

# Bismuth zinc niobate pyrochlore dielectric thin films for capacitive applications

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$\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  pyrochlore thin films were prepared on platinum coated Si wafers using a metalorganic deposition process. The structures, morphologies, and dielectric properties of films with two compositions:  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  and  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ , were investigated. Thin films of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  have a cubic pyrochlore phase when crystallized at 550 °C or higher. The crystal structure of  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  thin films was dependent on the firing temperature; the films showed the cubic pyrochlore phase at temperatures below 650 °C, and a pseudo-orthorhombic pyrochlore structure at 750 °C. A mixture of cubic and pseudo-orthorhombic structures was found in thin films crystallized at 700 °C.  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at 750 °C had a dielectric constant of  $\sim 150$  and a negative temperature coefficient of capacitance of  $-400$  ppm/°C.  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  thin films fired at 750 °C had a smaller dielectric constant of  $\sim 80$  and a positive temperature coefficient of capacitance of 150 ppm/°C. The dielectric constants of the thin films are composition, structure, and firing temperature dependent. The loss tangents of both types of films were smaller than 0.008. Bias voltage dependence of dielectric constant showed that the cubic  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at 750 °C were tunable, while the pseudoorthorhombic  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films were nearly field independent. The relatively large dielectric constants, small loss tangents, controllable temperature coefficients of capacitance, and tunability of the dielectric constant suggests that  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  thin films have potential applications for integrated microwave components and decoupling capacitors. © 2001 American Institute of Physics. [DOI: 10.1063/1.1328408]

## I. INTRODUCTION

The rapid development of communication technologies, especially mobile communication systems, is facilitated by miniaturization of devices. Integrated decoupling capacitors and microwave resonators are of interest for such systems. Dielectric materials for these applications must possess a moderate to large dielectric constant, low loss tangent ( $\tan \delta$ ), high dielectric quality factor  $Q$  ( $Q$  is equal to  $1/\tan \delta$ ), and a small temperature coefficient of resonator frequency (for resonators).  $\text{Bi}_2\text{O}_3\text{-ZnO-Nb}_2\text{O}_5$  (BZN) pyrochlore ceramics have previously been developed for low firing temperature multilayer capacitors.<sup>1-4</sup> Recent studies showed that some compositions in the BZN system also exhibit excellent microwave properties.<sup>5,6</sup> BZN ceramics with dielectric constants  $>100$ , temperature coefficient of resonant frequency  $|T_f| < 10$  ppm/°C and microwave  $Q \cdot f > 5000$  GHz have been reported.<sup>6</sup> The good dielectric properties shown by the BZN system suggest that thin films of this composition are potential materials for integrated microwave resonators and decoupling capacitors. Thin films may have the advantage of lower crystallization temperatures and smaller device size than bulk ceramics and can be integrated in microelectronic devices.  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  thin films deposited by a pulsed laser deposition technique were reported recently.<sup>7</sup>

In this article, we report on the fabrication and properties of BZN thin films prepared by a metalorganic deposition (MOD) process. The MOD process has been widely used to

deposit dielectric and ferroelectric thin films due to low processing temperatures, precise composition control, uniform deposition over large area substrates and low cost. The field tunability and dispersion of the relative permittivity in  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  and  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films are discussed.

## II. EXPERIMENTAL PROCEDURE

Two compositions of BZN thin films were investigated in this study:  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  and  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$ . These two compositions are members of the general family  $(\text{Bi}_{3x}\text{Zn}_{2-3x})(\text{Zn}_x\text{Nb}_{2-x})\text{O}_7$ , with  $x = 0.5$  and  $x = 2/3$ , respectively.

The starting materials in the MOD process were bismuth acetate, zinc acetate dihydrate, and niobium ethoxide (Aldrich, Chemical Company, Inc., Milwaukee, WI). 2-methoxyethanol, pyridine, and acetic acid (Aldrich, Chemical Company, Inc., Milwaukee, WI) were selected as solvents. Zinc acetate dihydrate was first mixed with 2-methoxyethanol and vacuum distilled at 110 °C to expel the water of hydration and to prevent niobium ethoxide from hydrolyzing. Niobium ethoxide was then added into the solution and refluxed at 120 °C for 1 h to form a (Zn, Nb) complex precursor, followed by vacuum distillation of byproducts. The solution was cooled down below 80 °C. In a separate flask, bismuth acetate was mixed with pyridine and stirred for 0.5 h. 30% by volume of acetic acid was added into the solution and stirred for 1 h until the solution became totally clear. The bismuth acetate solution was then added to

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the (Zn, Nb) precursor and the solution was refluxed at 120 °C for 0.5 h. After vacuum distilling off byproducts, the final precursor solution was diluted using 2-methoxyethanol to a concentration of 0.3 M.

The precursor solution was spin coated on platinum-coated Si wafers Pt/Ti/SiO<sub>2</sub>/Si (Nova Electronic Materials, Inc., Richardson, TX) at a speed of 3000 rpm for 30 s. The as-deposited films were pyrolyzed on a hot plate at a temperature of 350 °C for 1 min to remove the organics. The coating-pyrolysis procedure was repeated until the desired thickness was reached. The film was then crystallized in air using either a preheated tube furnace for 5 min or a rapid thermal annealer at a heating rate of 100 °C/s and a soaking time of 60 s. The thickness of the films prepared was 0.4–0.5 μm.

Both the solutions and the resulting films were analyzed by several techniques. The thermal decomposition of BZN precursor gels was studied using a TA TGA2050 thermogravimetric analyzer and a TA DTA1600 differential thermal analyzer (TA Instruments, Inc., New Castle, DE) at a heating rate of 10 °C/min. The gels were formed by drying the precursor solutions at 120 °C for 24 h. The crystallinity of the BZN thin films was characterized with a Scintag DMC-105 x-ray diffractometer (Scintag, Inc., Sunnyvale, CA) using Cu Kα radiation. A Digital Instruments Dimension 3100 atomic force microscope (AFM) (Digital Instruments, Santa Barbara, CA) was used in tapping mode to investigate the surface morphology and roughness of the thin films. To examine the electrical properties, platinum dots of 0.5 or 1.5 mm diameter were sputtered onto the films as top electrodes to form a Pt/BZN/Pt sandwich configuration. The dielectric properties of the BZN films were measured with a Hewlett Packard 4284A multifrequency inductance-capacitance-resistance LCR meter with a test signal of 0.03 V root mean square (rms) at 10 kHz. For temperatures between 200 and –175 °C, a computer-controlled Delta 9023 temperature oven (Delta Design, Inc., San Diego, CA) with a cooling ramp rate of 2 °C/min was used. A second sample chamber was employed for measurements between 300 and 4 K, again with a cooling or heating ramp rate of 2 °C/min. The measurement frequencies were between 20 Hz and 100 kHz. dc bias dependence measurements of dielectric properties were made using the dc bias voltage source provided by a HP4284A LCR meter. The maximum dc bias field for 0.48 μm thick samples was 830 kV/cm. Polarization–electric field (*P*–*E*) loops of the BZN films were measured by a RT66A ferroelectric test system (Radiant Technologies, Inc., Albuquerque, NM).

### III. RESULTS AND DISCUSSION

#### A. Thermal analysis

Figure 1 gives thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of the BZN gels. The TGA curve shows that the main weight loss started at ~250 °C and decomposition of the BZN gels was completed at ~400 °C, with a total weight loss of 27%. Only 0.37% additional weight loss was found between 400 and 850 °C. Assuming this weight loss to be caused by volatilization of

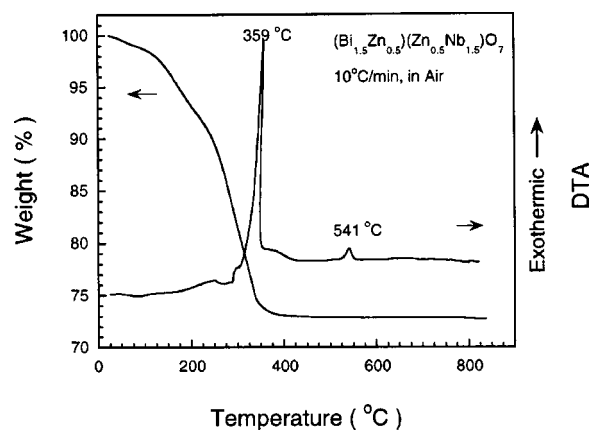


FIG. 1. TGA and DTA curves of the (Bi<sub>1.5</sub>Zn<sub>0.5</sub>)(Zn<sub>0.5</sub>Nb<sub>1.5</sub>)O<sub>7</sub> gels.

bismuth leads to 1.5 mol% of bismuth loss at a maximum. The result suggests that bismuth loss in BZN was not severe at firing temperatures below 850 °C. The DTA curve shows two exothermic peaks at 360 and 540 °C, respectively. The first exothermic peak at 360 °C (which was accompanied by a large weight loss) was associated with the decomposition of most of the organics. The second exothermic peak at 540 °C without any additional weight loss was attributed to crystallization of the BZN. This was confirmed by x-ray diffraction (XRD) studies on BZN films.

#### B. Crystallization

Previous results of the pyrochlore bulk ceramics have demonstrated that bulk ceramics of (Bi<sub>1.5</sub>Zn<sub>0.5</sub>)(Zn<sub>0.5</sub>Nb<sub>1.5</sub>)O<sub>7</sub> have a cubic pyrochlore structure with *a* = 1.056 nm.<sup>2,4</sup> However, Wang *et al.* suggest that Bi<sub>2</sub>(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)<sub>2</sub>O<sub>7</sub> is an orthorhombically distorted pyrochlore phase with *a* = 0.7202 nm, *b* = 0.7603 nm, and *c* = 1.064 nm.<sup>4</sup> The structure of Bi<sub>2</sub>(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)<sub>2</sub>O<sub>7</sub> ceramics is also firing temperature dependent and converts to a cubic phase at a higher firing temperature (~1100 °C).<sup>8</sup>

The XRD patterns of (Bi<sub>1.5</sub>Zn<sub>0.5</sub>)(Zn<sub>0.5</sub>Nb<sub>1.5</sub>)O<sub>7</sub> films fired at different temperatures are shown in Fig. 2(a). The films were amorphous at temperatures of 500 °C and below; no sharp diffraction peaks were observed in the films. Films fired at 550 °C were crystalline and showed a cubic pyrochlore structure. With increasing firing temperature, the intensities of the diffraction peaks strengthened, but the films maintained the cubic pyrochlore structure. No strong preferred orientation was found in the films. The lattice constant calculated from the films fired at 750 °C is 1.055 nm, which is close to the bulk value.

Figure 2(b) gives the XRD patterns of Bi<sub>2</sub>(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)<sub>2</sub>O<sub>7</sub> films fired at different temperatures. After the 500 °C anneal, the film was amorphous. Between 550 and 650 °C, the films appeared to have a cubic structure with a main peak (222) at 2θ = 29.3°. For the film fired at 750 °C, the diffraction pattern was found to be comparable to the bulk ceramic reported by Wang *et al.*<sup>4</sup> The film can be indexed to a pseudo-orthorhombic phase with lattice constants of *a* = 0.718 nm, *b* = 0.759 nm, and *c* = 1.058 nm. The XRD pattern showed the films still maintained a pseudo-

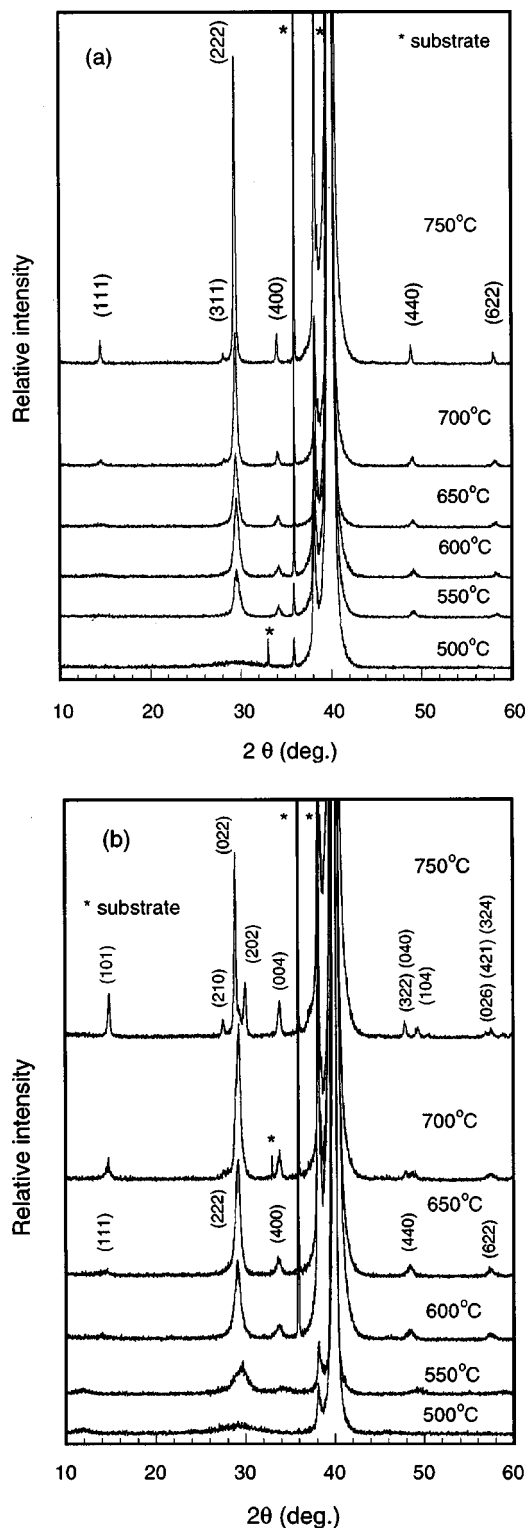


FIG. 2. XRD patterns of (a)  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films and (b)  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at different temperatures.

orthorhombic structure even when fired to 800 °C; no cubic phase was detected. A mixture of cubic and pseudo-orthorhombic structures was observed in films fired at 700 °C.

The phase evolution in the BZN thin films was found to be different from that of bulk ceramics. In bulk ceramics prepared by the mixed oxide route,  $\text{Bi}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  reacted

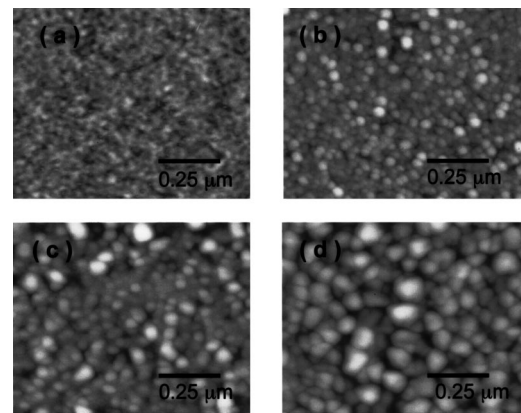


FIG. 3. AFM micrographs of  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at (a) 550 °C, (b) 650 °C, (c) 700 °C, and (d) 750 °C, respectively, for 5 min in a tube furnace.

first to form two kinds of  $\text{Bi}_2\text{O}_3$ – $\text{Nb}_2\text{O}_5$  compounds. These then reacted with  $\text{ZnO}$ .<sup>4</sup> A mixture of a pseudo-orthorhombic and cubic structures was formed at intermediate temperatures. At higher sintering temperatures, the cubic phase in  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  converted into the pseudo-orthorhombic phase, while for  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  the pseudo-orthorhombic phase transformed to the cubic phase. In thin films on the other hand, the cubic pyrochlore structure was directly formed at the low firing temperatures for both compositions. No pseudo-orthorhombic phase was ever observed in  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films over the temperature range investigated. The cubic phase in  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films transformed to the a pseudo-orthorhombic phase at higher firing temperatures. Single phase pseudo-orthorhombic  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films were obtained at 750 °C. The difference in phase evolution between the previous reports on bulk materials and the films prepared here is probably due in part to the better homogeneity of the MOD precursors. It is also possible that the bottom electrodes may play an important role in the phase formation sequence of the BZN thin films.

### C. Morphology

To investigate the surface morphologies of the BZN thin films, AFM micrographs were collected in tapping mode. Featureless AFM photos were found in the BZN films fired at 500 °C, which were amorphous as indicated by XRD. Figure 3 shows the results for  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at 550–750 °C. It can be seen that when the temperature was increased to 550 °C, very fine grains with a surface grain size of about 30 nm were observed in the films as shown in Fig. 3(a). The surface grain sizes increased with firing temperature. At temperatures of 750 °C, the grain size reached around 100 nm. The BZN films exhibited a dense microstructure with no cracks or defects. The surface roughness of the  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films calculated from the AFM data was very small as shown in Fig. 4. At a firing temperature of 550 °C, the average roughness was only 0.4 nm. The rms roughness increased with temperature and was 4.2 nm at 750 °C. AFM micrographs of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films showed similar features.

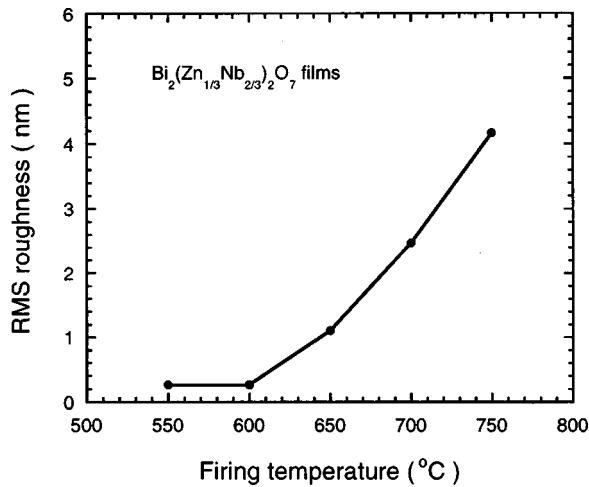


FIG. 4. Surface roughness of  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films calculated from AFM photographs.

#### D. Dielectric properties

Figure 5 gives the dielectric properties of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films as a function of firing temperature. The dielectric constants of the films increased monotonically with crystallization temperature and reached a value of 150 at 750 °C, which was comparable to the values of bulk ceramics with the same composition (140–170).<sup>2,4</sup> All films exhibited very low dielectric losses (loss tangent <0.008). The temperature dependence of the dielectric constant in the measuring temperature range  $-50$ – $100$  °C is given in Fig. 6(a). The dielectric constants changed linearly with temperature over this range. The temperature coefficient of capacitance (TCC) was calculated from Fig. 6(a) in terms of  $(C'-C)/C$ , where  $C$  and  $C'$  were the capacitance at  $-50$  and  $100$  °C, respectively. The result is shown in Fig. 7. The TCC of the films was also firing temperature dependent; it was  $-400$  ppm/°C for films fired at 750 °C and decreased towards zero at lower crystallization temperatures. The TCC of the  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at 750 °C was comparable to the reported values of bulk ceramics.<sup>2,4</sup>

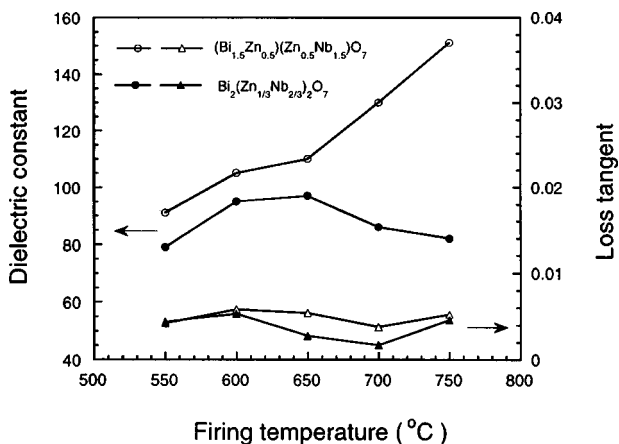


FIG. 5. Dielectric constant and loss tangent of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films and  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films as a function of firing temperature (measurement frequency = 10 kHz).

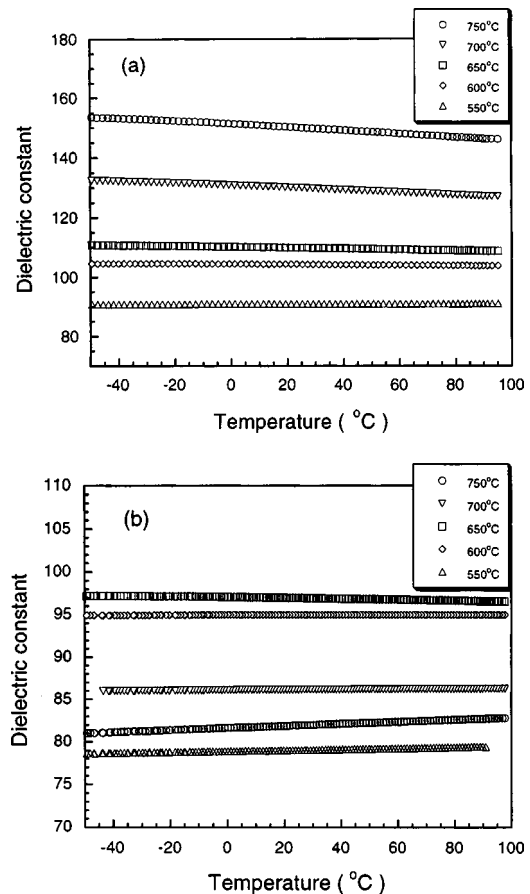


FIG. 6. Temperature dependence of dielectric constants of (a)  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films and (b)  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at different temperatures.

The dielectric properties of  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films versus firing temperature can be found in Fig. 5. The dielectric constant of the  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films was a function of firing temperature and had a maximum at 650 °C. The dielectric constant at 750 °C was 82, which was comparable to the bulk value.<sup>2,4</sup> The XRD in Sec. II indicated that  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films had a pseudo-orthorhombic pyrochlore phase at firing temperatures of 750 °C. Based on the

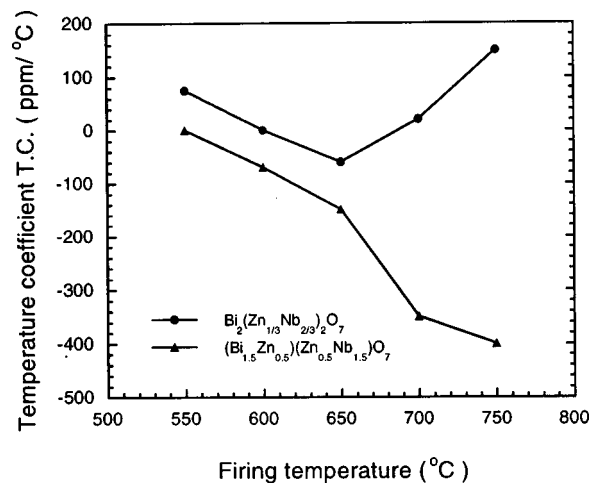


FIG. 7. TCC of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films and  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films as a function of firing temperatures.

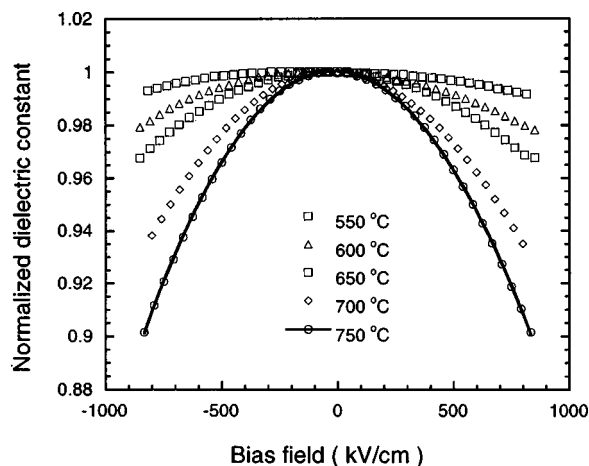


FIG. 8. Normalized dielectric constant vs dc bias field plots for  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at different temperatures. The measuring frequency was 10 kHz. The solid line was fitting curve for BZN films fired at 750 °C by Eq. (3).

above results, we can conclude that dielectric constant of BZN films with a pseudo-orthorhombic phase is smaller than that of the films with a cubic phase. Because of the cubic phase formed in  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films at firing temperatures of 650–700 °C, the dielectric constant in Fig. 5 increased with decreasing firing temperature. For firing temperatures of 600 °C and below the dielectric constant decreased due to weak crystallization of the films. The loss tangent of the films was lower than 0.008. The temperature dependence of dielectric constant of the  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films is shown in Fig. 6(b). The permittivity showed a good linear relationship in the measuring temperature range of  $-50$ – $100$  °C. The TCC calculated from Fig. 6(b) is shown in Fig. 7. TCC of the films fired at 750 °C was 150 ppm/°C, which was also comparable to the bulk values.<sup>2,4</sup> It can be seen from Fig. 7 that at the same firing temperature of 750 °C, the BZN films with a cubic phase had a negative TCC ( $-400$  ppm/°C), while films with a pseudo-orthorhombic phase had a positive TCC (150 ppm/°C). As the firing temperature decreased from 750 to 650 °C, the TCC of  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films decreased due to the cubic phase formed at low temperatures. A mixture of cubic and pseudo-orthorhombic phases in  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at 700 °C gives a very small TCC ( $\sim 20$  ppm/°C).

The bias electric field dependence of the dielectric properties of the BZN films was also investigated. Figure 8 gives normalized dielectric constant versus bias field plots for  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at different temperatures. The measuring frequency is 10 kHz. It can be seen that dielectric responses under the bias field are firing temperature dependent. For the cubic BZN films fired at 750 °C, the dielectric constant decreased with the bias field, while the loss tangent was constant (not shown in the figure). The dielectric constant changed 10% under a bias of 830 kV/cm. The curve was symmetric with respect to zero bias and had no hysteresis. The upper field attainable was limited by the dc bias the bridge was capable of applying, rather than the breakdown strength of the film. There is no evidence of saturation in the tunability up to the maximum measurement

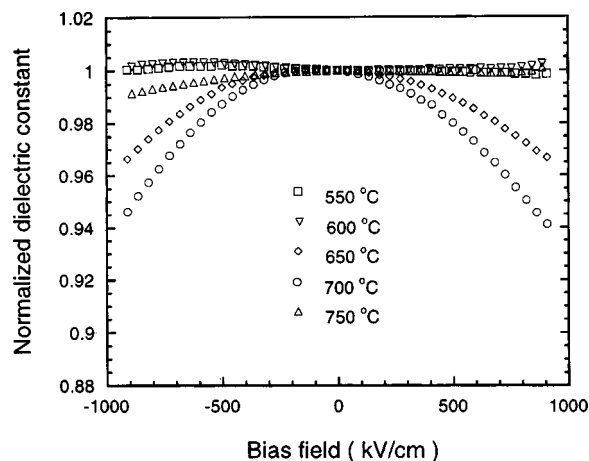


FIG. 9. Normalized dielectric constant vs dc bias field plots for  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at different temperatures. The measuring frequency was 10 kHz.

field. The tunability of the cubic BZN films decreased with decreasing firing temperature. At a firing temperature of 550 °C, the film was hard to tune by a bias field. The voltage variable dielectric constant makes cubic BZN thin films candidates for tunable microwave device applications.

Figure 9 shows normalized dielectric constants as a function of bias field for  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at different temperatures. Unlike  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films, the dielectric constants of the  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at 750 °C were almost constant. For the  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at 650 and 700 °C, their dielectric constants can be tuned by a bias field. This tunability is attributed to the cubic phase existing in the  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at lower temperatures. The pure pseudo-orthorhombic phase showed little evidence for tunability over the electric field range utilized.

The dielectric measurements demonstrate that the dielectric constants, TCC, and tunability of the BZN films depended not only on their composition, but also on the firing temperature and phase content. BZN films with the cubic pyrochlore phase have larger dielectric constants, negative TCC values, and larger tunability. Films with the pseudo-orthorhombic pyrochlore phase have smaller dielectric constants, positive TCC, and low tunability. The above results suggest that the dielectric properties of the BZN films can be tailored to a given application by adjusting composition, phase, and firing temperature.

It was also found that the cubic pyrochlore films showed a low temperature dielectric relaxation. It has been demonstrated previously on bulk ceramics<sup>3</sup> that many of the cubic bismuth pyrochlores showed evidence for a low temperature relaxation. Figure 10 gives the dielectric constant and loss of the  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at 750 °C as a function of measuring temperature. A frequency dispersion of dielectric properties was observed where the permittivity value dropped by almost a factor of 50%. The maxima in the dielectric constant curves were found to decrease and shift to higher temperatures with increasing measuring frequency. The corresponding maxima of loss tangent increased and shifted to higher temperature with increasing frequency. For temperatures below 65 K, the loss tangent was basically fre-

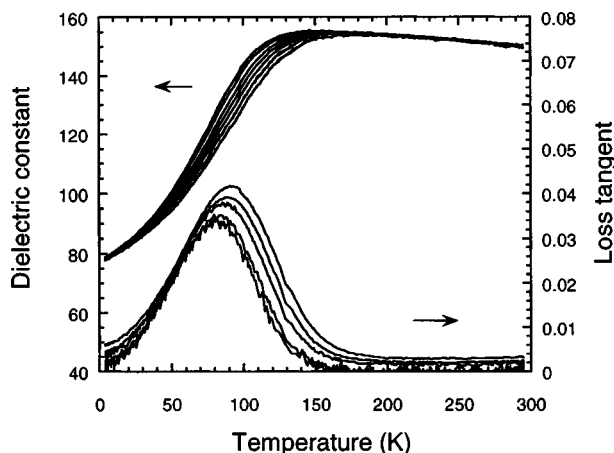


FIG. 10. Measuring temperature dependence of dielectric constant and loss tangent of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at  $750^\circ\text{C}$ . From top curve to bottom curve: 1, 2, 5, 10, 20, 50, and 100 kHz for dielectric constant; 1, 2, 5, 10 and 20 kHz for loss tangent. The cooling rate was  $2^\circ\text{C}/\text{min}$ .

quency independent. The dielectric constant and loss of  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films fired at  $750^\circ\text{C}$  versus temperature are shown in Fig. 11. The dielectric constant dropped rapidly below 100 K. No distinguished frequency dispersion was observed over the measured temperature range. The corresponding loss data showed no maxima.

The frequency dispersion characteristics of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films shows some analogies to the magnetic behavior of spin glasses.<sup>9</sup> Spin glasses are magnetic systems which cannot establish conventional long-range magnetic ordering due to some frozen-in structural disorder and/or frustration owing to competitive ferromagnetic and antiferromagnetic ordering process. As a result, the local symmetry is lower than the global one. Similar frequency dispersion is also observed in glass-like relaxor ferroelectrics such as lead magnesium niobate-lead titanate (PMN-PT),<sup>10</sup> dipole and quadrupolar glasses such as  $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  (RADP),  $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ , and

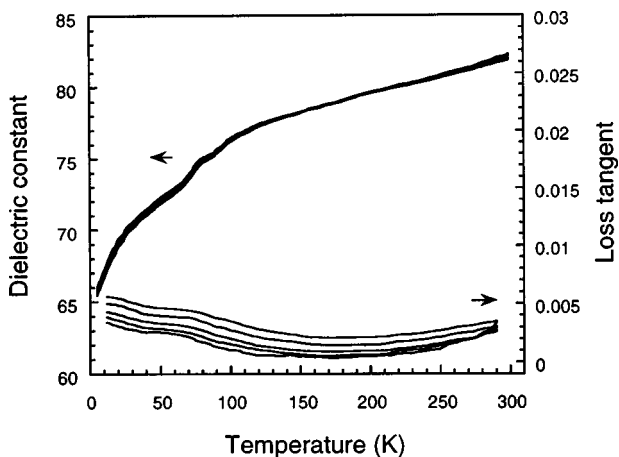


FIG. 11. Measuring temperature dependence of dielectric constant and loss tangent of  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films at frequencies of 0.5, 1, 2, 5, 10 kHz. For dielectric constant curves, the top curve has the lowest frequency, and for loss tangent curves, the top curve has the highest frequency. The cooling rate was  $2^\circ\text{C}/\text{min}$ .

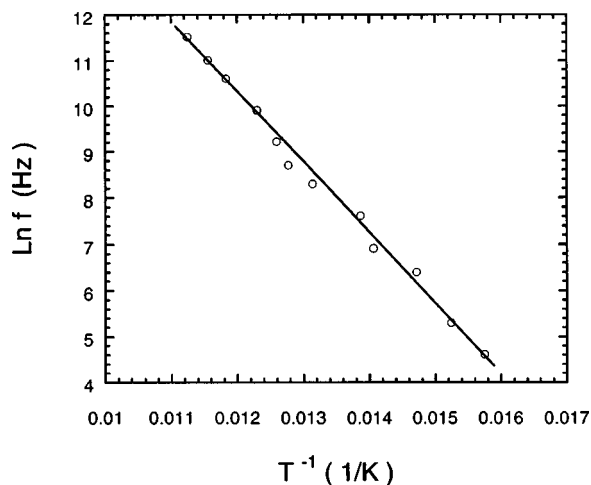


FIG. 12. An Arrhenius plot of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films based on the dielectric data in Fig. 10.

$\text{KBr}_{1-x}\text{CN}_x$ .<sup>11-13</sup> These similarities suggest that the BZN films also have glassy characteristics.

There are various empirical expressions to describe dielectric relaxation. Some dipole glasses like  $\text{KBr}_{1-x}\text{CN}_x$ <sup>13</sup> can be fitted to the Arrhenius equation

$$1/\tau_c = \nu_0 \exp[-E_a/k_B T], \quad (1)$$

where  $\tau_c$  is the characteristic relaxation time,  $\nu_0$  is attempt jump frequency,  $E_a$  is the activation energy, and  $k_B$  is Boltzmann constant.  $\nu_0$  and  $E_a$  are temperature independent. Figure 12 is an Arrhenius plot of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films based on dielectric data in Fig. 10. The logarithmic measuring frequency ( $f = \nu/2\pi = 1/2\pi\tau$ ) had a linear relationship with the reciprocal of the temperature at which the loss tangent was maximum.  $\nu_0$  and  $E_a$  calculated according to Eq. (1) were  $2 \times 10^{13}$  Hz and 0.13 eV, respectively. The jump frequency  $\nu_0$  of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films had the same order of magnitude as ionic vibrations of the lattice ( $\sim 10^{13}$  Hz), and was comparable to that reported for the  $\text{K}(\text{Br}, \text{CN})$  system.<sup>13</sup>

In contrast, for spin glasses,<sup>14</sup> ferroelectric relaxors like PMN-PT,<sup>10</sup> and dipole glasses like RADP,<sup>11</sup> their dielectric dispersion follows the Vogel-Fulcher equation

$$1/\tau_c = \nu_0 \exp[-E_a/(T - T_f)], \quad (2)$$

where  $T_f$  is the freezing temperature, which is defined as the temperature where the dynamic reorientation of dipolar cluster polarization can no longer be thermally activated.  $E_a$  and  $\nu_0$  in the Vogel-Fulcher relationship are temperature dependent. The temperature dependence of the activation energy and jump frequency were related to the temperature dependence of the correlation length, which is used to describe correlation between neighboring moments.<sup>15</sup> On cooling, the correlation length increases. For BZN films, the temperature independent  $E_a$  and  $\nu_0$  suggests a weak or an unchangeable correlation between polar clusters as a function of measurement temperature. Additional analysis of the full relaxation over a broader frequency range is necessary to identify whether  $T_f$  is finite in BZN films.

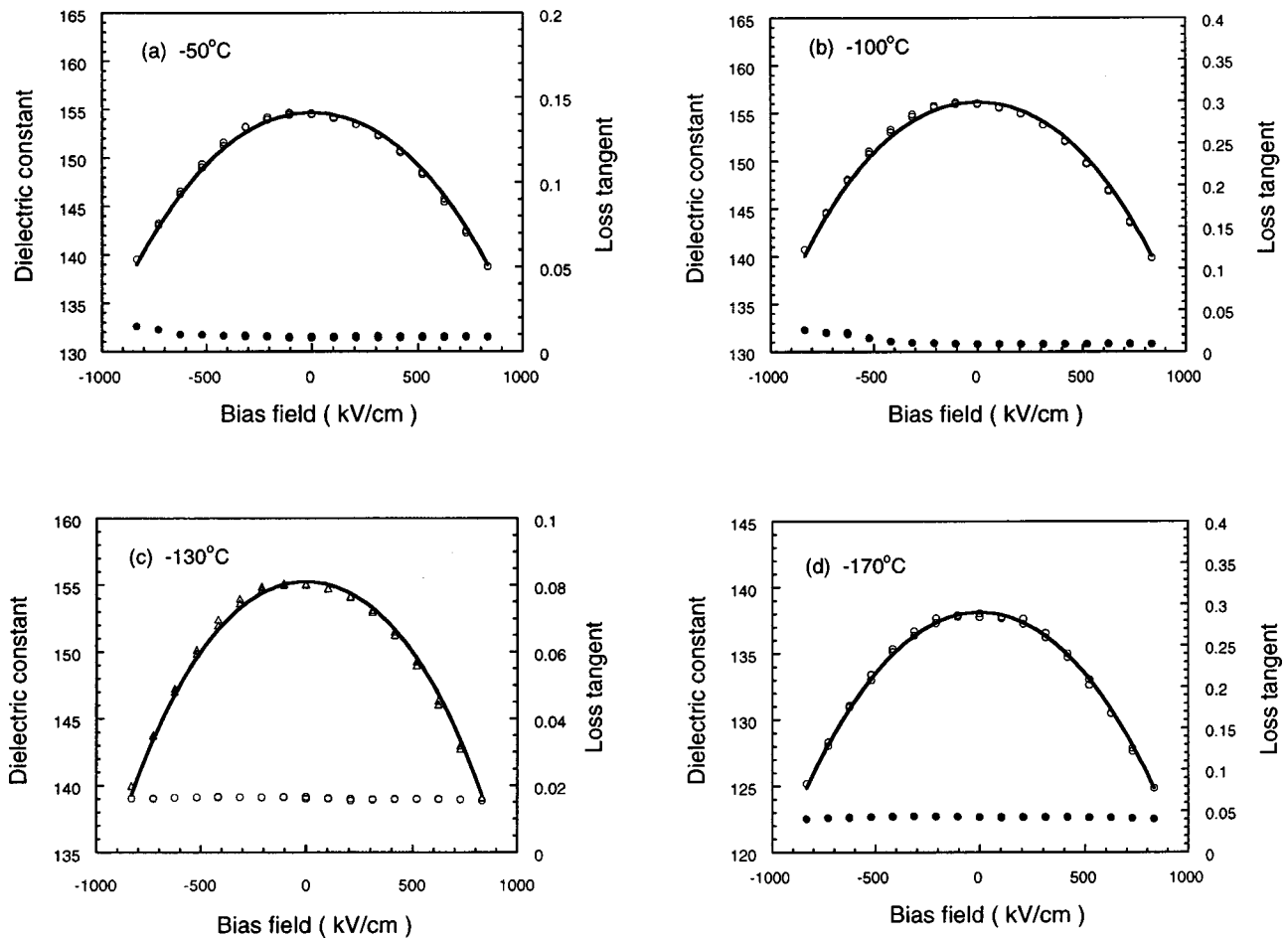


FIG. 13. Effect of bias field on dielectric properties of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at  $750^\circ\text{C}$  at the measuring temperatures of (a)  $-50^\circ\text{C}$ , (b)  $-100^\circ\text{C}$ , (c)  $-130^\circ\text{C}$ , and (d)  $-170^\circ\text{C}$ , respectively. The solid lines were fitting curves by Eq. (3). The measuring frequency was 10 kHz.

The bias field dependence of dielectric properties of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at  $750^\circ\text{C}$  was investigated at the different measuring temperatures. Figure 13 shows results measured for temperatures of  $-50$ ,  $-100$ ,  $-130$ , and  $-170^\circ\text{C}$ . It can be seen that all films demonstrated the same fractional tunability throughout the temperature range.

The bias field dependence of dielectric constant in  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films over this field range can be fitted by using a phenomenological power series expansion in the electric field

$$\epsilon(E, T) = \epsilon_0(T) + \epsilon_2 E^2 + \epsilon_4 E^4 + \dots, \quad (3)$$

where  $\epsilon$  is the dielectric constant,  $T$  is the measuring temperature,  $E$  is the bias field,  $\epsilon_0(T)$  is the zero field dielectric constant,  $\epsilon_2$  is the second order nonlinearity, and  $\epsilon_4$  is the fourth order nonlinearity. The solid lines in Figs. 8 and 13 are fits to the data at various measuring temperatures to the form of Eq. (3). The second order nonlinearity  $\epsilon_2$  was negative and had a weak dependence on measuring temperature, as shown in Fig. 14. The negative  $\epsilon_2$  suggested the stiffening of the dielectric response by dc bias. Studies by Viehland *et al.* showed that the second order nonlinearity of the PMN-PT was strongly temperature dependent<sup>15</sup> from negative to positive and then negative again on cooling, as shown in the inset of Fig. 14.

The dc field dependence of the dielectric response of the  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films was studied for bias levels of 0, 210, 415, and 830 kV/cm (see Fig. 15). The loss tangents were nearly independent of the bias field. This indicates that the peak temperatures of loss tangent  $T_{\text{max}}$  were bias field independent. It was found that in ferroelectric relaxors like PMN-PT, the bias field suppressed the frequency dispersion

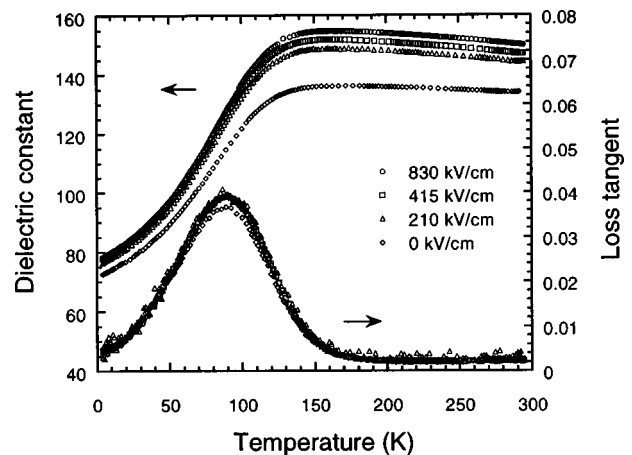


FIG. 15. Temperature dependence of dielectric constant and loss tangent of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films at 10 kHz with different bias fields.

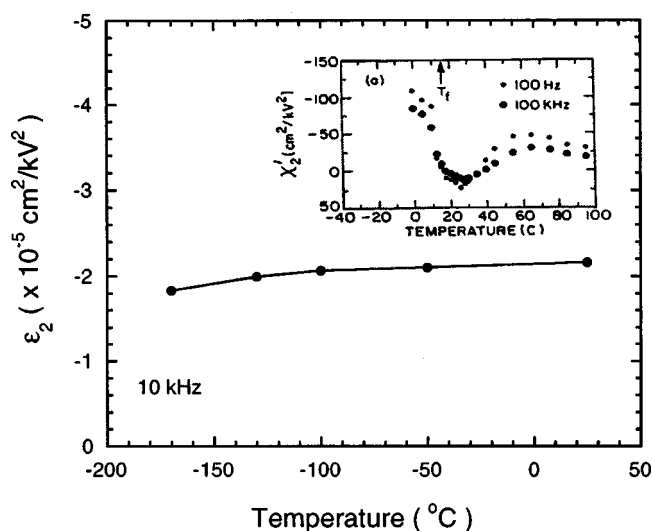


FIG. 14. The second order nonlinearity  $\epsilon_2$  calculated from Eq. (3) as a function of measuring temperature. In the inset, the second order nonlinearity of PMN-PT vs temperature is from Ref. 15.

and increased  $T_{\max}$ . It is believed that in relaxors, the large bias field destroys the glassy character and orders the local dipole field to establish a global equilibrium.<sup>10</sup> The correlation length increased with field and could reach a macroscopic scale at large enough fields. The BZN films studied here clearly differ in this way from such relaxor ferroelectrics. The films still showed strong frequency dispersion even at fields as high as 830 kV/cm. Thus, it is believed that at this field, the dipoles still cannot establish a long-range ordering. This, in turn, suggests that the dipole-dipole interactions are weak in this system.

One of the main characteristics of spin glasses and relaxors is that their field cooled state are anisotropic, with behavior like normal ferromagnets or ferroelectrics.<sup>10</sup> Thus, spin glasses and relaxors exhibit hysteresis at low temperatures when field cooled. However, in the BZN films, the data demonstrate that long-range ordering cannot be established at the fields investigated, which prevents the formation of either ferroelectric or antiferroelectric states at low temperatures. Figure 16 gives the  $P$ - $E$  loops of the BZN films measured at 4.2 K cooled under a bias field of 830 kV/cm. No hysteresis was observed in the BZN films. This result also suggests that a long range ordering of dipole moments cannot be established at the low temperatures under field cooling for the conditions investigated.

#### IV. CONCLUSIONS

$(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  and  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  thin films were successfully prepared by the MOD process.  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films showed the cubic pyrochlore structure, while the structure of  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  thin films depended on the firing temperature. Such films were a cubic in the temperature range of 550–650 °C and pseudoorthorhombic when crystallized at 750 °C. A mixture of cubic and pseudoorthorhombic pyrochlore structures was formed at 700 °C. The  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at 750 °C have a dielectric constant of 150 and a negative

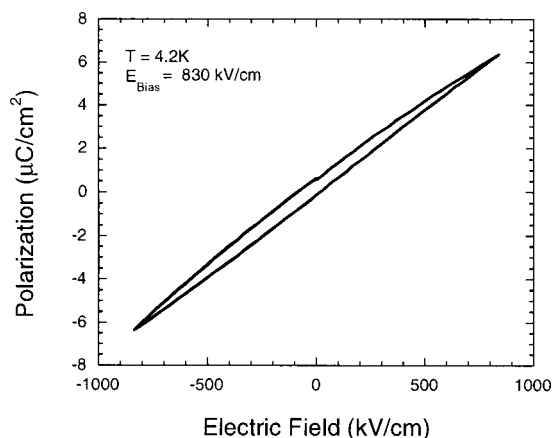


FIG. 16.  $P$ - $E$  loop of  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films measured at temperature of 4.2 K. The film was cooled down to 4.2 K at a rate of 2 °C/min. under a bias field of 830 kV/cm.

TCC.  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  thin films fired at 750 °C had a smaller dielectric constant of about 80 and a positive TCC. Loss tangents of both types of BZN films are below 0.008 at 10 kHz. The cubic  $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$  films fired at 750 °C had a large tunability and the pseudoorthorhombic  $\text{Bi}_2(\text{Zn}_{1/3}\text{Nb}_{2/3})_2\text{O}_7$  films had a low tunability. The cubic BZNs showed strong frequency dispersion in the dielectric responses at low temperature, which had glassy characteristics similar to spin glasses. Strong evidence suggests that the correlation between dipole clusters in the cubic BZN was very weak in the temperature range investigated. Even under field cooled conditions, the dipole clusters cannot establish a long-range ordering at 4.2 K. The tunability, large dielectric permittivity, and low dielectric loss make BZN interesting for capacitive components, as well as in microwave applications.

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