Abnormal behavior of the dielectric parameters of $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln=La–Gd) solid solutions

Anatolii Belous and Oleg Ovchar
V. I. Vernadskii Institute of General and Inorganic Chemistry, Ukraine Academy of Science, 32/34 Palladin Avenue, Kyiv-142, 03680 Ukraine

Matjaz Valant[a] and Danilo Suvorov
Department of Advanced Materials, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

(Received 14 February 2002; accepted for publication 8 July 2002)

The temperature dependence of the dielectric parameters ε and $\tan\delta$ for the entire x range of barium lanthanide titanate solid solutions (BLT ss) using the general formula $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln=La, Nd, Sm, Gd) was measured over wide frequency and temperature ranges. The results show the presence of diffuse regions of $\varepsilon(T)$ and $\tan\delta(T)$ anomalies, which are located below (in the La- and Nd-containing solid solutions) or above (in the Sm- and Gd-containing solid solutions) room temperature. However, no evidence of a structural transition responsible for these anomalies could be determined by differential scanning calorimetry and x-ray diffraction analysis. To examine the nature of the abnormal temperature behavior the dielectric parameters in the systems studied were considered in terms of a simple oscillator model. Within the framework of this model correlations among the average size of the *A*-site ions, tilting of the oxygen octahedra, and the lattice strain are discussed, and the effect of crystallographic peculiarities on the temperature behavior of the dielectric parameters is shown. As a consequence, the changes in $\varepsilon(T)$ and $\tan\delta(T)$ behavior in the BLT ss family were shown to originate from a varying relationship between the harmonic and anharmonic contributions to the phonons of the BLT ss crystal lattice. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1503855]

I. INTRODUCTION

For modern communication systems new ceramic materials that combine a high dielectric constant, low dielectric losses, and good temperature stability of the dielectric parameters are urgently required to reduce the size and weight of radio equipment, enhance its reliability, and lower the manufacturing and operational costs. In the ultrahigh frequency (UHF) range $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln=La–Gd) solid solutions, known as BLT ss, are, to date, the most promising candidates for the synthesis of new high-permittivity (≈80–100) dielectric ceramics.[1–3] BLT ss have a structure of tetragonal tungsten bronze, which also includes elements of the perovskite structure.[4–6] Within the network of corner-sharing TiO_6 octahedra three types of structural sites in the complex *A*-sublattice exist: pentagonal sites filled with Ba^{2+} ions, tetragonal sites shared by Ba^{2+} and Ln^{3+} ions, and empty trigonal sites.

In BLT ss the electrophysical characteristics strongly depend on the size of the *A*-site ions (r_A).[3,7,8] The characteristics are related to the unit-cell volume[7] and the magnitude of octahedral tilting, both of which decrease with r_A.[8] Whereas a change in the lanthanide ion from La to Gd results in a decrease in both the permittivity (ε) and the dielectric loss tangent ($\tan\delta$) of BLT ss for a fixed value of x, the temperature coefficient of the permittivity (τ_ε) increases and changes its sign when switching from Nd to Sm.[3,7] The changes in the sign and the magnitude of τ_ε with a decrease in the ionic radius of the lanthanide ion were ascribed to the decrease in the anharmonic contribution to the restoring forces affecting the *A*-site ions within the potential well.[8] When investigating $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ ($x=1.5$) using the dielectric resonator method in the frequency range of about 10^{10} Hz the authors of Ref 9 were the first to reveal anomalies in the temperature dependence of the permittivity which were ascribed to phase transitions of ''displace'' type. More recently, we observed anomalies in the temperature dependencies of the dielectric parameters (ε, and $\tan\delta$) in the entire range of Sm-containing BLT ss.[10] Within the solid solubility range of $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ the diffuse maxima of $\varepsilon(T)$ and the corresponding maxima of $\tan\delta(T)$ shift toward lower temperatures with increasing x (T_{max} ≈70–120 °C). So far, the nature of these anomalies remains unclear. Moreover, there are no data on the existence of temperature anomalies of dielectric parameters for other barium lanthanide analogs including those of La-, Nd-, and Gd-containing BLT ss. Therefore, the goal of this work was to examine the nature of the abnormal temperature behavior of the permittivity and the dielectric losses of BLT ss.

II. EXPERIMENT

Polycrystalline samples with chemical composition belonging to systems

$Ba_{6-x}La_{8+2x/3}Ti_{18}O_{54}$ $(0.75 \leqslant x \leqslant 2.0)$;

$Ba_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$ $(0.75 \leqslant x \leqslant 2.0)$,

[a]Electronic mail: matjaz.valent@ijs.si

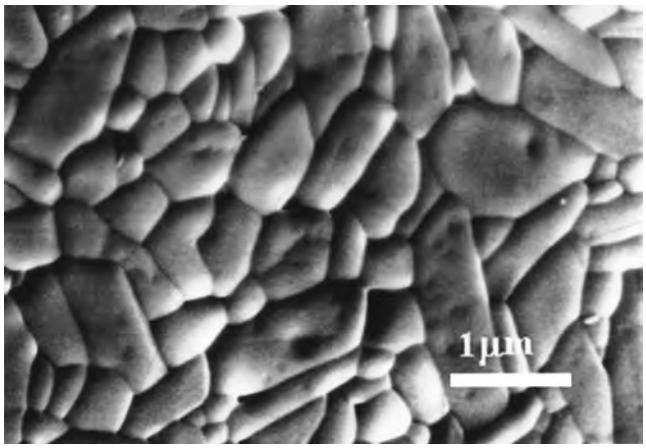

FIG. 1. Scanning electron microscope image of thermally etched $Ba_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$ $(x=1.5)$ samples sintered at 1380 °C for 5 h.

and

$$Ba_{6-x}Gd_{8+2x/3}Ti_{18}O_{54}\,(x=1.5)$$

were synthesized from extra-pure $BaCO_3$, La_2O_3, Nd_2O_3, Gd_2O_3, and TiO_2. The starting reagents were mixed in the appropriate ratios and homogenized by ball milling. The mixture was dried and pre-reacted at 1150–1200 °C to achieve equilibrium. The pre-reacted powders were then pressed into pellets and sintered at 1330–1380 °C. The phase composition and the lattice parameters of the materials were analyzed by powder x-ray diffraction (XRD) using a DRON (4 diffractometer, Burevestnik, Russia) and Cu $K\alpha$ radiation. Phase-composition analysis and elementary microanalysis of the sintered samples were performed with a scanning electron microscope (Joel, JSM 5800, Tokyo, Japan) using energy-dispersive x-ray (EDX) spectroscopy and the LINK software package (ISIS 3000). Typically, the sintered ceramics were single phase and dense with a relative density estimated to be >95%, as shown in Fig. 1. High-temperature XRD analysis was performed in a high-temperature chamber (HTK-16, Anton Paar, Graz, Austria) mounted on a diffractometer with θ–θ geometry (D-5000, Siemens, Karlsruhe, Germany). The heating rate of the powdered samples was 10 °C/min and the counting time was 50 s/step for steps of 2θ=0.02°. Variable divergence and antiscatter slits of 6 mm (V6) and a receiving slit of 0.6 mm were used. Low-temperature differential scanning calorimetry (LT-DSC) was carried out with a thermal analysis instrument (DSC 200 Netzsch, Selb, Germany) system in air with 80 mg samples placed in aluminum pans at heating and cooling rates of 10 °C/min. The nominal thermal sensitivity of the instrument is 3–6 μV/mW.

The dielectric characteristics of the materials (ε and tan δ) at frequencies around 10 GHz were examined using a modified-dielectric-resonator method.[11] The dielectric losses of the materials were estimated from the frequency dependence of the transfer constant in the vicinity of the resonant frequency (f_{res}).[12] Submillimeter-wave (SMM) frequency measurements were carried out using a backward-wave tube by measuring the optical path length and the absorption (α) in a parallel-plate sample coated with a quarter-wavelength antireflecting coating.[13]

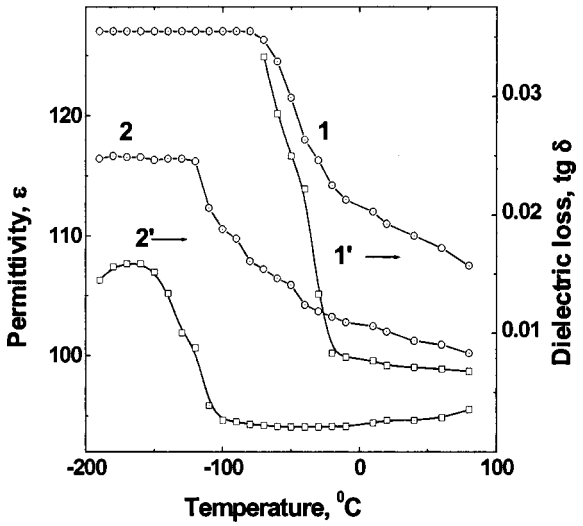

FIG. 2. Temperature dependencies of the permittivity (1), (2) and dielectric loss (1′), (2′) of materials with composition $Ba_{6-x}La_{8+2x/3}Ti_{18}O_{54}$ for $x=1.5$ (1), (1′) and $=2.0$ (2), (2′) at 10 GHz.

III. EXPERIMENTAL RESULTS

A. La-containing solid solutions

In the case of La-containing BLT ss the temperature anomalies of dielectric parameters (ε, and tan δ) were observed at temperatures below −100 °C (Figs. 2 and 3). The anomalies of $\varepsilon(T)$ were accompanied by anomalies in tan $\delta(T)$. For composition $Ba_{6-x}La_{8+2x/3}Ti_{18}O_{54}$ $(x=1.5)$ at temperatures below −80 °C the value of tan δ is not presented in Fig. 2 because the measurement technique used does not allow the precise determination of high dielectric losses. Figure 2 shows the shift of the anomalies with respect to the chemical composition of the BLT ss. It should also be noted that the anomalies in the La-containing BLT ss were observed over a wide frequency range including the SMM range (Fig. 3), which indicates no connection between them and any processing-induced phenomena.

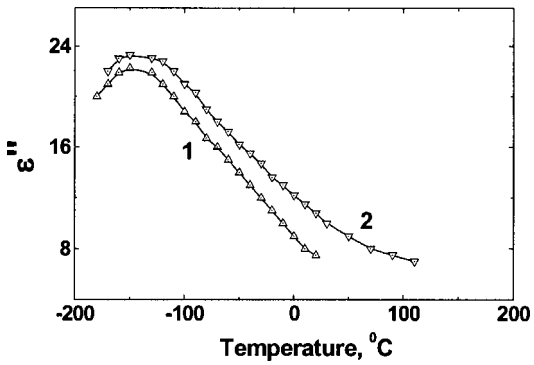

FIG. 3. Temperature dependencies of the imaginary component of the permittivity (ε'') at 96.7 (1), and 134 GHz (2) in $Ba_{4.5}La_9Ti_{18}O_{54}$ material $(x=1.5)$.

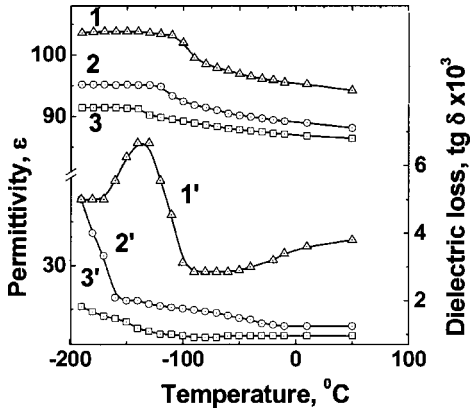

FIG. 4. Temperature dependencies of the permittivity (1)–(3), and the dielectric loss (1′)–(3′) of materials with composition $Ba_{6-x}Nd_{8+2x/3}Ti_{18}O_{54}$. $x=0.75$ (1), (1′), 1.5, (2), (2′), and 2.0 (3), (3′); measurement frequency 10 GHz.

B. Nd-containing solid solutions

In the case of Nd-containing BLT ss, temperature anomalies of the dielectric parameters similar to those observed in La-containing BLT ss were also observed at low temperatures (Fig. 4). The trends observed in the $\varepsilon(T)$ and $\tan\delta(T)$ curves (Fig. 4) indicate that the position of the anomalies on the T axis is dependent on the chemical composition of the BLT ss. It should also be noted that both the permittivity and dielectric loss tangent values of the Nd-containing BLT ss at fixed x are lower than those observed in La-containing solid solutions.

C. Sm-containing solid solutions

According to our findings presented in Ref. 10, for the case of Sm-containing solid solutions, anomalies in the $\varepsilon(T)$ and $\tan\delta(T)$ curves are observed at high temperatures. The position of the anomalies on the T axis is affected by varying the chemical composition of the BLT ss, and it shifts toward lower temperatures with an increase in x within the temperature region of $+120-+70$ °C (Fig. 5). It should be noted that similar behavior is observed in the case of solid solutions with ferroelectric and antiferroelectric properties. However, in the case of BLT ss the hysteresis loop is not detected, and Curie–Weiss behavior is not observed in the vicinity of the anomalies. The measurements in the SMM wavelength range reveal diffuse maxima in the temperature dependencies of both the absorption coefficient (α) and the imaginary component of the dielectric constant (ε'') at exactly those temperatures where the maxima of $\varepsilon(T)$ are observed at 10 GHz.[10] These results indicate the nonrelaxation nature of the anomalies of the dielectric parameters, and confirm that they are not related to the effects of processing.

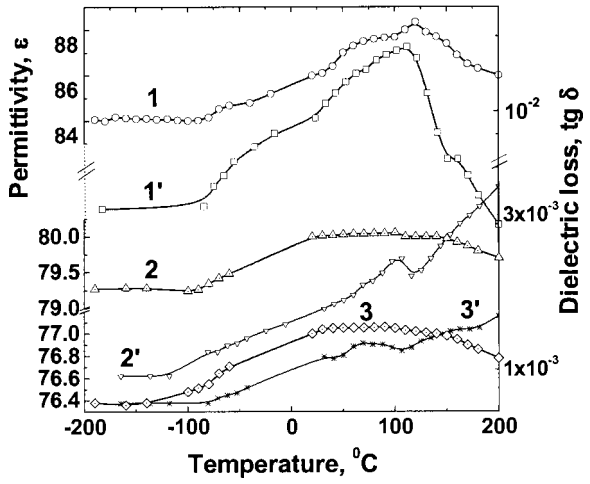

FIG. 5. Temperature dependencies of the permittivity (1)–(3) and dielectric loss (1′)–(3′) of materials with composition $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ for $x=1.0$ (1), (1′), 1.5 (2), (2′), and 2.0 (3), (3′), measurement frequency 10 GHz.

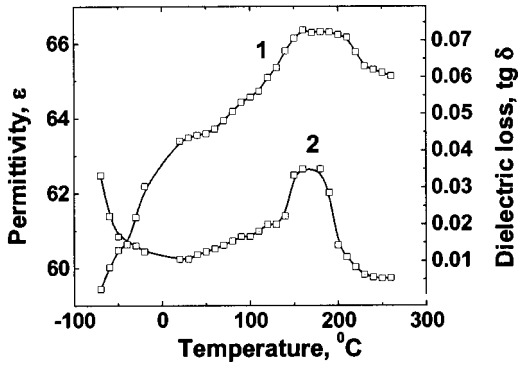

FIG. 6. Temperature dependencies of the permittivity (1) and the dielectric loss tangent (2) of materials with composition $Ba_{4.5}Gd_9Ti_{18}O_{54}$ ($x=1.5$) at 10 GHz.

D. Gd-containing solid solutions

In examining the temperature behavior of the permittivity and the dielectric losses of polycrystalline $Ba_{6-x}Gd_{8+2x/3}Ti_{18}O_{54}$ ($x=1.5$) at 10^{10} Hz the corresponding maxima of $\varepsilon(T)$ and $\tan\delta(T)$ were observed at higher temperatures ($T_{max}\approx 120-160$ °C) than in the case of their Sm-containing analogus (Fig. 6).

For a particular rare-earth analog the position of the anomalies on the temperature axis depends on the value of x in $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$. Regardless of the nature of the rare-earth ion, by increasing x both the permittivity and the corresponding dielectric loss anomalies shifted toward lower temperatures (Figs. 2, 4, and 5). Again, the position of the temperature anomalies varies when changing the rare-earth element in the BLT ss (Fig. 7). These results show that the position of the $\varepsilon(T)$ and $\tan\delta(T)$ anomalies on the temperature axis depends on the r_A of the complex A sublattice in BLT ss.

These experimental results suggest that the dielectric anomalies could be ascribed to unknown phase transitions. Therefore, samples with composition

$$Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}\,(x=1.0),$$

which are characterized by the strongest anomalies of the dielectric parameters at about of 120 °C amongst the Sm-containing BLT ss, were investigated by LT-DSC and high-

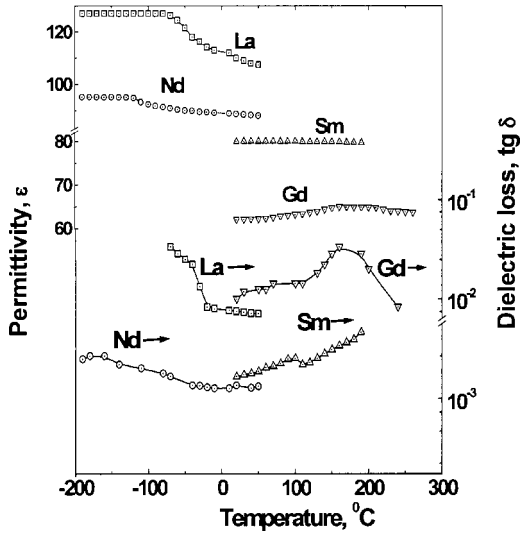

FIG. 7. Temperature dependencies of the dielectric parameters of materials with composition $Ba_{4.5}Ln_9Ti_{18}O_{54}$ ($x=1.5$) at 10 GHz.

temperature XRD. The analysis was carried out over a wide temperature range, including temperatures below and above the anomalies of $\varepsilon(T)$ and $\tan\delta(T)$.

XRD patterns in the range of $5°<2\Theta<55°$ were collected at room temperature, and 120 and 250 °C. No significant changes in the intensity or the position of the peaks (apart from those induced by the increase in temperature) or any kind of peak splitting were observed in the patterns. In addition, a detailed XRD analysis was performed for the 2Θ range where diffractions from superstructural phenomena were expected to appear ($10°<2\Theta<25°$). These patterns also did not indicate any structural changes (Fig. 8).

LT-DSC was performed in the temperature range from −30 to 250 °C. In agreement with the XRD analysis the LT-DSC revealed no thermal effects that could be associated with structural changes. We concluded that within the sensitivity limits of both analytical methods there was no evidence of a structural transition that could be responsible for the anomaly in the temperature dependence of the dielectric properties. Our structural investigations are fully supported by the work of Tang *et al.*[14] They performed synchrotron XRD studies on a $Ba_{4.5}Nd_9Ti_{18}O_{54}$ analog in the temperature range from 10 to 295 K. Their data revealed no evidence of any structural changes in this temperature range; the volume expansion was relatively smooth.

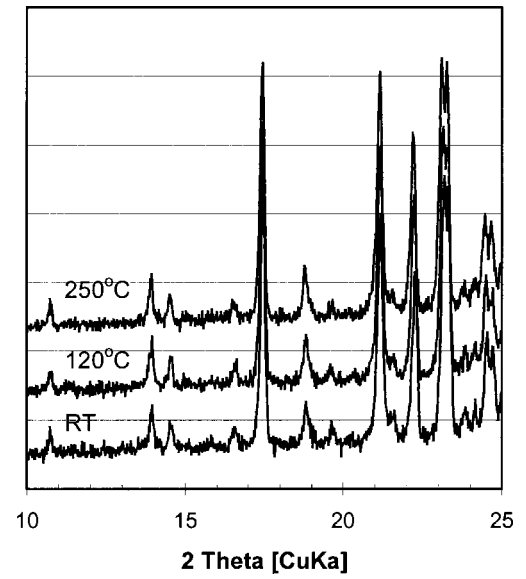

FIG. 8. X-ray diffraction pattern of the $Ba_{6-x}Sm_{8+2x/3}Ti_{18}O_{54}$ ($x=1.0$) sample at (a) room temperature and at (b) 120 and (c) 250 °C.

As a result of this we can state that the observed anomalies of the dielectric parameters are related neither to any processing peculiarities nor to the presence of structural transitions.

IV. DISCUSSION

In the microwave (MW) range the permittivity of dielectrics with high dielectric constant, for instance, those based on BLT ss, is predominantly determined by the contributions of the elastic strain, both ionic and electron polarization. In the literature these polarization mechanisms are known by the terms ''infrared'' and ''optical'' polarizations.[15] In the harmonic oscillator approximation, not taking into account either the cooperative interaction of different oscillators or the influence of electronic polarization, the infrared (IR) contribution to the dielectric constant (ε_{IR}) can be determined from by the following equation:[15]

$$\varepsilon_{IR}=\sum_i \frac{4\pi n_i q_i^2}{m_i\omega_{0i}^2}=\sum_i \frac{4\pi n_i q_i^2}{c_i-\frac{4}{3}\pi_i n q_i^2}, \tag{4.1}$$

where i is the number of possible oscillations (of different dipoles) that contribute to the permittivity, ω_{0i} is the frequency of the optical phonons, and it can be estimated as

$$\omega_{0i}^2=\frac{1}{m_i}(c_i-\tfrac{4}{3}\pi_i n q_i), \tag{4.2}$$

where m_i is the reduced mass of a dipole, q_i is the ionic charge, n_i is the concentration of i-type dipoles in the unit volume, and c_i is the elastic coefficient. By varying the chemical composition of BLT ss the value of ε_{IR}, which is inversely proportional to ω_{0i} [Eq. (4.1)], is determined by both the concentration of the oscillators in unit volume n_i and the magnitude of the elastic coefficient c_i. For BLT ss in the range from La to Gd n_i increases due to the decrease in unit-cell volume,[3,7,8] which could allow an increase in ε_{IR} assuming that c_i is constant. However, the experimental data indicate that by changing the lanthanide from La to Gd the permittivity decreases which, according to Eq. (4.1), may be related to an increase in the elastic coefficient c_i. It should be noted that the possible increase in c_i influences the permittivity more noticeably than the opposite effect, an increase in n_i.

Equation (4.1) allows estimation of the temperature behavior of permittivity in a harmonic approximation. The magnitude of the harmonic restoring force $f_{Ri}=-c_i x_i$ that acts on an ion shifted a distance x_i under the applied field (E) is equal to the distorting force $f_{Di}=q_i E$, and, therefore, the elastic coefficient can be written as $c_i=qE/x_i$. With an increase in temperature ionic interaction is reduced (x_i in-

creases due to the increase in unit-cell volume), thereby lowering c_i. A decrease in the magnitude of c_i, according to Eq. (4.2) results in a decrease of the phonon frequency, and a consequent increase in the permittivity. This is exactly the behavior observed in Sm- and Gd-containing solid solutions (Figs. 5 and 6). However, the temperature dependence of the permittivity across the entire BLT ss, particularly the presence of anomalies in $\varepsilon(T)$, cannot be described in terms of the harmonic oscillator mechanism [Eq. (4.1)].

The anharmonic contribution of the lattice oscillations to the restoring force f_R in the first approximation could be linearly dependent on the temperature component βT, which gives us the following equation: $f_R=-(c_{\text{sum}}+\beta T)x$,[15] where c_{sum} is the elastic coefficient that characterizes the total contribution of the harmonic components. Taking into account the equality of the distorting and restoring forces that affect the ion in the crystal lattice, $q_iE=(c_{\text{sum}}+\beta T)x_i$, the polarizability of a single ion,

$$\alpha_i=\frac{P_i}{E_i}=\frac{q_ix_i}{E_i}=\frac{q_i^2}{c_{\text{sum}}+\beta T},$$

is inversely proportional to the restoring force. With an increase in temperature the anharmonic contribution βT causes an increase in the restoring force f_R, and as a consequence, both the polarizability and the permittivity decrease in such a way that higher β values correspond to higher negative values of the temperature coefficient of the permittivity τ_ε, where $\tau_\varepsilon=(1/\varepsilon)(\partial\varepsilon/\partial T)$. Therefore, the $\varepsilon(T)$ behavior can be interpreted as a superposition of two different, competing contributions: an increase in the permittivity with the temperature (harmonic contribution), and a decrease in the permittivity with the temperature (anharmonic contribution). The resulting effect of these two contributions in a certain temperature interval causes changes of the $\varepsilon(T)$ behavior in BLT ss. In La- and Nd-containing BLT ss, which are characterized by small tilting angles of the oxygen octahedra and by the significant anharmonism of the lattice oscillations (high values of β),[8] the contribution of the βT component is already significant at low temperatures. In this case the anomalies of $\varepsilon(T)$ are observed at low temperatures (Figs. 2–4). In contrast, in Sm- and Gd-containing solid solutions, which are characterized by large tilting angles of the oxygen octahedra (low β values),[8] the anomalies occur at higher temperatures (Figs. 5 and 6).

When analyzing the origin of the dielectric losses in the BLT family it should be taken into account that, in the MW range, losses are predominantly determined by the fundamental phonon mechanisms of electromagnetic energy absorption, including three-quantum, four-quantum, and quasi-Debay mechanisms.[16] In general, the value of the fundamental losses in the MW range is proportional to $\varepsilon^k T^n$, where $k=1-4$; $n=1-8$.[16] However, the dielectric losses measured in BLT ss cannot be explained by this relationship because it does not presume the anomalies on the temperature dependencies of tan δ. Any qualitative estimation of the fundamental loss value in the MW range can be derived from the model of the harmonic oscillator, which takes into account oscillation damping. In the case where $\omega \ll \omega_0$, the value of tan δ is inversely proportional to the frequency of the optical phonons ω_0:[15]

$$\tan\delta \approx \Gamma_i \frac{\omega}{\omega_{0i}} \frac{\varepsilon_{\text{IR}}-\varepsilon_{\text{opt}}}{\varepsilon_{\text{IR}}}, \tag{4.3}$$

where Γ_i is the damping of the oscillator with frequency ω_{0i}.

Equation (4.3) allows qualitative estimation of the tan $\delta(T)$ behavior related to the temperature variation of the phonon frequency. Equation (4.3) shows that the temperature behavior of tan δ is determined by the frequency of the optical phonons, which is consequently dependent on both harmonic and anharmonic contributions to the restoring force. The harmonic contribution results in a decrease in ω_{0i} with the temperature and, as a result, in an increase in tan δ [Eq. (4.3)]. On the other hand, an increase in βT with the temperature causes an increase in ω_{0i} and, as a result, a decrease in tan δ. Within a certain temperature range, as a result of the competing effect of these two mechanisms, anomalies may appear in the temperature dependence of tan δ (Figs. 2–7).

Finally, it should also be emphasized that the origin of the lattice anharmonism in BLT ss family may be related to peculiarities of the cation distribution in the *A* sublattice.[7] According to considerations presented in Refs. 7 and 8 the latter can affect the values of both the internal lattice strain[7] and the tilting angle of oxygen octahedra.[8] Both these factors influence the oxygen network's flexibility. As a result, in the Sm- and Gd-containing solid solutions, where the oxygen octahedra are tilted at a larger angle in comparison with their La- and Nd-containing analogus, the anharmonic contribution (decrease in ε and tan δ) only becomes noticeable at high temperatures, where anomalies of the dielectric parameters are observed. In Gd-containing solid solutions an increase in temperature causes the most noticeable decrease in oxygen-network flexibility, which results in higher dielectric losses in comparison with Sm-containing analogs.

V. CONCLUSIONS

BLT ss are characterized by the presence of diffuse anomalies in the temperature dependencies of the permittivity and tan δ, which are located below (in La- and Nd-containing solid solutions) or above room temperature (in Sm- and Gd-containing solid solutions).

The observed anomalies originate from the competition between harmonic and anharmonic contributions to the phonons of the BLT crystal lattice, which exhibit an opposite effect on the temperature behavior of permittivity and tan δ.

[1] D. Kolar, Z. Stadler, S. Gaberščček, and D. Suvorov, Ber. Dtsch. Keram. Ges. **55**, 346 (1978).
[2] H. Ohsato, S. Nishigaki, and T. Okuda, Jpn. J. Appl. Phys., Part 1 **31**, 3136 (1992).
[3] T. Negas and P. K. Davies, Ceram. Trans. **53**, 179 (1995).
[4] R. G. Matveeva, M. B. Varfolomeev, and L. S. Il'yuhchenko, Russ. J. Inorg. Chem. **29**, 17 (1984).
[5] C. J. Rawn, D. P. Birnie, M. A. Bruck, J. H. Enemark, and R. S. Roth, J. Mater. Res. **13**, 187 (1998).
[6] R. Ubic, I. M. Reaney, and W. E. Lee, J. Am. Ceram. Soc. **82**, 1336 (1999).
[7] H. Ohsato, M. Imaeda, Y. Takagi, A. Komura, and T. Okuda, Proceedings

of the 11th IEEE Symposium on Applied Ferroelectrics ISAF 1998, 509 (1998).
[8] M. Valant, D. Suvorov, and C. J. Rawn, Jpn. J. Appl. Phys., Part 1 **38**, 2820 (1995).
[9] V. I. Butkov, A. G. Belous, Y. A. Nanasheva, Y. M. Poplavko, and E. F. Ushatkin, Sov. Phys. Solid State **26**, 1783 (1984) [translated from Fiz. Tverd. Tela (Leningrad) **26**, 2951 (1984)].
[10] A. Belous, O. Ovchar, M. Valant, and D. Suvorov, Appl. Phys. Lett. **11**, 1707 (2000).
[11] A. A. Bokrinskaya and M. E. Ilchenko, Izv. Vyssh. Uchebn. Zaved., Radioelecktron. **14**, 151 (1971).
[12] I. M. Buzin and I. M. Angelov, Prib. Tekh. Eksp. **4**, 114 (1974).
[13] V. V. Meriakri and E. F. Ushatkin, Prib. Tekh. Eksp. **2**, 143 (1973).
[14] C. C. Tang, M. A. Roberts, F. Azough, C. Leach, and R. Freer, J. Mater. Res. **17**, 675 (2002).
[15] Y. M. Poplavko, *Physics of Dielectrics* (Vyshcha Shkola, Kiev, 1980).
[16] V. L. Gurevich and A. K. Tagantsev, Adv. Phys. **40**, 719 (1991).