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Citation: Journal of Applied Physics **105**, 07D912 (2009); doi: 10.1063/1.3068477
View online: http://dx.doi.org/10.1063/1.3068477
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/105/7?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **105**, 07D912 (2009)

Dielectric constant at *x*-band microwave frequencies for multiferroic $BiFeO_3$ thin films

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(Presented 11 November 2008; received 21 September 2008; accepted 5 November 2008; published online 5 March 2009)

The magnetic-induced dielectric responses of $BiFeO_3$ (BFO) thin films were measured at the *X*-band microwave frequency ranged from 7 to 12.5 GHz. The measurement was given initially by a high-precision cavity microwave resonator without magnetic field. Both the real and imaginary parts of the permittivity showed its dielectric property as a function of the measuring frequency. The *X*-band dielectric responses of the BFO thin film were then measured by a controlled magnetic field at room temperature. The data demonstrated up to 2.2% dielectric tunability by using only 3.46 kOe magnetic field at TE_{107} mode (9.97705 GHz). © *2009 American Institute of Physics.*
[DOI: 10.1063/1.3068477]

I. INTRODUCTION

Materials possessing coupled electric, magnetic, and structural order characteristics that result in simultaneous ferroelectric, ferromagnetic, and ferroelastic reactions are known as multiferroics.[1,2] For them, electrical polarization can be induced by the magnetic field while the electrical field induces magnetization. This effect is called *magnetoelectric* effect (ME effect). Those materials recently became the focus of researches because of their magnetoelectric coupling phenomenon and their potential applications in multiple controlled devices[3–5] and sensors. At room temperature, however, the candidate materials for both magnetic and electrical controlled applications are very limited[6] because most of the currently known multiferroic materials exhibit a low magnetic-transition temperature (<273 K) in contrast to a high ferroelectric-transition temperature ($T_C > 350$ K).[6–8] This large difference between the magnetic and ferroelectric-transition temperatures is clearly one of the obstacles to the exploitation of multiferroics in real applications at room temperature.[9] From this point of view, $BiFeO_3$ (BFO) is the best candidate because it has both high antiferromagnetic ($T_N = 640$ K) and ferroelectric ($T_C = 1100$ K) transition temperatures,[10,11] which lead to wide application of this material in the design of actuators, transducers, and storage devices. The properties of BFO such as the domains, thermal properties, magnetization, magnetoelectric coupling, other element substitution such as Ba or La, and permittivity under megahertz region have been studied for years.[12–14] However, the permittivity at microwave region was poorly studied and it needs more attention for its benefits in the designing of dielectric devices. This motivated us to study the permittivity at *x*-band microwave frequencies. In this study, the BFO thin films were prepared by rf sputtering system, then perturbation method by using the cavity microwave resonator[15] was used for measuring both real and imaginary parts of the permittivity at *x*-band microwave frequencies (7–12.5 GHz) for TE_{10n} modes ($n = 3, 5, 7, 9$) generated by a vector network analyzer. X-ray diffraction (XRD) was used to perform the phase identification of the BFO films. Magnetization response to external magnetic field was measured by a superconducting quantum interference device (SQUID) magnetometer. The dielectric variation induced by the magnetic field was also examined on BFO thin films by adding the external magnetic field. From this study, the magnetoelectric coupling of the dielectric constant at *x*-band microwave frequencies was evident by the effect of magnetism and ferroelectricity simultaneously at room temperature in BFO thin films.

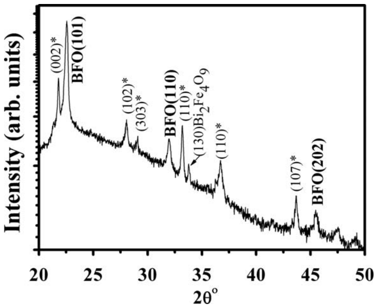

FIG. 1. XRD pattern of BFO thin film (100 nm thick). Peaks labeled with (*) belong to the quartz substrate.

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0021-8979/2009/105(7)/07D912/3/$25.00

TABLE I. The measured resonant frequencies with and without 100 nm BFO thin film (unit: GHz).

Resonant mode	TE_{103}	TE_{105}	TE_{107}	TE_{109}
Without BFO film	7.18815	8.41165	9.97705	11.74705
With BFO film	7.186675	8.4102	9.9756	11.74595

II. PERMITTIVITY MEASUREMENT AT MICROWAVE FREQUENCIES

The samples were prepared by rf sputtering deposition. High-quality BFO target (99.9%) was used to fabricate the BFO films on quartz substrates. Before deposition, the quartz substrate was cleaned before putting into the vacuum chamber. The system was pumped down to a 3×10^{-6} torr pressure. In depositing, the BFO target was cleaned by ion source for a few minutes and then deposited on the substrate with Ar and O_2 gas injected into the chamber. The deposition rate was steadily controlled around 1 Å/s. The samples were then annealed up to 900 °C by 4 °C/min heating up and maintained for 1 h at 900 °C then cooled down to room temperature at 4 °C/min. The whole annealing process was well controlled and maintained at air atmosphere. The phase identification of BFO(100 nm)/quartz(1.0 mm) structure was performed by XRD using Cu $K\alpha$ radiation. As can be seen in Fig. 1, the peak that was exhibited at $2\theta=22.509°$, 32.08°, and 45.827° demonstrated the (101), (110), and (202) BFO phases. The peak at $2\theta=33.774°$ belong to second phase of BFO having the form $Bi_2Fe_4O_9$.

By comparing the relative intensities of the peaks belong to both phases of BFO, we see explicitly that the second phase has less than 5% of the original phase $BiFeO_3$. This means that the 900 °C annealing shows a completion of crystallization process to form high purity BFO film having (101) preferential orientation.

The magnetization response to the external magnetic field showed diamagnetic signals without any hysteresis. This is consistent with a weak antiferromagnetic[12] contribution from the BFO films plus the diamagnetic signals of the quartz substrate.

In our experiment, an *X*-band microwave resonator with unloaded quality factor (*Q*-value) up to 5000 was designed for the permittivity measurement. This provided an enough sensitivity to extract the frequency S_{21} responses from the Agilent 8510C network analyzer with and without the BFO films in the microwave resonator. This was very important to sense the frequency shifting which was used to calculate the permittivity of BFO thin films in this study. Before our permittivity measurement, RT Duroid/6100[16] was used as a standard sample to make sure that the proper setup and measurement in the cavity microwave resonator were achieved. The sample was then measured by TE_{103}, TE_{105}, TE_{107}, and TE_{109} modes that were generated by the cavity resonator and 8510C network analyzer. Four resonant frequencies were undertaken from 7 to 12 GHz in our experiment. Table I demonstrates the resonant frequencies with and without a 100 nm BFO film. As can be seen, near megahertz frequency shift was detected in our measurement. Using resonant frequencies and the perturbation method, the real and imaginary parts of permittivity were obtained and given in Figs. 2 and 3, respectively. As can be seen in Fig. 2, the real part of permittivity is around 328 at 7.18 GHz and decreases to 205 at 11.74 GHz. The decreasing of ε' with increasing frequency can be understood by the dipole relaxation wherein at high frequencies the induced dipoles are unable to follow the frequency of the applied field.[14]

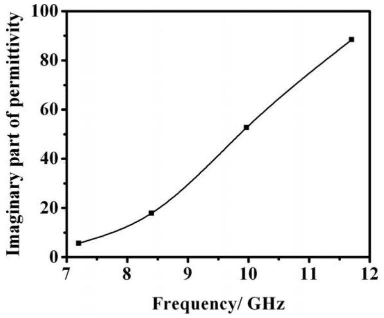

FIG. 3. Imaginary part of the permittivity for the BFO thin film.

Figure 3 shows that the imaginary part of the 100 nm BFO thin film is about 5.6 at 7.18 GHz and increases to 88 at 11.8 GHz. This increase in ε'' with the frequency is due to the effect of loss in the material.[12] The high loss in this material is generally originated from the higher conductivity and causes higher leakage current. Figure 4 gives the loss tangent of BFO thin film which shows a low loss (0.02) around 7.188 15 GHz and quickly raises up to 0.45 around 11.747 05 GHz.

III. MAGNETOELECTRIC PROPERTIES INDUCED BY THE MAGNETIC FIELD

The work concerned to the induced electric dipole moments by the magnetic field was set up by applying the mag-

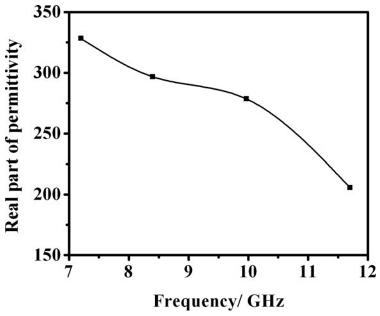

FIG. 2. Real part of the permittivity for the BFO thin film.

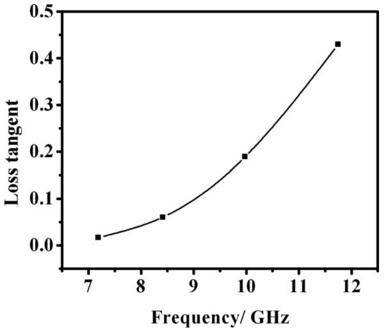

FIG. 4. Loss tangent of 100 nm BFO thin film at *X*-band frequency.

TABLE II. Real part of permittivity under the external magnetic field.

Magnetic field (kOe)	Real part of permittivity			
	TE_{103}	TE_{105}	TE_{107}	TE_{109}
0	328.3	296.8	278.4	205.7
0.46	330.5	297.3	280.3	206.6
1.39	332.17	298.3	282.3	207.7
2.33	333.4	298.5	283.2	208.7
3.26	335.2	299.1	284.7	209.8

netic field to the cavity microwave resonator. The sample was positioned at the maximum microwave electric field generated by the TE_{10n} modes. The S_{21} responses were around −30 dB with a 10 dBm input power. The external magnetic field that applied perpendicular to the film surface was used to induce the electric dipole moments of the BFO sample. The successful samples showed a clear frequency shift and obtainable permittivity variation as a function of magnetic field at TE_{10n} modes (Table II). Figure 5 shows the relation of permittivity variation $(\Delta\varepsilon'/\varepsilon')$ induced by the external magnetic field. As can be seen, a 0.17% permittivity variation was achieved by around 0.46 kOe magnetic field at 8.41 GHz and it increases up to 0.5% by 1.4 kOe at the same frequency. From the same figure, the permittivity shift for different modes shows the same tendency under the magnetic excitation. One can understand that such magnetic excitation is originating from the magnetoelectric coupling coefficient α_{ij} governed by polarization relation[4]

$$\vec{P}_i(\vec{E},\vec{H}) = -\frac{\partial F}{\partial E_i} = P_i^S + \varepsilon_o \varepsilon_{ij} E_j + \alpha_{ij} H_j + \dots , \qquad (1)$$

where F is the free energy contributed by the ME effect. P^S denotes the spontaneous polarization. The tensors ε_{ij} and α_{ij} correspond to the electric susceptibility and main electric polarization induced by the magnetic field. In our case, the magnetic-electric interaction of BFO thin film is up to 2.2% permittivity variation. This corresponds to the magnetoelectric coupling coefficient α_{ij} that characterized the magnetic-induced permittivity (the ME effect) in the BFO sample. Compared with Kimura *et al.*[7] who reported a 10% dielectric tunability for $TbMnO_3$ under 9 T magnetic field and Hemberger *et al.*[17] who found near a 500% dielectric tunability for $CdCr_2S_4$ by an external 5 T magnetic field in 2005, both tested at very low temperatures, our results reveals that magnetically tunable BFO films provide a more feasible solution for potential application of the high-frequency devices at room temperature. By going back to the XRD spectrum of the BFO film, we can expect that the highly oriented growth of the BFO film may be the reason for the high tunability of the permittivity by relatively low external magnetic field.

IV. CONCLUSION AND DISCUSSIONS

BFO thin films (100 nm) on quartz substrate have been prepared by rf sputtering followed by 900 °C annealing process. XRD pattern shows that the BFO film has a very high (101) preferential orientation. Magnetization response to external magnetic field measured by SQUID magnetometer is consistent with antiferromagnetic ordering in BFO films.

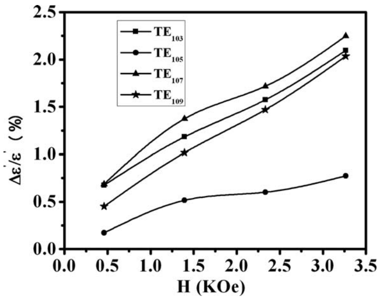

FIG. 5. The permittivity variation induced by the external magnetic field.

Permittivity measurements, which were done by the perturbation method, show the decrease in the real part of the permittivity and increase in the imaginary part as the frequency increased within the *x*-band microwave region. This decrease in ε' with increasing frequency was explained in terms of the dipole relaxation while the increasing of ε'' was explained in terms of the loss in the material.

Magnetoelectric coupling in the films has been tested by measuring the change in real and imaginary parts of the permittivity under the external magnetic field at room temperature, which show a magnetoelectric interaction up to 2.2 % permittivity variation under 3.26 kOe external magnetic field at frequency of ~9.97 GHz. This reveals a promising magnetically tunable BFO films for potential application of high-frequency devices at room temperature.

ACKNOWLEDGMENTS

This work was financially supported by the National Science Council, and Academia Sinica, Taiwan.

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