Relaxor behavior and Raman spectra of CuO-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ ferroelectric ceramics

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Abstract: In this work, Raman spectra and dielectricity–temperature dependence measurements were used to investigate the *B*-site order degree in CuO-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ ferroelectric ceramics. The measurement results indicated a typical relaxor characteristic for all samples. With the increasing of CuO doping content, the *B*-site order degree increased first and then decreased. However, the frequency dispersion and the relaxation degree decreased first and then increased while the CuO addition content was increasing, which was thought to be strongly correlated with the variations of the *B*-site order. The opposite variation tendency of the *B*-site order degree and the relaxation degree revealed that the phase transition dispersity is closely related to the order–disorder behaviors.

Keywords: relaxor ferroelectrics; dielectric properties; Raman spectra

1 Introduction

Lead magnesium niobate $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) based relaxor ferroelectrics have attracted extensive attention for their high permittivity, low temperature sensitivity, considerable electrostriction effects and slender hysteresis loops. They have been applied in many areas, such as multilayer ceramic capacitors (MLCC), high-energy pulsed power capacitors, electro-optic devices, micrometric displacement actuators, ferroelectric memories, and so on [1–3]. However, there are some disadvantages existing in such materials, such as high sintering temperature (about 1200 °C), low phase transition temperature (–12 °C, 1 kHz), high dielectric loss at negative

temperature, low breakdown strength, and difficulty to realize industrial production. At present, the main modifying method is solid solution doping.

It is easy for PMN and PbTiO_3 (PT) to form $(1-x)\text{PMN}-x\text{PT}$ (PMNT) solid solution. The relaxor behavior does not disappear until near the morphotropic phase boundary [4]. The relaxor characteristic of PMN has been carefully investigated on a consideration of atomic relaxation vibration, desiring to obtain giant dielectric response [5]. The effects of rear-earth doping and mixing with normal ferroelectrics on the relaxor characteristic have been intensively studied, which is aimed to improve the phase transition dispersivity and electrical properties [6,7]. In addition, PbO volatilizes seriously at the sintering temperature (~1200 °C) and oxygen vacancies are formed. Those defects not only make the ceramic composition deviate from stoichiometric ratio and deteriorate the properties [8], but also pollute the

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environment and waste energy. Therefore, it is significant to lower the sintering temperature and improve the electrical properties of PMN ceramics [9]. It is implied that doping can improve the properties of PMN ceramics. Wen *et al.* [10] found that in the case of PMNT ceramics co-doping with La^{3+} and Zn^{2+} , the degree of order-disorder is remarkably increased, and when 2 mol% La^{3+} and 3 mol% Zn^{2+} are co-doped, the maximal relative dielectric constant change decreases from 70% to 23% at 1 kHz (1000 V/mm). Gao *et al.* [11] prepared $\text{Zn}^{2+}/\text{Li}^{+}$ -doped PMNT ceramics, and found that the Curie temperature and dielectric constant decrease, but the ceramic with the Z/L ratio of 1:1 and the amount of 1 wt% has excellent piezoelectric properties. Li *et al.* [12] reported that temperature dependent diffusive dielectric loss peaks as a doping effect are found for Mn-doped PMNT. In addition, CuO is also one of important dopants and its function is superior to others'. Chou *et al.* [13] and Zhao *et al.* [14] reported that CuO doping not only improves the dielectric properties, but it also lowers the sintering temperature of BNT and KNN-LNS ceramics, respectively. However, there are only few works concerned with the properties and Raman spectra of the CuO singly doped PMNT system. Recently, CuO addition was found to be useful for lowering sintering temperature of PMN based ceramics [15,16].

In this work, the CuO-doped PMNT ceramics were prepared by the columbite method [17]. Their microstructures, dielectric properties, phase transition dispersion and B-site order, together with the influence of CuO doping on above features, were all investigated.

2 Experiment

The starting materials were high-purity oxide powders: yellow lead oxide (PbO), niobium oxide (Nb_2O_5), magnesium oxide (MgO), titanium dioxide (TiO_2) and cupric oxide (CuO). The experiments in this paper were based on the composition of $0.94\text{PMN}-0.06\text{PT}-x\text{CuO}$ ($x=0, 0.015, 0.03, 0.06$), defined as PMNT, PMNT1, PMNT2 and PMNT3, respectively. Preparing samples contained the following steps. First, PbO and TiO_2 powders were used to synthesize PT. Next, PMNT powders were obtained using the columbite method [17], which involved mixing and batching (800 °C) MgO, Nb_2O_5 , PbO, PT and CuO powders.

Finally, the powders with 5 wt% PVA solution as binder were pressed into pellets with 30 mm in diameter and 5 mm in thickness. The pellets were sintered at different temperatures (1050–1200 °C) for 2 h in air.

A scanning electron microscope (SEM, Hitachi TM-1000) was used to observe the micro-morphology. The phase identification of the samples was performed using a X-ray diffractometer (XRD, Rigaku D/max-RB). The Raman spectrum measurements were carried out using a Renishaw Ramanor InVia spectrometer. The temperature dependence of dielectricity was measured using an Agilent 4284A LCR meter.

3 Results and discussion

Figure 1 shows a dense section morphology for all samples. With the increasing of CuO content, the sintering temperature is gradually reduced and the particle size becomes uniform and fine. The indexed planes in Fig. 2 indicate that there is only perovskite phase for all samples. The XRD data illustrates that the CuO doping causes a shifting of diffraction peaks, which indicates a lattice distortion in doped samples. It is possible that the Cu ions incorporate into the lattice and lead to the distortion. As well known, metal cations prefer to take the place of the ions with similar electrovalence and radius. CuO doping makes the cell bigger because Cu^{+} ions (radius ~ 0.77 Å) take the place of Mg^{2+} ions (radius ~ 0.72 Å). The electron configurations of Cu^{+} and Cu^{2+} are $3s^23p^63d^{10}$ and $3s^23p^63d^9$, respectively. According to Hund's rules, a completely filled d orbit is relatively stable, so Cu^{+} ion is more stable than Cu^{2+} ion. In fact, CuO will decompose into Cu_2O when the temperature reaches 1273 K [18]. As can be seen from Fig. 3, the binding energy of Cu 2p is significantly decreased, which indicates that the dispersion of CuO into the lattice is increased [19]. In addition, from the peak position and shape, the peak of the sample binding energy is superimposed from the peak of Cu^{+} and Cu^{2+} ions, the intensity of the peak spectrum is remarkably lower, and the peak area of Cu^{2+} ion can also be seen lower than that of Cu^{+} ion simultaneously. This shows that the content of Cu^{2+} ion is relatively lower compared with that of Cu^{+} ion, and the possibility that Cu^{+} ion occupies the lattice grid of Mg^{2+} is greater than that of Cu^{2+} . As a result,

Fig. 1 SEM section images of PMNT- x CuO ceramics: (a) $x=0$ (1200 °C); (b) $x=0.015$ (1080 °C); (c) $x=0.03$ (1050 °C); (d) $x=0.06$ (1050 °C).

Fig. 2 XRD patterns of PMNT- x CuO ceramic powders: (a) $x=0$; (b) $x=0.015$; (c) $x=0.03$; (d) $x=0.06$.

Cu^+ exists stably at sintering temperature (1323–1473 K), and an unequivocal replacing affects the structural ordering. The effect of ion replacement

on the B -site order is also investigated with Raman analysis.

Figure 4 shows the Raman spectra of all ceramic samples. The characteristic peaks in Fig. 4 and the corresponding peak positions are listed in Table 1. Compared with non-doped sample, frequency shift is found on the doped samples. Especially, the frequency of peak C decreases at first and then increases. For PMN based ferroelectrics, 260 cm^{-1} , $500\text{--}600\text{ cm}^{-1}$ and 780 cm^{-1} wave numbers are related to O–B–O bending modes (peak A), Nb–O–Nb stretching modes (peak B) and Nb–O–Mg bending modes (peak C, named A_{1g} mode), respectively [20].

Peak A around 260 cm^{-1} (as shown in Fig. 4 and Table 1) originates from O–B–O bending modes. The frequency shift in Raman spectra reveals that the O–B–O bending vibration is affected when CuO is introduced. Cu^+ ions could increase the composition fluctuation on B -sites, resulting in a change on B -site polarity.

Fig. 3 XPS spectra of Cu 2p of CuO-doped PMNT ceramics.

Fig. 4 Raman spectra of PMNT-*x*CuO ceramics.

Table 1 Raman spectrum peaks of PMNT-*x*CuO ceramics

Sample	<i>x</i>	Peak A (cm ⁻¹)	Peak B ₁ (cm ⁻¹)	Peak B ₂ (cm ⁻¹)	Peak C (cm ⁻¹)
PMNT	0	270	512	592	788
PMNT1	0.015	272	503	589	785
PMNT2	0.03	273	506	587	783
PMNT3	0.06	275	507	583	787

Nb–O–Nb stretching modes, originating from the polarization displacement of Nb⁵⁺ ion in oxygen octahedron [21], are corresponding with the peak B in Fig. 4. The peak B does not split when the temperature is above 77 °C. Below 77 °C, peak B will split into peaks B₁ and B₂ (500–600 cm⁻¹) [20]. After CuO

doping, the variations of peaks B₁ and B₂ indicate that CuO doping has an apparent effect on the Nb–O–Nb stretching modes.

Peak C around 780 cm⁻¹ is caused by the Nb–O–Mg bending modes (A_{1g} modes). The A_{1g} modes are similar to free oxygen octahedron vibration modes, related to the nano-ordered region in space group *Fm3m*. As an effective indicator of *B*-site order, the A_{1g} modes reflect the change of oxygen octahedron in perovskite structure.

There are two different models: the space charge model and the random layer model, used to study PMN Raman behaviors [22]. In the space charge model, B^I and B^{II} sublattices are occupied by Mg²⁺ and Nb⁵⁺, respectively. Nanoscale ordered regions emerge with a local Mg²⁺/Nb⁵⁺ ratio of 1:1, instead of the 1:2 stoichiometry at *B*-site. Then a super structure of [Pb²⁺(Mg²⁺_{1/2}Nb⁵⁺_{1/2})O₃²⁻]^{-0.5} with negative charge forms, which is twice bigger than the normal lattice period. This will prevent the growth of ordered structure because of unbalanced charges. In the random layer model, the *B*-site 1:1 ordered structure is corresponding to Pb[(Mg²⁺_{2/3}Nb⁵⁺_{1/3})_{1/2}Nb⁵⁺_{1/2}]O₃ stoichiometry, and the B^I and B^{II} sublattices are occupied by Mg²⁺/Nb⁵⁺ and Nb⁵⁺, respectively. Thus the ordered regions are consistent with the 1:2 stoichiometry. Jiang *et al.* [23] employed a simple harmonic oscillator model to discuss the effect of *B*-site order on A_{1g} mode frequency ω :

$$\omega = \sqrt{k/m^*} \quad (1)$$

where k represents the force constant related to the O–O and O–B band strengths; m^* is the reduced mass of this mode. In the random layer model, the space group of PMN is explained by the stoichiometry of $\text{Pb}[(\text{Mg}_{2/3}\text{Nb}_{1/3})_{1/2}\text{Nb}_{1/2}]\text{O}_3$. B^{I} sublattice represents $2/3\text{Mg}^{2+} + 1/3\text{Nb}^{5+}$, and its average atomic mass is 47, while B^{II} sublattice represents Nb^{5+} with atomic mass of 93. In this work, the distribution of $\text{Mg}^{2+}/\text{Nb}^{5+}$ on B -site is changed by Cu^+ doping. The introduction of Cu^+ ions leads to Nb^{5+} entering B^{I} sublattice when a little amount of CuO is doped, which would increase the m^* value and B -site order. The decrease of A_{1g} mode frequency in PMNT1 and PMNT2 is related to the increase of m^* value (Table 1). However, the A_{1g} mode frequency increases when excessive CuO is doped, because the replacement of Mg^{2+} by Cu^+ makes the composition deviate from stoichiometry of $\text{Mg}^{2+}:\text{Nb}^{5+} = 1:2$. This serious unbalanced stoichiometry also prevents Nb^{5+} entering B^{I} sublattice, and decreases B -site order. By applying Eq. (1) and the random layer model, the peak shifting of Raman spectra is explained. In a word, the A_{1g} mode frequency variations indicate that B -site order increases at first and then decreases with the introduction of Cu^+ ions. Subsequently, the dielectric properties are discussed in terms of B -site order.

As shown in Fig. 4, we can also find that the peak intensities become stronger with increasing CuO doping concentration. Especially, the peak intensities of B_1 and B_2 are become stronger and sharper compared with those of the non-doped sample that are broad; it may be closely related to the structure order. Siny *et al.* [24] proposed that samples with high order degrees exhibit strong Raman peaks and Raman active modes, which are also closely related to the structure order. So the change of the peak intensity is attributed to the B -site order degree. In addition, the intensity of the Raman spectrum peak is also correlated with the polarizability and it has effect on the intensity of the peak simultaneously. When doping content increases, it will raise the atomic distance and lead to the change of the polarizability. While the polarizability increases with increasing of atomic distance, the vibration intensity of the modes also will increase. Therefore, the intensity of the Raman spectrum peak will become stronger.

Figure 5 shows the temperature dependences of dielectric constant and loss at 1 kHz. The dielectric properties of all samples are listed in Table 2. The

Fig. 5 Temperature dependences of dielectric constant and loss at 1 kHz.

Table 2 Dielectric properties and diffusive factors of PMNT- x CuO at 1 kHz

Sample	x	ϵ_m	T_m (°C)	δ (°C)	ϵ at 25 °C
PMNT	0	20296	30	41.44	20203
PMNT1	0.015	22708	20	40.99	22362
PMNT2	0.03	19942	20	42.88	19506
PMNT3	0.06	18411	20	44.04	18237

results indicate that the peak temperatures (T_m) of doped samples are about 10 °C lower than that of non-doping. This shift is probably related to the compositional differences and microstructure characteristic, particularly the degree of crystallinity and grain size [25]. Therefore, the changes in grain size, shape and composition by CuO doping result in the change of T_m . With the increasing of doping amount, the maximum dielectric constant of samples shows a tendency to increase at first and then decrease. However, the dielectric loss keeps nearly unchanged above the room temperature. The maximum dielectric constant reaches the highest (22 708) when the CuO content is 1.5 mol%, but it decreases to 19 942 and 18 411 when the CuO content is 3 mol% and 6 mol%, respectively (Table 2). The reason of this phenomenon is that a minor amount of CuO doping causes the B -site order to increase. Meanwhile, a lot of unbalanced space charges form, which contribute to the polarization and dielectric constant. Unfortunately, excessive doping leads to incomplete ion replacement and decreasing of B -site order. Consequently, the dielectric constant is reduced. On the other hand, the dramatic decline of dielectric loss around phase transition temperature is due to the polarization disappearance. It can be seen that the dielectric loss is reduced to less than 1% for all doped samples while

the temperature is above 30 °C (Fig. 5). Attributed to the suppression of PbO volatilization and lowering of sintering temperature, the dielectric loss retains relatively low when the temperature is above the room temperature. However, the dielectric loss of the doped ceramic samples is higher than that of non-doped samples at negative temperature. It may originate from the increase in the oxygen vacancies. As mentioned above, Cu^+ ions dissolved into lattice will substitute for Mg^{2+} ions on the *B*-site and oxygen vacancies are simultaneously generated with the increasing of CuO concentration, and the appearance of oxygen vacancy can lead to lattice distortion and decreasing of *B*-site order [26]. In addition, the vacancies in the system can be polarized under an alternating electric field. Therefore, the dielectric loss increases [27].

One characteristic of relaxor ferroelectrics is diffusive phase transition. The relationship between maximum dielectric constant and dispersion degree could be used to analyze the order–disorder behavior of ferroelectric ceramics. The diffusive factor δ can be calculated from the quadratic formula [28]:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{1}{2\varepsilon_m\delta^2}(T - T_m)^2 \quad (2)$$

where ε and ε_m are the relative and maximum dielectric constants, respectively; T and T_m are the temperatures corresponding to ε and ε_m , respectively. The curve of $(1/\varepsilon - 1/\varepsilon_m)$ vs. $(T - T_m)^2$ is linear fitted, as shown in Fig. 6. The diffusive factor δ could be calculated with the slope of the curve. It is obvious that the dispersities of samples decrease at first and then increase with the CuO content increasing (Table 2 and Fig. 6). According to the order–disorder transition model [29], the dispersion and dielectric

Fig. 6 Linear fitting graph of $(1/\varepsilon - 1/\varepsilon_m)$ vs. $(T - T_m)^2$.

relaxation degree decrease with the *B*-site order increasing. In this work, the related *B*-site order increases at first and then decreases, which is confirmed by the Raman analysis. Additionally, it could be seen that the variation tendency of the maximum dielectric constant is opposite to that of phase dispersion degree, which is another evidence that the dispersion degree is closely related to the order–disorder behaviors.

4 Conclusions

CuO-doped PMN–PT ferroelectric ceramics with a single perovskite-type phase were fabricated by solid state reaction method. The Raman measurement results showed that the A_{1g} peak firstly shifted to low frequency and then to high frequency with increasing CuO content, which meant the *B*-site order degree increased and then decreased. The variations in the *B*-site order degree resulted in the changes in the relaxor behavior. The relaxation degree and the dispersion degree decreased first and then increased with the increasing of CuO addition content. This paper further provided an evidence on the relationship between the ferroelectric relaxation degree and the *B*-site order degree in the PMN based ceramics.

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