Incommensurate phase in barium sodium niobate: Thermal-analysis study

Shining Zhu and Niaben Ming
Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210008, People's Republic of China

Qingping Dai
Center for Materials Analysis, Nanjing University, Nanjing 210008, People's Republic of China
(Received 18 November 1992)

Differential-scanning-calorimetry measurements have been performed on single-crystalline barium sodium niobate from 400 to 900 K. Special attention was paid to measurements in the temperature range 500–650 K. Three thermal peaks were detected; one was at 850 K near the ferroelectric transition temperature, the two others were at 532 K and 549 K, respectively, and their latent heat was estimated. A specific-heat-capacity anomaly was also observed at 590 K within experimental accuracy. These thermal anomalies are discussed in the framework of the available structure-transition and incommensurate-phase models.

Since the 1980s the incommensurate phase (ICP) of barium sodium niobate (BSN) has been the focus of intensive studies that have used x-ray diffraction,[1,2] neutron scattering,[3] transmission-electron microscopy (TEM),[4] and optics.[5] Recently, some experiments[6,7] revealed that the temperature range previously assigned to a single ICP may actually be occupied by two ICP's, one being an orthorhombic incommensurate structure with modulation along one axis ($1q$ phase), the other a tetragonal incommensurate structure with identical modulation along two orthogonal axes ($2q$ phase). However, this is not without controversy; some authors believe that there is no $2q$ phase at all, only a superposition of $1q$ domains with different orientations. So the hypothesized $1q$-$2q$ transition in BSN remains to be confirmed using various experiment techniques.

A thermal-analysis method can be used to study the crystal transition. Generally speaking, it should be possible to infer the thermodynamic order of a transition from the result of a thermal measurement. In a differential scanning calorimetry (DSC) or a differential thermal-analysis (DTA) diagram, a first-order transition associated with a latent heat will give rise to a peak, while a second-order one will only determine a displacement of the recorded base line due to a discontinuous specific heat.

The DTA's of BSN have been studied by Scott, Giess, and Kane,[8] Abell, Harris, and Cockayne,[9] and Loiacono.[10] Their experiments all showed a thermal effect at ~580 °C Curie point but failed to detect the thermal anomalies in the temperature range 250–320 °C. Toledano and Pateau[11] only detected a thermal effect at 260 °C, and did not give a convincing explanation, for the ICP of a crystal had not been understood in those days.

In this paper the study of the thermal behaviors of a BSN crystal using the DSC method across the temperature range 400–900 K is presented, and we got, for the first time, the evidence related to the occurrence of the two ICP's.

A high-quality single crystal of BSN was cut into several wafers and then polished mechanically to the thickness of about 0.2 mm. Samples weighed from 19 to 76 mg and laid flat on the bottom of the crucible in measurements. It has been known that the composition of all real samples of BSN depart from the stoichiometric formula $Ba_2NaNb_5O_{15}$. The main structural defect introduced by nonstoichiometry was likely to be the occurrence of vacancies at the sodium sites.[5] The formula determined for our samples by an electron microprobe analysis was $Ba_{0.1}Na_{0.9}Nb_5O_{15}$.

The DSC data of BSN were obtained with a Perkin-Elmer model DSC-2 differential scanning calorimeter at a scanning rate of 20 K/min with a temperature precision less than 2 K. Details on the techniques can be found in another work.[12]

The results of the DSC measurements are reproducible. Figure 1 shows an experimental result from 400 to 900 K for a sample having a mass of about 34 mg. An examination of the DSC curve indicates the existence of two thermal anomaly ranges. A single thermal peak $P1$ can be observed near 850 K in the upper range, while a multiple thermal effect can be found from 520 to 590 K in the

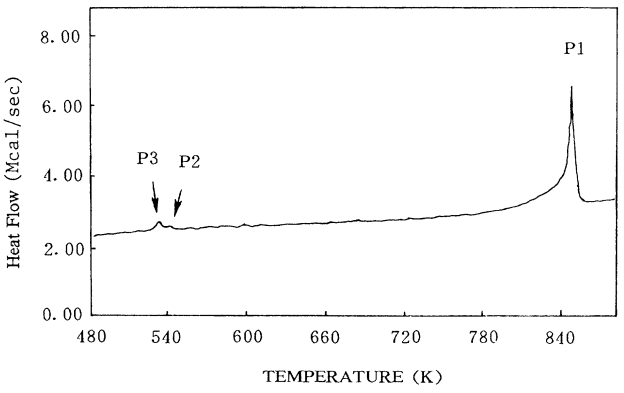

FIG. 1. The DSC curve of the BSN single crystal from 480 to 880 K.

lower range. Let us first consider the upper thermal peak at 850 K. Toledano and Pateau have given a convincing explanation according to their DTA result, the peak $P1$ is related to the ferroelectric transition in BSN. Since this is a latent-heat peak, we can infer that the transition is first order in nature. The conclusion is in agreement with other experimental results. The latent-heat peak appeared at 850 K on heating and 838 K on cooling, a 12-K hysteresis could be observed in the heat cycle. From the area of the $P1$ peak we get the latent-heat value of 0.68 cal/g for the ferroelectric transition in BSN, which is bigger than the previous one of 0.18 cal/g from the DTA.[11]

Let us now consider the thermal anomolies in the range 520–590 K. Figure 2 shows the DSC curve in the temperature range for a bigger sample (74.6 mg). Two thermal peaks, $P3$ and the $P2$, appeared at 532 and 549 K on heating, respectively. The $P3$ peak is about three times the area of the $P2$ peak, so the latent heat associated with $P3$ is three times that associated with $P2$. From DSC data we get, respectively, 0.03 cal/g for $P3$ and 0.01 cal/g for $P2$. Since the latent-heat value for $P2$ is only $\sim\frac{1}{70}$ that for peak $P1$, it is too small to be detected in some previous thermal measurements, and neglected. We paid attention to the observation of the temperature range especially and detected the small latent peak. We also disclosed that the DSC curve on cooling displayed two reproducible latent peaks at 537 K (for $P2$) and 503 K (for $P3$), respectively, at the same scanning rate. The $P3$ peak has a bigger hysteresis (30 K) than the $P2$ peak (10 K). The observation alone cannot constitute the evidence of the phase transition but, based on recent x-ray and TEM studies, we can analyze the two peaks, $P2$ and $P3$ are related to the ICP transitions of BSN in the temperature range. Barre, Mutka, and Roucau sketched a crude phase diagram of BSN from room temperature to 580 °C based on their TEM study, they conjectured that there are two ICPs, $1q$ and $2q$, between the lock-in transition temperature (T_L) and the normal-incommensurate transition temperature (T_i), that the $1q$ phase is stable in the lower temperature range nearby the lock-in transition, and metastable above this range, and that the $2q$ phase is stable in the upper temperature range nearby the normal-incommensurate transition, and metastable in the lower range. In view of this, a phase transition was assumed to exist which connects the two ICP's. We extend the temperature range of the diagram to above 850 K. The situation containing the total measurement range is shown in Fig. 3. In Fig. 3, $1q$-$2q$ transition temperature is denoted with T_n. Referring to the phase diagram, we are able to interpret that the thermal peak $P1$ is attributed to ferroelectric transition, while the peaks $P3$ and $P2$ can be assigned to the lock-in transition and the $1q$ to $2q$ ICP transition, respectively.

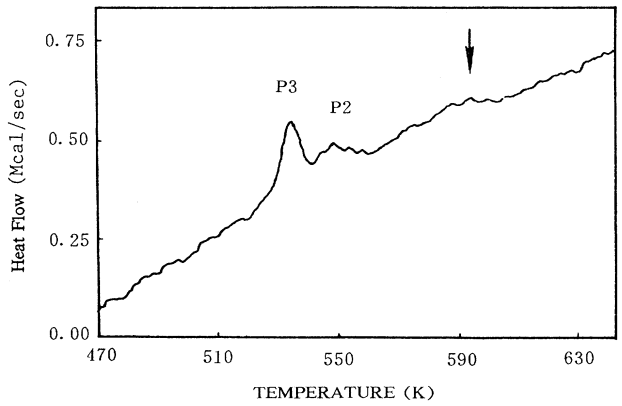

FIG. 2. The DSC curve of the BSN single crystal from 470 to 640 K. Both latent-heat peaks, $P1$ and $P2$, are obviously distinguishable. The anomaly of specific-heat capacity at about 590 K is denoted with an arrow.

The lock-in transition and the $1q$-$2q$ transition can be safely asserted as first-order transitions because both $P2$ and $P3$ are well-defined latent-heat peaks. The two peaks are obviously distinguishable in Fig. 2. This suggests that there should be a clear distinction indeed between the two ICP's. Some authors, using electron microscopes, observed the disappearance of ferroelastic domain walls and the onset of microdomains and a bidimensional modulation state near the temperature T_n. It is the procedure that may make contribution to the latent-heat peak $P2$. It can be seen clearly that if the averaged 4-mm structure of the $2q$ ICP is sufficient to produce short-range tetragonality, the ferroelasticity should onset at the $1q$-$2q$ transition. Earlier tentative assignment to the transition as a second-order one was based on the failure to detect a latent heat at the transition temperature. The present result gives that there is a latent-heat peak at the temperature, therefore the $1q$-$2q$ transition is first order in nature. The $P2$ peak, such as the $P3$ peak, has a thermal hysteresis between the heating and cooling measurements, but its hysteresis is smaller than $P3$. Peak $P3$ has a large thermal hysteresis up to 30 K from a DSC, which is consistent with other measurements (x-ray, TEM, or optics). This indicates it is not due to the dynamical measuring methods while it suggests that one is dealing with a first-order transition and the metastability of the ICP.

In the DSC diagram an evolution of the record base line of the DSC depends on the variation of the specific-heat capacity with temperature. On the basis of the Debye model and Landau theory, considering the total contribution of the phonons and the structure, we can know

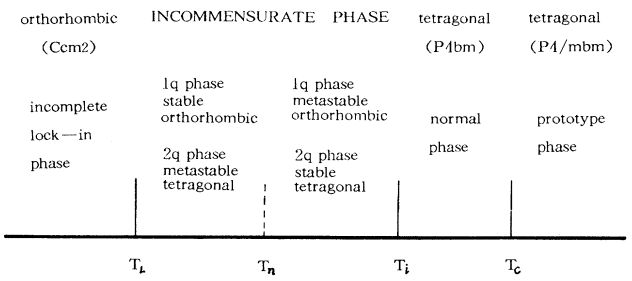

FIG. 3. Phase diagram of BSN from room temperature to 900 K.

that a second-order transition will give rise to a jump of the specific-heat capacity at transition temperature, which leads to a displacement of the DSC base line and changes the slope of the DSC curve before and after transition. On performing the experiment we found a thermal anomaly similar to a jump (denoted with an arrow in Fig. 2) at about 590 K within experimental accuracy, and that the slope of the base line of the DSC changed at the temperature. We infer that the anomaly is related to the incommensurate-normal transition. When approaching the temperature, the structure changes from incommensurate tetragonal to crystalline tetragonal. The structural change led to the change of the specific-heat capacity. From the DSC data, we get that the specific-heat capacities are $3.62\times10^{-1}+4.49\times10^{-4}T$ ($J\,g^{-1}K^{-1}$) in orthorhombic phase and $4.80\times10^{-1}+2.63\times10^{-4}T$ ($J\,g^{-1}\,K^{-1}$) in the tetragonal phase, respectively. The specific-heat-capacity anomaly is at 590 K. We estimate that the jump of the specific-heat capacity is about 5.53×10^{-2} ($J\,g^{-1}\,K^{-1}$).

In summary, three latent-heat peaks were found in our DSC measurements, the first corresponds to the ferroelectric transition, and the second and the third to the $1q$-$2q$ transition and lock-in transition, respectively. The three transitions are of first order in nature. Due to defect pinning and the existence of metastable states, both peak 2 and the peak 3 exhibit obvious thermal hysteresis effect. One specific-heat-capacity jump was detected at ICP to crystalline tetragonal transition temperature, however, the jump may have been blurred by the pinning of the defect. Our experimental results support the previous qualitative models of nucleation and growth of discommensurations in ICP of BSN.

One of the authors (Shining Zhu) would like to express his sincere thanks to Professor X. K. Zhang for his guidance and encouragement throughout his study and work. The authors wish to thank Professor Z. R. Xu for supplying the samples. The work was supported by a grant for a key research project from the State Science and Technology Commission of China.

[1]J. Schneck, J. C. Toledano, B. Joukoff, F. Denoyer, and C. Joffrin, Ferroelectrics **26**, 661 (1980).
[2]J. Schneck and F. Denoyer, Phys. Rev. B **23**, 383 (1981).
[3]J. Schneck, J. C. Joledano, C. Joffrin, J. Aubree, B. Joukoff, and A. Gabelotaud, Phys. Rev. B **25**, 1766 (1982).
[4]C. Manolikas, J. Schneck, and J. C. Joledano, Phys. Rev. B **35**, 8884 (1987).
[5]J. Schneck, Ph.D thesis, Paris University, 1982.
[6]S. Barre, H. Mutka, and C. Roucau, Phys. Rev. B **38**, 9113 (1988).
[7]X. Q. Pan and D. Feng, Phys. Status Solidi A **106**, K117 (1988).
[8]B. A. Scott, E. A. Giess, and D. F. O Kane, Mater. Res. Bull. **4**, 107 (1969).
[9]J. S. Abell, I. R. Harris, and B. Cockayne, J. Mater. Sci. **8**, 667 (1973).
[10]G. M. Loiacono, Ferroelectrics **5**, 101 (1973).
[11]J. C. Toledano and L. Pateau, J. Appl. Phys. **45**, 1611 (1974).
[12]X. X. Qu, H. Xia, X. Y. Xu, W. Zhang, and X. K. Zhang, J. Phys.: Condens. Matter **2**, 55 (1990).