Dielectric properties characterization of La- and Dy-doped $BiFeO_3$ thin films

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The dielectric response of La- and Dy- doped $BiFeO_3$ thin films at microwave frequencies (up to 12 GHz) has been monitored as a function of frequency, direct current (dc) electric field, and magnetic field in a temperature range from 25 to 300 °C. Both the real and imaginary parts of the response have been found to be non-monotonic (oscillating) functions of measuring frequency. These oscillations are not particularly sensitive to a dc electric field; however, they are substantially dampened by a magnetic field. The same effect has been observed when the volume of the characterized sample is increased. This phenomenon is attributed to the presence of a limited number of structural features with a resonance type response. The exact origin of these features is unknown at present. Leakage current investigations were performed on the whole set of films. The films were highly resistive with low leakage current, thereby giving us confidence in the microwave measurements. These typically revealed 'N'-type I-V characteristics.

I. INTRODUCTION

Multiferroic (MF) materials are those in which more than one ferroic order (magnetic, electric, elastic) coexists and is coupled.[1] The possibility of including extra functionality with a device makes MF materials very attractive for application in microwave technology. However, there are no (or very few) papers reporting the properties of MF materials at frequencies higher than a few megahertz. The main reason for the lack of published high-frequency [radio frequency (rf) and microwave] measurement data is the high leakage current in these materials and especially in samples of thin films.

$BiFeO_3$ (BFO) is one of the very few single-phase multiferroic materials and is the subject of increased scientific interest.[2–4] The challenges with $BiFeO_3$ (BFO) arise from its large leakage current[4] and from the fact that at room temperatures bulk BFO is ferroelectric and antiferromagnetic.[3] Doping of BFO with Dy and La helps in the stabilization of the perovskite phase and in the reduction of leakage current. The idea of La doping is known to restrain the formation of a non-ferroelectric second phase and to stabilize the perovskite phase. Also, as observed in Ref. 4, doping $BiFeO_3$ films with La gradually changes the film structure from a monoclinically tilted state to a nontilted tetragonal like state. The

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spatially inhomogeneous spin-modulated incommensurate structure of BFO gradually disappears with increasing concentration of La, leading to the structural phase transition at $x < 0.2$ in $Bi_{1-x}La_xFeO_3$, which corresponds to the change in the unit-cell symmetry from $R3c$ to $C3v$. The authors have also shown increase in magnetization and fatigue-free ferroelectric switching characteristics with La doping in $BiFeO_3$. Therefore, we studied film characteristics of Dy-modified $BiFeO_3$ thin films with and without La doping.

In this work, we present the results of a comprehensive study on the dielectric response of doped BFO thin films in microwave-frequency range as well as the effect of applied direct-current (dc) electric and magnetic fields. Also reported are the current–voltage characteristics of the samples.

II. EXPERIMENTAL

Thin films of $Bi_{0.7}Dy_{0.3}FeO_3$ and $Bi_{0.6}La_{0.1}Dy_{0.3}FeO_3$ were deposited on single-crystal $LaAlO_3$ and MgO substrates using pulsed laser deposition (PLD). A PM882 GSI-Lumonics (Kanata, Ontario, Canada), 248 KrF excimer laser was used for the ablation process. For the deposition, stoichiometric targets of $Bi_{0.7}Dy_{0.3}FeO_3$ and $Bi_{0.6}La_{0.1}Dy_{0.3}FeO_3$, synthesized by a partial coprecipitation route, were used. NaOH was used as the precipitating agent. The precipitate was filtered out, washed, and then dried under an infrared lamp. The dried powders were pulverized and calcined at 600 °C for 1 h to obtain the reacted material. The calcined powder was pressed to form a pellet and sintered at 800 °C for 2 h to obtain a dense target for laser ablation. Pulsed laser ablation conditions were optimized to achieve phase-pure, granular, homogeneous, and insulating thin films of both the compounds. The typical film thickness was ~220 nm.

The crystal structure of the samples was investigated by x-ray diffraction (XRD) using a PANalytical X'Pert MRD system (Almelo, The Netherlands) with Cu K_α radiation. Measurements were performed using an X'Celerator diffractometer with monochromator attached. The sample microstructure was examined on Hitachi 4500 field-emission SEM (Tokyo, Japan).

For electrical testing planar capacitors, structures with 3 and 5 μm gap-size were patterned on the film surface; 0.5-μm-thick Au/Ti electrodes were formed using E-beam evaporation followed by photolithography and ion-milling performed on an Oxford Applied Research OAR–IM150 system (Witney, Oxfordshire, UK).

Electrical measurements were performed on a Signatone probe station (Gilroy, CA). The current–voltage characteristics were measured using an Agilent B1500A semiconductor device analyzer (Santa Clara, CA). An Agilent 4287A RF LCR meter was used for direct measurement of the sample capacitance and Q-factor (up to 3 GHz). At higher frequencies (up to 12 GHz), these values were evaluated from the Agilent 8722 ES VNA measured S11-parameter using the procedure described in Ref. 5. To examine the effect of dc electric field on the dielectric response of the material, a dc bias up to 100 V was applied to the samples via a Picoprobe bias-tee (Naples, FL). A home-made temperature stage (accuracy ±1 °C) was used for temperature measurements up to 300 °C, while a 0.15T permanent magnet was used for dielectric measurements under a magnetic field.

III. RESULTS AND DISCUSSION

In this work, we refer to $Bi_{0.7}Dy_{0.3}FeO_3$ films on $LaAlO_3$ and MgO substrates as DL and DM, respectively, and $Bi_{0.6}La_{0.1}Dy_{0.3}FeO_3$ films on $LaAlO_3$ and MgO substrates as DLL and DLM, respectively. These abbreviations will be used further in this paper.

A. Crystal structure

XRD analysis showed that all samples have good crystallinity. Films grown on $LaAlO_3$ were single-faced (010) oriented [Fig. 1(a)], while (104) and (110) peaks were observed as well on the films grown on MgO substrates [Fig. 1(b)]. Lattice spacings *d/n*(*0k0*) evaluated from the position of the observed peaks were 3.888 Å for

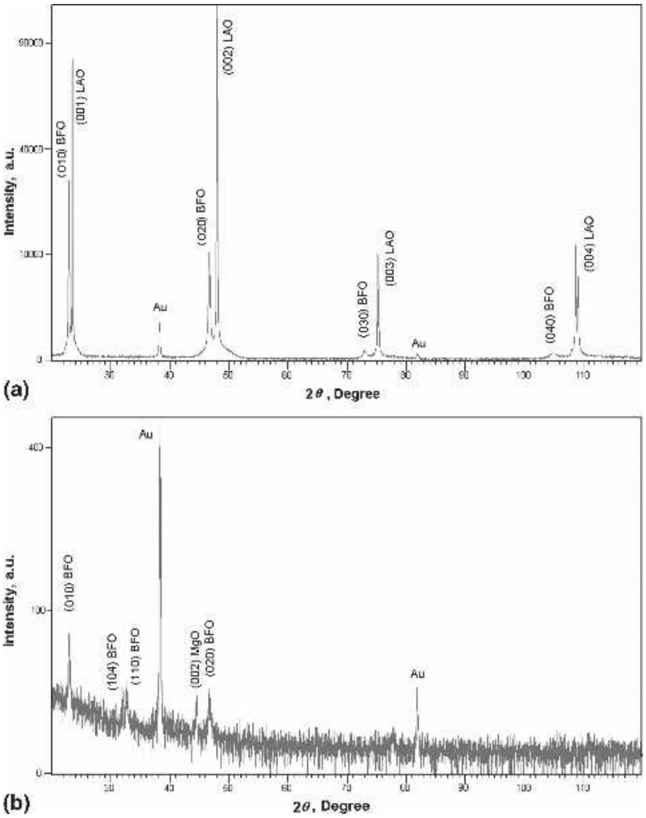

FIG. 1. XRD patterns of Dy- and La-doped $BiFeO_3$ thin films grown on (a) $LaAlO_3$ substrate and (b) MgO substrate. (Au peaks are from the electrodes, formed to enable electrical measurements.)

the films on the LAO substrate and 3.885 Å for the films on MgO substrate.

Scanning electron microscopy revealed that all films have nano-scale granular structure. Also observed were granules randomly distributed on the sample' surface [Fig. 2(a)].

B. I-V measurements

A typical I-V characteristic of the materials is presented in Fig. 3. In addition to the fact that the conductivity in the samples is low enough to allow them to be measured at high frequency, this investigation revealed some unexpected and very interesting results.

Note that Ohm's law does not hold for these samples. For the sake of comparison, let us divide the I-V curve into three regions, as shown in Fig. 3, and estimate the conductivity in these regions. The conductivity in region 1 is ~$1 \times 10^{-4}\ \Omega^{-1}\text{cm}^{-1}$, a value typical for the pure BFO. In region 2, there is negative resistance. In region 3, the system reduces its conductivity by 2–3 orders of magnitude compared with pure BFO. It is important to note that the values of the samples' conductivity varied from sample to sample (even those patterned on the same substrate); however, 'N'-type I-V was observed in about 80% of the samples. At present, we do not have a good explanation for this behavior, and work is in progress to find a convincing reason for the observed phenomenon.

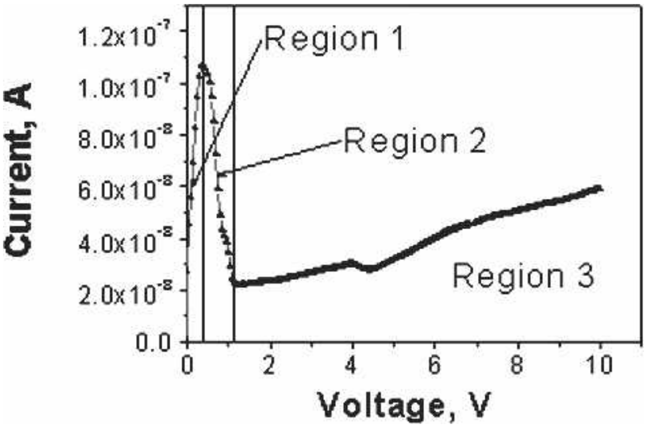

FIG. 3. Typical I-V characteristic showing 'N'-type behavior.

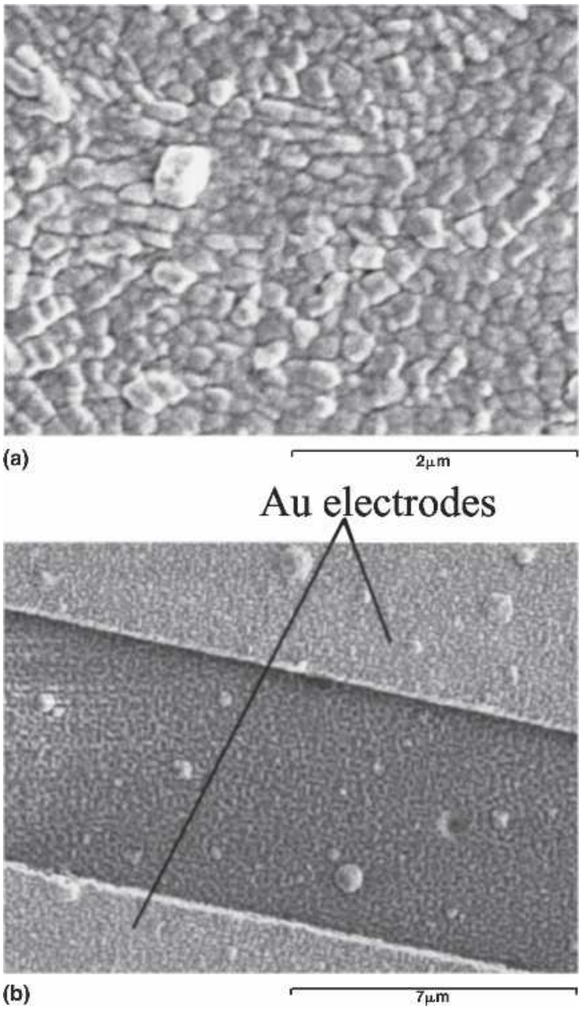

FIG. 2. SEM images of Dy- and La-doped BiFeO$_3$ thin films showing (a) the nano-scale granular structure of the films and (b) the observed granules randomly distributed on the sample surface.

C. Capacitance and the Q-factor versus frequency

Figure 4(a) shows the typical behavior of the capacitance and the Q-factor at microwave frequencies. We observe many local peaks (oscillations) in both characteristics, which occur in the measurements of all samples [see Fig. 4(b)]. The non-monotonic variation of the capacitance with frequency strongly suggests that the dielectric response is controlled by the coupling of the electric field with structural features exhibiting the resonance rather than relaxation type response, which is rare in the microwave-frequency range. A remarkable feature of these oscillations is that these can be "damped" by increasing the distance between the electrodes of the measuring capacitor (see Fig. 5). Such behavior can be attributed to a small number of resonating species in the gap of the planar capacitor: the oscillations are smeared or damped more in the case of a wider gap, which contains a larger number of the features. Thus, it seems that we are dealing with a situation reminiscent of the classical mesoscopic effect,[6] where not the average of the spatial distribution of impurities, but rather the inhomogeneity of their distribution governs the properties of the materials and results in fluctuations of their conductance.

We note that only the capacitance and Q-factor are presented. This eliminates the uncertainty introduced by the dielectric permittivity–dielectric loss tangent evaluation procedures. The measurement uncertainty of the measured capacitance and Q-factor is less than 5%,[7] allowing us to discuss the observed oscillations with confidence. When dielectric permittivity–dielectric loss

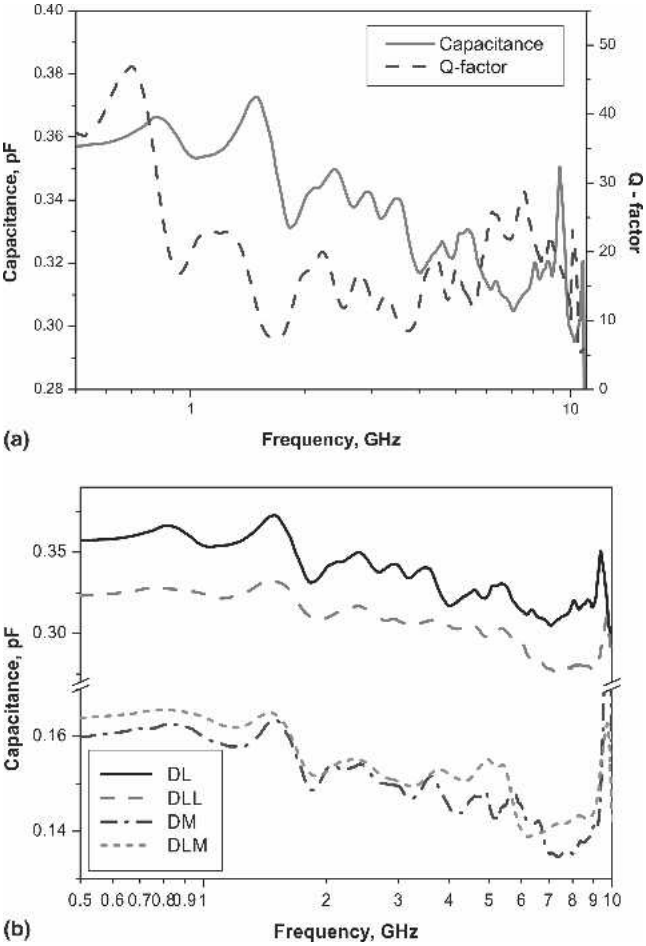

FIG. 4. Frequency dispersion of the dielectric properties of Dy- and La-doped $BiFeO_3$ thin films measured at 0 V, 25 °C: (a) typical behavior of the capacitance and Q-factor versus frequency and (b) frequency dispersion of the capacitance.

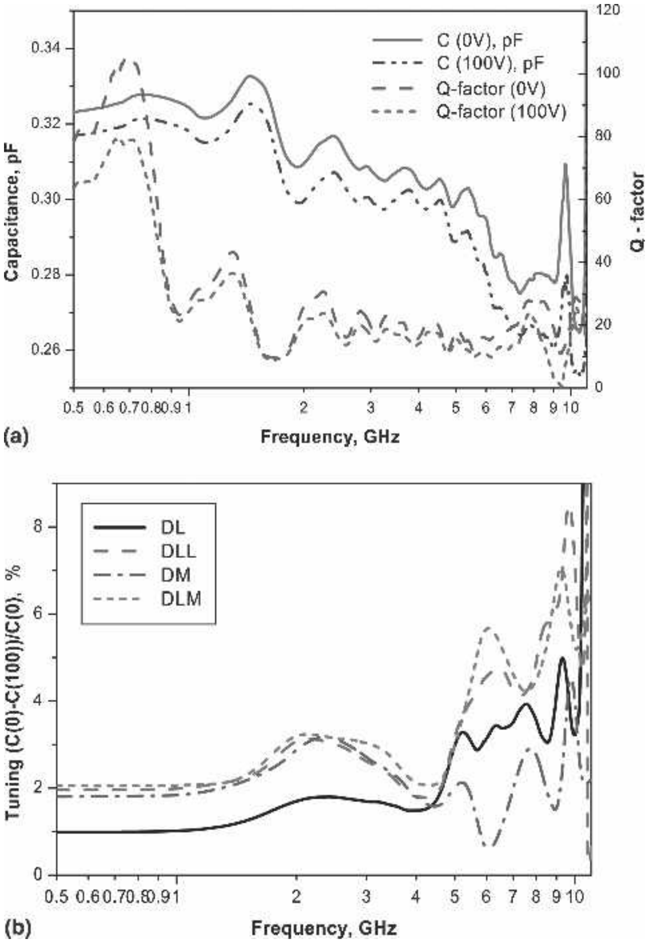

FIG. 6. Effect of the electric field of dielectric response of the Dy- and La-doped $BiFeO_3$ thin film: (a) typical behavior of the capacitance and Q-factor versus frequency at 0 and 100 V and (b) tuning versus frequency.

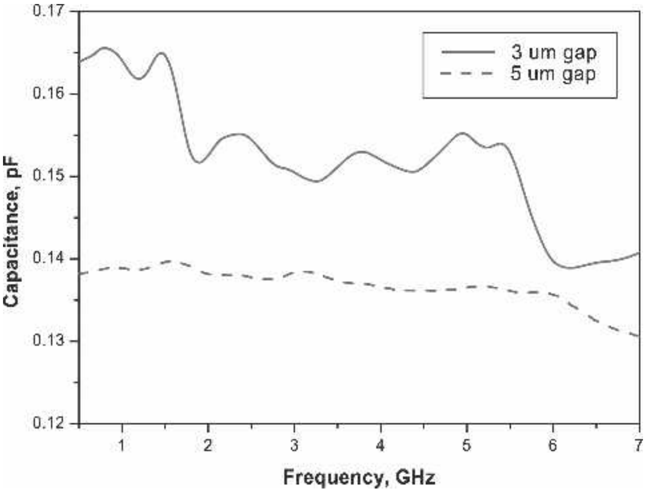

FIG. 5. Frequency dispersion of the capacitance measured for capacitors with 3- and 5-μm gap size, at 0 V, 25 °C.

tangent evaluation procedures are used, the measurement uncertainty is further increased to 20–30% (due-to the model limitations and effect of the electrodes and interface layers),[5,8,9] which makes the above discussion less credible. Thus, we are confident that the observed oscillation in capacitance and Q factor is a true electrical effect. The error introduced in the evaluation of relative permittivity (film thickness, electrode dimensions, etc.) makes us less certain of these quantities. Nevertheless, taking this into account, we estimate that in the 0.1–12 GHz frequency range, the dielectric permittivities for films on LAO and MgO substrates, were about 300 and 200, respectively, while the loss tangent, calculated as $1/Q$, was between 0.01 and 0.1.

D. Effect of dc electric field

Tuning of the capacitance (calculated as {[C(0V) − C(100V)]/C(0V)} × 100%) by 2–4% was measured under an electric field of 200kV/cm (see Fig. 6). Samples on MgO substrates exhibited higher tuneability, which might be related to a higher residual strain in the films as

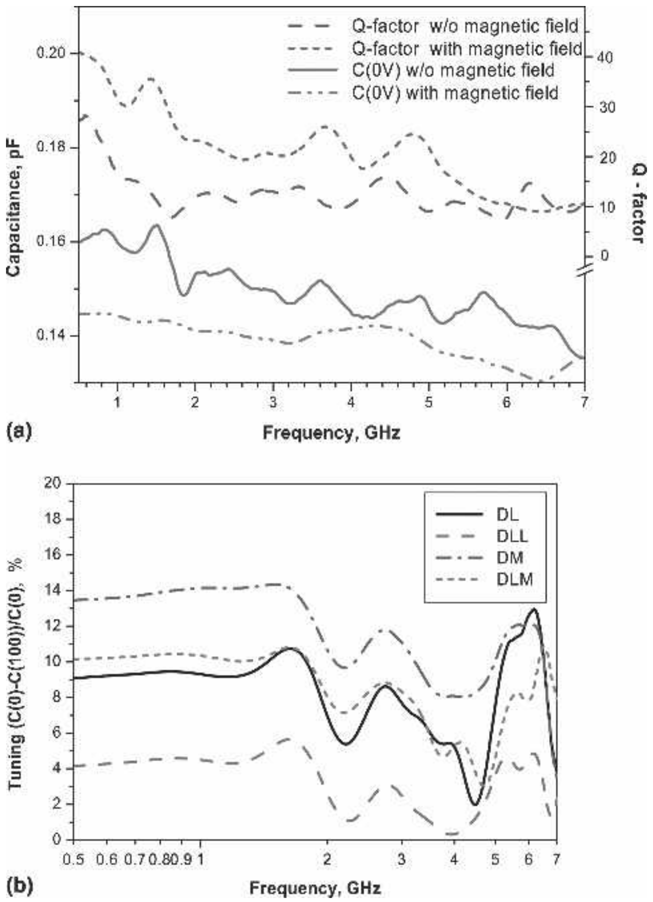

FIG. 7. Effect of permanent magnetic field on the dielectric response of the Dy- and La-doped $BiFeO_3$ thin films: (a) typical behavior of the capacitance and Q-factor versus frequency at a magnetic field of 0 and 0.15 T and (b) magnetic tuning versus frequency.

a consequence of the lattice mismatch. The presence of La further enhances the tuneability (on average) by a factor of two. It seems that the mechanism of tuneability is different from that active in traditional ferroelectrics such as $(Ba,Sr)TiO_3$; in our materials, the reduction of permittivity (with increasing frequency) is accompanied with an appreciable increase of the tuneability, a trend opposite that observed in typical ferroelectric systems.[10]

E. Effect of permanent magnetic field

As one can see in Fig. 7, the effect of the magnetic field on the dielectric response was larger for the samples deposited on MgO substrates. However, now the La doping causes a decrease in the response. The Q-factor however, increases when a magnetic field is applied. Remarkably, the application of the magnetic field leads to an appreciable smearing of the oscillations in the $C(f)$ curves, an effect similar to that caused by increasing the capacitor gap.

F. Effect of elevated temperature

Elevated temperature seems not to affect the oscillation in the $C(f)$ curves. They exist [see Fig. 8(a)] at temperatures up to 300 °C, the maximum temperature we could apply. The temperature dependence of the capacitance is very weak, as seen from Fig. 8(b).

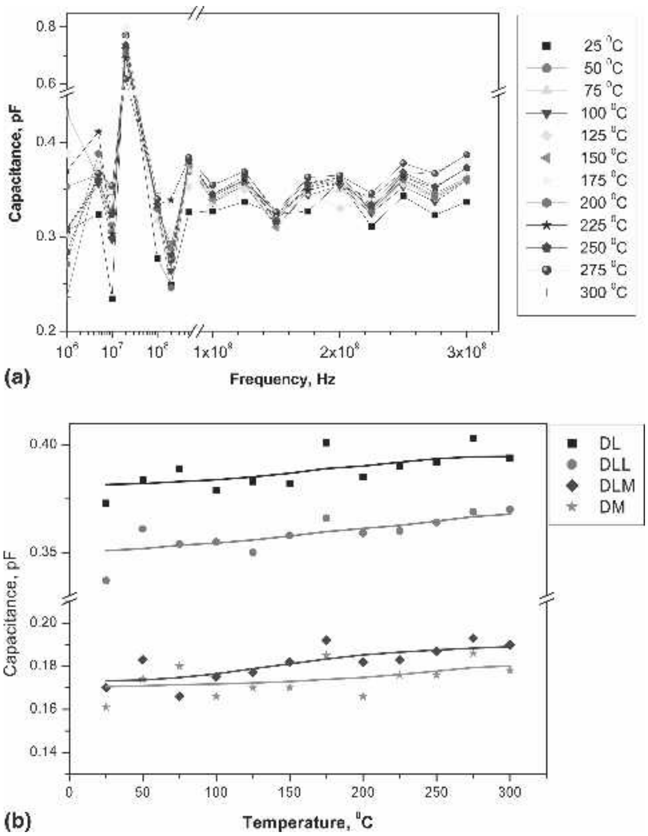

FIG. 8. Dielectric response of the Dy- and La-doped $BiFeO_3$ thin films at elevated temperature: (a) typical behavior of the capacitance versus frequency as a function of temperature and (b) capacitance versus temperature measured at 1.25 GHz.

IV. CONCLUSIONS

The microwave dielectric response and the conductivity of La- and Dy-doped $BiFeO_3$ thin films was examined under dc electric and magnetic fields and in a temperature range from 25 to 300 °C . We observed strong oscillations in the $C(f)$ characteristic, which we interpreted as a manifestation of a small number of structural features with a dielectric resonance. Further evidence supporting this speculation was a damping of the $C(f)$ characteristic when the capacitor gap-size was increased; i.e., the number of features involved in the response was increased. These resonating features are rather sensitive to the magnetic field and less sensitive to the dc electric field. One region in the I-V characteristic of the samples shows a negative differential resistance. Finally, doping with Dy and La leads to a leakage reduction. However the presence of La weakened the magnetic response of the system.

The novel phenomena revealed in this study are true electrical effects, even though at present (because of uncertainty introduced by the evaluation procedure) we are unable to state the exact values of thin films' dielectric permittivity and loss tangent with confidence. This requires the use of other measurement techniques and evaluation procedures with lower uncertainty level. Nevertheless, the observed results show the potential applicability of multiferroic materials at rf and microwave frequencies.

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