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$$(\text{Ba}_{0.77}\text{Ca}_{0.23})_{1-x} (\text{Sm}, \text{Nd}, \text{Pr}, \text{Yb})_x \text{TiO}_3$$

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The structural, dielectric, and vibrational properties of pure and rare earth (RE)-doped $\text{Ba}_{0.77} \text{Ca}_{0.23} \text{TiO}_3$ (BCT23; RE = Sm, Nd, Pr, Yb) ceramics obtained via solid-state reaction were investigated. The pure and RE-doped BCT23 ceramics sintered at 1450 °C in air for 4 h showed a dense microstructure in all ceramics. The use of RE ions as dopants introduced lattice-parameter changes that manifested in the reduction of the volume of the unit cell. RE-doped BCT23 samples exhibit a more homogenous microstructure due to the absence of a Ti-rich phase in the grain boundaries as demonstrated by scanning electron microscopy imaging. The incorporation of REs led to perturbations of the local symmetry of TiO$_6$ octahedra and the creation of a new Raman mode. The results of Raman scattering measurements indicated that the Curie temperature of the ferroelectric phase transition depends on the RE ion and ion content, with the Curie temperature shifting toward lower values as the RE content increases, with the exception of Yb$^{3+}$ doping, which did not affect the ferroelectric phase transition temperature. The phase transition behavior is explained using the standard soft mode model. Electronic paramagnetic resonance measurements showed the existence of Ti vacancies in the structure of RE-doped BCT23. Defects are created via charge compensation mechanisms due to the incorporation of elements with a different valence state relative to the ions of the pure BCT23 host. It is concluded that the Ti vacancies are responsible for the activation of the Raman mode at 840 cm$^{-1}$, which is in agreement with lattice dynamics calculations.


I. INTRODUCTION

Barium titanate, BaTiO$_3$ (BT), has been the subject of intense research for several decades because it is a model system for understanding ferroelectric materials and is used in many other applications as well. In recent decades, research on BT has been focused on its potential for photorefractive applications, such as optical data storage and image processing. The large values of the electrooptic coefficients and the remarkable holographic sensitivity of BT make it a promising material for applications in this field. However, this material has some limitations that prevent its use in photorefractive devices designed for operating close to room temperature because it is extremely difficult to grow as a monocrystal, presents very low growth rate, and has a tetragonal-orthorhombic phase transition that occurs at about 8 °C.

The addition of Ca$^{2+}$ to the BT host is one way of overcoming these difficulties. Previous works have shown that Ba$_{1-x}$Ca$_x$TiO$_3$ (BCT) monocrystals can be grown easily using the Czochralski method in which high growth rates are achieved and the tetragonal-orthorhombic phase transition temperature is prevented because its critical temperature is lowered down to about –120 °C, depending on the Ca composition. Furthermore, some components of the electrooptic tensor in BCT with a concentration x = 0.23 (BCT23) are larger than in BT. These features make BCT23 a potential alternative material for replacing BT in photorefractive related applications. The introduction of Fe as a dopant in BCT23 also improves the photorefractive properties, thus reducing its time response and increasing its sensitivity.

Alkaline earth metal doping is very important for defining the properties of perovskites, although their role is not yet very well understood. The introduction of Ba, Ca, and Sr ions in the lattice induces charge carriers. Perovskite materials containing 3d transition metals present a dependence of...
their physical and chemical properties as a function of temperature, pressure, and the transition metal composition. The interactions among the orbitals of alkaline metals and the 3d transition metals, together with the amount of covalent hybridization of 2p states from oxygen and 3d states from the transition metal, are fundamental issues to be addressed in these perovskite materials.

In addition to having applications as photorefractive materials, the BCT ceramics are also appropriate for preparing multi-layer ceramic capacitors (MLCs) with the advantage of being produced on cheap electrodes while keeping dielectric properties similar to those of BT. Considerable efforts in the preparation and characterization of BCT ceramics have been made. Some authors have observed the behavior of the ferroelectric-paraelectric phase transition depends on the preparation method. One of the main drawbacks is the formation of a liquid phase localized in the grain boundaries that is rich in titanium. Irregular grain growth is also observed. Both effects affect the dielectric properties of the ceramics to a great extent. Recently, several authors have proposed the use of dopants such as Zr, Mn, and rare earth (RE) ions as an alternative for controlling the grain size and for improving the dielectric properties of BCT ceramics. Among the several dopants, the RE oxides are important additives, and they are used for the preparation of BT-based materials aimed at the production of MLCs. Some studies have investigated the addition of RE elements in the BCT ceramic, but the basic mechanism behind the effect of the addition of RE ions (Nd, Sm, Pr, and Yb) on the physical properties (structural, electrical, vibrational, and optical) of BCT ceramics is not yet understood.

In this paper, we report the investigation of RE (Sm, Nd, Pr, Yb) doped BCT ceramics using different experimental techniques. Analyzing the vibrational and electronic paramagnetic resonance (EPR) data led us to conclude that RE-doped BCT presents titanium vacancies, and the RE ions occupy both A and B sites of the ABO3 perovskite structure. Changes in the physical properties of doped BCT ceramics are discussed in terms of the A-site occupancy by the RE trivalent ions. The results contribute to a better understanding of the physical properties of RE doped perovskites.

II. EXPERIMENTAL DETAILS

Undoped and RE-doped BCT ceramics were prepared with the composition (Ba_{0.77}Ca_{0.23})_{1−x}RE_xTiO_3, where x = 1% and 2% and RE = Sm, Nd, Pr, and Yb, via solid-state reaction. Appropriate amounts of reagent-grade barium carbonate (BaCO_3, AlfaAesar, 99%), calcium carbonate (CaCO_3, Merck, 99%), titanium oxide (TiO_2, Merck, 99%), and rare earth oxide (RE_2O_3) were mixed for up to 72 h by ball milling in isopropyl alcohol. ZrO_2 balls (0.94 × 0.96 mm² in size) were used to produce an optimized grain size. After milling, the powders were calcined in an open platinum crucible at 1400 °C for 4 h and submitted to further ball milling in isopropyl alcohol for 48 h. The ceramics were shaped into disks (6 mm in diameter and 2 mm in thickness) by uniaxial pressing at 10⁷ Pa and sintered at 1450 °C for 4 h in air.

The phase formation was investigated via x-ray diffraction (XRD) using a Rigaku Rotaflex-RU-200B diffractometer and Cu Kα radiation. The microstructure was examined via scanning electron microscopy (SEM) using a Zeiss DSM 960. The dielectric properties of the ceramics were measured at a frequency of 1 kHz in the temperature range from 20 °C to 205 °C using an impedance analyzer (Solartron model SI 1260).

Raman scattering measurements were carried out on undoped and RE-doped BCT23 samples using the 514.5 nm line of an Ar⁺ laser with a power density of 1 MW/cm² on the sample surface. This laser power density was found to optimize the signal-to-noise ratio without overheating the sample. The scattered light was analyzed with a Jobin Yvon T64000 spectrometer equipped with a N₂-cooled charge-coupled device detector. An Olympus microscope lens with a focal distance = 20.5 mm and a numeric aperture = 0.35 was used to focus the laser beam on the polished sample surface.

Room temperature EPR measurements were carried out with a Bruker EleXsys E-500 spectrometer. The X-band spectrometer consists of an SHQE-W1 cavity, a SuperX bridge, a NMR Tesla meter, a field/frequency stabilizer, and a 13 in. magnet. Data were acquired by taking the first derivative of the absorption curve with a field modulation of 100 kHz and an amplitude of 0.4 mT. The typical microwave power applied to the sample was 40 mW. Powder samples were placed in a fused silica tube and inserted into the microwave cavity for measurement.

III. RESULTS AND DISCUSSION

A. X-ray diffraction and scanning electron microscopy

Figure 1 shows the XRD patterns for the undoped and RE doped BCT ceramics. It is observed that Pr-, Sm-, and Nd-doped samples have an XRD pattern typical of a single tetragonal, while for the Yb-doped samples additional reflections at 2θ = 31° and 35° are observed. These additional reflections are identified as coming from the Yb_2Ti_2O_7 phase. The shift toward higher 2θ values, observed for some of the diffraction peaks of the RE-doped BCT23 sample, indicates a decrease in the volume of the unit cell. The contraction of the lattice parameters a and c obtained from the x-ray data are listed in Table I. Rare earth doping introduced lattice parameter changes, thereby leading the system to develop internal stress in the so-called grain core and grain shell structures, as evidenced by the unresolved peak observed at 2θ = 45° for doped samples.

The morphology of the sintered samples was characterized via SEM and with selected images of the RE-doped BCT23 ceramics shown in Fig. 2. The results indicate that RE doping favors a smaller grain-size formation (around 2 μm), thus improving the homogeneity. Furthermore, RE doping prevented abnormal grain growth and the formation of a liquid phase segregated in the grain boundaries, which are normally observed in both pure BCT and BT ceramics prepared using conventional methods. For the Yb-doped samples, we observed the formation of cubiclike grains (indicated by arrows in Fig. 2), which are likely to correspond to the Yb_2Ti_2O_7 pirochlore phase that was detected in the x-ray patterns (see inset to Fig. 1(d)).
B. Dielectric constant measurements

The relative dielectric constant measurements of pure and RE-doped BCT23 ceramics as a function of temperature measured with a frequency of 1 kHz are shown in Fig. 3. The dielectric properties of BCT in the ferroelectric state are extremely sensitive to the addition of impurities. The temperature dependence of the dielectric constant is typical of a diffuse phase transition (DPT). This result points out that the Ca ions are exclusively occupying the Ba site. The occurrence of this DPT is due to the intrinsic disorder effect introduced by the replacement of A or B cation sites in the ABO₃ structure. The dielectric results show that RE doping modifies the dielectric properties of the ceramics (Figs. 3(a), 3(c), and 3(d)) significantly. We observe that increasing Pr, Sm, and Nd doping progressively downshifts the Curie temperature from 125°C to 50°C, which indicates that these dopants are incorporated into the crystal lattice. In contrast, the peak in the dielectric response does not change for the Yb-doped samples (see Fig. 3(b)). This result points out that this ion has not been incorporated into the lattice, in agreement with the XRD and SEM results that show the formation of the secondary phase Yb₂Ti₂O₇. It should be pointed out that the incorporation of Yb is related to the solubility limit of Yb₂O₃ in BCT23. Therefore, this limit should be very low, because 1% of Yb is already enough to induce the formation of Yb₂Ti₂O₇ as identified in the XRD diffractograms.

C. Raman spectroscopy

Figure 4 shows the Raman spectra of (Ba₀.₇₇Ca₀.₂₃)₁₋ₓ(RE)ₓTiO₃ ceramics recorded at room temperature. The
spectra are very similar to that of BT. Also, the Raman spectrum of undoped BCT23 agrees well with previous reports on Ba0.85Ca0.15TiO3 ceramic,25 thus indicating that these two compositions have the same structural phase at room temperature as expected from the BCT phase diagram.26 However, some variations in the frequencies and in the relative intensity of the modes were observed. The mode (E + B1) located at about 300 cm$^{-1}$ is not as pronounced as it is in BT. The spectrum is characterized by strong light scattering in the low frequency region E(1TO), attributed to the overdamping mode. We also note that the Fano interference27 (absorption-like peak) located at about 180 cm$^{-1}$ is less evident in the BCT23 Raman spectrum than in BT.

A comparison of the Raman spectra of the RE-doped BCT ceramics shows that the spectra of Yb doped samples (1% and 2%) are similar to the spectrum of undoped BCT23, indicating that Yb$^{3+}$ does not introduce significant changes in the crystalline lattice. This is consistent with the XRD, SEM, and dielectric measurement results, which pointed out the existence of a Yb segregated phase. Undoped and Yb$^{3+}$ doped BCT have the same crystalline structure at room temperature as BT. These results corroborate the morphology results obtained by SEM, which indicate the presence of cubiclike grains and suggest the presence of secondary phase Yb$_2$Ti$_2$O$_7$. Therefore, the Yb does not replace Ca/Ba, and the Raman spectra are dominated by the BCT phase because it has a much larger scattering volume than the secondary phase.

A vibrational mode is observed at about 850 cm$^{-1}$ for the Nd, Sm, and Pr doped samples, and its intensity increases as the dopant concentration increases. It presents a peculiarly narrow linewidth as compared with the other Raman modes. This mode is due neither to the RE oxide phase segregated in the ceramic nor to luminescence from impurities in Nd$_2$O$_3$, Sm$_2$O$_3$, and Pr$_2$O$_3$ because it appears at the same frequency for samples with different dopants and different excitation lights, indicating that it is an intrinsic property of the RE-doped ceramics. BaTiO$_3$ and CaTiO$_3$ do not present first order Raman phonons with a frequency larger than 750 cm$^{-1}$, and we can assign the mode at 850 cm$^{-1}$ due to a local effect induced by the incorporation of RE ions in the crystalline structure of BCT23.28 We attributed these modes to the local distortion of the TiO$_6$ octahedra introduced by the ion doping in the BCT structure. We have identified this mode as originating from a Ti-vacant octahedron. This vacancy is created by a charge compensation mechanism wherein RE$^{3+}$ ions are incorporated into the BCT lattice. This vacancy state is supported by EPR measurements and lattice dynamics calculations that are discussed in the next section.

The thermodynamic stability of ferroelectrics is associated with a low frequency vibrational mode, the so-called soft mode.29 In order to eliminate the temperature effects in the Stokes spectrum, we corrected the spectrum intensity by the Bose-Einstein factor $[1 - \exp(h\nu/k_BT)]^{-1}$. A noticeable change in the Raman spectrum is evident when both the doping ion and its concentration are changed, i.e., the frequency of the E(1TO) soft mode decreases with increasing concentrations of Nd, Sm, and Pr. For the Yb-doped samples, the frequency of the soft mode is exactly the same as that observed in BCT.

The incorporation of Nd, Sm, and Pr into the BCT lattice affects the frequency of the E(1TO) mode considerably. The $\omega^2_{E(1TO)}$ values (see Fig. 5(b)) as a function of RE concentration decrease (see Fig. 5(a)), exhibiting the same trend as the Curie temperature ($T_c$) (see Fig. 5(b)) obtained from dielectric measurements. The decrease of $T_c$ and the frequency of the E(1TO) mode are correlated because the tetragonal-cubic phase transition is characterized by the softening of the E(1TO) mode—that is, the frequency of the mode should assume a constant value in the point transition, and the dielectric constant response should exhibit a peak.29–31 A smaller $\omega^2_{E(1TO)}$ value means that the material is closer to the transition temperature ($T_c$), in agreement with the experimental observations. When this frequency reaches the limiting value, the material undergoes a transition from the tetragonal to the cubic phase. Extrapolation of the results presented in Figs. 5(a) and 5(b) suggests that for concentrations larger than 2%.

![FIG. 2. (Color online) SEM images of RE-doped ceramics. (a) 1% Nd, (b) 2% Nd, (c) 1% Sm, (d) 2% Sm, (e) 1% Pr, (f) 2% Pr, (g) 1% Yb, and (h) 2% Yb. The arrows in (g) and (h) indicate the secondary phase.](image-url)
of Nd, Sm, and Pr, the BCT samples will present cubic symmetry at room temperature. The effect of the incorporation of RE ions (Nd, Sm, and Pr) into the structure of the BCT ceramic is similar to that of BaTiO₃ under hydrostatic pressure, where the $T_c$ value decreases with increasing pressure, i.e., $(dT_c/dP) < 0$. The partial substitution of Nd, Sm, and Pr for (Ba, Ca) reduces the volume of the unit cell and decreases the tetragonality $(c/a)$ parameter, as shown by the XRD results. These changes promote the formation of a more cohesive structure and reveal a trend toward the cubic phase.

D. Electronic paramagnetic resonance

In Fig. 6(a) we show the mass-corrected EPR spectra recorded at room temperature of undoped BCT (BCT23) and BCT doped with 1% Nd, 2% Nd, 2% Pr, and 2% Sm. The spectra exhibit a sextet of lines between 3250 and 3750 G, and these lines have previously been assigned to Mn²⁺, which is incorporated as an impurity during the synthesis procedure. A simulation using XSophe software confirms that the sextet is due to the presence of Mn²⁺ with hyperfine splitting due to the nuclear spin of Mn $(I = 5/2, 100\%$ abundant), with $g = 2.001, A = 85$ G, and a linewidth of 7 G (see Fig. 7). The addition of RE dopants to the BCT samples did not seem to significantly affect either the parameters of the Mn²⁺ signal or the intensity of the signal.

The RE-doped BCT samples clearly exhibit an axially symmetric signal with $g_k = 2.0075$ and $g_\| = 1.98$ and a linewidth varying from 10 to 13 G (taken from simulations similar to that shown in Fig. 7). The signal is present but weak in the undoped (BCT23) sample, and the signal intensity is nearly doubled for the 1% Nd doped sample as compared to the 2% Nd doped sample. As this signal is not characteristic of the RE ions, it likely represents a charge compensating defect. The signal is consistent with an axially symmetric signal near $g = 2.004$ seen in previous studies. In order to satisfactorily fit the RE-doped BCT samples using the XSophe simulation program, a hyperfine coupling with a Ba nucleus of 11 to 15 G had to be included in the simulation of this axially symmetric signal. An obvious choice for the origin of this signal would be an electron trapped at an oxygen vacancy (a F⁻ center), as the g value is near the free electron value; the signal shows hyperfine coupling to a Ba nucleus, which would be the nearest neighbor to an oxygen vacancy in the BCT structure, and F⁻ centers could be the charge compensation mechanism for the incorporation of RE ions. However, Lu et al. ruled out the possibility of oxygen vacancies ($V_O$) in a BaTiO₃ structure due to the presence of oxygen during the sintering process, the absence of conductivity from oxygen vacancies, and the absence of Fe³⁺.$V_O$
complexes upon intentional doping with Fe$^{3+}$. We did not intentionally dope our samples with Fe$^{3+}$, but we did use a similar sintering procedure, and the RE-doped BCT samples did not show an increase in conductivity. In addition, Tsur et al. found that only dopants with ionic radii smaller than 0.89 Å produced oxygen vacancies as compensating defects in BaTiO$_3$, and all of the dopants used in our studies have ionic radii larger than 0.964 Å. Therefore, it is unlikely that the described axially symmetric signal in our samples is due to F$^+$ centers.

Previous studies have attributed the axially symmetric signal near $g = 2.004$ to singly ionized Ti vacancies in BaTiO$_3$. The presence of charge-compensating Ti vacancies is consistent with Raman spectroscopy data, which show a narrow peak originating from the Ti-vacant octahedron. The totally symmetric breathing of the oxygen case is most likely responsible for the 840 cm$^{-1}$ mode. In fact, the EPR spectra do not show a resonance near $g = 1.974$, which has previously been seen and attributed to Ba vacancies. Further-

more, Tsur et al. concluded that dopants with ionic radii larger than 0.94 Å (which includes the dopants used in our studies) would be incorporated in the A site and result in charge-compensating Ti vacancies. Therefore, we conclude that the observed axially symmetric EPR signal near $g = 2.004$ is due to singly ionized Ti vacancies. However, the presence of hyperfine coupling with the next-nearest neighbor Ba nucleus is somewhat surprising due to the low abundance of Ba isotopes with nuclear moments, and it introduces some doubt as to the Ti vacancy identification. Future experiments and modeling with different dopants (i.e., dopants with smaller ionic radii) and annealing in a reducing atmosphere in order to promote oxygen vacancies could help to clarify this identification.

E. Lattice dynamics calculations

Two unexpected sharp bands at 863 and 842 cm$^{-1}$ were observed in the Raman spectra. We assign these bands to the distortion of TiO$_6$ octahedra by the titanium vacancies created...
in order to maintain charge neutrality due to the introduction of REs. Defect-induced bands are observed in other systems such as hexagonal bronze systems and titanosilicates.\textsuperscript{39,40} In the hexagonal bronze systems, tungsten vacancies break down the force equilibrium among adjacent W–O bonds (associated with adjacent WO\textsubscript{4} octahedra), resulting in the shortening of W–O bonds and the appearance of high wavenumber bands at around 900 cm\textsuperscript{-1}. In titanosilicates, such as BaTiSi\textsubscript{2}O\textsubscript{7} for example, some high wavenumber modes are observed due to interstitial Ti defects. In that case, the defect centers present a bipyramidal structure associated with short Ti–O bonds. Based on these and other, similar cases, we propose that the additional bands observed in the BCT system (mode at about 850 cm\textsuperscript{-1}) are associated mainly with short Ti–O bonds resulting from Ti vacancies in the lattice structure.

In order to further support the assignment of the Ti vacancies in the BCT lattice structure, we performed lattice dynamics calculation in the cubic BT system (closely related to BCT system) by using the Rigid ion model and the GULP code by Gale.\textsuperscript{41} We have computationally constructed a supercell consisting of 64 cubic BT unit cells (320 atoms), and we have arbitrarily diluted the defects in that supercell. The pair potentials $U_{ij}(r)$ used in the calculations were derived by Lewis and Catlow.\textsuperscript{42} The structure was optimized through energy minimization, and the final deviation from experimental results\textsuperscript{43} was kept within 1\% with a lattice formation energy of −9401.8 eV. In Fig. 8 we show some Ti–O bonds around the defect center after geometrical optimization (in this case, the Ti vacancy is labeled as the D point in Fig. 8). We observed that the absence of B bonds (dotted lines in Fig. 8) results in short A type Ti–O bonds of the order of 1.78 Å. The bond lengths of the other bonds around the defect center are almost unchanged after the optimization (~2.0 Å). This result is in good agreement with our hypothesis. It is pertinent to say that a Ti vacancy generates a lattice charge imbalance that must be compensated for by either oxygen vacancies or cationic interstitials. In our study, we have diluted both kinds of defects and observed different local structures (vacancy or interstitial configurations). Among them, it is interesting to note the formation of bipyramidal structures, similar to the defect configuration proposed by Stassen et al. for titanosilicates.\textsuperscript{44} It is remarkable that this kind of structure, as well as many other tested configurations for the interstitial Ti defects, results in short Ti–O bonds (~1.7 Å). So we must further consider the possibility that these bonds can contribute to the high wavenumber vibrational modes observed in RE doped BCT.

Additionally, we have derived the force constants $f_{ij}$ by using Eq. (1), and we have performed phonon calculations using the Wilson’s FG matrix method.\textsuperscript{45}

$$f_{ij} = -\frac{1}{r} \frac{\partial U_{ij}(r)}{\partial r}$$  \hspace{1cm} (1)

This process resulted in a number of modes (3 x 320 modes) ranging from 23 to 783 cm\textsuperscript{-1}. In order to simulate a covalent effect (not considered in the ionic model), we slightly increased the force constants (~1.5 mDyn/Å) in the A short bonds around the defect centers. The calculations predicted an additional mode at 857 cm\textsuperscript{-1} (see the atomic displacements in Fig. 8) that is very close to the frequency of the extra band we observed experimentally. This calculation further supports our hypothesis that the additional observed modes in the BCT system arise from a tight interaction in A bonds resulting from vacancy centers.

IV. CONCLUSIONS

In summary, we have investigated RE-doped BCT ceramics by probing their vibrational, structural, and morphological properties using different experimental and modeling techniques. The changes in the materials’ properties due to RE doping allowed us to conclude that the REs are likely to be occupying the A site of the perovskites. The charge compensating effect is manifested through the
creation of Ti vacancies, a result that is suggested by EPR measurements. The presence of Ti vacancies was simulated by means of lattice dynamic calculations, and the geometrical optimization pointed to the presence of shorter Ti–O bonds. Phonon calculations showed a vibrational mode at 857 cm\(^{-1}\) related to these short Ti–O bonds, the frequency of which is very close to the band observed in the Raman spectra of Nd, Sm, and Pr doped BCT23 ceramics. By using different experimental techniques and modeling, this paper contributes to a better understanding of the physical properties of rare earth doped perovskites.

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