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Permalink

https://escholarship.org/uc/item/51w852q9

Journal

Applied Physics Letters, 86(3)

ISSN

0003-6951

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Publication Date

2005

Peer reviewed

The temperature dependence of the dielectric tunability

of pyrochlore bismuth zinc niobate thin films

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Abstract

The change in permittivity of bismuth zinc niobate (BZN) films with the cubic pyrochlore structure under an applied electric field was measured as a function of temperature. Dielectric measurements were performed using planar capacitor structures with Pt electrodes on sapphire substrates. The electric field tunability of the permittivity was weakly temperature dependent and increased with decreasing temperature up to the onset of dielectric relaxation. At temperatures below the onset of the dielectric relaxation (~ 150 K at 1 MHz), larger electric fields were required to achieve the highest tunabilities. A simple model of hopping, non-interacting dipoles was not suited to describe the dielectric tunability of BZN thin films. A better description of the experimentally observed behavior at temperatures above the onset of the dielectric relaxation was obtained using a simple random-field model with hopping dipoles in a uniform distribution of random fields.

Recently, $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) thin films have attracted interest for integrated capacitor applications because of their relatively high permittivity (~170-220) [1-4] and very low dielectric losses (tan δ ~ 5 × 10^{-4} at 1 MHz) [3]. Furthermore, BZN thin films exhibit a large electric field dependence of their dielectric permittivity [1-4]. The electric field tunability n can be defined as $\varepsilon(0)/\varepsilon(E)$, where $\varepsilon(0)$ is the dielectric constant at zero applied field and $\varepsilon(E)$ is the dielectric constant at an applied DC field E. At a maximum applied bias field of 2.4 MV/cm, the tunability was greater than 2:1 at room temperature [3]. Films that combine a high tunability with low losses are attractive for tunable microwave device applications. Figure 1 shows that the films maintain a high tunability into the GHz frequency range.

To date, large electric field tunabilities have mostly been observed in ferroelectrics close to the paraelectric/ferroelectric phase transformation temperature or in incipient ferroelectrics at low temperatures [5]. In contrast, BZN has the cubic pyrochlore structure (space group $Fd\overline{3}m$) and is not ferroelectric [1]. Zn randomly substitutes for Bi on the A-site and Nb on the B-site of the pyrochlore structure (general formula $A_2B_2O_6O'$ where O' is the seventh oxygen bonded only to the A-site) [6]. Both the A-cations and O' ions are randomly displaced from their ideal positions in cubic pyrochlore with 6 possible positions for the A site and 12 for the O' site [6,7]. Vacancies on A-site and oxygen positions have also been reported [6,7]. The displacements of ions is thought to strongly affect the dielectric constant and a low temperature dielectric relaxation, i.e., a time lag between the applied electric field and the polarization [6,8-11]. The frequency dependence of the dielectric relaxation is characterized by a shift of the

drop in the dielectric constant and the associated dielectric loss peak to higher

temperatures with increasing measurement frequency.

The origin of the large electric field tunability of the permittivity of BZN is not

yet understood. The goal of this paper is to provide an initial understanding of the nature

of the tunability of BZN.

Thin films were deposited by radio-frequency (rf) magnetron sputtering from a

stoichiometric 3 inch $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ target (Praxair Surface Technology Inc.) using a

$(Ar+O_2)$ sputter gas mixture, with an Ar/O_2 flow ratio of 85/15, an overall gas pressure of

50 mTorr, and a sputter power of 150 W. The substrates were (0001) sapphire single

crystals coated with 100 nm Pt layer bottom electrodes that were deposited by electron

beam evaporation. The substrate temperature was 300 ˚C during deposition. An *ex situ*

post-deposition anneal was performed for 5 minutes in air at 750 C to crystallize the

films. The film thickness, determined by cross-section transmission electron microscopy

(TEM), was about 160 nm. X-ray powder diffraction and TEM detected only the cubic

pyrochlore phase [12]. For dielectric measurements, planar capacitor structures with 50

$\mu m \times 30\ \mu m$ Pt top electrodes were fabricated, as described elsewhere [3]. The dielectric

properties were measured with a 500 mV oscillating test field using an impedance

analyzer (Agilent model 4294A) connected to an air coplanar probe (Cascade Microtech,

Inc.). Unless stated otherwise, all measurements were carried out at 1 MHz. For

measurements between 100 and 320 K, the impedance analyzer was attached to a

cryogenic wafer probe station (RMC Cryosystems). Measurements above 320 K were

performed using an MMR probe station. The loss tangents of the films, as calculated

from the measured device quality factor Q, i.e. $\tan \delta = Q^{-1}$, were ~ 0.0005 at room temperature.

Figure 2 shows the applied electric DC field E_n necessary to achieve a tunability n, as a function of temperature. E_n decreases with decreasing temperature, i.e. at a given applied field, the tunability increases with decreasing temperature. The increase in tunability is correlated with the increase in the zero-bias dielectric constant with decreasing temperature (Fig. 3). However, the dielectric nonlinearity is not a simple linear function of the zero-bias permittivity. The field required to achieve the highest tunabilities decreases more rapidly with decreasing temperature than that for the small tunabilities. At temperatures below 250 K, tunabilities up to $n = 2.5$:1 (or 60 % relative tunability, defined as $n_r = \varepsilon(0) - \varepsilon(E)/\varepsilon(0)$) can be achieved. The higher tunabilities are also due to the higher breakdown strength at low temperatures, which allows the application of higher fields. As reported by others [4], BZN films are tunable well into the dielectric relaxation region, shown in Fig. 3. The onset of the dielectric relaxation appears in the permittivity curve at ~150 K (at a measurement frequency of 1 MHz), but is visible as an increase in loss at temperatures below about 175 K (details of the dielectric relaxation behavior of these films have been reported elsewhere [12]). At temperatures below the onset of the dielectric relaxation, a larger E_n is needed with decreasing temperature for the highest tunabilities.

The simplest description of the electric field tunability of a non-ferroelectric material involves the field-induced hopping of random, non-interacting dipoles in a double-well potential. Assuming the total number N of dipoles per unit volume is given

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by N_1+N_2, where N_1 is the number of occupied wells 1 and N_2 the number of occupied wells 2, then the relative populations of the wells is given by

$$N_1/N_2 = \exp(-2 p_0 E/kT) \tag{1}$$

where p_0 is the dipole moment, E is the applied field, k is the Boltzmann constant and T is the temperature [13]. The polarization P of the system is controlled by the number of dipoles in one direction that are not compensated by dipoles in the other direction [13], i.e.

$$P = p_0(N_2 - N_1)/V \tag{2}$$

Eqns. (1-2) can be combined to give

$$P = p_0 N/V \cdot \tanh(p_0 E/kT) \tag{3}$$

The dielectric constant ε is given by

$$\varepsilon = \partial P/\partial E = N p_0^2/kTV \cdot \mathrm{sech}^2(p_0 E/kT) \tag{4}$$

and tunability n is given by:

$$n = \varepsilon(0)/\varepsilon(E) = \cosh^2(p_0 E/kT) \tag{5}$$

Rearranging gives the applied field E_n necessary to achieve a tunability n:

$$E_n = kT/p_0 \ln(\sqrt{n} + \sqrt{n-1}) \tag{6}$$

Comparison with the data shown Fig. 1(a) shows that Eqn. (6) does not describe the experimentally observed behavior, as an extrapolation of a linear fit to the data would not intercept the temperature axis at 0 K. This implies that an additional field is required to achieve a given tunability and that additional interactions exist that limit the tunability at low temperatures. For example, the reorientation of dipoles may be affected be random fields [14]. In BZN, likely sources of random fields are the randomly off-centered ions and the chemical disorder on A- and B-sites. In bulk BZN, a uniform

distribution of random fields has been suggested to be responsible for the relatively broad low-temperature dielectric relaxation [8].

To model the influence of random fields on the polarization response described by Eqn. (3), E in Eqn. (3) should be substituted with $E+E_{rf}$, where is E_{rf} the projection of the local random field along the direction of the applied electrical field and an averaging over the distribution of E_{rf} must be performed [15]. To obtain a qualitative description of the experimental results, only the simplest case, which assumes a uniform distribution of random fields (E_{rf}), is considered here. In this case, the polarization is given by [15]:

$$P = \frac{N}{V}\frac{p_0}{2E_r}\int_{-E_r}^{+E_r}\tanh\left(p_0\frac{E+E_{rf}}{kT}\right)dE_{rf} = \frac{N}{V}\frac{kT}{E_r}\tanh^{-1}\left[\tanh\left(\frac{p_0 E_r}{kT}\right)\tanh\left(\frac{p_0 E}{kT}\right)\right]$$

(7)

The permittivity ε and the tunability n are obtained by differentiating Eqn. (7) (cf. Eqns. (4-5)):

$$n = \frac{\cosh^2(p_0 E/kT)-1}{\cosh^2(p_0 E_r/kT)}+1$$

(8)

The electric field E_n to achieve a tunability n is then given by:

$$E_n = \frac{kT}{p_0}\ln\left(\sqrt{1+(n-1)\cosh^2(p_0 E_r/kT)}+\sqrt{(n-1)\cosh^2(p_0 E_r/kT)}\right)$$

(9)

Eqn. (9) predicts that materials with a wide distribution of random fields (large E_r) require larger applied fields to achieve a given tunability n and that random fields reduce the temperature dependence of E_n at low temperatures (E_n can even increase on cooling, see Fig. 2). The solid lines in Fig. 2 are least-square fits to the data above 150 K to Eqn. (9). The data affected by the dielectric relaxation (i.e., below ~ 150 K) cannot be described by a quasi-static model.

The average values for p_0 and for E_r obtained from the fits were $3.21\pm0.21\times10^{-29}$ C m and $1.66\pm0.33\times10^{8}$ V/m, respectively (Table I). The dipole moment corresponds to a charge separation of the electronic charge e by a distance x of ~ 0.4 nm ($p_0 = 1/2 e \cdot x$). Considering that the hopping charge is likely greater than e, this compares reasonably well with the off-centering of the A-site cations of 0.039 nm, and of the O' ions of 0.046 nm [6] or with hopping between empty sites. The random field is of the same order as the field of an electron charge at a distance of ~ 3 nm. In a first approximation, the physically reasonable values obtained by the model described by Eqn. (9) indicate that dielectric behavior of BZN is described by the random-field model.

Better agreement between the experimental data and the model may be obtained with a less simplistic model for the random field distribution. For $E_n / E_r \ll 1$, tails of the random field distribution only weakly influence the response and the "top-hat" distribution function for E_{rf} may be considered a reasonable approximation. For larger tuning fields ($E_n \geq E_r$) the exact shape of the distribution function has a greater influence on the response. This may explain why the fit values for E_r are field dependent (see Table I). However, the model seemed to match the experimental data better at larger applied fields. At smaller fields, the increase in E_n with temperature is found to be less rapid than predicted. The increase in E_n at low temperatures predicted by the model cannot be experimentally confirmed, because of the onset of the dielectric relaxation, which is not described by the model. The development of improved models using more realistic random field distributions is currently underway.

In summary, we have shown that the dielectric tunability of BZN films is only weakly temperature dependent at temperatures above the onset of the dielectric

relaxation. BZN films thus have a practical advantage over tunable ferroelectric materials, as they would allow temperature-stable tunable devices. We have also shown that, in a first approximation, at temperatures above the dielectric relaxation, the temperature dependence of the BZN film tunability can be described by a simple model of hopping dipoles under the influence of random fields. This is consistent with the chemical and displacive randomness of the BZN structure that controls the dielectric behavior [6,8]. Differences between the model and the experimental data are likely due to specifics in the random field distribution that are not included in the simple model presented here.

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Table I: Fit results for p_0 and E_r in Eqn. (9), using the experimental data above 150 K shown in Fig. 2.

Tunability n	Relative tunability n_r	p_0 [C m]	E_r [V/m]
10/9	10 %	$3.30\times10^{-29} \pm 1.02\times10^{-30}$	$1.29\times10^{8} \pm 1.45\times10^{6}$
5/4	20 %	$3.37\times10^{-29} \pm 8.26\times10^{-31}$	$1.36\times10^{8} \pm 1.11\times10^{6}$
10/7	30 %	$3.39\times10^{-29} \pm 9.09\times10^{-31}$	$1.48\times10^{8} \pm 9.06\times10^{5}$
5/3	40 %	$3.36\times10^{-29} \pm 1.16\times10^{-30}$	$1.68\times10^{8} \pm 8.02\times10^{5}$
2	50 %	$2.89\times10^{-29} \pm 4.99\times10^{-31}$	$1.97\times10^{8} \pm 3.94\times10^{5}$
20/9	55 %	$2.92\times10^{-29} \pm 4.37\times10^{-31}$	$2.20\times10^{8} \pm 3.61\times10^{5}$
Average values		**$3.21\times10^{-29} \pm 0.21\times10^{-29}$**	**$1.66\times10^{8} \pm 0.33\times10^{8}$**

Figure Captions

Figure 1 (color online)

Bias field dependence of the permittivity of BZN films in a planar Al_2O_3/Pt/BZN/Pt capacitor structure, measured at 1 GHz.

Figure 2 (color online)

Applied electric DC field E_n required to achieve an electric field tunability n, defined as $\varepsilon(0)/\varepsilon(E)$, for BZN films grown on platinized sapphire substrates. The markers and dashed lines represent the experimental data, and the solid lines represent least-square fits using Eqn. (9), using p_0 and E_r as the parameters for the fit.

Figure 3 (color online)

Permittivity and loss as a function of temperature and frequency between 1 kHz and 10 MHz (permittivity) and 1 kHz and 1 MHz (loss). Above 1 MHz the losses increased due to conductor losses in the electrode and are not shown. The dashed line indicates the temperature of the drop in the permittivity at 1 MHz due to the onset of the dielectric relaxation.
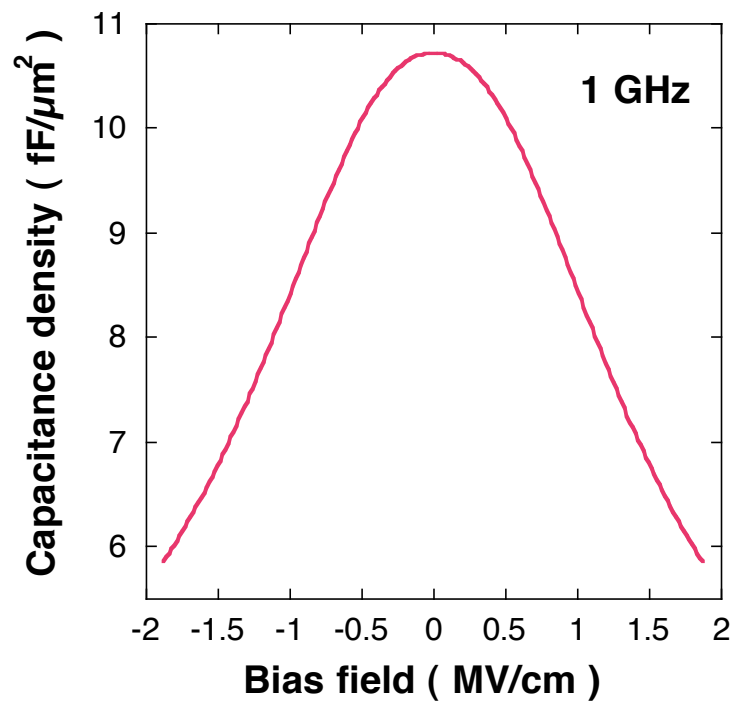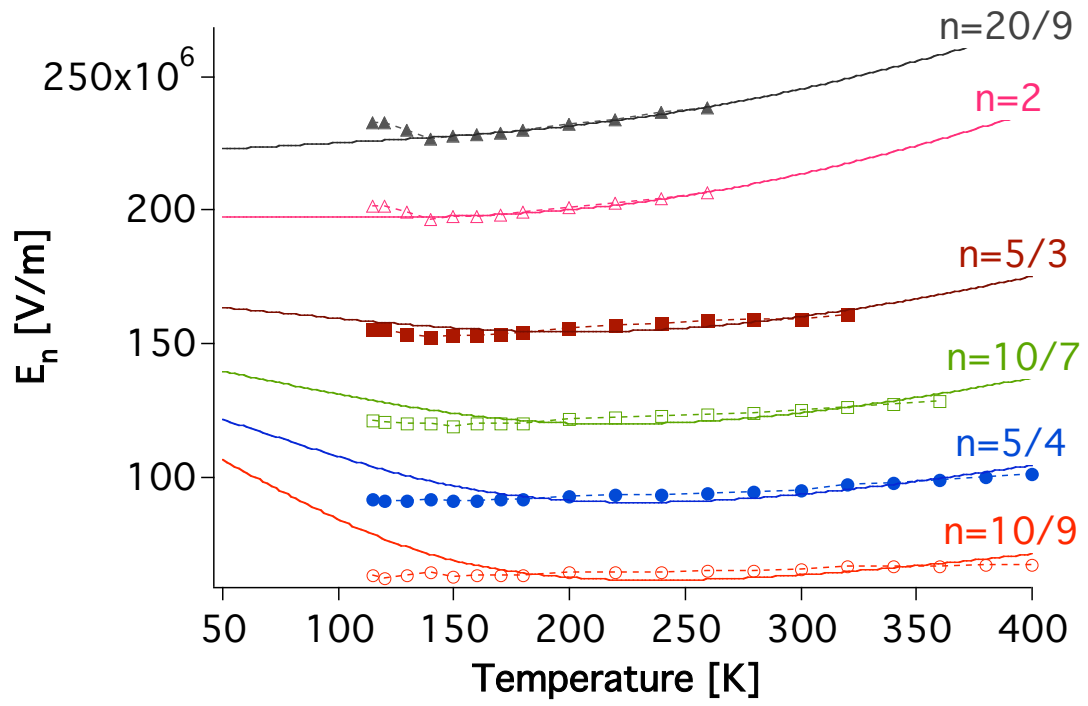
Figure 1

Figure 2

Figure 3