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SPECIFIC HEAT ON $Sr_2Nb_2O_7$ AND $Sr_2Ta_2O_7$

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Specific heats on the single crystals of $Sr_2Nb_2O_7$, $Sr_2Ta_2O_7$ and $(Sr_{1-x}Ba_x)_2Nb_2O_7$ were measured in a wide temperature range of 2–600 K. Heat anomalies of a λ-type were observed at the incommensurate phase transition of T_{INC} (=495 K) on $Sr_2Nb_2O_7$ and at the super-lattice phase transition of T_{SL} (=443 K) on $Sr_2Ta_2O_7$; the transition enthalpies and the transition entropies were estimated. Furthermore, a small heat anomaly was observed at the low temperature ferroelectric phase transition of T_{LOW} (=95 K) on $Sr_2Nb_2O_7$. The transition temperature T_{LOW} decreases with increasing Ba content x and it vanishes for samples of x>2%.

Keywords: *phase transition, specific heat, $(Sr_{1-x}Ba_x)_2Nb_2O_7$, $Sr_2Nb_2O_7$, $Sr_2Ta_2O_7$*

Introduction

$Sr_2Nb_2O_7$ (abbreviate as SN) and $Sr_2Ta_2O_7$ (abbreviate as ST) belong to $A_2B_2O_7$-type ferroelectrics with a layered perovskite structure. SN has a very high ferroelectric Curie temperature of T_C=1615 K [1], and takes place a normal incommensurate phase transition at T_{INC}=493 K [2, 3]. Above T_C the space group is assumed to be $Cmcm$-D_{2h}^{17} in analogy to the paraelectric phase of ST, and below T_C the established space group is $Cmc2_1$-C_{2v}^{12} [4]. Furthermore, SN takes place another ferroelectric phase transition at a low temperature of T_{LOW}≈100 K [5, 6]. Since SN has a low coercive field and a low dielectric constant at room temperature, it is promising for lead-free and non-volatile ferroelectric memory-devices based on FETs, as pointed out by Fujimori *et al*. [7]. On the other hand, ST shows a super-lattice phase transition at T_{SL}=443 K [3, 8], and a ferroelectric phase transition at T_C=166 K [1, 8]. In a solid solution of $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$, the ferroelectric Curie temperature T_C decreases steeply from 1615 to 166 K with increasing Ta content [1]. By contrast, the incommensurate phase transition temperature T_{INC} changes little even if the Ta content increases, and the T_{INC} connects to the super-lattice phase transition temperature T_{SL} of ST [9]. Recently, we have investigated a new system of $(Sr_{1-x}Ba_x)_2Nb_2O_7$ and found that the phase transitions at T_{INC} and T_{LOW} decrease with increasing Ba content x and disappear near x=2–4% [10, 11]. As for the specific heat C_p on these crystals, a peculiar heat anomaly was observed at T_{INC} recently [10, 12], but no anomaly was observed near T_{LOW} [10]. Furthermore, there is no useful information about C_p on ST, as long as we know. In this paper, we investigate in detail the specific heat on the single crystals of $Sr_2Nb_2O_7$, $Sr_2Ta_2O_7$ and $(Sr_{1-x}Ba_x)_2Nb_2O_7$ with x<2%, in a wide temperature range of 2–600 K.

Experimental

The single crystals were grown in an O_2 flow by a floating zone method using a FZ furnace (Crystal systems Inc). The starting materials were $SrCO_3$ (99.9%), $BaCO_3$ (99.9%), Nb_2O_5 (99.98%) and Ta_2O_5 (99.98%). Heat capacity was measured using two types of equipment: a fully automated measurement system of relaxation heat capacity (Quantum Design, a heat capacity module of PPMS) and an AC calorimeter (ULVAC, ACC1-M/L). They were used in a temperature range of 2–250 and 200–600 K, respectively. For the heat capacity measurement using PPMS, a single crystal with weight of about 20 mg was put with apiezon L grease on the sample stage. For the AC calorimeter, a thin plate-like crystal prepared by cleavage was attached to an E type thermocouple with a diameter of 20 μm using a silver paste. A heat capacity anomaly by the E type thermocouple at 410 K was removed numerically after the measurement.

Results and discussion

Specific heat C_p *vs*. T curves, measured on the single crystals of SN and ST, are shown in Figs 1 and 2, respectively. The C_p is composed of two kinds of data obtained by PPMS below 250 K and by an AC calo-

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rimeter above 230 K. Because the AC calorimeter gives only relative values of C_p, the absolute values were determined as the data of the AC calorimeter coincide with those of PPMS in a temperature range of 230–250 K. A broad anomaly of the specific heat is seen around T_{INC} on SN (the inset of Fig. 1); similarly, a typical λ-type anomaly is seen around T_{SL} on ST (the inset of Fig. 2). However, at the temperatures below 300 K, we cannot see any heat anomalies on the both crystals of SN and ST (Figs 1 and 2, respectively).

For estimating excess specific heat ΔC_p caused by the phase transition, we must draw a baseline that is the normal portion of the specific heat. The solid lines in Figs 1 and 2 were obtained on an assumption that a polynomial function holds for C_p(base) in a limited temperature range of 260–590 K for SN, and of 300–465 K for ST: $C_p(\text{base})=a+bT+cT^2+dT^3+eT^4$, where *a*, *b*, *c*, *d* and *e* are constants. These constants were calculated by the method of least squares fitting to the data in the ranges of 260–360 and 530–590 K for SN, and in the ranges of 260–350 and 455–465 K for ST.

The obtained excess specific heats, $\Delta C_p = C_p - C_p(\text{base})$, for the two phase transitions at T_{INC} and T_{SL} are shown together in Fig. 3 for comparison. As seen in the figure, the incommensurate phase transition shows broad change over a wide temperature region of 350–520 K. By contrast, the super-lattice transition shows a relatively sharp change in comparison with that of T_{INC}; the maximum value of ΔC_p reaches about 11 J mol^{-1} K^{-1} and the phase transition occurs in a rather narrow temperature region of 350–460 K. These relatively broad and continuous behaviors near the transition temperatures indicate that the both transitions at T_{INC} and T_{SL} are of the second order.

The ΔC_p *vs*. *T* curves have small bumps near 410 K (Fig. 3). They are probably due to a heat anomaly of the E-type thermocouple used in this experiment. Most of the thermocouple's anomaly was removed numerically from the raw data after the experiment, but a small anomaly would be able to remain if there were another heat anomaly near 410 K.

The transition enthalpy ΔH was calculated from the excess specific heat ΔC_p, as shown in Fig. 4. The transition temperature can be determined as an inter-

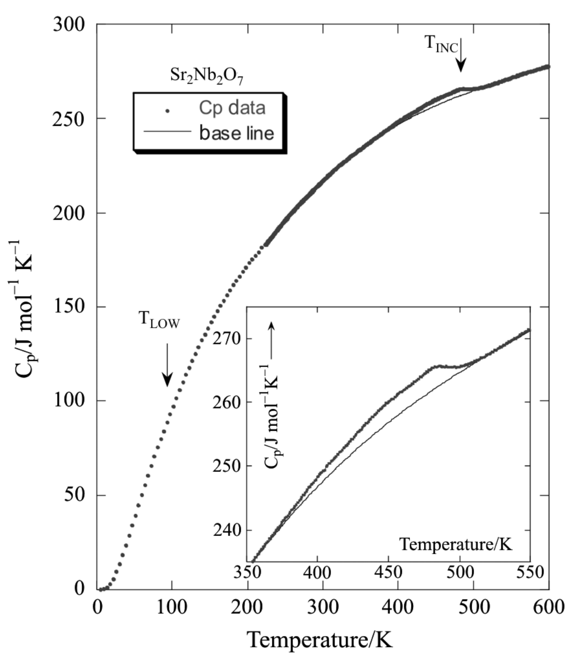

Fig. 1 Specific heat C_p on the $Sr_2Nb_2O_7$ single crystal

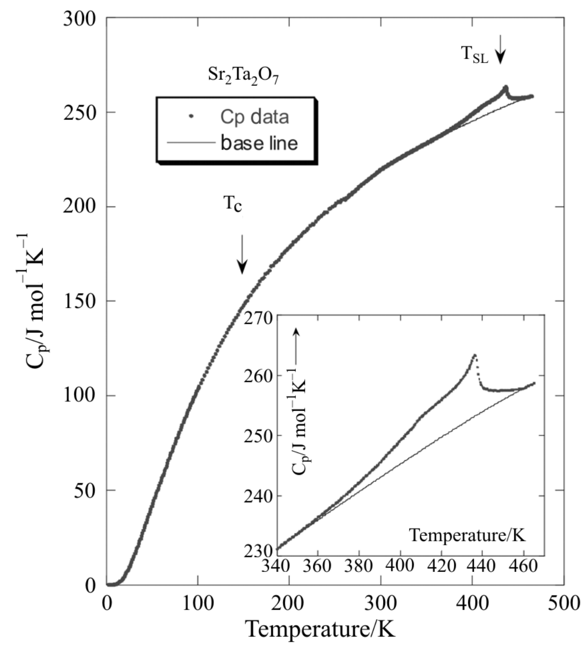

Fig. 2 Specific heat C_p on the $Sr_2Ta_2O_7$ single crystal

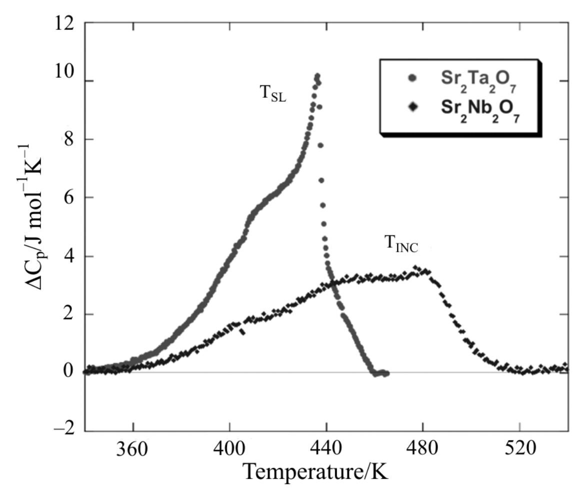

Fig. 3 Excess specific heat ΔC_p associated with the incommensurate phase transition at T_{INC} on SN and the super-lattice phase transition at T_{SL} on ST

section of the extrapolated lines of ΔH from the straight portions above and below the transition point: that is, T_{INC} and T_{SL} become 495 and 443 K, respectively. These values of the transition temperatures agree well with results of the dielectric constant [2, 8], the Raman scattering [13, 14], and the electron microscope [3]. The transition enthalpy ΔH and transition entropy ΔS are respectively estimated as $2.91\cdot10^2$ J mol^{-1} and $5.87\cdot10^{-1}$ J mol^{-1} K^{-1} for T_{INC}, and as $3.56\cdot10^2$ J mol^{-1} and $8.04\cdot10^{-1}$ J mol^{-1} K^{-1} for T_{SL}. These small values of the transition entropy may be attributed to that the phase transitions are a displacive type, as confirmed by existence of soft modes near T_{INC} and T_{SL} [13, 14].

Previously, Shabbir and Kojima reported the ΔC_p of SN [12], where they measured the heat capacity of SN using DSC. Curiously, their absolute values of C_p around T_{INC} are half of our results. Moreover, the data showed a sharp peak around 487 K, like as the ΔC_p of ST in Fig. 2. They estimated the transition entropy ΔS at T_{INC} as 0.71 J mol^{-1} K^{-1}, which is a little larger than the present value of ΔS=$5.87\cdot10^{-1}$J mol^{-1} K^{-1}. Since the temperature resolution of AC calorimetry is higher than that of DSC in general, we must mention why the ΔC_p on SN in Fig. 1 does not show a sharp peak. In order to check this point, we measured C_p using several samples of SN, but all of our samples showed a broad anomaly at T_{INC} like Fig. 1. In our AC calorimetry, a thin crystal sample is attached to a thermocouple by a silver paste of small amounts, so that it may be possible that a kind of elastic strain induced by the contact gives unfavourable influence on the phase transition.

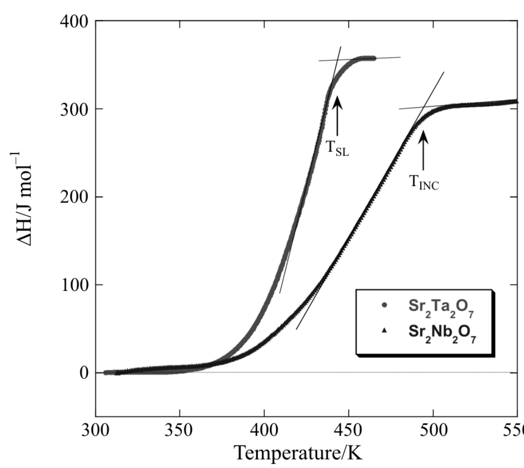

Fig. 4 Transition enthalpy ΔH associated with the incommensurate phase transition at T_{INC} on SN and with the super-lattice phase transition at T_{SL} on ST

	T/K	ΔH/J mol^{-1}	ΔS/J mol^{-1}K^{-1}
T_{SL}	443	356	0.804
T_{INC}	495	291	0.587

In order to reveal the specific heat anomaly around T_{LOW}, we reinvestigated C_p on SN in detail. The C_p/T values on SN and ST are shown in Fig. 5 as a function of temperature. The specific heat of ST changes smoothly over the whole temperature range. Comparing the C_p *vs*. T curves between ST and SN, we can notice that C_p of ST is larger than that of SN at temperatures between 50 and 200 K and C_p of ST coincides with those of SN at temperatures below 30 and above 200 K. These differences of C_p between SN and ST at temperatures of 50–200 K are probably due to a broad and dispersive nature of the ferroelectric phase transition at T_C=166 K on ST, as it is known that the dielectric constant of ST behaves like relaxor near T_C [8]. Another peculiar behavior is that SN shows a small jump of $\Delta C_p/C_p$=0.58% at 95 K, as clearly shown in the inset of Fig. 5.

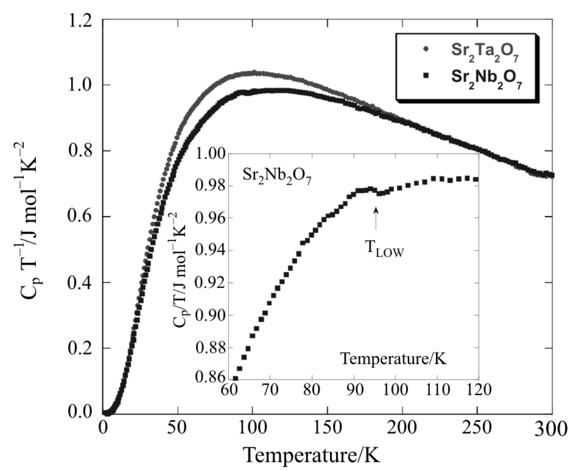

Fig. 5 C_p/T *vs*. T relations on $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$ single crystals

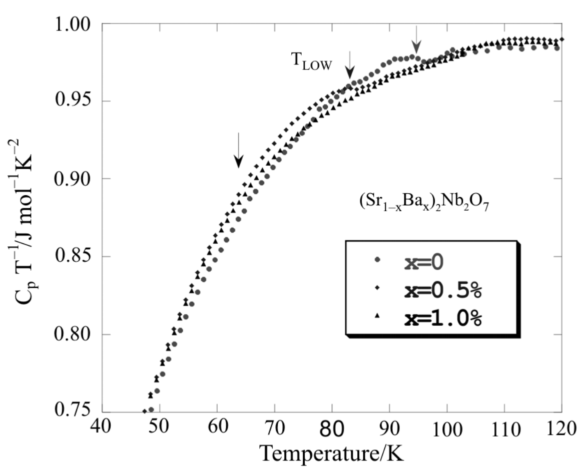

Fig. 6 C_p/T *vs*. T relations on $(Sr_{1-x}Ba_x)_2Nb_2O_7$ single crystals

Figure 6 shows the C_p/T behavior in the low temperature region for the Ba doped crystals,

$(Sr_{1-x}Ba_x)_2Nb_2O_7$. As seen in the figure, the small jump at 95 K for *x*=0% decreases its temperature as the Ba content increases: the jump occurs at 83 K for *x*=0.5% and at 63 K for *x*=1.0%. Above about *x*=2%, we could not observe these small changes in C_p. These results agree well with our primitive results of the dielectric constant ε_b along the *b*-axis. The ε_b shows a peak around $T_{LOW}\approx100$ K for *x*=0 crystals. The T_{LOW} decreases with increasing Ba content and disappears for *x*=2–4% crystals. Thus the small heat anomaly in Fig. 6 is certainly due to the phase transition at T_{LOW}.

Conclusions

Specific heats on the single crystals of $Sr_2Nb_2O_7$, $Sr_2Ta_2O_7$ and $(Sr_{1-x}Ba_x)_2Nb_2O_7$ were measured in a wide temperature range of 2–600 K. Specific heat anomalies were observed at the incommensurate phase transition of T_{INC} (=495 K) on $Sr_2Nb_2O_7$ and at the super-lattice phase transition of T_{SL} (=443 K) on $Sr_2Ta_2O_7$. The transition enthalpy ΔH and transition entropy ΔS were respectively estimated as $2.91\cdot10^2$ J mol^{-1} and $5.87\cdot10^{-1}$ J mol^{-1} K^{-1} for T_{INC}, and as $3.56\cdot10^2$ J mol^{-1} and $8.04\cdot10^{-1}$ J mol^{-1} K^{-1} for T_{SL}. A small heat anomaly was observed at the low temperature ferroelectric phase transition of T_{LOW} (=95 K) on $Sr_2Nb_2O_7$. The transition temperature T_{LOW} decreases with increasing Ba content *x* and vanishes around *x*=2%.

Acknowledgements

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References

1 S. Nanamatsu, M. Kimura and T. Kawamura, J. Phys. Soc. Jpn., 38 (1975) 817.
2 K. Ohi, M. Kimura, H. Ishida and H Kakinuma, J. Phys. Soc. Jpn., 46 (1979) 1387.
3 N. Yamamoto, K. Yagi, G. Honjo, M. Kimura and T. Kawamura, J. Phys. Soc. Jpn., 48 (1980) 185.
4 N. Ishizawa, F. Marumo, T. Kawamura and M. Kimura, Acta Crystallogr., B 31 (1975) 1912.
5 Y. Akishige, Y. Kobayashi, K. Ohi and E. Sawaguchi, J. Phys. Soc. Jpn., 55 (1986) 2270.
6 V. Bobnar, P. Lunkenheimer, J. Hemberger, A. Loidl, F. Lichtenberg and J. Mannhart, Phys. Rev., B 65 (2002) 155115.
7 Y. Fujimori, N. Izumi, T. Nakamura and A. Kamisawa, Jpn. J. Appl. Phys., 37 (1998) 5207.
8 Y. Akishige and K. Ohi, J. Phys. Soc. Jpn., 61 (1992) 1351.
9 N. Yamamoto, M. Nakamura, K. Yagi and K. Ohi, J. Phys. Soc. Jpn., 49 Suppl. B (1980) 95.
10 Y. Akishige, M. Kamata and K. Fukano, J. Korean Phys. Soc., 42 (2003) S1187.
11 A. Hushur, Y. Akishige and S. Kojima, Ceramics International, 30 (2004) 2023.
12 S. Shabbir and S. Kojima, J. Phys. D: Appl. Phys., 36 (2003) 1036.
13 S. Kojima, M. Takashige, T. Nakamura, K. Ohi and H. Kakinuma, Solid State Commun., 31 (1979) 755.
14 S. Kojima, K. Ohi and T. Nakamura, Solid State Commun., 35 (1980) 79.

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