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Phase Transition Behavior between Normal and Diffuse Transitions in Lead based Perovskite Compounds.

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The phase transition behavior in the system (1-x)$Pb(Ni_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ (PNN-PT) relaxor ferroelectric material has been investigated to explore the nature of diffused phase transition (DPT) in this material. All the dielectric constant (ε) -temperature (T) characteristics for the materials above the Curie point have been found to be described by the equation $(1/\varepsilon-1/\varepsilon_m)^{1/n}=(T-T_m)/C'$, where ε_m is the maximum dielectric constant of a material, T_m is the temperature giving ε_m, and n and C' are constants changing with composition. This material exhibited the broad maximum, whose value was about 1.8 near T_m=0°C, in the n-T_m characteristics. The n-T_m characteristics above T_m=0°C was the same results obtained in the systems, (1-x)$Pb(Mg_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$ and $Pb_{1-y}La_{2y/3}TiO_3$.

1.Introduction

The temperature dependence of the dielectric constant above the Curie point in normal ferroelectrics, such as $BaTiO_3$ and $PbTiO_3$ (PT), is well known to obey the Curie-Weiss law, $1/\varepsilon=(T-T_c)/C$, where ε is the dielectric constant at T, T_c is the Curie point and C is the Curie constant, while those for many complex perovskite ferroelectrics, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), are known to obey the equation $(1/\varepsilon-1/\varepsilon_m)^{1/2} = (T-T_m)/C$, where T_m is the peak temperature of the dielectric constant and ε_m is the maximum dielectric constant. The latter dielectric behavior characterized by broad peaks of the dielectric constant, associated with a significantly large low-frequency dielectric dispersion, has been interpreted by a diffused phase transition (DPT) model[1]. There have been many studies which dealt with DPT in relaxor ferroelectrics and these results seem to support the model for DPT proposed by Cross[2] based on the electrical analogues of superparamagnets. Although this model certainly explains qualitatively the dielectric aspects of DPT, there still remain some questions, for instance, as to how the variation of their behavior patterns with composition can be consistently explained.

The authors have been doing a quantitative and systematic study on the dielectric constant-temperature characteristics for (1-x)PMN-xPT($0\le x\le 1.0$) and $Pb_{1-y}La_{2y/3}TiO_3$ (PLT, $0\le y\le 0.3$) to explore the nature of DPT in relaxor ferroelectrics[3]. The dielectric behavior of these materials was found to be completely described by the equation $(1/\varepsilon-1/\varepsilon_m)^{1/n} = (T-T_m)/C'$, continuously changing with composition. In this paper, a systematic study has also been done for (1-x)$Pb(Ni_{1/3}Nb_{2/3})O_3$-xPT (PNN-PT,

$0 \leq x \leq 0.8$). (PNN is a typical relaxor.) Comparing the results on PNN-PT with those on PMN-PT and PLT, a possible interpretation for the nature of DPT is presented. structure change (morphotropic phase boundary: MPB) from a rhombohedral structure to a tetragonal one between the compositions x=0.35 and 0.40.

2.Experimental

PNN-PT samples with the composition (1-x)$Pb(Ni_{1/3}Nb_{2/3})O_3$-x$PbTiO_3$; x=0, 0.2, 0.3, 0.35, 0.4, 0.6, 0.8, were produced by the columbite method using PbO, $NiNb_2O_6$, $PbTiO_3$ powders as raw materials[4]. The sintered density of all the obtained materials was greater than 95% of the theoretical density. All the sample prepared were confirmed to have no phase other than the perovskite phase by powder X-ray diffraction (XRD) analysis. Measurements of ε-T characteristics in all the present samples were conducted at -200 to 600 °C using an impedance analyzer (YHP-4192A) at various frequencies.

3.Results and discussion

Figure 1 shows the ε-T characteristics for the PNN-PT samples. It is evident that the phase transition behavior of the materials changes with composition from normal phase transition (NPT) characterized by a sharp peak of the dielectric constant for PT to DPT characterized by broad peak for PNN. It was confirmed that there exists a crystal structure change (morphotropic phase boundary : MPB) from a rhombohedral structure to a tetragonal one between the compositions x=0.35 and 0.40.

Figure 2 shows the T_m-composition x characteristics at various frequencies. It was confirmed that the T_m shifted to the higher

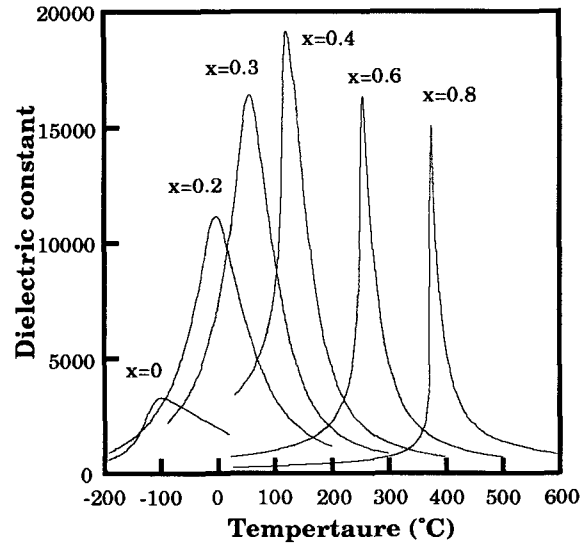

Figure 1. Temperature dependence of dielectric constant for the PNN-PT samples at 100kHz.

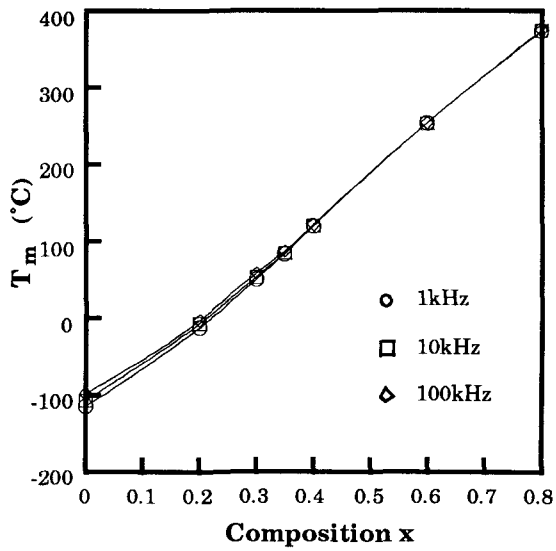

Figure 2. Composition x dependence of T_m for the PNN-PT samples at various frequencies.

temperature with an increase of the measuring frequency in the composition range, $0 \leq x < 0.4$, indicating the rhombohedral structure.

To examine the behavior pattern of ε-T characteristics above the Curie point for these materials, the data shown in Fig.1 were plotted on a $\log(1/\varepsilon - 1/\varepsilon_m)$ versus $\log(T-T_m)$ plot, revealing linear relationships between $\log(1/\varepsilon - 1/\varepsilon_m)$ and $\log(T-T_m)$, as shown in Fig.3. This figure clearly demonstrates that all the ε-T characteristics above the Curie point for the materials in the system can be completely described by the equation $(1/\varepsilon - 1/\varepsilon_m)^{1/n} = (T-T_m)/C'$ with constants n and C' which depend upon the composition of the materials.

The values of n and C' in the equation of $(1/\varepsilon - 1/\varepsilon_m)^{1/n} = (T-T_m)/C'$ were obtained for all the present samples from the straight lines in the $\log(1/\varepsilon - 1/\varepsilon_m)$ versus $\log(T-T_m)$ plots and plotted as functions of T_m, as shown in Figs. 4 and 5, respectively. The n indicated the maximum

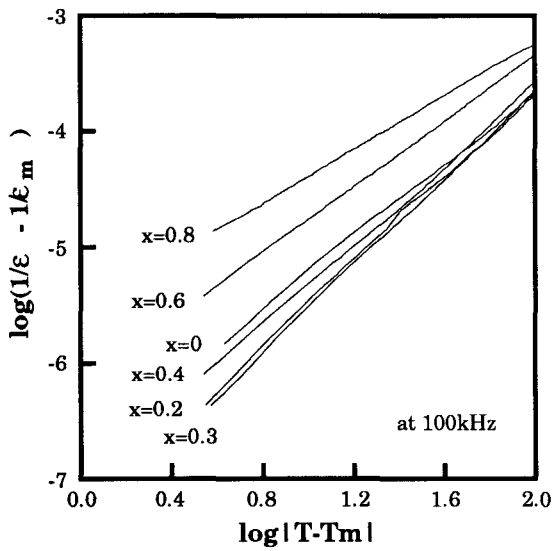

Figure 3. $\log(1/\varepsilon - 1/\varepsilon_m)$ versus $\log(T-T_m)$ plots for the samples at 100kHz.

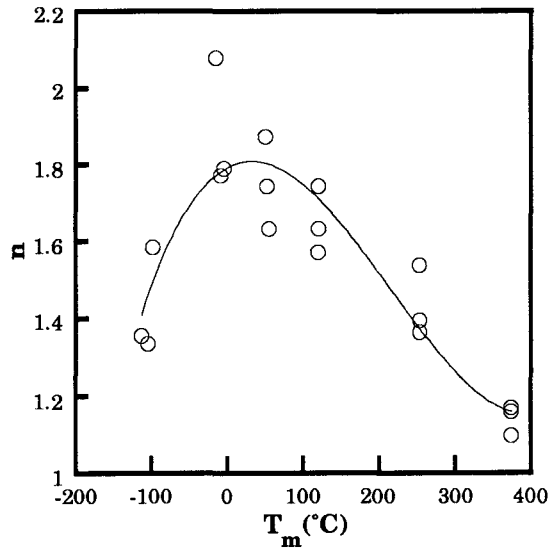

Figure 4. Variation of n plotted as a function T_m obtained for all the samples at various frequencies.

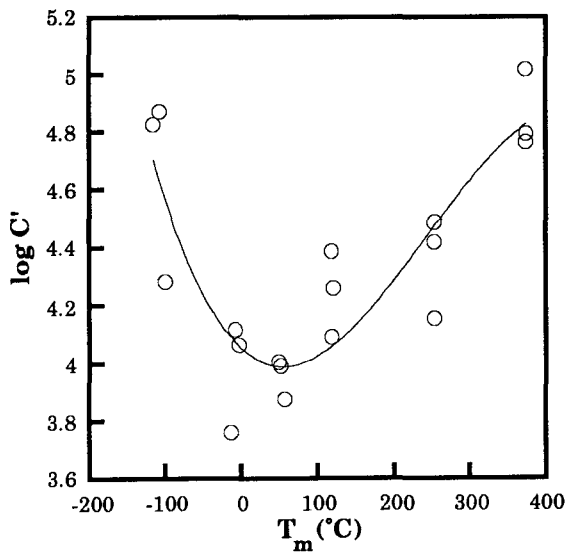

Figure 5. Variation of logC' plotted as a function of T_m obtained for all the samoles at various frequencies.

value of about 1.8 and the C' indicated the minimum value of about 4 near T_m=0°C. The n-T_m characteristics above T_m=0°C was the same results obtained in the systems, (1-x)PMN-xPT($0 \le x \le 1.0$) and $Pb_{1-y}La_{2y/3}TiO_3$ (PLT, $0 \le y \le 0.3$)[3], demonstrating that the values of n and C' continuously vary with T_m (thus with composition) without any specific fluctuation independent of the kind of elements in corporated into the lattice of lead titanate. The exact physical meaning of C' has not been clarified yet. On the other hand, the value of n is obviously an index indicating the broadness of the dielectric constant peak (thus the degree of diffuseness of phase transition) in these materials. Since the value of n continuously varies with T_m, as seen in Fig. 5, it is thus obvious that the diffuseness of the phase transitions the present materials continuously varies with the compositional change. Although the local compositional fluctuation model, proposed by Smolenskii[5], has been accepted as that which most appropriately interprets the origin of DPT, this model does not adequately interpret the experimental results shown in Figs.4 and 5, because the n depended on the T_m rather than the composition in the relaxor-normal ferroelectrics solid solution systems mentioned above. We are discussing a new model to interpret the continuous change of n with T_m shown in Fig.4.

4.Summary

The phase transition behavior in the system PNN-PT have been investigated by analyzing the dielectric constant-temperature characteristics above the Curie point in the materials. All the dielectric characteristics obtained for the materials were found to be described by the equation $(1/\varepsilon - 1/\varepsilon_m)^{1/n} = (T-T_m)/C'$ with constants n and C' continuously varying withcompositional change. Particularly, the value of n, by which the phase transition behavior is characterized, was confirmed to continuously vary from 1.0 to 1.8 above Tm=0°C. This result was consistent with the results in the systems, (1-x)PMN-xPT($0 \le x \le 1.0$) and $Pb_{1-y}La_{2y/3}TiO_3$ (PLT, $0 \le y \le 0.3$).

REFERENCES

1. V.V.Kirillov and V.A.Isupov, Feroelectrics 5 (1973) 3
2. L.E.Cross, Ferroelectrics 76 (1987) 241.
3. M.Kuwabara, S.Takahashi, K.Goda, K. Oshima and K.Watanabe, Jpn. J. Appl. Phys., 31 (1992) 3241
4. S.Takahashi, S.Miyao, S.Yoneda and M. Kuwabara, Jpn.J.Appl.Phys., to be published.
5. G.A.Smolenskii, Proc. 2nd Int. Meet. Ferroelectricity, J. Phys. Soc. Jpn., 28 (1970) Suppl.,26