

# Dielectric properties of 1:1 ordered $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ ceramics

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## Abstract

Thermally induced coarsening of the chemically ordered domains in  $\text{Pb}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$  (PMT) ceramics was recently reported to support the “random site” model rather than the “space charge” model for the B-site cation ordering in PMN-related complex perovskite relaxors. However, a systematic comparison of the dielectric behavior of the ordered and disordered material has not yet been reported. In this work, PMT ceramics with different degrees of order were prepared by appropriate heat treatment, and their ordering state was characterized by XRD and TEM observation. The dielectric, and ferroelectric properties of disordered and ordered ceramics are 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 behavior showed an ordering-degree dependence at low temperature range.

*Keywords: B. X-ray methods; C. Dielectric properties; C. Ferroelectric properties*

## 1. Introduction

$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (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  $\text{Pb}(\text{B}_{1/3}^{2+}\text{B}_{2/3}^{5+})\text{O}_3$  ( $\text{B}^{2+} = \text{Mg}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$ , etc,  $\text{B}^{5+} = \text{Nb}^{5+}, \text{Ta}^{5+}$ ), and the sub-micro-scale heterogeneous distribution of the divalent and pentavalent cations are believed to be the origin of their relaxor nature, typically having a the diffuse and frequency-dependent maximum in the variation of relative permittivity with temperature<sup>1,2</sup>. It was found that in PMN-related materials there exist some chemical ordered nano regions that are dispersed in the disordered matrix<sup>3</sup>. Unlike some  $\text{Ba}(\text{B}_{1/3}^{2+}\text{B}_{2/3}^{5+})\text{O}_3$  compounds, the ordered nano regions in PMN exhibit a 1:1 structure of  $\text{Pb}(\beta'_{1/2}\beta''_{1/2})\text{O}_3$ , where  $\beta'$  and  $\beta''$  are arranged on a face-centered rock-salt structure with a doubled perovskite repeat unit<sup>2</sup>. The 1:1 chemical ordering of PMN-family materials can be modeled with a “random site” structure, where the  $\beta''$  site is exclusively occupied by  $\text{B}^{5+}$  cation, whereas on  $\beta'$  site the  $\text{B}^{2+}$  and the remanent  $\text{B}^{5+}$  are randomly distributed. The ordered domain is overall electro-neutral, and can be generally

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formulated as  $Pb([B_{2/3}^{2+}B_{1/3}^{5+}]_{1/2}B_{1/2}^{5+})O_3$ . The “random site” model has been demonstrated by many recent investigations<sup>4-6</sup>.

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<sup>7, 8</sup>, 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<sup>8</sup>. 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  $\beta'$  sublattice<sup>10, 11</sup>. 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 different annealing procedure. The dielectric and ferroelectric properties are measured as a function of temperature, frequency and electrical field. The non-linear behavior at low 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 12h, followed by a calcination at 1100°C for 10h. 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 24h using isopropanol as the milling medium. The resultant mixture was calcinated at 800°C for 2h and then ball-milled for 12h to obtain fine perovskite powder. Pellets with the size of 9mm in diameter and 1mm in thickness were dry pressed and sintered at 1230°C for 2h. Annealing treatments were then conducted at 1350°C with different dwelling time of 16h and 64h 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,  $CuK\alpha$ , 40kV, 35mA) 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<sup>12</sup>:

$$S = \left[ \frac{(I_{1/2(111)}/I_{(001)})_{observed}}{(I_{1/2(111)}/I_{(001)})_{calculated,S=1}} \right]^{\frac{1}{2}} \quad \text{and} \quad S = \left[ \frac{(I_{1/2(311)}/I_{(111)})_{observed}}{(I_{1/2(311)}/I_{(111)})_{calculated,S=1}} \right]^{\frac{1}{2}} \quad (1)$$

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 100Hz-1MHz under ac field level from 1 to 40V/mm, using a high precision LCR meter (HP4284A) and an computer controlled environmental chamber (Delta 9023). High-field polarization measurement was conducted using a standard Sawyer-Tower ferroelectric test system.

### 3. Results and discussions

Ceramics with different order degrees 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 64h 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 Tab. 1. Fig. 2 (a) shows the real part of the relative permittivity varying as a function of temperature for the PMT-PZ (5%) ceramics. The 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,  $\epsilon_{max}$  and the corresponding temperature,  $T_m$ , apparently decrease with the order degree. The diffuseness degree of the relaxor phase transition is characterized by the parameter of  $\gamma$ , which can be evaluated via fitting the  $\epsilon'$ -T curve over the temperature range of ( $T > T_m$ ) with the modified Curie-Weiss law<sup>13</sup>:

$$\frac{1}{\epsilon'} = \frac{1}{\epsilon'_{max}} + \frac{(T - T_m)^\gamma}{C} \quad (2)$$

where C is the Curie constant. The diffuseness index  $\gamma$  also shows a decrease with the order degree (from 1.949 to 1.880). It is noticeable that at a fixed frequency, the  $\epsilon'$ -T curves merge with each other both at high temperature range and at low temperature range, as illustrated in Fig. 2 (b). At temperatures higher than ~430K, 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  $1.05 \times 10^5 \text{K}$  and  $308 \text{K}$ , respectively, by linear fitting of the curve over high temperature range. At the temperature of about  $430\text{-}440 \text{K}$ , 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.

The dielectric properties under different ac fields (from  $0.01 \text{kV/cm}$  to  $0.4 \text{kV/cm}$ ) were also measured as a function of temperature. The non-linearity behavior is evident for all samples especially in the frequency-dispersive regimes. Resembling PMN, the variation of relative dielectric constant on ac field strength can be fitted using a power function:  $\Delta\epsilon' \propto E^\xi$ <sup>14</sup>. The  $\xi$  value also undergoes a step-like change from  $\sim 1.1$  at temperatures above  $T_m (-70^\circ\text{C})$  to  $\sim 1.8$  at temperature around  $T_m - 40 \text{K}$  ( $\sim -110^\circ\text{C}$ ), and the change with temperature exhibits a weak dependence on the chemical order degree, as is illustrated in Fig. 4. At temperatures lower than  $-110^\circ\text{C}$ , the field dependence of the dielectric constant deviates from the power function and one negative minimum appears on the  $\Delta\epsilon'$ - $E$  curve. It is interesting that the negative minimum of the relative dielectric constant and the corresponding ac field strength is order-degree sensitive. For the highly ordered sample, the dielectric constant minimum emerges at about  $-117^\circ\text{C}$ , whereas for the disordered sample it does not appear until the temperature is lowered to  $-155^\circ\text{C}$  (Fig. 5 c). It is also apparent that the higher order degree corresponds to the more apparent dielectric constant minimum and higher ac field strength to reach the minimum (Fig. 5 b, c). The low temperature non-linearity of present PMT-PZ system is quite different from that for PMN ceramics, of which the negative minimum of dielectric permittivity varying on ac field strength is not yet reported. Another point is that over the low temperature range the relative dielectric permittivity for the samples with different degrees of order is provided with almost the same value. Therefore the order degree sensitivity of the non-linear behavior cannot be ascribed to the possible difference in the ensemble dielectric response. That means although that while the weak field relaxor behavior shows little change on the chemical ordering, the non-linearity of the considered system, especially at very low temperatures, is significantly affected. The emerging of the dielectric minimum suggests that there exist an unknown competitive mechanism that controls the dielectric response to the ac field, and the chemical ordering of B-site cations can influence this competition. More extensive investigations are needed to understand this point.

The 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. 6 a) and exhibit little difference. At temperatures higher than  $T_m$ , the polarization is a

single-valued non-linear 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 (108K) of our measurement. Correspondingly the remanent polarization increases with the lowering of the temperature over a broad range, experimentally from  $T_m-10K$  to  $T_m-90K$ , and no limit seems emerge at the lowest temperature points, as is illustrated in Fig. 6 (b).

## **5. Conclusions**

All PMT-PZ(5%) ceramic samples show typical weak field relaxor behavior in spite 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. The dielectric non-linearity, characterized by the exponent  $\xi$ , exhibits ignorable difference between different samples at frequency dispersion regime. However at lower temperatures, a negative minimum appears on the  $\Delta\epsilon'-E$  curve, and the dielectric minimum is sensitive to the temperature and the degree of chemical order: the higher order degree and lower temperature lead to lower dielectric minimum and higher corresponding ac field strength. The minimum of the relative dielectric permittivity suggests an unknown competitive mechanism that controls the dielectric response of the considered system. More extensive research is needed to clarify this point.

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

| Sample                                                       | AS         | A16       | A64        |
|--------------------------------------------------------------|------------|-----------|------------|
| Order degree $S$                                             | $\sim 0.1$ | 0.60      | 0.92       |
| Ordered domain size (nm)                                     | $\sim 3-5$ | $\sim 30$ | $\sim 150$ |
| $T_m$ at 1kHz (K)                                            | 197.9      | 193.9     | 192.3      |
| $\epsilon'_m$ at 1kHz                                        | 8548       | 7438      | 6590       |
| Diffuseness index $\gamma$                                   | 1.949      | 1.898     | 1.880      |
| $\Delta T_m(100\text{Hz}-1\text{MHz})(\text{K})$             | 24.5       | 26.9      | 25.7       |
| $\Delta \epsilon'_m / \epsilon'_m(100\text{Hz}-1\text{MHz})$ | 22%        | 20%       | 23%        |

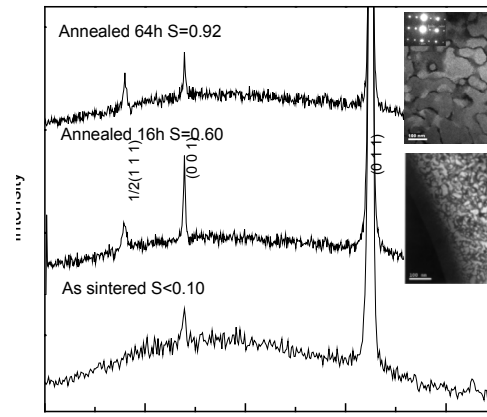


Fig. 1 XRD patterns and related chemical ordered domains for PMT-PZ (5%) ceramics with different annealing time, the centered dark field TEM images were collected using the  $(\frac{3}{2} \frac{3}{2} \frac{3}{2})$  supercell reflection

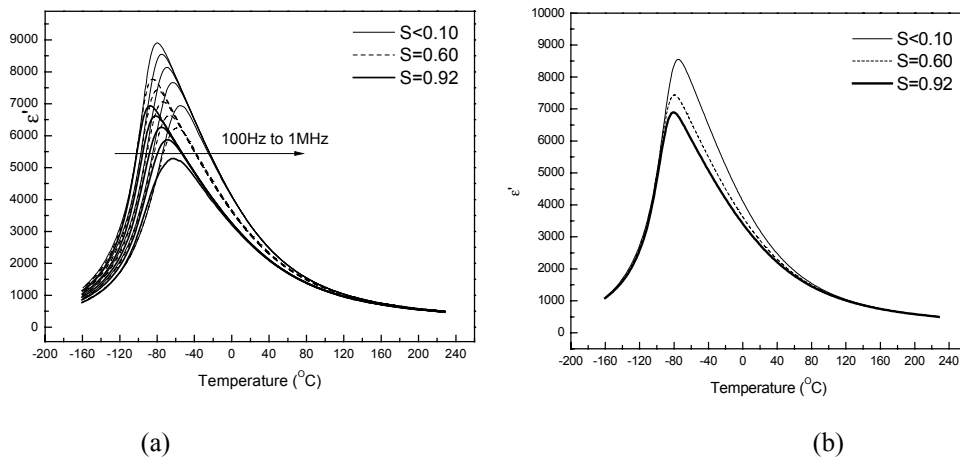


Fig. 2 The temperature and frequency dependence of relative dielectric permittivity of PMT-PZ (5%) ceramics under weak field of 1V/mm; (b) is extracted from (a) with the fixed frequency of 1kHz

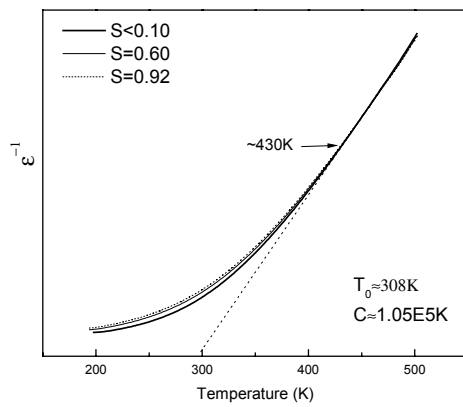


Fig. 3 The reciprocal real part of the dielectric permittivity at temperatures above  $T_m$

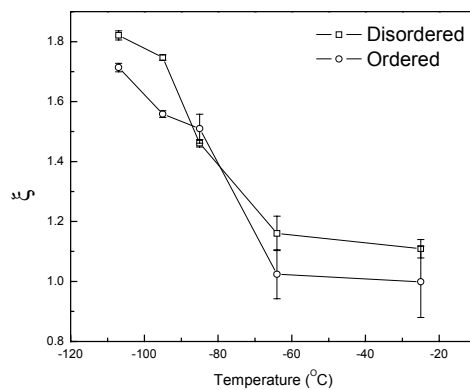


Fig. 4 Temperature dependence of exponent  $\xi$  corresponding to the fit of  $\Delta\epsilon' \propto E^\xi$



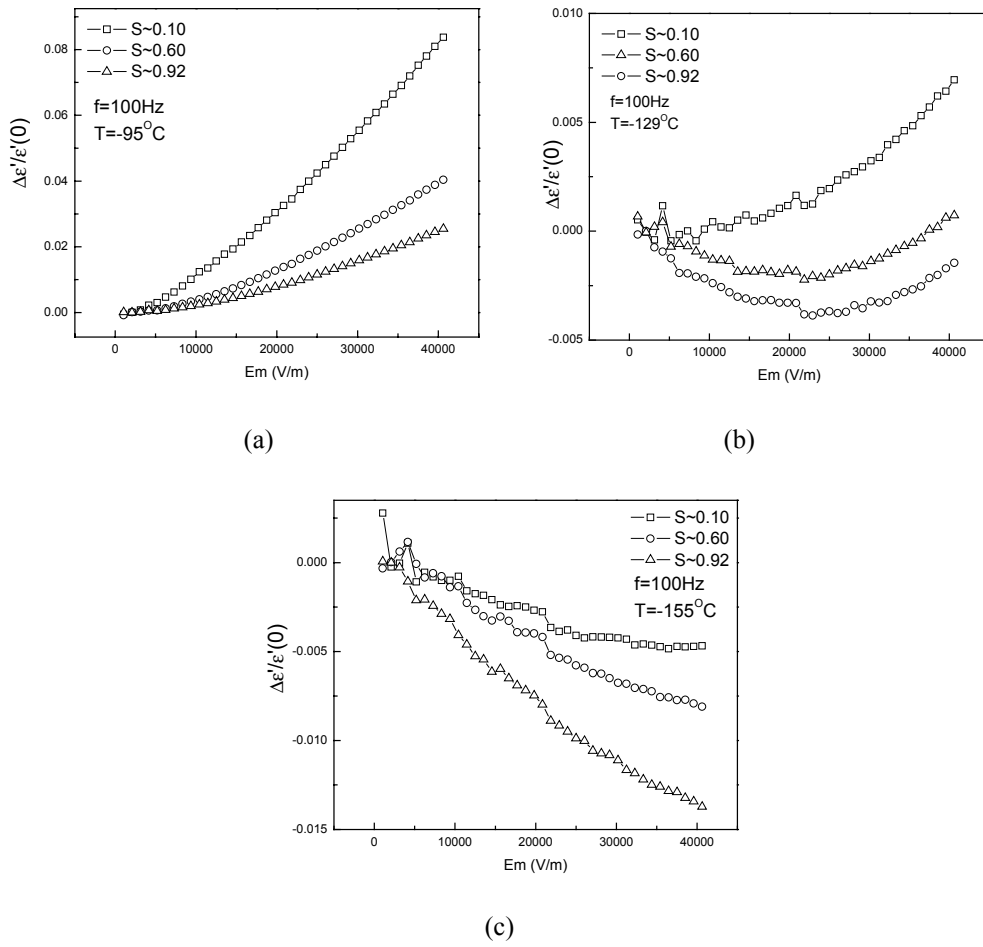


Fig. 5 ac field dependence of the dielectric permittivity at different temperatures

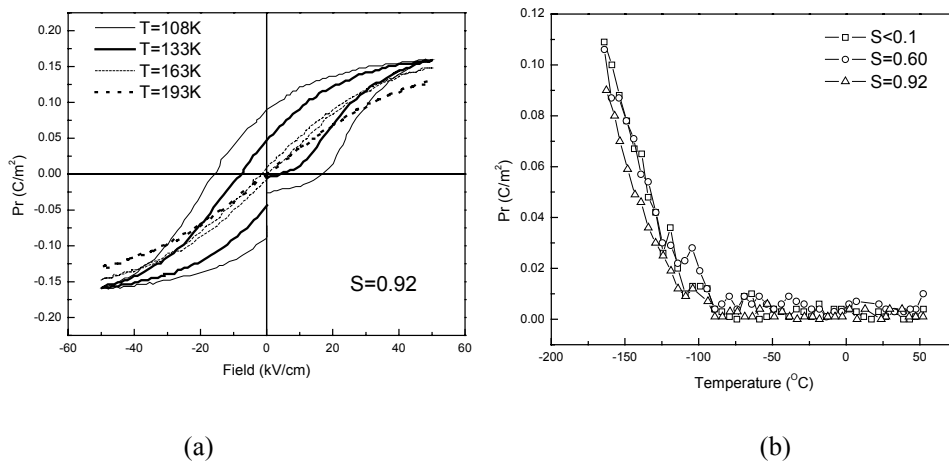


Fig. 6 The hysteresis loops measured at different temperatures (a) and the temperature dependence of the remanent polarization (b)