4)$$

The heat of transition and the entropy change associated with the second transition are small compared to those of the first transition.

In order to confirm the nature of the transitions observed in the above studies, X-ray powder diffraction studies have been carried out as a function of temperature and the results obtained are as follows.

The XRD pattern obtained for BiV at room temperature (300 K) is shown in Fig. 3 and the corresponding data are given in Table I. This pattern could be indexed to an orthorhombic system with unit cell parameters (called super cell parameters)

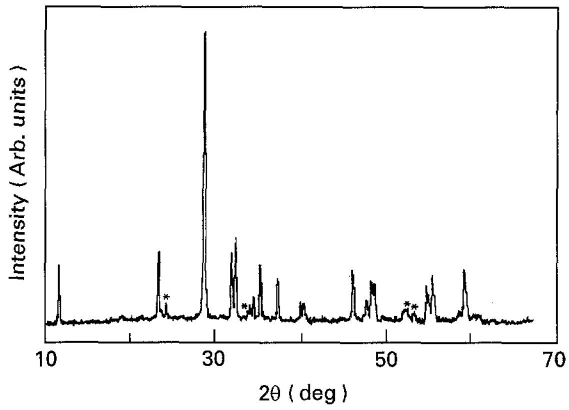

Figure 3 X-ray powder diffraction pattern for $Bi_2VO_{5.5}$ ceramic.

TABLE I The X-ray powder diffraction data for $Bi_2VO_{5.5}$ at 300 K ($a_0 = 1.6586(3)$ nm, $b_0 = 0.5607(1)$ nm and $c_0 = 1.5276(3)$ nm)

h	k	l	d(obs)(nm)	d(cal)(nm)	I/I_0
0	0	2	0.7632	0.7637	21
3	1	1	0.3814	0.3812	25
0	1	3	0.3772	0.3769	6
1	**1**	**3**[a]	0.3682	0.3676	8
3	1	3	0.3116	0.3114	100
0	2	0	0.2804	0.2803	25
6	0	0	0.2767	0.2765	30
2	**2**	**0**[a]	0.2654	0.2656	4
0	2	2	0.2633	0.2632	6
6	0	2	0.2600	0.2599	8
0	0	6	0.2547	0.2546	19
3	1	5	0.2415	0.2414	16
0	2	4	0.2259	0.2260	8
6	0	4	0.2239	0.2239	8
6	2	0	0.1968	0.1968	19
3	1	7	0.1908	0.1908	9
0	2	6	0.1885	0.1885	15
6	0	6	0.1872	0.1872	14
1	**3**	**3**[a]	0.1749	0.1745	4
2	**3**	**3**[a]	0.1718	0.1717	4
3	3	3	0.1672	0.1672	13
9	1	3	0.1655	0.1655	17
3	1	9	0.1558	0.1558	13
1	3	5	0.1531	0.1531	3
9	1	5	0.1519	0.1519	3

[a] Super lattice reflections.

$a_0 = 1.6586(3)$ nm, $b_0 = 0.5607(1)$ nm and $c_0 = 1.5276(3)$ nm by taking into account the superlattice reflections (1 1 3), (2 2 0), (1 3 3) and (2 3 3) which are marked by asterisk in Fig. 3. However, one could also index this pattern to an orthorhombic system with unit cell parameters (called mean cell parameters) $a = a_0/3 = 0.5528(1)$ nm, $b = b_0 = 0.5607(1)$ nm and $c = c_0 = 1.5276(3)$ nm (where a_0, b_0 and c_0 are super cell parameters) by leaving behind the superlattice reflections.

The mean cell parameters have been computed based on X-ray data collected as a function of temperature up to 860 K in close intervals. The variations of the mean cell parameters and mean cell volume with temperature are shown in Fig. 4a and b, respectively. On heating, the lattice parameters as well as the cell volume of BiV increase almost linearly with increasing temperature up to ~730 K. The lattice parameter, a, is found to expand at a faster rate than b and, as a consequence, the orthorhombic distortion (b/a) decreases with increasing temperature (Fig. 4b). At 730 K, a and c parameters, as well as the volume of the cell, expand while b contracts. A sudden drop in b/a ratio has also been observed at 730 K (Fig. 4b). However, the cell continues to be orthorhombic well beyond this temperature (730 K) with a very small difference between a and b parameters. This small orthorhombic distortion could be detected in the reflections (0 2 0), (2 0 0), (1 3 3) and (3 1 3) upto ~835 K. The lattice parameters a, b and c obtained below 835 K are in good agreement with that of Mairesse [9]. High-temperature X-ray single-crystal studies carried out by Mairesse suggest that BiV at 730 K, goes from a polar orthorhombic ($mm2$) system to a non-polar centrosymmetric orthorhombic (mmm) system with the lattice parameters $a = 1.1226$ (2×0.5613) nm, $b = 0.5639$ nm, and $c = 1.5351$ nm. Our present studies indicate that the orthorhombic distortion (b/a) disappears and the symmetry becomes tetragonal above 835 K (Fig. 4b). Table II depicts the X-ray powder data obtained for BiV at 860 K, based on which the cell is indexed to a tetragonal symmetry ($a = 0.3984$ nm and $c = 1.5422$ nm). This observation is in agreement with that of Abraham *et al.* and Mairesse [6, 9]. The following sequence of phase transitions for BiV is in order.

Non-centrosymmetric orthorhombic ($mm2$) $\xrightarrow{\sim 730\text{ K}}$ centrosymmetric

Orthorhombic (mmm) $\xrightarrow{\sim 835\text{ K}}$ centrosymmetric tetragonal ($4/mmm$)

The temperature dependence of the dielectric constant for BiV ceramic measured at 100 kHz is illustrated in Fig. 5a. On heating, the dielectric constant, ε_r, increases with increasing temperature, and exhibits a broad maximum around 620 K and later it undergoes a sharp maximum at 730 K. Subsequently, it exhibits yet another broad maximum around 850 K. On cooling, it is found that the dielectric constant also undergoes a thermal hysteresis with a sudden drop around 810 and 650 K. The first transition temperature agrees well with that of DSC data, while the second transition temperature is different by about 15 K. Fig. 5b shows the variation of loss tangent, tan δ, as a function of temperature. The loss tangent increases with increase in temperature and raises

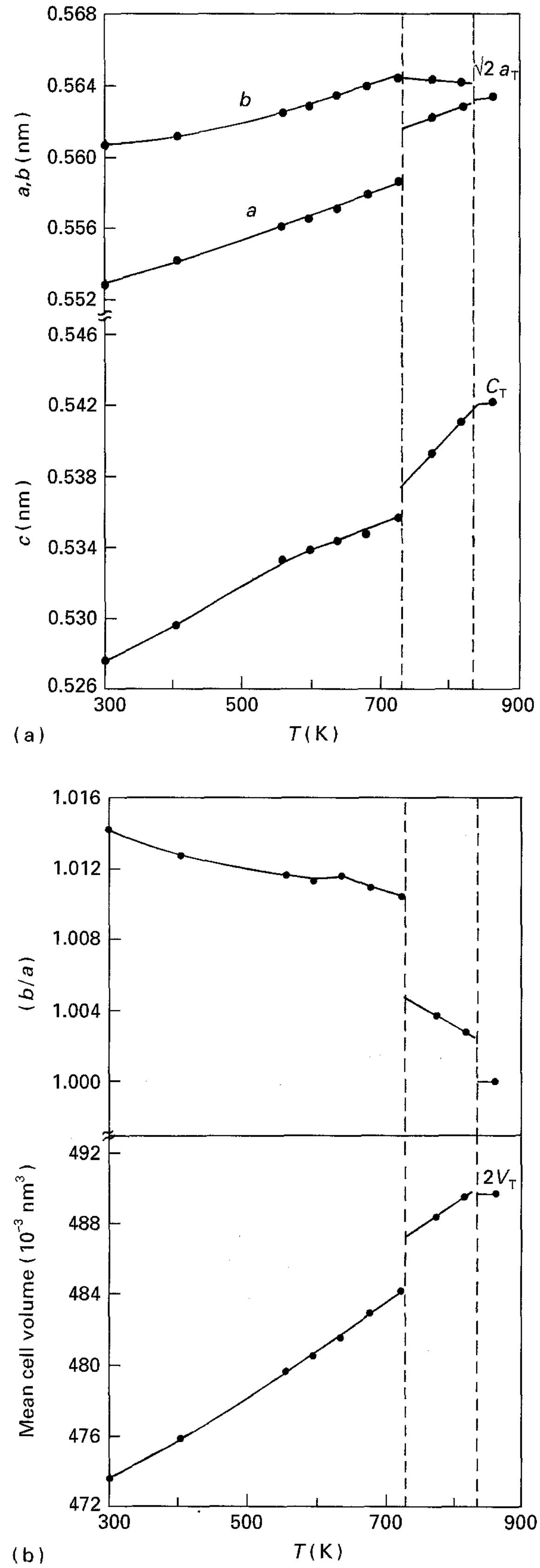

Figure 4 (a) The variation of mean cell parameters of $Bi_2VO_{5.5}$ as a function of temperature. (b) Temperature response of mean cell volume and b/a ratio of $Bi_2VO_{5.5}$.

TABLE II The X-ray powder diffraction data for $Bi_2VO_{5.5}$ at 860 K ($a = 0.3984(1)$ nm, and $c = 1.5422(3)$ nm)

h	k	l	d(obs)(nm)	d(cal)(nm)	I/I_0
1	0	1	0.3861	0.3857	21
1	0	3	0.3152	0.3149	100
1	1	0	0.2816	0.2817	36
1	1	2	0.2645	0.2646	16
0	0	6	0.2570	0.2570	15
1	0	5	0.2438	0.2439	18
1	1	4	0.2274	0.2274	15
2	0	0	0.1992	0.1992	18
2	0	2	0.1926	0.1928	18
1	1	6	0.1898	0.1898	26
2	1	3	0.1683	0.1683	30
1	0	9	0.1574	0.1574	25

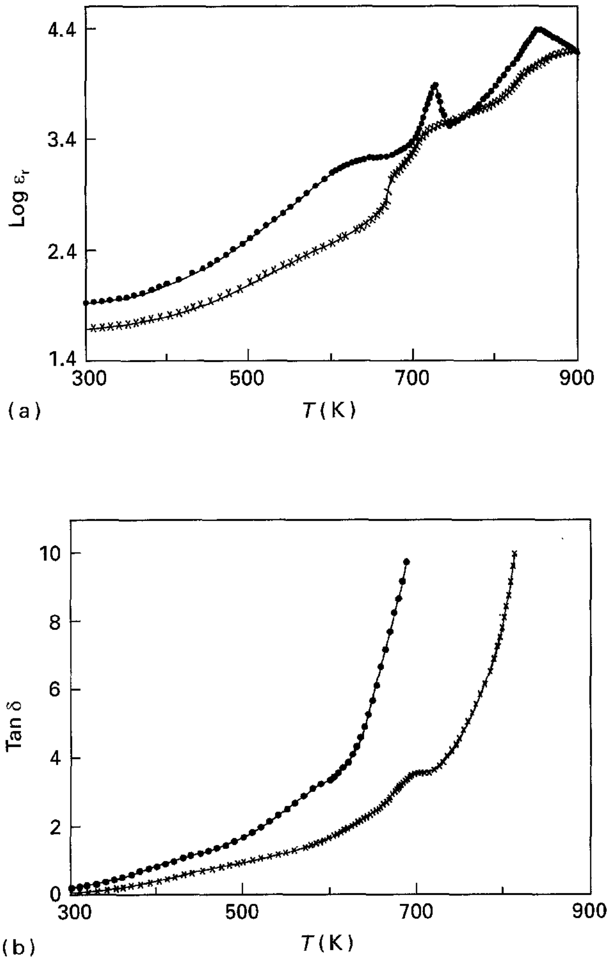

Figure 5 Temperature variation of (a) the dielectric constant, ε_r, and (b) the dielectric loss, tan δ, of $Bi_2VO_{5.5}$ ceramic, at 100 kHz; (●) heating, (×) cooling.

sharply beyond 600 K. The dielectric constant at room temperature is found to decrease with increase in frequency up to 10 MHz (Fig. 6). The dielectric loss, tan δ, increases initially and exhibits a broad maximum around 600 Hz and subsequently decreases up to 10 MHz (Fig. 6). The variation of reciprocal of the dielectric constant with temperature is shown in Fig. 7. It demonstrates that the dielectric constant of BiV obeys the Curie–Weiss law above 730 K with a Curie constant, $C = 0.95 \times 10^5$ K, while it does not obey it above the second transition (850 K). The value

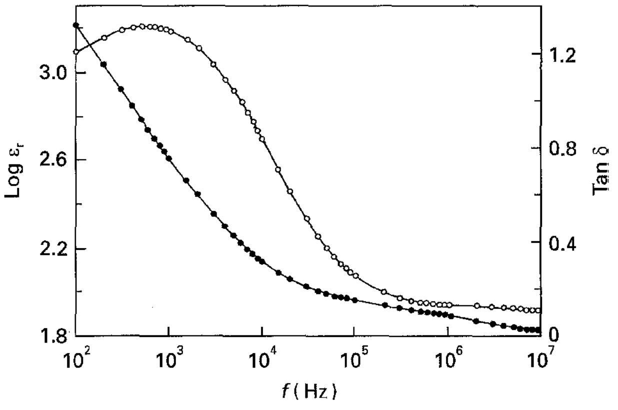

Figure 6 The frequency response of (●) the dielectric constant and (○) the dielectric loss of $Bi_2VO_{5.5}$ ceramic at 300 K.

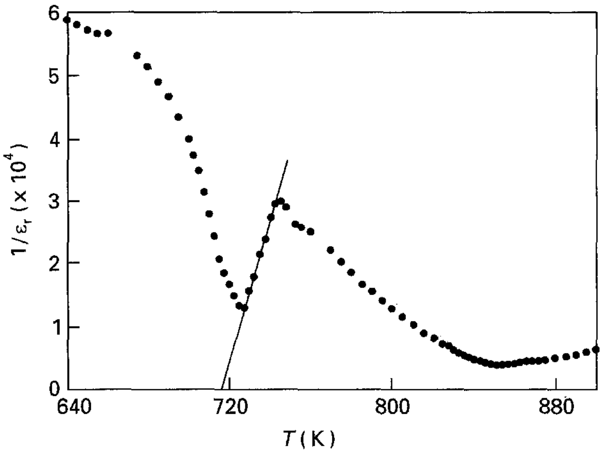

Figure 7 The variation of the reciprocal dielectric constant, $1/\varepsilon_r$, of $Bi_2VO_{5.5}$ ceramic with temperature.

of the Curie constant is of the same order as that of well-known displacive-type ferroelectrics such as $BaTiO_3$ ($C = 1.7 \times 10^5$ K) and $KNbO_3$ ($C = 2.4 \times 10^5$ K) [10].

The ferroelectric hysteresis loop studies have been carried out as a function of temperature on the ceramic as well as single-crystalline samples to confirm the Curie temperature [11, 12]. It was found that the hysteresis loop disappears around 730 K in both the cases. Further, the ferroelectric domain patterns obtained for single crystals by polarizing microscopic studies were also found to disappear around 730 K [12]. Based on these two experimental facts in addition to the anomalies observed around the same temperature in both ε_r and C_p, it is evident that the Curie temperature of BiV is 730 K.

The dielectric constant is found to increase with increase in temperature well beyond the Curie temperature due to the second transition involved at 835 K. The unusually high ε_r around this temperature may be due to the high ionic conductivity associated with the sample [5, 6]. It should be noted that around this temperature, BiV goes from a centrosymmetric orthorhombic to a centrosymmetric tetragonal system as a consequence of an elongation of one of the face diagonals perpendicular to the c-axis. The relation between the orthorhombic and the prototype tetragonal modification is shown in Fig. 8.

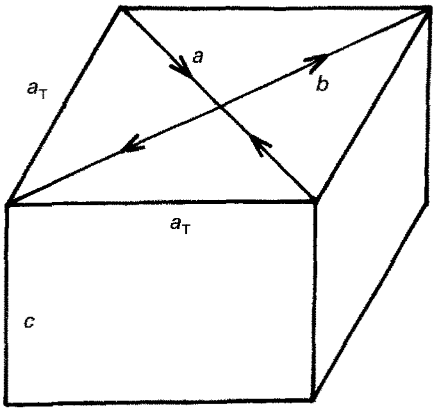

Figure 8 Schematic representation of the unit cell axes of the layer-type compounds, showing the relation of the axes of the high-temperature tetragonal modification, a_T, to those of orthorhombic form, *a* and *b*.

4. Conclusion

The Curie temperature (730 K) of BiV has been determined by both dielectric and specific heat studies. High-temperature X-ray diffraction studies clearly demonstrated that BiV undergoes two major phase transitions at 730 and 835 K. It transforms into a non-polar centrosymmetric orthorhombic at 730 K and subsequently into a centrosymmetric tetragonal at 835 K. While the anomaly at 730 K is associated with both the ferroelectric and the crystallographic transitions, that at 835 K is associated with only the crystallographic transition.

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