Specific-Heat Anomaly Caused by Ferroelectric Nanoregions in $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(Mg_{1/3}Ta_{2/3})O_3$ Relaxors

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The specific heat of typical relaxors, $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT), was measured by adiabatic and relaxation methods between 2 and 420 K. A broad anomaly was found in the specific heat curve over the wide temperature range between 150 and 500 K for PMN, and between 50 and 400 K for PMT, which provides evidence for the formation of ferroelectric nanoregions (FNR) in the paraelectric matrix. The entropy of the anomaly was estimated as $3.3\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and $2.9\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for PMN and PMT, respectively, which implies an order-disorder-type mechanism for the formation of FNR.

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$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is a typical relaxor showing a large, broad and frequency-dependent peak in the dielectric constant curve around 300 K. Its properties have been studied quite extensively. Although such a broad peak implies a "diffuse phase transition"[1], no macroscopic structural change had been found and the cubic symmetry remains down to liquid helium temperature. Later studies employing neutron and x-ray diffractometry on PMN [2–4] indicate a heterostructure composed of two phases, i.e., ferroelectric nanoregions (FNR) (space group $R3m$) formed in paraelectric matrix ($Pm\bar{3}m$). Nowadays such heterostructure is considered to be essential to relaxors. In general, two phases can coexist at a first-order phase transition point, where an anomaly in specific heat should be observed. Even if the ferroelectric phase transition in relaxors is smeared by some reasons, e.g., the random field interactions [5], a specific heat anomaly would be expected due to the formation of FNR. So-called "domain state model" [5] should be dismissed if there is no specific heat anomaly in relaxors. In previous specific heat measurements on PMN by the adiabatic method [6,7], however, no remarkable anomaly was reported between 2 and 300 K, where the dielectric peak is observed below the middle frequency range. On the other hand, the existence of the specific heat anomaly in PMN has been argued from the result of differential scanning calorimetry between 140 and 790 K [8], but the result was not in good agreement with that of adiabatic calorimetry in the overlapping temperature range [6,7]. Such uncertainty of the experimental results might originate from both the essential complexity of relaxors and experimental restrictions, e.g., precision, accuracy, and measurable temperature range. For further understanding of the nature of relaxors, thermodynamic information is indispensable, and the precise data of specific heat over a wider temperature range are highly desired. In the present study, we performed precise specific heat measurements for PMN up to 420 K. In order to examine the generality of our findings, we have also performed for the first time specific heat measurements on $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT), which is a member of the PMN family with a similar dielectric peak around 200 K.

The samples of single crystals of PMN and PMT were prepared by the PbO-flux method. The details of the synthesis of PMN were described previously [7], and PMT was also synthesized with a similar procedure. The crystals of about 2 mm in size were separated from the products. The crystal structure of the samples was identified to be cubic perovskite by powder x-ray diffraction. The specific heat of PMN and PMT was measured between 13 and 420 K using a homemade adiabatic calorimeter with the accuracy of 0.1% and 0.2% at 100 and above 300 K, respectively. The amount of the samples of PMN and PMT put into a calorimeter vessel was 7.7 and 8.0 g, respectively. The details of the calorimeter and the method of measurements were described elsewhere [9–11]. In order to obtain the specific heat below 13 K, the specific heat was also measured between 2 and 60 K by the thermal relaxation technique using Physical Property Measurement System (Quantum Design Inc.). The mass of the single crystals of PMN and PMT used for the measurements was 6.5 and 16.6 mg, respectively. The results were in good agreement with those of the adiabatic calorimetry within 0.5% in the overlapping temperature range. The dielectric constant was measured between 10 and 370 K with frequencies of 1, 3, 10, 30, 100, 300, and 1000 kHz using an HP 4284A Precision *LCR* meter. The measurements were carried out in both cooling and heating runs at the rate of 1 K/ min. No hysteresis was observed in either compound.

The measured specific heat of PMN and PMT is shown in Fig. 1. At a glance, no remarkable anomaly is seen in either specific heat curve. PMT shows larger specific heat than that of PMN at low temperatures, which is probably due to the mass effect of heavier Ta ions. Since both

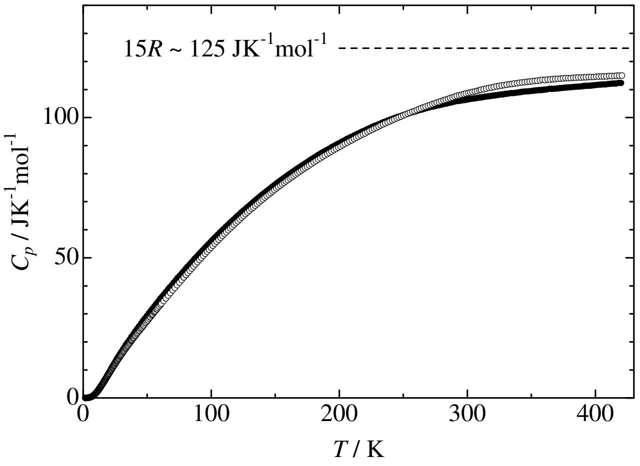

FIG. 1. Measured molar specific heat C_p of PMN (open circles) and PMT (closed circles). The broken line represents the classical value of Dulong-Petit law, which is $15R$ for perovskite compounds.

compounds have the same crystal structures, both specific heat curves are expected to approach asymptotically the classical value of Dulong-Petit law ($15R$ in perovskites, where R is gas constant) without any remarkable features as temperature increases. However, the two curves intersect at 250 K, which implies some effects causing the extra specific heat at least in PMN.

A small or broad anomaly in specific heat can be seen more clearly in the corresponding Debye temperature curve, which is calculated from measured specific heat using the Debye function. Figure 2 shows the Debye temperatures of PMN and PMT thus calculated assuming $15N$ degrees of freedom, where N is the Avogadro constant. The deviation of Debye characteristic temperature from a constant value denotes the deviation from Debye model. A deep hollow in the low temperature region (around 10 K in Fig. 2) is commonly observed in a variety of compounds, which is due to the contribution of low frequency optical phonons and other contributions reported previously [7,13]. On the other hand, in the higher temperature region, a broad hollow is clearly seen with a minimum at about 250 K for PMT and 320 K for PMN. A minimum in this temperature region is quite unusual because Debye temperature usually approaches a constant value as specific heat saturates to a classical value with increasing temperature. No such anomalous curve has been found in related compounds, e.g., $PbTiO_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ [14]. Thus the present results clearly demonstrate the existence of the specific heat anomaly in such a high temperature region for PMN and PMT.

In order to obtain the excess specific heat, ΔC_p, the lattice contribution was estimated using a simple model for the lattice vibrations as shown in the inset of Fig. 2. A Debye function was used for the contribution of acoustic phonons with $3N$ degrees of freedom. Because of a nonphonon contribution to the low temperature specific heat

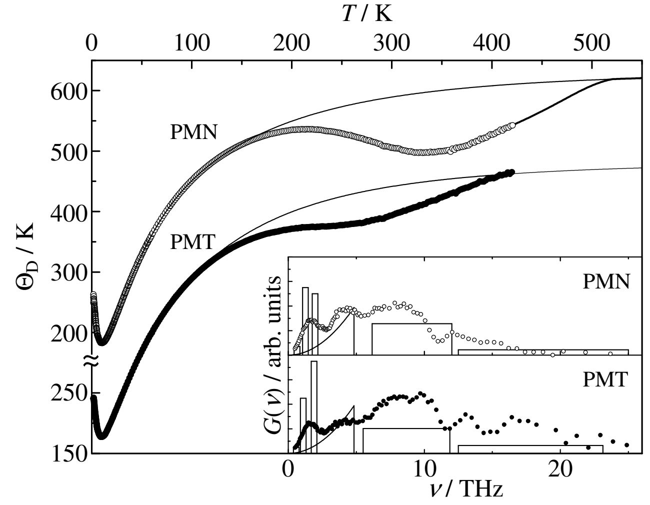

FIG. 2. Debye temperature Θ_D calculated from the measured molar specific heat C_p of PMN and PMT assuming $15N$ degrees of freedom. Solid lines denote Θ_D of the estimated lattice contribution mentioned in the text. In PMN, C_p data are extrapolated above 420 K and it is shown as a thick solid line. The inset shows generalized density of states $G(\nu)$ obtained from the estimation of the lattice contribution (solid lines) and the result of inelastic neutron scattering experiments at 50 K [12].

in PMN [7,13], the cutoff temperature of the function, Θ_D, was determined from the elastic data [15–17]. For perovskites, Θ_D is usually derived for $15N$ degrees of freedom, and we scaled it for $3N$ degrees of freedom as $\Theta_{D3N} = 5^{-1/3}\Theta_{D15N}$ and obtained 230 K for PMN. The same Θ_D value was used for PMT as no elastic data are available. For the other contributions of $12N$ degrees of freedom, we used Einstein functions and their characteristic temperatures and degrees of freedom were fitting parameters for nonlinear least square fitting to the specific heat data. The estimation of the lattice contribution was carried out by trial and error, where the temperature regions of the data used for the fitting were adjusted until a valid result was obtained. For PMT, the data below 50 K and above 400 K were used for the fitting. On the other hand, in PMN, the specific heat data in the high temperature region obviously include the extra contribution and could not be used for the fitting. Thus the estimated lattice contribution for PMT at high enough temperatures was considered as the high temperature specific heat of PMN, as both compounds were expected to show the same specific heat value at high temperatures. Consequently, only the data below 120 K was used for the fitting. The resultant distribution of the density of states is shown in the inset of Fig. 2, which is in good agreement with the result of inelastic neutron scattering experiments [12]. The Debye temperatures of the lattice contribution are denoted by thin solid lines in Fig. 2. The excess specific heat obtained by subtracting the lattice contribution from the measured specific heat is shown in Fig. 3 together

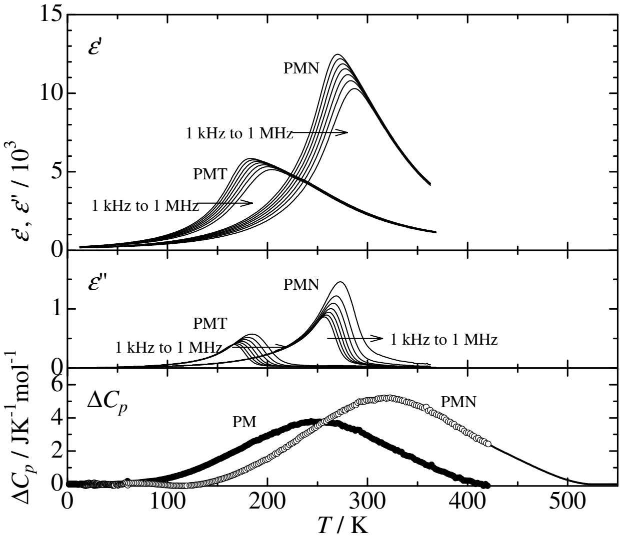

FIG. 3. Complex dielectric constant ϵ', ϵ'' and excess specific heat ΔC_p of PMN and PMT.

with the complex dielectric constant. The specific heat of PMN was smoothly extrapolated above 420 K as shown with a thick solid line in Figs. 2 and 3.

The first evidence for the nucleation of ferroelectric regions in PMN was provided as a deviation in the index of refraction from the linear temperature dependence starting around 600 K with decreasing temperature [18]. Later structural studies revealed [2–4] that the ferroelectric regions grow gradually with decreasing temperature, but the growth ceases around 150 K. Consequently, they become nanoregions with a size of a few 10 nm and most of the crystal remains in the cubic paraelectric phase down to liquid helium temperature. Thus two phases coexist below 600 K. As shown in Fig. 3, the specific heat anomaly of PMN is found between 150 and 500 K, which coincides with the temperature region of the nucleation and growth of FNR. The anomaly is thus likely to be caused by the formation of FNR. The same phenomenon should take place in PMT between 50 and 400 K. The excess specific heat forms a very broad peak, and the phase transition seems to be "smeared" or "diffused" as compared with a normal first-order phase transition. The value of the excess entropy ΔS of PMN and PMT was estimated to be 3.3 and 2.9 $\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively, which suggests an order-disorder-type mechanism for the formation of FNR; a displacive mechanism should not have such a large value of ΔS. In the case of the order-disorder phase transition, the expected value of ΔS between fully ordered and disordered states should be considered in detail, and we presumed the ordering of Pb ions at off-center positions [2–4]. In PMN, the polarizations of FNR resulting from the ordering of ionic shifts are randomly oriented along the eight equivalent $\langle 111 \rangle_{\mathrm{cub}}$ directions, which means eight ionic positions for ordering. Taking this into account, the expected value of ΔS is $R\ln 8$, and the experimental values are about 20% of this value. On the other hand, profile analyses of powder neutron diffraction peaks of PMN [3,4] revealed that the maximum volume ratio of FNR to the whole crystal is also about 20%. In Fig. 4, the temperature dependence of the ratio of the entropy to $R\ln 8$ ($\Delta S/R\ln 8$) and the volume ratio of FNR to the whole crystal (V_{FNR}/V) [4] for PMN are shown, where both are in good agreement. According to this concept, the phase transition is not completed in the crystals of PMN and PMT, which should be in a glassy state at low temperature with residual entropy of $0.8R\ln 8$. However, the enumeration of entropy is not so simple because individual Pb ions must be ordered at one in eight possible positions at low temperatures in addition to the ordering as FNR. More detailed calculation of the entropy is needed for the individual ionic ordering and their clustering. The order-disorder-type description is supported by recent studies on the local structure of PMN, where antiferroelectric ordering, as well as ferroelectric ordering, is deduced [19,20].

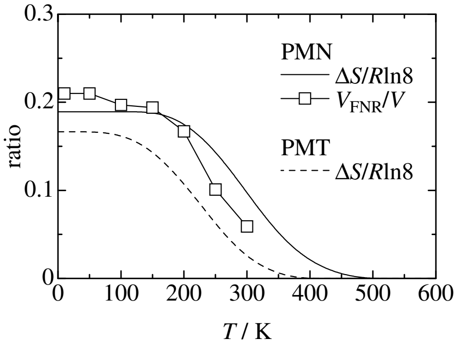

FIG. 4. Temperature dependence of the ratio of excess entropy to $R\ln 8$ ($\Delta S/R\ln 8$) of PMN and PMT and the volume ratio of FNR to the whole crystal (V_{FNR}/V) of PMN [4].

Although the large value of ΔS can be explained to some extent assuming an order-disorder-type mechanism, we should also consider the energetic contribution of the dipolar interactions among FNR. So far, several models related to the orientational glasslike characteristics of relaxors have been proposed[21–23] on the analogy of the spin glass system, where long range dipolar interactions are involved. A number of studies focused on the glasslike freezing in relaxors have been carried out since a "dipolar glass model" [22] was proposed for PMN, where the dielectric relaxation process in the middle frequency range can be well described by the Vogel-Fucher law and the freezing temperature is found to be about 220 K[22]. If there are strong dipolar interactions among FNR, it is expected to observe hysteresis and/or an anomalous thermal relaxation phenomenon caused by the reorientational relaxation around a temperature where the relaxation time becomes comparable to the measurement time scale [24]. According to the dipolar glass model [22], such a phenomenon should be observed around an apparent freezing temperature, i.e., 240 K for PMN and 140 K for PMT in adiabatic calorimetry because the heat input corresponds to about 10^{-3} Hz [9–11]. However, no anomalous relaxation or hysteresis was observed during all the specific heat measurements. This suggests that the dipolar interactions among FNR are not strong enough to be thermally detected relative to the inside of FNR. Thus although several orientational glass models have been proposed for relaxors, it seems that quantitative consideration taking into account energetic contribution of dipolar interactions is required for further understanding of the orientational glasslike nature of the relaxors.

In conclusion, we performed precise specific heat measurements for PMN and PMT relaxors over the wide temperature range between 2 and 420 K and found specific heat anomaly showing for the first time the thermodynamic signature of the formation of FNR. The entropy value is about $0.2R\ln 8$, which suggests an order-disorder-type mechanism for the formation of FNR and both crystals may be in a glassy state at low temperatures. Concerning a orientational glasslike behavior in PMN and PMT, no anomalous thermal relaxation phenomenon was observed in the specific heat measurements, which suggests little energetic contribution of dipolar interactions among FNR.

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