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Heat capacity studies of phase transitions in $K_3Nb_3O_6(BO_3)_2$

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Abstract

Heat capacity measurements of $K_3Nb_3O_6(BO_3)_2$, a borate that exhibits superionic conductivity and ferroelectric properties, have been performed in the 60–220 K temperature range. In this work, the presence of two heat capacity anomalies has been documented. The first anomaly occurs at 198.3 K and it has been attributed to a first-order phase transition. The second anomaly suggests presence of second-order phase transition at around 80 K.

Keywords: Borate; Heat capacity; Phase transitions; Ferroelectric; Non-linear

1. Introduction

Among the known crystalline materials in nonlinear optics, boron containing materials play an important role since these materials usually have rather high $\chi^{(2)}$- and $\chi^{(3)}$-nonlinear susceptibilities [1]. Moreover, borates have cut-off wavelength in the near ultra-violet region and have outstanding resistance to laser damage [1–3]. Among borates, materials composed of both the BO_3 and octahedral groups attract recently considerable attention since they may exhibit especially large nonlinear coefficients [3]. One of the promising nonlinear borate, containing both the BO_3 and NbO_6 groups, is $K_3Nb_3O_6(BO_3)_2$. It has been recently shown that this material is an attractive $\chi^{(3)}$-active crystal for picosecond stimulated Raman scattering generation in the visible and near-IR region [4]. This material crystallizes in $P\bar{6}2m$ structure above 783 K which consists of triple groups of NbO_6 octahedra linked by planar BO_3 triangles [5,6]. The characteristic feature of this structure is the presence of large tunnels occupied by the K^+ ions. The ionic conductivity studies showed that this borate exhibits superionic properties at elevated temperature [7,8]. It was also shown that $K_3Nb_3O_6(BO_3)_2$ exhibits successive ferroelastic and ferroelectric phase transitions below 783 K [7,8], and its structure at room temperature was shown to be $P2_1ma$ [6]. The nature of these transitions has not yet been explained.

In the present paper, we report heat capacity studies of this material in the 60–220 K range in order to get some insight in the phase transition mechanism. Our studies show that $K_3Nb_3O_6(BO_3)_2$ has high values of heat capacity. They also confirm the presence of a phase transition at 198.3 K and indicate that this material may exhibit another, possibly second-order phase transition near 80 K, which has not yet been reported.

2. Experimental

The $K_3Nb_3O_6(BO_3)_3$ crystals were grown from the flux. The mixture of K_2CO_3 (99%), Nb_2O_5 (99.9%) and B_2O_3 (99%), corresponding to the composition $K_3Nb_3O_6(BO_3)_2$ and $K_2B_4O_7$ in a ratio 1:1, was placed in a platinum crucible, heated to 1000 °C, kept at this temperature for 20 h, cooled to 840 °C with a rate 2 °C/h and then cooled to room temperature with a rate of 10 °C/h. The crystals were extracted from the crucible by washing with hot water. Single crystals had the form of hexagonal rods up to 5 mm in length and up to 2 mm × 2 mm in cross-section. The obtained crystals were characterized by single crystal X-ray diffraction which showed that these crystal are of good quality. The established lattice parameters ($a = 17.526(3)$, $b = 15.182(3)$ and $c = 3.9696(8)$ Å) are in good agreement with those reported previously by Becker et al. [6].

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The specific heat measurements were carried out in the automated adiabatic calorimeter as described in reference [9]. The sample was located on a flat holder of the heat capacity equivalent to ∼200 mg Cu at the room temperature. The absolute calorimeter temperature was measured by a Pt resistance thermometer (EL700U, HY-CAL Engineering). The resistivity of this thermometer is 1000 Ω at 300 K and the accuracy of temperature determination is ±1 mK. The continuous heating method was used to scan the 60–230 K region. The heating rate was 8 mK/s. The mass of the sample was 104.79 mg. The heat capacity measurements were repeated several times showing good reproducibility of the data. The comparison of the results with a standard reference material (a 360 mg monocrystalline copper sample) showed that the accuracy of heat capacity measurements was about ±1.5%.

3. Results and discussion

The relationship between the measured heat capacity of the $K_3Nb_3O_6(BO_3)_2$ crystals on heating and temperature is shown in Fig. 1. The $K_3Nb_3O_6(BO_3)_2$ has relatively large heat capacity (271 J mol^{-1} K^{-1} = 445 J kg^{-1} K^{-1} at 210 K). Such a large value of heat capacity, comparable to heat capacity of excellent nonlinear crystal $Ca_4YO(BO_3)_3$ (729.7 J kg^{-1}K^{-1} at 373 K [10]) indicates that pulsed laser beam can only cause minor temperature variation in the crystal, and the damage threshold might be high.

The heat capacity versus temperature plot shows very clear anomaly at 198.3 ± 0.5 K. The full line in Fig. 1 represents the lattice heat capacity estimated by fitting the experimental data with a single Debye and Einstein functions (the experimental points in the temperature ranges 74–110 and 177–207 K were not included in the fit). Three Einstein functions were chosen since the Raman spectra consist of three spectral ranges: 43–327, 637–857 and 1066–1240 cm^{-1}. The fitting parameters determined for $K_3Nb_3O_6(BO_3)_2$ are summarized in Table 1. As can be noticed, the obtained Einstein temperatures agree reasonably well with the average frequencies obtained for every spectral range from the Raman studies (see Table 1).

After subtracting the background thus determined, the excess heat capacity ΔC_p in the vicinity of the 198.3 K phase transition temperature is shown in Fig. 2. The latent heat of this transition equals to 95.7 ± 5 J mol^{-1} and the corresponding value of the entropy change can be evaluated as $\Delta S = 1.2 \pm 0.1$ J mol^{-1} K^{-1} (see Fig. 3).

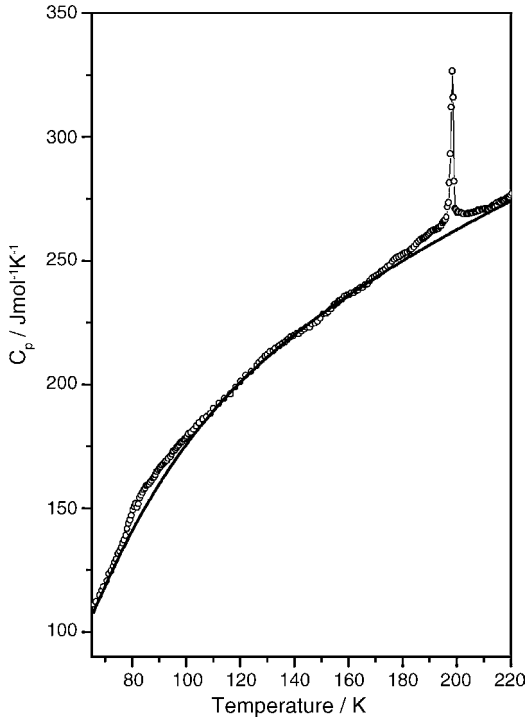

Fig. 1. The heat capacity of $K_3Nb_3O_6(BO_3)_2$. The full line is the lattice heat capacity.

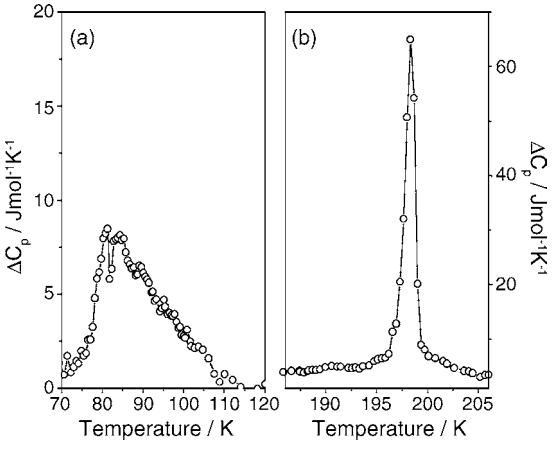

Fig. 2. Excess heat capacity of $K_3Nb_3O_6(BO_3)_2$ near 80 (a) and 198 K (b).

Table 1
Parameters obtained from the analysis of heat capacity for $K_3Nb_3O_6(BO_3)_2$ together with Raman frequencies

Mode	Θ		Raman frequencies (cm^{-1})	Average value of Raman frequency (cm^{-1})
	K	cm^{-1}		
D	106	74		–
E_1	253	176	43, 71, 77, 83, 89, 113, 137, 143, 150, 164, 177, 212, 218, 244, 257, 270, 289, 317, 327	178
E_2	1048	724	637, 647, 699, 780, 857	724
E_3	1682	1168	1066, 1198, 1240	1168

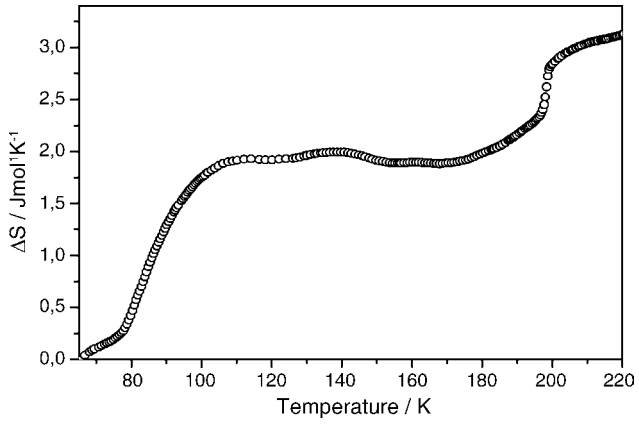

Fig. 3. Temperature dependence of transition entropy of $K_3Nb_3O_6(BO_3)_2$.

The previous dielectric studies showed the presence of one dielectric peak with a shoulder near 180 K [7,8]. On that basis, it was concluded that there are two closely located phase transitions at about 188 and 176 K temperature [7,8]. It has been argued that the nature of these phase transitions is close to second order [7]. The authors suggested also that the phase stable in the 176–188 K range may be incommensurate [7]. Our present measurements, repeated a few times, always show the presence of only one clear anomaly at 198.3 K which corresponds to the 188 K phase transition reported in references [7,8]. It is worth noting that the temperature of this transition is about 10 K higher than that reported previously by Voronkova et al. [7,8]. This discrepancy can be partly attributed to different accuracy of the experimental methods used in the previous and present reports. However, it cannot be excluded that this difference in the phase transition temperature is also partially due to difference in the crystal stoichiometry, since it was shown previously that phase transitions in this material are very sensitive to dopants [7,8]. For example, it was shown that for $K_{2.68}Na_{0.32}Nb_3O_6(BO_3)_2$, the discussed phase transition shifted to 438 K (by 250 K) in comparison with pure potassium niobium borate [8]. As has been mentioned above, our heat capacity results do not show any indication of the second phase transition near 176 K, observed in dielectric studies [7]. Our recent Raman studies did also not show the presence of this transition [11]. The origin of this discrepancy is not clear, but it shows that the presence of the 176 K phase transition is not certain and its confirmation needs further studies with other techniques. Our results also show that the heat capacity peak is very narrow and nearly symmetric. Although due to experimental reasons, we could not established whether this transition is associated with thermal hysteresis, the observed shape of the heat capacity anomaly and the previous observation of discontinuous changes in phonon frequencies [11], give strong indication that the 198 K phase transition has strongly first-order character. We cannot, therefore, confirm that this transition is close to second order. The heat capacity studies show also that the entropy change $\Delta S/R$ is very small, less than 0.15. Such a small change indicates that this transition is of displacive type. Since the crystal structure is composed of NbO_6 octahedra, we may suppose that this transition, similarly as in the case of perovskites, may be connected with small tilts of NbO_6 octahedra. Our recent temperature-dependent Raman study supports this conclusion (see reference [11]). It is known that such tilts in perovskite-like crystals are, as a rule, characterized by rather small entropy change ($\Delta S/R \leq 0.2$) [12]. However, it is worth noting that phase transitions in perovskites have usually significant contribution of an order–disorder character [13,14]. Typical example is $KNbO_3$, which exhibits a few phase transitions [13]. The comparison of the observed entropy change for the $K_3Nb_3O_6(BO_3)_2$ crystal shows that it is at least an order of magnitude smaller than that usually observed for perovskites. For example, $\Delta S \approx 5$ J mol^{-1} K^{-1} for the cubic-tetragonal phase transition in $PbTiO_3$ and 14.1 J mol^{-1} K^{-1} for Pb_2MgWO_6 [14,15]. Such a small value of ΔS for $K_3Nb_3O_6(BO_3)_2$ indicates that contribution of an order–disorder mechanism to the 198 K phase transition is negligible.

It is worth noting that our results show also another anomaly near 80 K (see Figs. 1–3). The presence of this anomaly suggests that the crystal may exhibit another phase transition, previously not reported for pure potassium niobium borate. It is worth noting, however, that the dielectric studies of $K_3Nb_3O_6(BO_3)_2$ doped with Na^+ ions also revealed the presence of a new phase transition, not reported for undoped $K_3Nb_3O_6(BO_3)_2$, near 276 and 333 K for $K_{2.87}Na_{0.19}Nb_3O_6(BO_3)_2$ and $K_{2.68}Na_{0.32}Nb_3O_6(BO_3)_2$, respectively [8]. Since substitution of K^+ by Na^+ in this material was shown to lead to very large increase of phase transitions temperatures [7,8], it is very likely that the observed by us heat capacity anomaly near 80 K has the same origin as the dielectric anomalies observed near 276 and 333 K for the $K_{2.87}Na_{0.19}Nb_3O_6(BO_3)_2$ and $K_{2.68}Na_{0.32}Nb_3O_6(BO_3)_2$ crystals, respectively. The entropy change near 80 K is small, 1.9 ± 0.1 J mol^{-1} K^{-1}, indicating that this anomaly may be associated with a displacive phase transition. It is worth noting that although the observed heat capacity anomaly near 80 K is not very clear, our recent Raman study also suggested that $K_3Nb_3O_6(BO_3)_2$ may exhibit a second-order phase transition near 80 K, i.e. we observed a very significant and abrupt change in depolarization ratio around 80 K as well as some changes in the slopes of frequency versus temperature plots for a number of vibrational modes (see reference [11]). However, except of large change in depolarization ratio, the other observed changes were very weak, indicating that this transition is associated with some subtle structural changes.

4. Conclusions

The performed heat capacity study revealed the presence of only one clear anomaly near 198 K, instead of two expected at 188 and 176 K on the basis of previous dielectric studies reported in the literature. It has been shown that this transition has very clear first-order character and may be associated with rotation of NbO_6 octahedra. Our results indicate also that this material may exhibit another phase transition near 80 K.

References

[1] A.A. Kaminskii, P. Becker, L. Bohaty, S.N. Bagaev, H.J. Eichler, K. Ueda, J. Hanuza, H. Rhee, H. Yoneda, K. Takaichi, I. Terashima, M. Maczka, Laser Phys. 13 (2003) 1385.
[2] G. Aka, A. Kahn-Harari, F. Mougel, D. Vivien, F. Salin, P. Coquelin, P. Colin, D. Pelenc, J.P. Damelet, J. Opt. Soc. Am. (b) 14 (1997) 2238.
[3] J.F.H. Nicholls, B. Henderson, B.H.T. Chai, Opt. Mater. 16 (2001) 453.
[4] A.A. Kaminskii, P. Becker, L. Bohaty, H.J. Eichler, A.N. Penin, K. Ueda, J. Hanuza, K. Takaichi, H. Rhee, Phys. Stat. Sol. (a) 201 (2004) 2154.
[5] P. Becker, L. Bohaty, J. Schneider, Kristallografiya 42 (1997) 250.
[6] P. Becker, P. Held, L. Bohaty, Z. Kristallogr. 211 (1996) 449.
[7] V.I. Voronkova, E.P. Kharitonova, V.K. Yanovskii, S. Yu. Stefanovich, A.V. Mosunov, N.I. Sorokina, Kristallografiya 45 (2000) 888.
[8] E.P. Kharitonova, V.I. Voronkova, V.K. Yanovskii, S. Yu. Stefanovich, Neorg. Mater. 38 (2002) 978.
[9] D. Włosewicz, T. Plackowski, K. Rogacki, Cryogenics 32 (1992) 265.
[10] J. Luo, S.J. Fan, H.Q. Xie, K.C. Xiao, S.X. Qian, Z.W. Zhong, G.X. Qian, R.Y. Sun, J.Y. Xu, Crys. Res. Technol. 36 (2001) 1215.
[11] M. Maczka, K. Hermanowicz, J. Hanuza, J. Phys. Condens. Matter. 17 (2005) 3355.
[12] I.N. Flerov, M.V. Gorev, K.S. Aleksandrov, Ferroelectrics 106 (1990) 207.
[13] N. de Mathan, E. Prouzet, E. Husson, H. Dexpert, J. Phys. Condens. Matter. 5 (1993) 1261.
[14] I.N. Flerov, M.V. Gorev, Ph. Sciau, J. Phys. Condens. Matter. 12 (2000) 559.
[15] H. Shigematsu, H. Nakadaira, T. Matsui, A. Tobo, K. Ohoyama, J. Nucl. Sci. Technol. 39 (2002) 395.