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Fabrication and dielectric properties of transparent PZN–BT ceramic

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Abstract

Transparent ceramic of $0.85Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.15BaTiO_3$ has been successfully prepared by a two-stage sintering method using conventional raw materials. The ceramics exhibited an excellent crystallinity, high density and clean grain boundary. The transmittance keeps about4 0% from visible to near infrared regions. The frequency dependence of T_m and relaxor behavior has also been investigated using Vogel–Fulcher model and Power model.

Keywords: C. Dielectric properties; C. Optical properties; PZN

1. Introduction

Transparent ferroelectric ceramics (TFC) with high optical transmittance and large electro–optic(EO) coefficients have great potential for optoelectronic devices[1] such as light valves, deflectors, displays, and so forth. Compared to ferroelectric single crystals, TFC have less cost, variable composition and considerable size, which make them suitable for widespread applications. Since PLZT(lead lanthanum zirconate titanate) transparent ceramics was firstly reported by Land and Haertling [2] in the 1970s, a large number of TFC such as BLN–PZT [3], PZT–SLN [4], PLMN–PT [5,6], and so forth, have been successfully prepared and studied.

Recently, relaxor ferroelectric PZN based single crystals exhibits ultrahigh dielectric, piezoelectric constants, superior electrostrictive properties and large electro–optic coefficients [7,8]. However, PZN single crystals have high production cost. Moreover it still faces many technical challenges for growing large-size crystals with uniform properties. Another choice is PZN based ceramic. Unfortunately, it has been found that perovskite structure PZN is thermal unstable and will turn to pyrochlore phase due to its inherently low tolerance factor and small absolute value of the bond valence sum of oxygen [9,10]. To fabricate pure perovskite structure PZN, the addition of normal ferroelectric compounds such as $BaTiO_3$ [11] and $PbTiO_3$ [11] is purposed as the most effective way.

As is well known, PLZT [2] and PLMN–PT [5] transparent ceramics can be successfully prepared by atmosphere sintering in oxygen flow, isostatic hot pressing of sintered samples in an inert or oxygen atmosphere and Vacuum/oxygen pressing. However, to our knowledge, only translucent 70PLZT–30PZN [12] and 90PSN–10PZN [13] ceramics were fabricated by such technology. In this study, we report our work on preparation of transparent PZN based ceramic by two-stage sintered method. And the PZN–BT transparent ceramic was fabricated.

2. Experimental procedures

The powder of 0.85PZN–0.15BT was synthesized by the conventional solid state method. Reagent-grade powders of PbO, ZnO, Nb_2O_5, TiO_2, and $BaCO_3$ were used as raw materials. These powders were mixed in the required stoichiometric ratios (small amount of excess PbO was added for liquid-phase sintering and PbO volatility), and ball-milled with zirconium balls in ethanol for 24 h. After drying at 80 °C, the mixture was calcined at 900 °C for 4 h using a double crucible configuration. The calcined powers were remilled for 3 h and dried. The finally obtain powder was cold isostatically pressed into pellets at a pressure of 150 MPa. The pellets were first sintered in an oxygen

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atmosphere (OA) at temperatures between 1050 and 1150 °C. The sintered pellets were then hot pressed (HP) at a temperature 1050–1300 °C for more than 8 h at pressure of 50–100 MPa.

The obtained samples were polished to a thickness of 0.5 mm for transparency measurement. The crystal structure was examined with an XRD powder diffraction (scan rate of 4° /min, step of 0.02°, D/max-2550VX, Japan).The microstructures of the samples were investigated by a scanning electron microscopy (SEM) (JSM-6510A, Japan). The optical transmission was measured using a UV–vis-NIR spectrophotometer (HitachiU4100, Japan). The dielectric properties were obtained with a Novocontrol Broadband Dielectric Spectrometer, Germany.

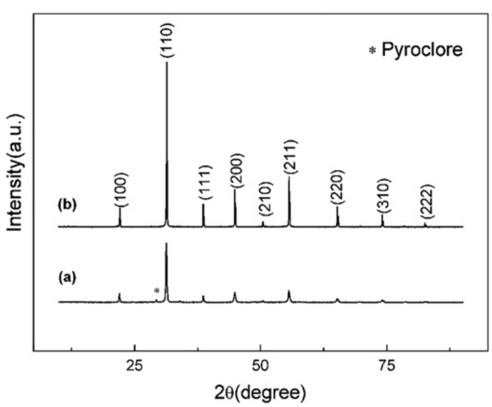

Fig. 1. X-ray diffraction patterns of PZN–BT powder (a) and PZN–BT ceramic sintered with HP (b).

3. Results and discussion

Fig. 1 shows the XRD patterns for the powder and sintered sample of 0.85PZN–0.15BT ceramic. It is found that a slight amount of pyroclore phase exists in the obtained powder. After OA-HP sintering, no pyroclore phase could be detected. And the diffraction peaks of crystalline PZN–BT ceramic exhibits much sharper, narrower and stronger, showing clearly separated Cu-K_{a1} and Cu-K_{a2} doublets for each peak, indicating an excellent crystallinity. All the diffraction peaks can be well indexed as the cubic structure of PMN (JCPDS 88–1861)

Fig. 2 reveals the SEM image from thermal etched surface and natural cross-section of 0.85PZN–0.15BT transparent ceramic. It can be seen that the sample is of full dense and have clean grain boundary. There are no pores observed. The grain size is not quite uniform, ranging from 1 to 5 μm. Many grains with small size about 1 μm could be found from thermal etched surface. Note that some write pieces observed on etched surface might be PbO from etching procedure.

Fig. 3 reveals the optical transmittance spectra of PZN–BT ceramics in the wavelength ranging from 200 to 2500 nm. The sample exhibits good line-transmittance, we can clearly see the character at a distance of 2 mm (the insert of Fig. 3). The maximal transmittance is 40%, which is not very high. However, it can be seen that it shows a sharp increase in visible region (380–500 nm) and keeps about 40% from visible to near infrared regions (700–2500 nm).The main scattering mechanisms might be correspond to the nonuniform grain size. The works on improving the uniform of grain size and optical transmittance is on the progress now.

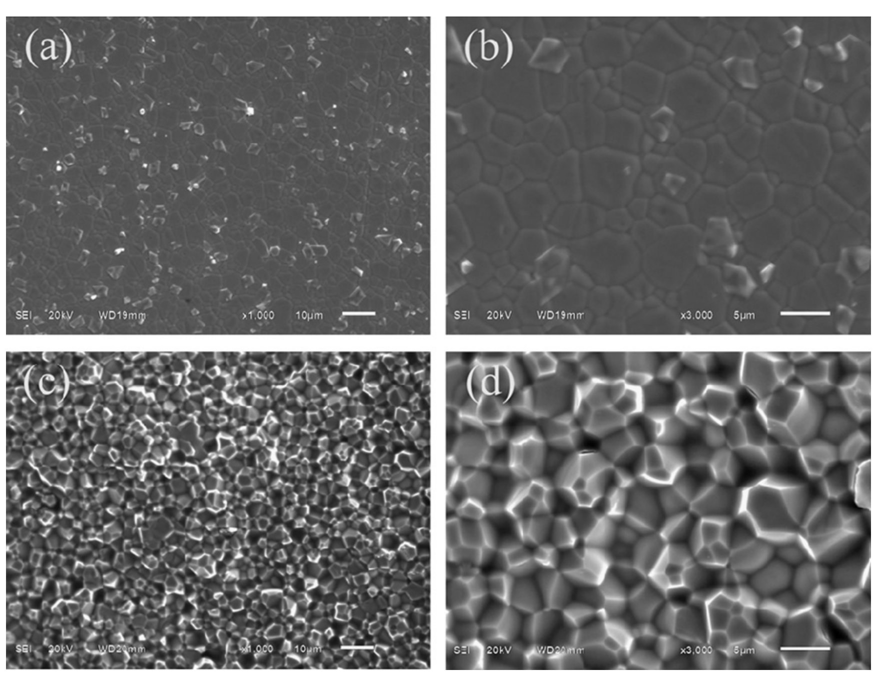

Fig. 2. SEM image from surface after thermal etching (a,b) and fracture surface (c,d) of 0.85PZN–0.15BT.

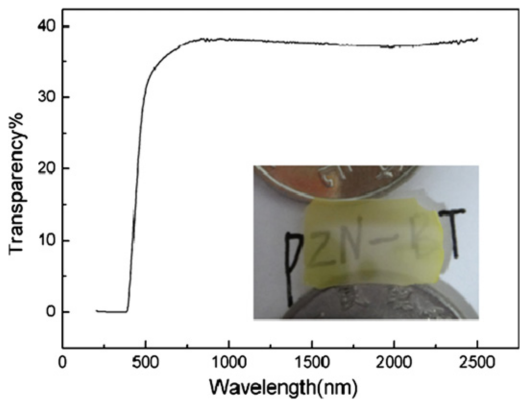

Fig. 3. Optical transmitting spectra of 0.85PZN–0.15BT ceramic at a thickness of 0.5 mm ranging from 200 to 2500 nm.

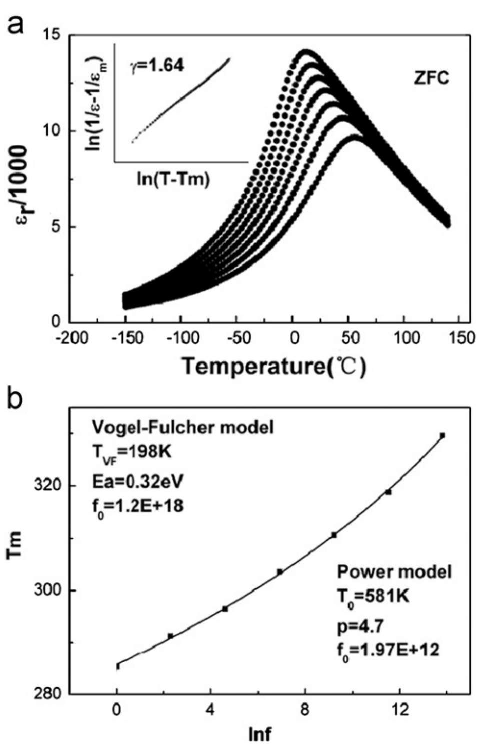

Fig. 4. Dielectric property of 0.85PZN–0.15BT as a function of temperature (frequency range: 10^0–10^6 Hz).

The dielectric property as a function of temperature from 10^0 to 10^6 Hz is shown in Fig. 4(a). The sample of 0.85PZN–0.15BT shows a typical relaxor behavior. The ΔTm, defined as $\Delta T_m = T_{m100\ kHz} - T_{m100\ Hz}$, is 22 K, where T_m is the temperature at dielectric maxima. The insert of Fig. 4(a) exhibits the temperature dependence of dielectric constant above Tm according to Martirena and Burfoot modified Curie–Weiss law [14] and is given as

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{(T - T_M)^{\gamma}}{K} \quad (1)$$

where γ is the diffuseness exponent whose values vary between 1 and 2, K is a constant. We find that the γ is 1.64.

We also investigated the frequency dependence of T_m and relaxor behavior using Vogel–Fulcher model (Eq. (2)) [15] and Power model (Eq. (3)) [16] (Fig. 4(b)).

$$f = f_0 \exp\left(-\frac{E_a}{k(T_m - T_{VF})}\right) \quad (2)$$

$$f = f_0 \exp\left(-\left(T_0/T_m\right)^p\right) \quad (3)$$

where T_{VF} is the freezing temperature of the polar regions in the material, f_0 is the Debye frequency, k is the Boltzmann constant, E_a is the activation energy, T_0 is the equivalent temperature of activation energy, f is the applied probing frequency. The fitting curve is the solid line of Fig. 4(b). Both the Vogel–Fulcher and Power model could be well fitted for the measurement results. However, the f_0 obtained from Vogel–Fulcher model is 1.2 E+18 Hz and is invalid for the present system. The values of f_0, T_0 and p for Power model were found to be 1.97 E+12 Hz, 581 k and 4.7, respectively, which were more physically reasonable.

4. Conclusion

The transparent 0.85PZN–0.15BT was firstly successfully fabricated by two-stage sintered method. The transmittance keeps about 40% from visible to near infrared regions. The main scattering mechanisms might correspond to the nonuniform grain size. Dielectric measurements showed the sample of 0.85PZN–0.15BT ceramic is a typical relaxor. The ΔT_m is 22 K, diffuseness exponent γ is 1.64. The values of fitted results were more physically reasonable by using Power model. And the values of f_0, T_0 and p for Power model were found to be 1.97E+12 Hz, 581 K and 4.7, respectively.

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