Ceramics International 30 (2004) 1627–1630

CERAMICS INTERNATIONAL

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Magnetic field effect on dielectric properties of $Pb(Fe_{1/2}Nb_{1/2})O_3$ single crystal

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Received 24 November 2003; received in revised form 12 December 2003; accepted 22 December 2003

Abstract

Single crystal was grown by precursor flux-melt method. It was characterized by X-ray diffraction (XRD) and was found perovskite and the surface index of the crystal is (2 1 0). Scanning electron microscopic image also confirms no explicit defect on the crystal surface. The dielectric response as a function of temperature and frequency was measured in a frequency range from 100 to 10^6 Hz with temperatures varying from 25 to 300 °C without and with an applied magnetic field up to 14 T. The directions of applied magnetic field with respect to the direction of the applied electric field and the crystal orientation are in two configurations and three rotation angles, about the electric field direction, 0, 45, and 90°. We carefully analyzed the data and believe that the magnetic field affects on the dielectric properties of the PFN single crystal.

PACS: 77.80. - e; 75.30.Ds; 75.80. +q; 75.50.G

Keywords: Single crystal; PFN; X-ray; Dielectric constant; Magnetic field effect

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1. Introduction

Magnetic and electric phenomena are two inseparable physical scenarios. The magnetic moment of a free atom has three principal sources: the spin with which electrons are endowed; their orbital angular momentum about the nucleus; and the change in the orbital moment induced by an applied magnetic field [1]. The dielectricity of a solid, on the other hand, is due to the polarization defined as the electrical dipole moments per unit volume. It closely depends on the charge distribution of the system. Specifically, the ferroelectricity and piezoelectricity in a solid is originated by the shift of the oppositely charged ions in the opposite direction or the break of the centrosymmetry of the crystal (due to the large internal electric field) [1]. The fundamentals of the two phenomena are closely related. The two phenomena usually coexist in ferric perovskites that are the focus of our investigation in this paper, because perovskite-like (ABO_3) compounds have large internal field that is necessary for the appearance of ferroelectric state. Simultaneously, the angles between the connecting lines "cation B–oxygen-B" are equal to 180°, forming a facilitating condition for the existence of magnetic ordering due to the indirect exchange interaction, if cation B is partially or entirely magnetic element [2]. Lead-based complex perovskite ferroelectric compound $Pb(Fe_{1/2}Nb_{1/2}O_3)$ (PFN) is one of the materials under this category, and it was first discovered by Smolenskii et al. [2,3]. Other similar compounds $RMnO_3$ with R = rare-earth have attracted attention lately [4]. The Fe–O–Fe interaction in PFN and Mn–O–Mn interaction in $YMnO_3$ provide the magnetic ordering condition, and the noncentrosymmetric space group in both compounds is the natural source for the ferroelectromagnetism in these compounds [4–8]. In the later 1990s, other interesting compounds, $(RBi)FeO_3$ which also possesses ferroelectromagnetic characteristics, but with another type of interaction [9,10]. Experiment including the materials preparation, characterization and the measurements of magneto-electric coupling effects in these materials were mostly carried out in 1960s and 1970s by the scientists in the former Soviet Union [4,11,12]. Because the

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doi:10.1016/j.ceramint.2003.12.172

great application potential of these materials and the variety of the scientific interests in the magnetoelectric inherent in the materials, the research efforts on them have been resumed and intensified among the world scientific communities. Ed Gerstner has recently observed both ferroelectric and ferromagnetic nano-domain coexisting in $YMnO_3$ [13] and T. Kimura et al. found gigantic magnetoelectric and magnetocapacitance effects [14]. The magnetoelectric effect has been used in a variety of applications such as microwave field and precise current measurements [1,15–17]. We have systematically investigated the magnetic field effect on the dielectric properties of PFN single crystal. The results are reported in this paper.

2. Experiment procedure

The single crystal $Pb(Fe_{1/2}Nb_{1/2})O_3$ was prepared by a modified PbO flux-melt method. The regent grade FeO and Nb_2O_5 were first thoroughly mixed by ball-milling followed by calcinations at 1000 °C for 4 h to form a precursor $FeNbO_4$. The precursor then was mixed with PbO according to the composition $Pb(Fe_{1/2}Nb_{1/2})O_3$ plus 70 mol% PbO as the flux. The mixture contained in a Pt crucible was heat treated with a temperature profile for crystal growth. After the crystal growth process is completed, the crucible with the material was rinsed in a boiled 50% nitride acid for over 20 h to separate the crystals from the residual flux.

A small piece of the crystals were ground into powder for X-ray diffraction (XRD) using Rigaku D/Max2100B-PC, Cu Kα radiation. The orientation of the relatively flat surface of one of the crystal was also determined by X-ray diffraction. The crystal microstructure was observed with Hitach S-2460N scanning electronic microscope (SEM). The crystal then was cut and polished into a 0.63 mm thick plate, and its surfaces were coated with Pt thin films by Cressington 108 auto Sputter Coater as electrodes and then fired at 600 °C for 10 min to ensure bonding of the electrodes to the surfaces. The magnetization was measured in Quantum Design PPMS (Model 6000) at magnetic field 500 G. The dielectric response as a function of temperature and frequency was measured with LCR precision meter (Hewlett-Packard 4284A) in a frequency range from 100 to 10^6 Hz in a Delta 9039 test chamber with temperatures varying from 25 to 300 °C without magnetic field and with an applied magnetic field up to 14 T in Quantum Design PPMS. The directions of applied magnetic field with respect to the direction of the applied electric field and the crystal orientation are in two configurations: (1) both electric field and magnetic field perpendicular to the crystal plane (2 1 0), the surface of the crystal, and (2) electric field perpendicular to the crystal plan (2 1 0), but the magnetic field parallel the crystal plane (2 1 0). In the second field configuration, we rotate the direction of the magnetic field about the electric field direction for three angles, 0, 45 and 90°.

3. Results and discussions

The color of the obtained crystals is shiny dark gray and the morphological images of them are in pyramid shape of the size in several millimeters. The powder X-ray diffraction pattern showing that the crystal structure is rhombohedral perovskite. The X-ray diffraction pattern from the relatively flat surface of a crystal shows that the sample is a single crystal and its flat surface is (2 1 0) crystal plane. SEM image also demonstrates the single crystal feature of the sample.

Fig. 1 shows the magnetization as a function of temperature indicating an anomaly around 150 K, which is possibly a *para*-antiferromagnetic transition. According to the crystal structure analysis, Fe occupied one half B-sites in the unit cell. Fe–O–Fe forms a chain optimizing the Fe magnetic moments interaction. The coupling effect of magnetic field with the dielectric properties is expected orientation dependent. For this anticipation we preceded the dielectric constant and loss measurements with an applied magnetic field in two configurations mentioned in the previous section. The dielectric constants as a function of applied magnetic field at different temperatures and frequencies are shown in the figures below. Fig. 2 shows the dielectric constants as a function of applied magnetic field at 77 °C for frequency 1.0 MHz at the first field configuration. The dielectric constants increase with increasing applied magnetic field monotonically. The percentage changes of the dielectric constant at frequency 1.0 MHz and at temperature 27 and 77 °C is shown in Fig. 3. From this figure, one can see that for the same frequency the magnetic field effect on the dielectric constant at different temperatures is similar. For the configuration of magnetic field perpendicular to the electric field, i.e. the magnetic field in plane situation, the dielectric constant as a function of magnetic field at temperature 77 °C and frequency 1.0 MHz for three rotation angles is shown in Fig. 4. Similar results at temperature 77 °C and frequency 1.0 kHz were also observed. From these figures we observed that the aspect of

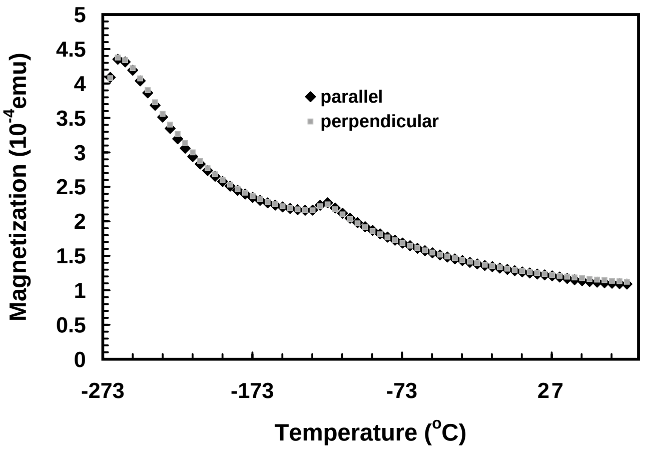

Fig. 1. Magnetization of PFN single crystal as a function of temperature at 500 G with the magnetic field perpendicular or parallel to the (2 1 0) plane.

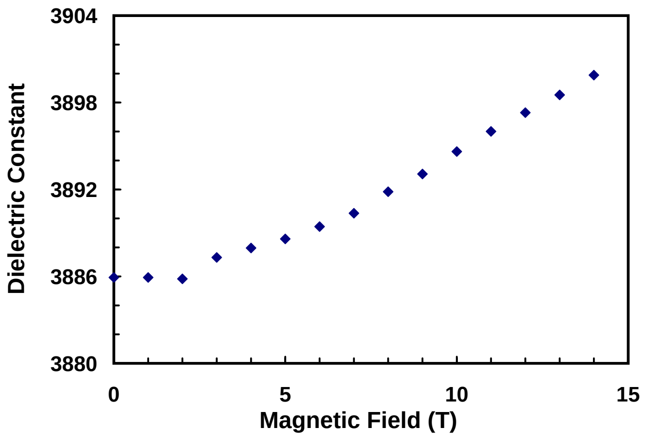

Fig. 2. Dielectric constant as a function of applied magnetic field with both electric field and magnetic field perpendicular to the crystal plane (2 1 0).

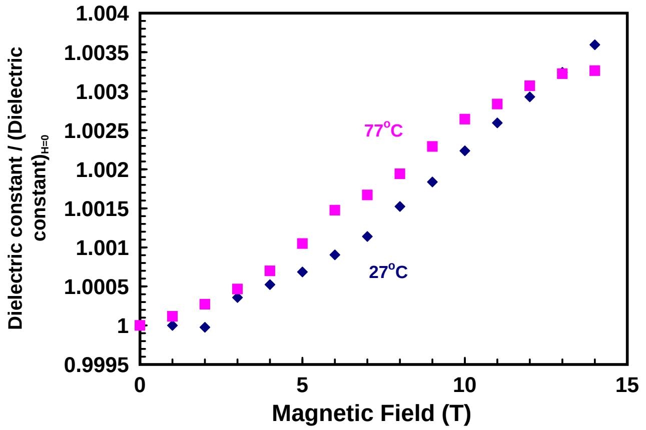

Fig. 3. Percentage change of the dielectric constant with magnetic field over the one without magnetic field at 1.0 MHz at two different temperatures.

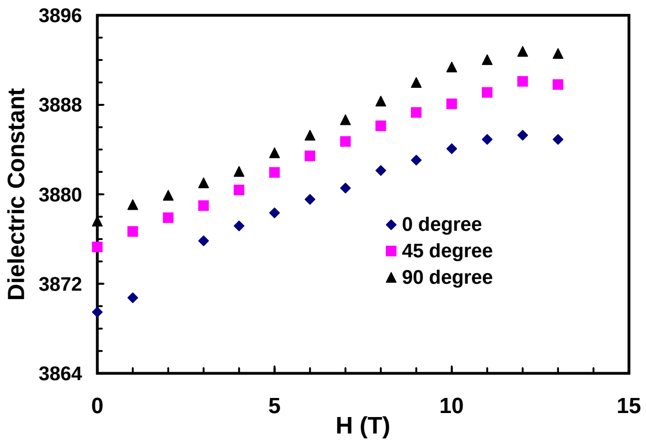

Fig. 4. Dielectric constant as a function of magnetic field perpendicular to the electric field for three rotation angles at 77 °C and 1.0 MHz.

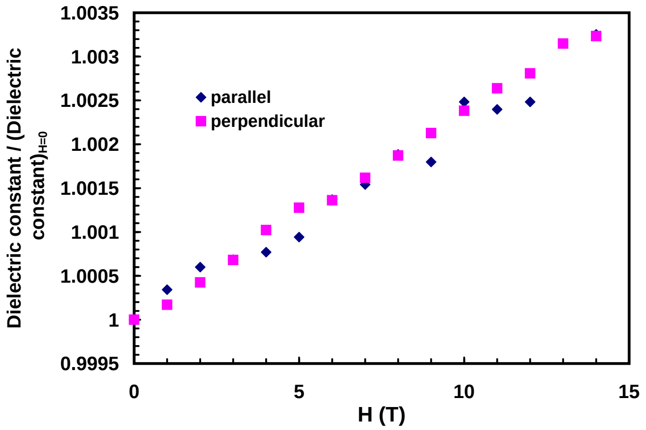

Fig. 5. Percentage changes of the dielectric constant as a function of magnetic field parallel and perpendicular to the electric field at 77 °C and 10 kHz.

the relations of dielectric constant with magnetic field for the three rotation angles in this field configuration is similar to each other. However, the absolute values of the dielectric constant for the three angles are different. It means that in this field configuration, the rotation angles do not affect the dielectric constant in this case. The percentage changes of the dielectric constant as a function of magnetic field at frequency 10 kHz and temperature 77 °C for the above two field configurations is shown in Fig. 5. The field orientation seems not to affect the dielectric properties of this sample in this study. Fig. 6 shows the percentage change of dielectric constant as a function of the magnetic field at temperature 77 °C and frequencies 10 and 100 kHz. It can be seen that the rate of the increase of the dielectric constant for higher frequencies seems higher. It is understandable that at higher frequency the contribution from the charge polarization in unit cell to the dielectric constant is greater and the magnetic field has stronger influence to the charge distribution in the unit cell than to the domain wall motion. Therefore, the

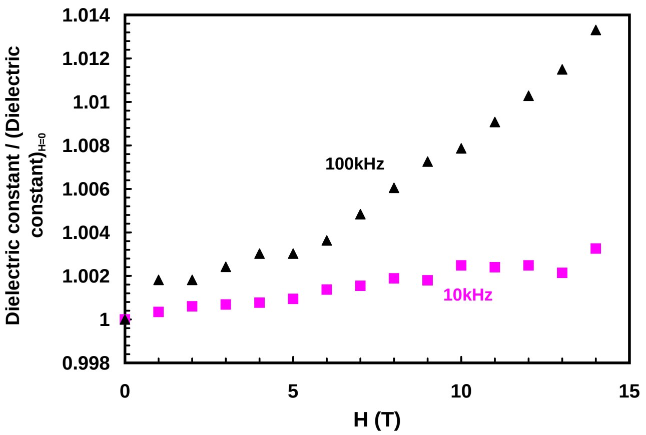

Fig. 6. Percentage change of the dielectric constant as a function of the magnetic field at 77 °C and frequencies 10 and 100 kHz.

magnetic field effect on the dielectric constant is expected stronger at higher frequencies.

Since the change of dielectric constant in this investigation is relatively small, we carefully examined the experimental results with the following two possible error sources. (1) The temperature deviation causes the change of the dielectric constant. During the measurement, no temperature change was found within the PPMS accuracy and we found the change of dielectric constant due to this temperature should be within 4 at 1 kHz and 0.7 at 1 MHz and (2) the Faraday's induction due to an applied magnetic field.

$$\varepsilon = -\frac{\mathrm{d}\Phi}{\mathrm{d}t}$$

may cause the rise of dielectric constant. We have estimated this effect. It was found that there are two reasons to exclude this concern: (a) the dielectric constant change should be a fix constant proportional to the rate of increasing the magnetic field; (b) the magnitude of the change of the dielectric constant due to the Faraday's induction is in the order of 10^{-3} much smaller than measured values (in the order of 10^{3}). Therefore, these suspicions mentioned above can be ignored.

Acknowledgements

This work is supported by Office of Naval Research, US Navy, grant N00014-02-1-0275.

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