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Ceramics International 30 (2004) 307–310

CERAMICS
INTERNATIONAL

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Ordered micro-regions and dielectric properties of La^{3+}-doped $Pb(Zn_{1/3}Nb_{2/3})O_3$-based ceramics with Nb^{5+} deficiency

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Received 8 March 2003; received in revised form 27 March 2003; accepted 28 April 2003

Abstract

La^{3+}-doped $0.85Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.10BaTiO_3$–$0.05PbTiO_3$ (abbreviated as PZN-based ceramics hereafter) ternary system ceramics with Nb^{5+} deficiency were synthesized by the columbite method. The effect of deficient Nb^{5+} on the phase structure, ordered micro-region size and dielectric properties of lanthanum-doped PZN-based ceramics was investigated in detail. With the increase of Nb^{5+} deficiency, the content of pyrochlore phase decreased significantly. Especially, when Nb^{5+} deficiency was >3 mol%, the pyrochlore phase resulting from La^{3+} doping was eliminated completely. From the viewpoint of the phase structure affected by Nb^{5+} deficiency, it could come to the conclusion that the non-stoichiometric 1:1 ordered micro-regions do exist in PZN-based ceramics. The analysis of Raman scattering spectra demonstrated that Nb^{5+} deficiency enlarged ordered micro-region size of the lanthanum-doped PZN-based ceramics. Nb^{5+} deficiency increased the dielectric constant, but it hardly affected dielectric loss. The increase of dielectric constant results not only from the elimination of pyrochlore phase but also from the size increase of "effective ordered micro-regions".

Keywords: B. Spectroscopy; C. Dielectric properties; D. Perovskites; Lanthanum

1. Introduction

Relaxor ferroelectrics based on $Pb(Zn_{1/3}Nb_{2/3})O_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ (abbreviated as PMN) exhibit excellent physical properties such as high dielectric constant, large electrostriction and little hysteresis. They have drawn special attention as electrostrictive materials applied to actuators, micro-positioners and optical instruments [1]. However, the research on PZN-based ceramics is much less extensive and intensive than that of PMN-based ceramics. Especially, the ordered region of PZN-based ceramics was very seldom reported. Though the dielectric properties of PZN-based ceramics doped with La^{3+} and K^+ have been yet reported in the literature, the effect of La^{3+}/K^+-doping on ordered micro-regions and the effect of micro-regions on dielectric properties were rarely investigated. In the present study, the effect of La^{3+}-doping on ordered micro-regions and dielectric properties of PZN-based ceramics was explored. The effect of Nb^{5+} deficiency on ordered micro-regions and dielectric properties was also explored in detail at constant amount of La^{3+} dopant. It is hoped that this study could help to understand the role of ordered micro-regions and the mechanism in the dielectric response of relaxor ferroelectrics.

Two ways of doping La^{3+} were adopted. In the first one, La^{3+} was directly added to the PZN-based ceramics according to the formula $0.85PZN$–$0.10BT$–$0.05PT + x(\text{mol})\ La^{3+}$. In the other way, the content of La^{3+} was kept at 2 mol%, and meanwhile, Nb^{5+} content was deficient by comparison with stoichiometric specimens.

2. Experimental procedure

The specimens studied in this research were fabricated according to the formulas $0.85Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.10BaTiO_3$–$0.05PbTiO_3$–$xLa^{3+}$ and $0.85Pb(Zn_{1/3}Nb_{2/3})$

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doi:10.1016/S0272-8842(03)00104-4

O_3–$0.10BaTiO_3$–$0.05PbTiO_3$–0.02 La^{3+}–yNb^{5+}, where $x = 0$, 0.01, 0.02, 0.05, 0.10, and $y = 0$, 0.01, 0.03, 0.04.

The specimens were prepared by the columbite precursor method [2] and the purity of all starting raw powders is 99.9%. The columbite precursor $ZnNb_2O_6$ was first prepared by mixing pre-determined amounts of ZnO and Nb_2O_5 and ball-milled for 12 h in polyethylene jars, then the slurry was dried and calcined for 4 h at 1000 °C to form $ZnNb_2O_6$. The columbite precursor was then mixed and ball-milled with pre-determined amounts of PbO, TiO_2, $BaCO_3$ and La_2O_3 powders and calcined at 880 °C for 4 h. The calcined powders were ground, ball-milled again and pressed into disks using PVA as a binder. After burning off PVA, the pellets were sintered in a sealed alumina crucible at soaking temperature of 1100 °C for 1 h. In order to compensate for PbO loss from the pellets, a PbO-rich atmosphere was maintained by placing an equi-molar mixture of PbO and ZrO_2 into the covered alumina crucible.

The relative amounts of pyrochlore and perovskite phase was determined using XRD patterns of powder samples by measuring the major X-ray peak intensities for perovskite and pyrochlore phase, i.e., (110) and (222), respectively. The percentage of perovskite phase was calculated by the following equation:

$$\text{Content of perovskite phase (\%)} = I_{\text{perov}(110)}/I_{\text{perov}(110)} + I_{\text{pyro}(220)},$$

where I_{perov} and I_{pyro} stand for the intensities of the major peaks (110) and (220) for perovskite and pyrochlore phase respectively.

The dielectric response was measured at the frequency of 1 kHz using an automatic LCR meter (WK4225) at the temperature ranging from −70 to 120 °C.

Raman spectra were measured with an instrument Ramanor U1000 (Jpbin-Yvon, France) spectrometer using the 514.5 nm line of an Ar-ion laser as an excitation source in the scanning range of 100–1000 cm^{-1}, and scanning speed of 3 cm^{-1}/s.

3. Results and discussion

3.1. Phase structure and dielectric properties of La^{3+}-doped PZN-based ceramics

At first, La^{3+} was directly added to the PZN-based ceramics according to the formula 0.85PZN–0.10BT–0.05PT + xLa^{3+}. The specimens containing 0, 1, 2, 5, 10 mol% La^{3+} are numbered PLZN0, PLZN1, PLZN2, PLZN3 and PLZN4 respectively. According to XRD patterns, their perovskite and pyrochlore phase contents and other physical parameters are shown in Table 1.

As listed in Table 1, with the increase in La^{3+} content, the amounts of perovskite phase of the specimens decreased gradually, which is similar to the case of lanthanum-doping in PMN-based ceramics [3]. It was explained that the charge unbalance due to lanthanum-doping was compensated for by the adjustment of the B-site cation concentrations. Ti^{4+} and Nb^{5+} ions have approximately the same ionic radii, i.e., 0.68 and 0.70 a.u., respectively, so we believe that charge unbalance was compensated for by removing Nb^{5+} ions and entering an equivalent amount of Ti^{4+} onto their positions [3]. The experiment proved that La^{3+} substitution resulted in Nb^{5+}-rich and Ti^{4+}-rich regions. The Nb^{5+}-rich regions became pyrochlore phase and Ti^{4+}-rich regions became perovskite phase. It can be concluded that more lanthanum content there is, more pyrochlore and less perovskite phase will be produced.

As shown in Table 1, the perovskite phase lattice shrank gradually with the increase of lanthanum content. Obviously, the radius of La^{3+} ion is smaller than that of Pb^{2+} ion. When La^{3+} ions entered the perovskite structure, the lattice parameter would decrease.

Table 1 also shows the effect of La^{3+} dopant on dielectric property parameters. With the content of lanthanum ions increasing, both the relative dielectric constant and Curie temperature decreased significantly.

There are several possible reasons for the decrease of the relative dielectric constant in lanthanum-doped PZN-based ceramics. First and foremost, the pyrochlore phase content increased with lanthanum content. It is

Table 1
The effect of La^{3+}-doping on the phase structure and dielectric parameters of PZN-based ceramics

Specimens	PLZN0	PLZN1	PLZN2	PLZN3	PLZN4
La^{3+} content (%)	0	1	2	5	10
Pyrochlore phase (%)	–	1.2	3.8	6.1	11.7
Perovskite phase (%)	100	98.8	96.2	93.9	88.3
Lattice constant (nm)	0.4051	0.4049	0.4041	0.4034	0.4032
Diffusion degree (°C)	44.2	68.1	72.5	78.8	80.2
Curie temperature(°C)	80	60	35	−5	−50
Peak relative dielectric constant (at 1 kHz)	6598	5916	3943	3402	1388

known that the pyrochlore phase is detrimental to dielectric properties. Second, lanthanum-doping made the Nb^{5+} ions content decrease and Ti^{4+} ions content increase in the perovskite phase, i.e., the number of NbO_6 octahedrons decreased whereas the number of TiO_6 octahedrons increased. The space charge of polarization caused by NbO_6 octahedrons was less than that by TiO_6 octahedrons, which also decreased dielectric constant. Third, as shown in Table 1, the lattice constant of the perovskite phase was reduced by lanthanum-doping, which made movable space of B-sites ions become smaller, thus affecting dielectric properties. Finally, lanthanum-doping might result in some Lead vacancies that also had a strong effect on dielectric properties.

3.2. The effect of Nb^{5+} deficiency on phase structure of La^{3+}-doped PZN-based ceramics

In Table 2, the phase structure and dielectric parameters of 2 mol% La^{3+}-doped PZN-based ceramics with Nb^{5+} deficiency are listed, where Nb^{5+} deficiency was 0, 0.01, 0.03 and 0.04 respectively.

As shown in Table 2, the pyrochlore phase content was 3.8% in the specimen PLZN2 with the content of 2 mol% La^{3+}. When Nb^{5+} deficiency increased, the pyrochlore phase decreased gradually, in particular, when Nb^{5+} deficiency was more than 3 mol%, pyrochlore phase was eliminated completely and the La^{3+}-doped specimens became pure-perovskite-structured. La^{3+} doping made ordered micro-region sizes in PZN-based ceramics increase a great deal, which resulted in a lot of excess Nb^{5+} cations. It is well known that pyrochlore phase mainly results from the rich Nb^{5+} cations. Nb^{5+} deficiency decreased the content of rich Nb^{5+} cations, so the pyrochlore phase content decreased. With the increase of Nb^{5+} deficiency, the specimens come to 100% perovskite phase structure.

There are three possible types of ordered structure in PZN-based ceramics, mixed 1:1, 1:2 and non-stoichiometric 1:1 structures [4]. Assuming that there exists mixed 1:1 or 1:2 structure rather than non-stoichiometric 1:1 in ordered micro-regions, Nb^{5+} would distribute uniformly in both ordered and disordered regions, and moreover, the concentration of Nb^{5+} would not vary with the size of ordered micro-regions. Nb^{5+} deficiency would unbalance the stoichiometric ratio, so detrimental pyrochlore or other phases may result. The results shown in Table 2, however, indicated that Nb^{5+} deficiency could decrease and even eliminate pyrochlore phase. Obviously, the above assumption is not correct, i.e., there could not exist in PZN-based ceramics ordered micro-regions with mixed 1:1 or 1:2 structures. The non-stoichiometric 1:1 ordered micro-regions do exist in PZN-based ceramics only from the angle of the variation of pyrochlore phase.

3.3. The effect of Nb^{5+} deficiency on ordered micro-region of La^{3+}-doped PZN-based ceramics

Raman scattering study is important for the interpretation of the properties of such relaxors as PMN and PZN-based ceramics and has been reported by some authors [5–9].

Fig. 1 shows Raman spectra of the specimens PLZN2 and PLZN22 with 0 and 3% Nb^{5+} deficiency respectively. The 780 cm^{-1} line is assigned to the stretching mode of Nb–O–Zn bonds that are the most rigid in the structure. The very large band at 600–500cm^{-1} is assigned to the Nb–O–Nb bonds, and 430 cm^{-1} line corresponds to Zn–O–Zn bonds [7, 9]. The intensity ratio of these two lines indicates an increase of the Nb–

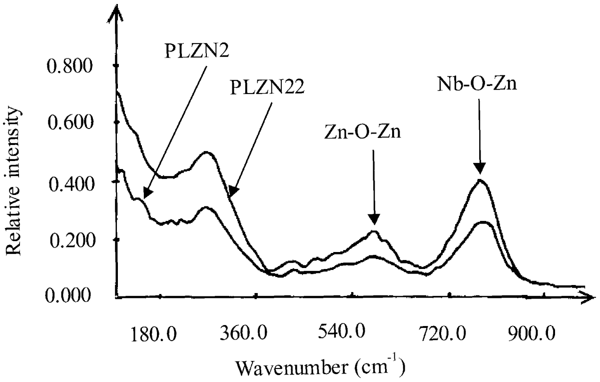

Fig. 1. Raman scattering spectroscopy of 2 mol% La^{3+}-doped PZN-based ceramics PLZN2 and PLZN22, which contain 0 and 3 mol% Nb^{5+} deficiency respectively.

Table 2
The effect of Nb^{5+} deficiency on phase structure and dielectric parameters of 2 mol% La^{3+}-doped PZN-based ceramics

Specimens	PLZN2	PLZN21	PLZN22	PLZN23
La^{3+} content (%)	2	2	2	2
Nb^{5+} deficiency (%)	0	1	3	4
Zn/Nb ratio	0.5	0.505	0.515	0.520
Pyrochlore phase (%)	3.8	1.8	0	0
Perovskite phase (%)	96.2	98.2	100	100
Diffusion degree (°C)	72.5	66.8	65.2	70.3
Curie temperature (°C)	35	35	40	40
Peak relative dielectric constant (at 1 kHz)	3943	5167	5509	5021

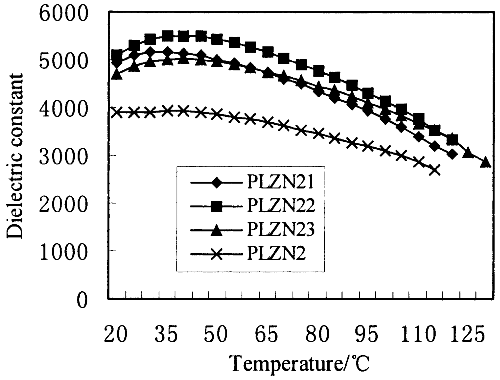

Fig. 2. Temperature dependence of dielectric constants (1 kHz) for the PZN-based specimens PLZN2, PLZN21, PLZN22 and PLZN23.

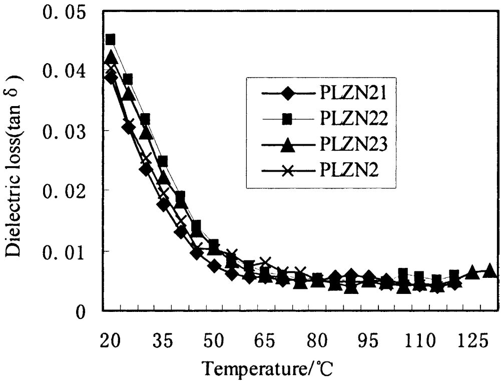

Fig. 3. Temperature dependence of dielectric loss (1 kHz) for the PZN-based specimens PLZN2, PLZN21, PLZN22 and PLZN23.

O–Zn number with Nb^{5+} deficiency, owing to an obvious growth of the ordered regions size.

3.4. The effect of Nb^{5+} deficiency on dielectric properties of La^{3+}-doped PZN-based ceramics

Figs. 2 and 3 show the dependence of dielectric constant and loss on temperature of the specimens PLZN2, PLZN21, PLZN22 and PLZN23 respectively. When Nb^{5+} deficiency was $<3\%$, with the increase of Nb^{5+} deficiency the dielectric constant increased greatly. The dielectric constant reached its maximum value 5509 with 3 mol% Nb^{5+} deficiency. When Nb^{5+} deficiency was >3 mol%, dielectric constant began to fall, however, its dielectric constant is still higher than that of the specimen with no Nb^{5+} deficiency.

Nb^{5+} deficiency resulted in the increase of the dielectric constant of La^{3+}-doped PZN-based ceramics. The most important reason is that Nb^{5+} deficiency made ordered micro-regions size increase, so the "effective ordered micro-regions" size also increased. It was proved that "effective ordered micro-regions" played a vital role in dielectric response of PMN-typed relaxor ferroelectrics [4]. At the same time, Nb^{5+} deficiency decreased pyrochlore phase significantly, which also resulted in the increase of dielectric constant. With the increase of Nb^{5+} deficiency, the dielectric loss increased only slightly.

4. Conclusions

La^{3+}-doping caused the perovskite phase and dielectric constant to decrease largely. The dielectric constant of 2 mol% La^{3+}-doped specimen was 3943 while that of stoichiometric specimen was 6598. Nb^{5+} deficiency made pyrochlore phase of La^{3+}-doped PZN-based ceramics decrease. When Nb^{5+} deficiency was >3 mol%, the content of perovskite phase of 2% La^{3+}-doped ceramics attained 100%, so we could draw the conclusion that non-stoichiometric 1:1 ordered micro-regions do exist in PZN-based ceramics just from the angle of the variation of pyrochlore phase. The analysis of Raman spectrum demonstrated that Nb^{5+} deficiency increased the size of ordered micro-regions in La^{3+}-doped PZN-based ceramics. The Nb^{5+} deficiency also increased the dielectric constant significantly, but it affected dielectric loss very weakly.

Acknowledgements

This work was supported by a Science Fund from Air Force Engineering University.

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