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Journal of the European Ceramic Society 25 (2005) 2521–2525
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Dielectric properties of 1:1 ordered $Pb(Mg_{1/3}Ta_{2/3})O_3$ ceramics

Y.L. Wang*, S.S.N. Bharadwaja[1], A.K. Tagantsev, N. Setter

Ceramics Laboratory, Swiss Federal Institute of Technology (Lausanne) – EPFL CH-1015 Lausanne, Switzerland

Abstract

Thermally induced coarsening of the chemically ordered domains in $Pb(Mg_{1/3}Ta_{2/3})O_3$ (PMT) ceramics promotes the studying of dielectric behavior of the 1:1 B-cations ordered PMN-style complex perovskites. In this work, PMT ceramics with different degrees of chemical order were prepared, and their dielectric, and ferroelectric properties of disordered and ordered ceramics were studied as a function of temperature, frequency, and electrical field. It was found that the weak field relaxor nature is insensitive to the chemical order, whereas some non-linear behaviors showed ordering-degree dependence at the low temperature range.

Keywords: Dielectric properties; Ferroelectric properties; Perovskites

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) family relaxors, characterized by high dielectric and piezoelectric properties, have been widely studied both in terms of applications and theoretical view points during the past decades. In general, the compounds of this family have the formula of $Pb(B^{2+}_{1/3}B^{5+}_{2/3})O_3$ ($B^{2+} = Mg^{2+}$, Ni^{2+}, Zn^{2+}, etc, $B^{5+} = Nb^{5+}$, Ta^{5+}), and the sub-micro-scale heterogeneous distribution of the B-cations are believed to be the origin of their relaxor nature, typically having a diffuse and frequency-dependent maximum in the variation of relative permittivity with temperature.[1] It was found that in PMN-related materials there exist some chemical ordered nano regions that are dispersed in the disordered matrix.[2] Unlike some $Ba(B^{2+}_{1/3}B^{5+}_{2/3})O_3$ compounds, the ordered nano regions in PMN exhibit a 1:1 structure of $Pb(\beta'_{1/2}\beta''_{1/2})O_3$, where β' and β'' are arranged on a face-centered rock-salt structure with a doubled perovskite repeat unit.[2] The 1:1 chemical ordering of PMN-family materials can be modeled with a "random site" structure, where the β'' site is exclusively occupied by B^{5+} cation, whereas on β' site the B^{2+} and the remanent B^{5+} are randomly distributed. The ordered domain is overall electro-neutral, and can be generally formulated as $Pb([B^{2+}_{2/3}B^{5+}_{1/3}]_{1/2}B^{5+}_{1/2})O_3$. The "random site" model has been demonstrated by many recent investigations.[3,4]

It is well known that the 1:1 chemical ordering of different B-site cations in some complex perovskites plays an important role on the dielectric and ferroelectric characteristics. In $Pb(Sc_{1/2}Ta_{1/2})O_3$ related ceramics, perfect ordering of B-site cations usually leads to the suppression of the relaxor nature and gives rise to a ferroelectric phase transition,[5] whereas in $Ba(Mg_{1/3}Ta_{2/3})O_3$-based materials, the 1:1 ordering of the octahedron cations produces a great improvement in the microwave dielectric properties.[6] Davis reported that the relaxor nature was conserved even in highly ordered $Pb(Mg_{1/3}Ta_{2/3})O_3$-$PbZrO_3$ ceramics, and the weak field dielectric properties were quite insensitive to the chemical order degree as well as the ordered domain size because of the random distribution of cations on the β' sublattice.[7] The influence of the 1:1 chemical order on the high field non-linear behavior of PMN family perovskites, however, is not sufficiently reported. In this paper, the $Pb(Mg_{1/3}Ta_{2/3})O_3$-5% $PbZrO_3$ ceramics with different degrees of order are prepared using proper annealing procedures. The dielectric and ferroelectric properties are measured as a function of temperature, frequency and electrical field. The non-linear behavior at low

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* Corresponding author. Tel.: +41 21 6935805; fax: +41 21 6935805.
E-mail address: yongli.wang@epfl.ch (Y.L. Wang).

[1] Present address: 0143 Materials Research Laboratory, University Park, PA 16802, USA.

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doi:10.1016/j.jeurceramsoc.2005.03.094

temperature is found to be sensitive to the degree of chemical order of this system.

2. Experimental methods

Complex perovskite $Pb(Mg_{1/3}Ta_{2/3})O_3$-5% $PbZrO_3$ ceramics were prepared via a modified "columbite route". The stoichiometric quantities of the high purity (Aldrich, >99.5%) raw materials, $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, Ta_2O_5, and ZrO_2 were mixed and ball milled for 12 h, followed by a calcination at 1100 °C for 10 h. As-obtained trirutile powder (solid solution of ZrO_2 in $MgTa_2O_6$) was then mixed with PbO in molar ratio and subjected to a ball-milling of 24 h using isopropanal as the milling medium. The resultant mixture was calcinated at 800 °C for 2 h and then ball-milled for 12 h to obtain fine perovskite powder. Pellets with the size of 9 mm in diameter and 1 mm in thickness were dry pressed and sintered at 1230 °C for 2 h. Annealing treatments were then conducted at 1350 °C with different dwelling time of 16 and 64 h to control the order degree. An inverse crucible method was used to depress the lead volatility during high temperature procedures.

The phase content was monitored by powder XRD measurements (SIMENS KRISTALLOFLEX 805, Cu Kα, 40 kV, 35 mA) and conventional TEM (PHILIPS CM300-UT-FE). The order degree, *S*, is evaluated from the ratio of the observed superlattice reflection to the nearest base lattice reflection with the calculated ratio of corresponding intensities for perfect ordering:[8]

$$S=\left[\frac{(I_{1/2(1\,1\,1)}/I_{(0\,0\,1)})_{\text{observed}}}{(I_{1/2(1\,1\,1)}/I_{(0\,0\,1)})_{\text{calculated},S=1}}\right]^{1/2}\quad\text{and}$$

$$S=\left[\frac{(I_{1/2(3\,1\,1)}/I_{(1\,1\,1)})_{\text{observed}}}{(I_{1/2(3\,1\,1)}/I_{(1\,1\,1)})_{\text{calculated},S=1}}\right]^{1/2}\qquad(1)$$

The chemical ordered domain size was determined from the centered dark field TEM images that were collected using the (3/2 3/2 3/2) supercell reflection. The dielectric properties were measured as a function of temperature over the frequency range of 100 Hz–1 MHz under ac field level from 0.02 to 1.0 kV/cm, using a high precision LCR meter (HP4284A) and a computer-controlled environmental chamber (Delta 9023). High-field polarization measurement was conducted using a standard Sawyer-Tower ferroelectric test system.

3. Results and discussions

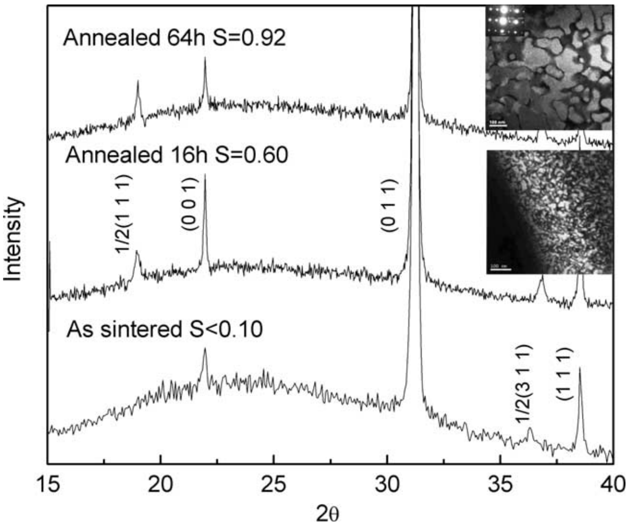

Fig. 1. XRD patterns and related chemical ordered domains for PMT-PZ (5%) ceramics with different annealing time, the centered dark field TEM images were collected using the (3/2 3/2 3/2) supercell reflection.

Table 1
Dielectric properties of PMT-PZ (5%) samples with different order degrees

Sample	AS	A16	A64
Order degree *S*	∼0.1	0.60	0.92
Ordered domain size (nm)	∼3–5	∼30	∼150
T_m at 1 kHz (°C)	−75	−79	−81
ε'_m at 1 kHz	8548	7438	6590
Diffuseness index γ	1.949	1.898	1.880
ΔT_m (100 Hz–1 MHz) (°C)	24.5	26.9	25.7
$\Delta\varepsilon'_m/\varepsilon'_m$ (100 Hz–1 MHz)	22%	20%	23%

Ceramics with different degrees of order and ordered domain sizes were obtained by high temperature annealing method. The *S* value increases from ∼0.10 for the as-sintered samples (AS) to 0.92 for 64 h annealed ones (A64). The chemical ordered domain size also increases with the annealing time, as is showed in Fig. 1 and summarized together with the related dielectric properties in Table 1. Fig. 2 shows the real part of the relative permittivity varying as a function of temperature for the PMT-PZ (5%) ceramics. The

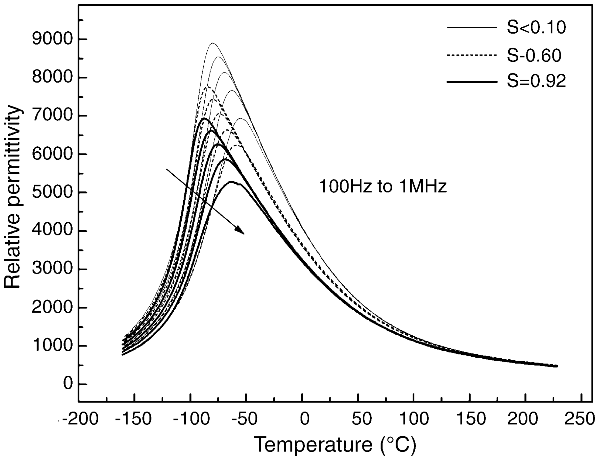

Fig. 2. The temperature and frequency dependence of the relative dielectric permittivity of PMT-PZ (5%) ceramics under weak field of 0.01 kV/cm.

tendency is similar to that reported by Davis et al., although the real permittivity is some 35% higher. Typical relaxor behavior, the diffuse and frequency dependent dielectric constant maximum, is apparent for samples with different chemical order degrees. The maximum dielectric constant, $\varepsilon_{\max}$ and the corresponding temperature, T_{m}, apparently decrease with the order degree. The diffuseness degree of the relaxor phase transition, characterized by the parameter of γ, was evaluated via fitting the ε'–T curve over the temperature range of ($T > T_{\mathrm{m}}$) with the modified Curie-Weiss law:[9]

$$\frac{1}{\varepsilon'} = \frac{1}{\varepsilon'_{\max}} + \frac{(T - T_{\mathrm{m}})^{\gamma}}{C} \tag{2}$$

where C is the Curie constant. The diffuseness index γ also shows a slight decrease with the order degree (from 1.949 to 1.880). It is noticeable that at a fixed frequency, the ε'–T curves merge with each other both at high temperature range and at low temperature range. At temperatures higher than ~160 °C, the variation of dielectric constant on temperature follows the Curie-Weiss law. Fig. 3 plots the reciprocal real part of the dielectric permittivity at temperatures above T_{m}. The Curie-Weiss constant (C_{cw}) and the Curie-Weiss temperature (T_0) are determined as 1.05×10^5 K and 35 °C, respectively, by linear fitting of the curve over high temperature range. At the temperature of about 160–170 °C, the relative dielectric constant deviates from the Curie-Weiss law, and the deviation temperature for different samples is not the same. The higher order degree corresponds to the higher deviation temperature.

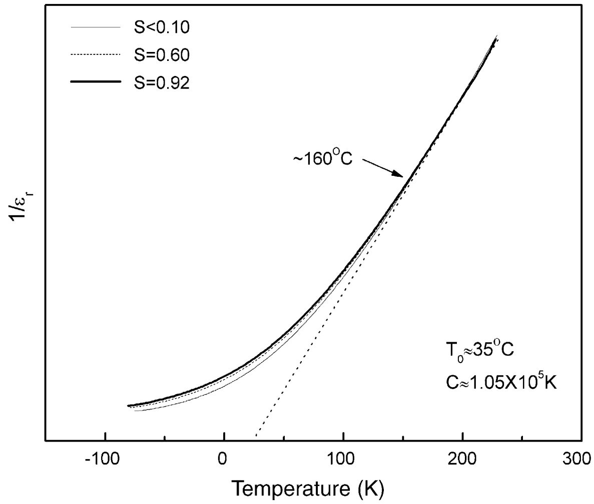

Fig. 3. The reciprocal real part of the dielectric permittivity at temperatures above T_{m}.

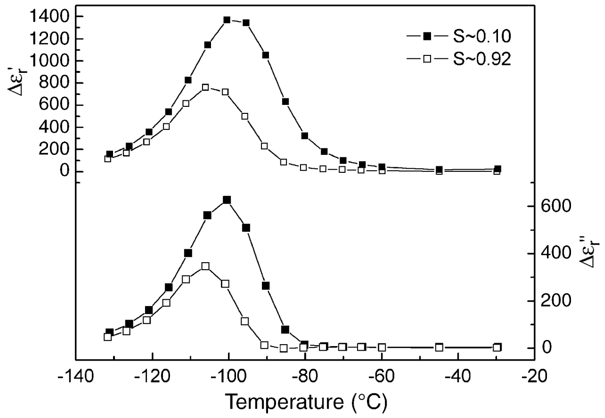

Fig. 4. The temperature dependence of the difference in dielectric permittivity when measured with 0.02 and 1.0 kV/cm ac fields ($\Delta\varepsilon'_{\mathrm{r}} = \varepsilon'_{\mathrm{r}}$(1.0 kV/cm)–$\varepsilon'_{\mathrm{r}}$(0.02 kV/cm)).

The dielectric properties under different ac fields (from 0.02 to 1.0 kV/cm) were also measured as a function of temperature. Fig. 4 shows the temperature dependence of the variation of the dielectric permittivity under different measuring ac signals ($\Delta\varepsilon'_{\mathrm{r}} = \varepsilon'_{\mathrm{r}}(1.0\,\mathrm{kV/cm})$–$\varepsilon'_{\mathrm{r}}(0.02\,\mathrm{kV/cm})$). For both ordered and disordered samples, the ac field dependence of the dielectric permittivity evidenced in the frequency dispersive regime, resembles that in PMN single crystal.[10] The change of the dielectric permittivity under different measuring ac field, both in real and imaginary part, is substantially stronger for disordered samples than that for highly ordered ones. Reasonably one might ascribe the large difference in $\Delta\varepsilon'_{\mathrm{r}}$ to the difference of relative dielectric constant between the ordered and disordered samples, according to the non-linear behavior of the ferroelectric relaxors:[10,11]

$$\Delta\varepsilon'_{\mathrm{ac}} = -\frac{3}{4}\beta\varepsilon_{\mathrm{s}}^4\varepsilon_0^3E_{\mathrm{m}}^2 \tag{3}$$

where ε_{s} is the linear static dielectric permittivity of the materials and $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m, E_{m} is the ac field strength using in measurement and β non-linear coefficient. However, it is not the exact case for the present results: at the temperature of around −105 °C, the difference in linear static dielectric constant is quite small (~5%), whereas the value of $\Delta\varepsilon'_{\mathrm{r}}$ shows a maximum difference between two samples; in contrast, at a higher temperature (−75 °C), the maximum difference in ε_{s} (~36%) corresponds to a smaller variation of $\Delta\varepsilon'_{\mathrm{r}}$ for ordered and disordered samples. Fig. 5 illustrate the ac field dependence of the dielectric permittivity for disordered samples at several typical temperature points. Similar behaviors are also observed for ordered samples (not shown). The dielectric permittivity non-linear nature of the PMT ceramics is quite different below and over the temperature point that corresponds to the maximum $\Delta\varepsilon'_{\mathrm{r}}$. At low temperature interval (lower than −100 °C), the value of $\Delta\varepsilon'_{\mathrm{r}}$ and $\Delta\varepsilon''_{\mathrm{r}}$ are quadratically related with the measuring ac signal ($\Delta\varepsilon'_{\mathrm{r}} \propto E_{\mathrm{m}}^2$). With the increase of temperature, this relationship deviates from the quadratic form and an inflection point appears on the curve at the field value of around 0.6 kV/cm. The quadratic relation is conserved only at low field regime (0.02 to 0.2 kV/cm). This transformation is qual-

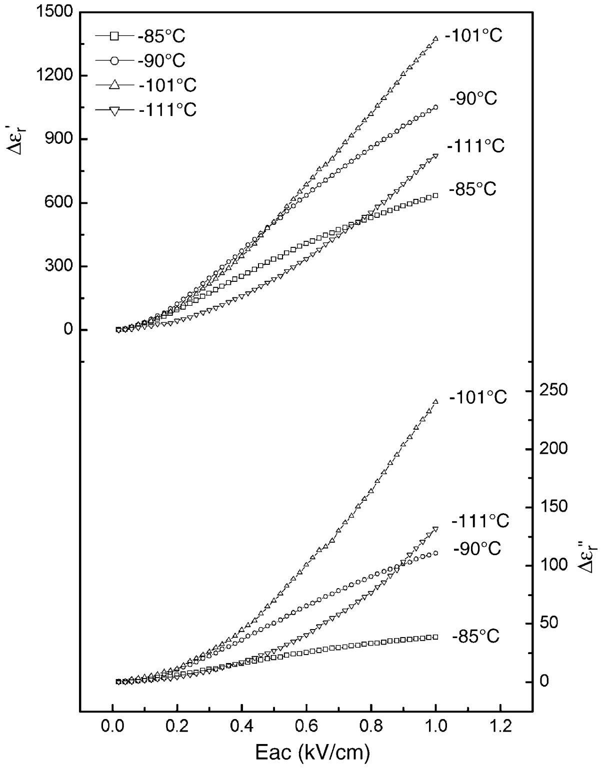

Fig. 5. ac Field dependence of the dielectric permittivity at different temperatures.

itatively consistent with the non-linear behavior of PMN single crystal reported in Ref. [10] where one exponent equation, $\Delta\varepsilon_r' \propto E_m^{\xi}$, was adopted to fit the change of $\Delta\varepsilon_r'$ on measuring ac field. The exponent ξ was found to undergo a crossover from 1.2 to 1.9 over the frequency dispersive regime when cooling, and the corresponding mechanism was interpreted with the "breathing" model. Apparently it is insufficient to fit the present $\Delta\varepsilon_r'(E_m)$ curves with a single exponent equation, and more complicated relation seems to respond for the non-linear behavior of PMT-PZ (5%) ceramics. Additionally, the non-linearity of the dielectric permittivity exhibits higher sensitivity on the chemical order of PMT-PZ (5%) than other dielectric properties do, and more extensive research is necessary to clarify this point.

The static field dependent properties of the PMT-PZ (5%) ceramics were also measured as a function of temperature during a cooling cycle. For samples with different order degree, the hysteresis loops are always typical of those observed in relaxors (Fig. 6a) and exhibit little difference. At temperatures higher than T_m, the polarization is a single-valued nonlinear function of the electrical field, which changes to tilted loops below T_m. The hysteresis loops become more rectangular with the further decrease of temperature, but the real rectangular loop does not appear even at the lowest temperature (−165 °C) of our measurement. Correspondingly the remanent polarization increases with the lowering of the temperature over a broad range, experimentally from $T_m - 10$ to $T_m - 90$ °C, and no limit seems emerge at the lowest temperature points, as is illustrated in Fig. 6b.

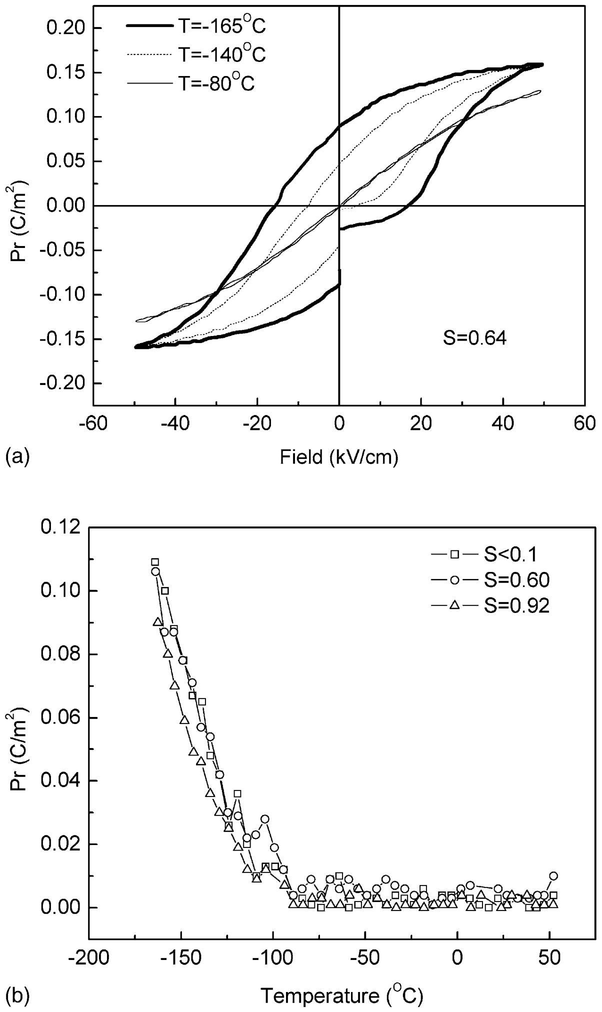

Fig. 6. The hysteresis loops measured at different temperatures (a) and the temperature dependence of the remanent polarization (b).

4. Conclusions

All PMT-PZ(5%) ceramic samples show typical weak field relaxor behavior regardless of their different order degrees. The relative dielectric permittivity maximum, the corresponding temperature T_m, and the diffuseness index of the DPT decrease with the order degree. Over the temperature interval of frequency dispersion, the dielectric permittivity exhibits strong dependence on the measuring ac field. The $\Delta\varepsilon_r'(E_m)$ curve follows a quadratic relation at temperatures lower than −100 °C, whereas it strongly deviates from this form at higher temperature. The non-linearity of the dielectric permittivity is found to be sensitive to the chemical order of PMT-PZ (5%) ceramics, although the corresponding mechanism is not yet clear. More extensive research is necessary to clarify this point.

Acknowledgements

This work was supported by the Swiss Federal Office of Science and Technology (COST 525 program). The authors would like to acknowledge Dr. M. Cantoni and Dr. D. Su for the TEM observation on the chemical ordered domains.

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