

Structural and dielectric properties of La substituted polycrystalline $\text{Ca}(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$

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Polycrystalline $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ were prepared by the standard solid state reaction technique. Pellet shaped samples prepared from each composition were sintered at 1573 K for 5 h. The X-ray diffraction analysis indicated the formation of a single-phase orthorhombic structure. The lattice parameters as well as densities increased but the average grain sizes decreased with the increase of La content. The dielectric measurements were carried out at room temperature as a function of frequency and composition. The experimental results revealed that dielectric constant (ϵ') decreased but dielectric loss ($\tan \delta$) and ac electrical conductivity (σ_{ac}) increased as frequency increased. The composition dependence of ϵ' and $\tan \delta$ indicated that they decreased with the increase of La content. The σ_{ac} was derived from the dielectric measurements and it is concluded that the conduction in the present samples is due to mixed polarons hopping.

Keywords: *ceramics; chemical synthesis; X-ray diffraction; dielectric properties*

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1. Introduction

Considerable attention have been given to high-permittivity dielectric materials with ABO_3 perovskite structure for both scientific study and their numerous technological applications in industries such as capacitors, memory devices, sensors etc, which are possible to realize due to the miniaturization and integration of electronic devices [1–3]. Usually, high-dielectric properties are observed in the perovskite ferroelectric or relaxor oxides, e.g., $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and $\text{Pb}(\text{Mg,Nb})\text{O}_3$, however, these materials show strong temperature dependence due to the ferroelectric phase transition. Most perovskite oxides contain Pb [4, 5]. The Pb based ceramics have outstanding ferroelectric as well as dielectric properties. However, Pb is a toxic substance which can cause damage to the environment and human health; therefore, some countries now require that all electronic products that enter its borders should be Pb free. Due to growing awareness of global environmental pollution and danger to human health,

many scientists have now focused greatly on finding Pb free ceramics [6, 7].

In recent literature, Pb free perovskite-like oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) and Li, Ti co-doped NiO (LTNO) ceramics have been reported to possess high dielectric constant at room temperature, which is almost constant over a wide range of temperature and frequency [8, 9]. However, Both of CCTO and LTNO materials have not yet found applications because of their high dielectric losses around room temperature. Therefore, the production of Pb free dielectric materials with high dielectric constant, low dielectric loss and good stability in a wide range of temperature and frequency are highly desired.

The researchers paid more attention to improve the dielectric properties of pure CaTiO_3 via partial substitution of either Ca-ions (A-site doping) or Ti-ions (B-site doping), which may result in high permittivity of ferroelectric CaTiO_3 . So far, many new compositions with excellent properties have been developed, such as $\text{Ca}_{1-x}\text{Nd}_{2x/3}\text{TiO}_3$, $\text{Ca}_{1-x}\text{Sm}_{2x/3}\text{TiO}_3$ and $\text{Ca}_{1-x}\text{Bi}_x\text{Ti}_{1-x}\text{Cr}_x\text{O}_3$ [10–12].

Literature survey has revealed that no study has been made on $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ which

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is Pb free. For the present experiment, $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ compositions were chosen and the results of the study of structural and dielectric properties are reported in this paper.

2. Experimental methods and procedures

2.1. Sample preparation

The polycrystalline samples of $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ (CLTFO) with $0 \leq x \leq 0.5$ were prepared by the standard solid state reaction technique. The stoichiometric amounts of CaCO_3 (99.9 %), La_2O_3 (99.9 %), TiO_2 (99.9 %) and Fe_2O_3 (99.9 %) were mixed thoroughly by ball milling in distilled water for 10 h. The slurry was dried and the mixed powders were calcined at 1223 K for 12 h in air. The calcined powders were re-milled for 10 h and then dried. Finally, the dried powders were ground, and from the fine powders, disk-shaped pellets with diameter of 0.01 m and thickness of 0.001–0.002 m were prepared under uniaxial pressure of 35 MPa. The pellets were sintered at 1573 K for 5 h. During the sintering, the heating and cooling rates were maintained at 0.16 K/s and 0.08 K/s, respectively.

2.2. Sample characterization

The phase-purity and the crystal structure of the compositions were investigated by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation at room temperature. The XRD patterns of all compositions were collected over a 2θ range of 15 – 65° using a step size of 0.02° . The physical or bulk density, ρ_B , of the compositions was determined using the expression:

$$\rho_B = \frac{W}{W - W'} \times \rho \quad (1)$$

where W and W' are the weights of the compositions in air and water, respectively, and ρ is the density of water at room temperature. The theoretical density, ρ_{th} , was calculated using the expression:

$$\rho_{th} = \frac{4M}{N_A abc} \quad [\times 10^3 \text{ Kg/m}^3] \quad (2)$$

where N_A is the Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$), M is the molecular weight, a , b and c

are lattice parameters. The porosity, P , was calculated from the relation:

$$P(\%) = \frac{\rho_{th} - \rho_B}{\rho_{th}} \times 100 \quad (3)$$

The surface morphology of sintered and polished pellets was studied with a high resolution optical microscope (Olympus DP-70) and the average grain sizes were determined by the linear intercept technique [13]. In order to measure the dielectric properties, gold electrodes were deposited on both sides of the pellets and then gold wire was attached on each electrode with silver paste. The frequency dependence of the capacitance and the loss were measured by LCR meter at room temperature in the frequency range of 10 Hz to 32 MHz. The dielectric constant was calculated from the capacitance using the following equation:

$$\epsilon' = \frac{Cd}{\epsilon_0 A} \quad (4)$$

where C is the capacitance (F), ϵ_0 is the permittivity ($8.854 \times 10^{-12} \text{ Fm}^{-1}$) of free space, A is the area (m^2) of electrode and d is the thickness (m) of the pellet. The ac conductivity was calculated using room temperature dielectric data from the relation:

$$\sigma_{ac} = \epsilon' \epsilon_0 \omega \tan \delta \quad (5)$$

where ω is the angular frequency and $\tan \delta$ is the dielectric loss.

3. Results and discussion

3.1. Crystal structure, lattice parameters and density of the compositions

The XRD patterns for various $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ are shown in Fig. 1. Analyzing the XRD patterns, it is observed that there is a single phase perovskite structure but there is no trace of a second phase which implies that La cations diffuse into the $\text{Ca}(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ lattice and form a solid solution [7]. The XRD patterns are indexed similar to orthorhombic CaTiO_3 on the basis of space group $Pnma$ [12, 14]. With increasing La content (x), the stability of perovskite phase increases because the ionic size of La^{3+} ($1.36 \text{ \AA}$, CN = 12) ion

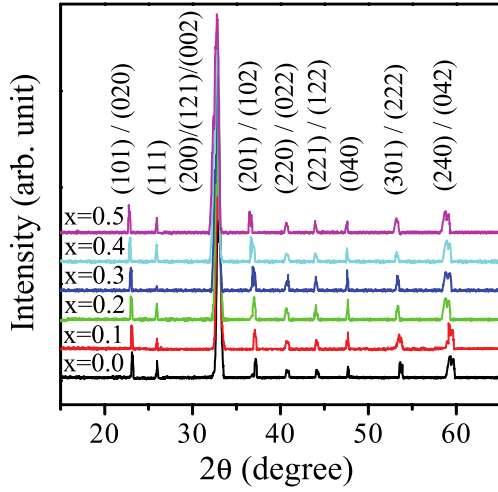


Fig. 1. X-ray diffraction pattern of various $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ sintered at 1573 K.

is larger than that of Ca^{2+} (1.34 Å, CN = 12) ion [15], which is confirmed by the increase of tolerance factor, $t = (R_A + R_O) / \sqrt{2}(R_B + R_O)$ (where R_A , R_B , and R_O are the ionic radii of the A site, B site, and oxygen ion, respectively, in ABO_3 perovskite) from 0.9567 (for $x = 0.0$) to 0.9603 (for $x = 0.5$).

The lattice parameters were calculated from the XRD patterns by using the formula:

$$d_{hkl} = \left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right]^{-\frac{1}{2}} \quad (6)$$

where d_{hkl} is the interplanar distance; h , k , and l are the Miller indices of the crystal planes; and a , b and c are the dimensions of an orthorhombic unit cell. The variation of lattice parameters a , b and c of the orthorhombic phase obtained from the above relation and are shown in Fig. 2 for different La contents. It is observed from Fig. 2 that the substitution of Ca cations by La in the $\text{Ca}(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ phase slightly increased the lattice parameters because of the larger ionic size of La^{3+} compared to Ca^{2+} , obeying Vegard's law [16].

The variations of ρ_B , ρ_{th} and P (%) with La content of various CLTFO are shown in Fig. 3. It is obvious from Fig. 3 that the substitution of Ca by La leads to the increase of density of the CLTFO solid solutions. The increase of ρ_B with increasing La content may be attributed to the difference in

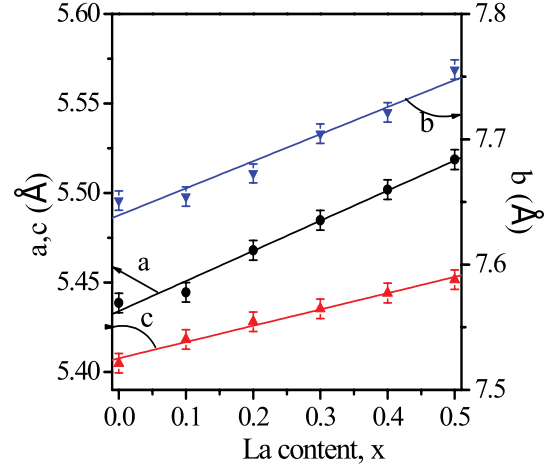


Fig. 2. Variation of lattice parameters with La content of various $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ sintered at 1573 K.

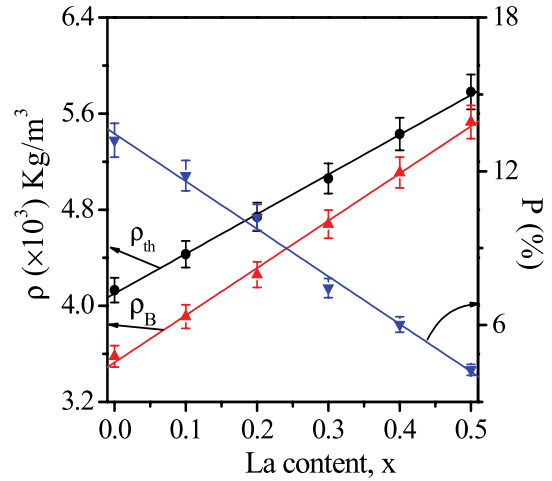


Fig. 3. Variation of density and porosity with La content of various $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ sintered at 1573 K.

atomic weight and density of initial and substituted cations. The ρ_{th} increases with increasing La content because the molecular weight of each composition increases significantly with the substitution of La. It is also noticed in Fig. 3 that the ρ_{th} is larger in magnitude compared to the corresponding ρ_B . This is due to the existence of pores which are forming and developing during the sintering process [17]. On the other hand, porosity (P) of the compositions has the opposite behavior as that of density, which is shown in Fig. 3. The P of the compositions de-

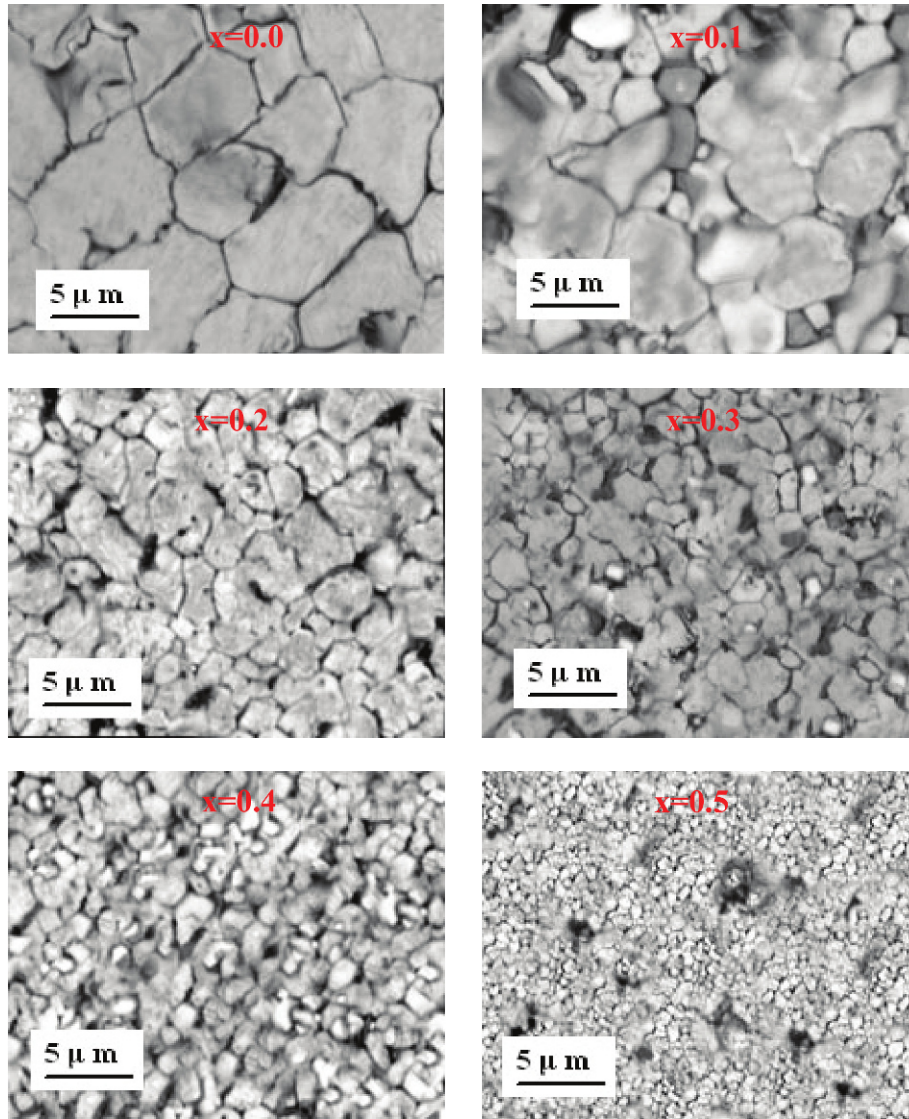


Fig. 4. Optical micrographs of various $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ sintered at 1573 K.

creases with the increase of La content; this is due to the substitution of higher density La cations.

3.2. Microstructure

The optical micrographs for various CLTFO sintered at 1573 K are shown in Fig. 4. It is observed that the average grain sizes decrease from ~ 4.45 to ~ 0.65 μm with the increase of La content. It has been reported that heterovalent dopants (donors as well as acceptors) are segregated at the grain boundaries in perovskite titanates. The segregation of dopants at the grain boundaries inhibits the grain

growth [18, 19]. Decrease in the average grain sizes with increasing La content in all the compositions investigated in this study can be accounted for the segregation of dopants at the grain boundaries.

3.3. Frequency dependence of dielectric properties

Fig. 5 shows the frequency dependence of the dielectric constant (ϵ') and dielectric loss ($\tan \delta$) for various compositions, measured at room temperature. An examination of Fig. 5(a) shows that all the compositions reveal dielectric dispersion. The ϵ' is

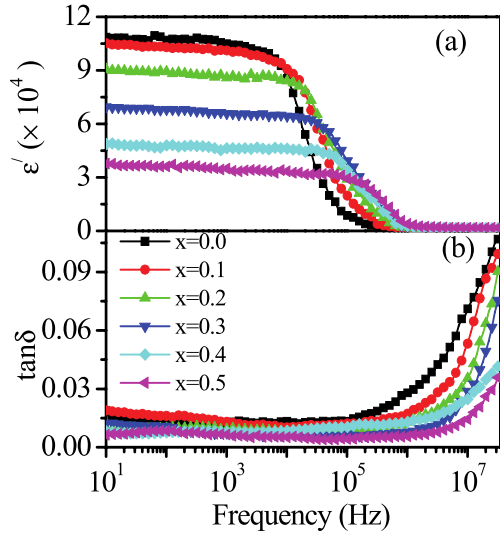
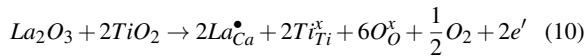
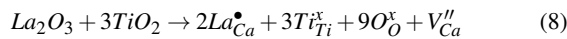
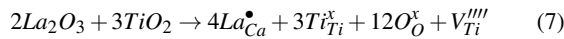
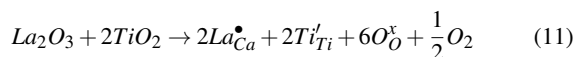


Fig. 5. Frequency dependence of (a) dielectric constant (ϵ') and (b) dielectric loss ($\tan \delta$) of various $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ sintered at 1573 K.

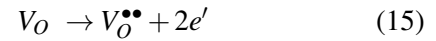
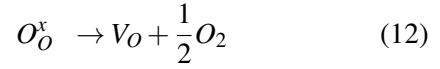
high at low frequency and remains fairly constant up to a certain frequency (depending upon compositions). Thereafter it decreases with the increase in frequency. The higher value of ϵ' at lower frequencies is due to the dislocations and cation or oxygen vacancies present in the materials. As a result of the substitution of Ca^{2+} by La^{3+} at the lattice site A, there is a strong possibility of creation of cation or oxygen vacancies (as illustrated below). These vacancies are created in order to maintain localized charge neutrality because of different valence states of the cations that are occupying the lattice sites A and B [20, 21]. In the present perovskite material, (La^{3+} , Ca^{2+}) ions occupy the lattice site A and (Ti^{4+} , Fe^{3+}) ions occupy the lattice site B.



If the electrons are primarily associated with Ti, then Eq. (10) can be written as:



All the above symbols have been used in accordance with Kroger-Vink notation [22], where $\text{V}_{\text{Ti}}^{\prime\prime\prime}$ and $\text{V}_{\text{Ca}}^{\prime\prime}$ are denoted Ti and Ca vacancies leading to four and two extra negative charges respectively and $\text{V}_{\text{O}}^{\bullet\bullet}$ represents the oxygen vacancy with two positive charges. In the present study, the samples have been sintered at higher temperatures; a slight amount of oxygen is lost according to the reaction such as:



where V_{O} is the oxygen vacancy, $\text{V}_{\text{O}}^{\bullet}$ and $\text{V}_{\text{O}}^{\bullet\bullet}$ are single and double ionized oxygen vacancies respectively and e' is the electron released or captured. These oxygen and cation vacancies act as intrinsic donors or acceptors. The electron released in the above equations during the sintering process induces trivalent La^{3+} ion to substitute for Ca^{2+} acting as extrinsic donors. Similarly trivalent Fe^{3+} ion substitutes for Ti^{4+} acting as extrinsic acceptor. The overall charge neutrality condition requires that the sum of charges on the positive and negative charge defects should be equal. Therefore, the vacancies of $\text{V}_{\text{O}}^{\bullet}$, $\text{V}_{\text{O}}^{\bullet\bullet}$, $\text{V}_{\text{Ca}}^{\prime\prime}$ and $\text{V}_{\text{Ti}}^{\prime\prime\prime}$ are combined with $\text{Fe}_{\text{Ti}}^{\prime}$ or $\text{La}_{\text{Ca}}^{\bullet}$ to form the dipoles of the types of $(\text{Fe}_{\text{Ti}}^{\prime} - \text{V}_{\text{O}}^{\bullet})$, $(2\text{Fe}_{\text{Ti}}^{\prime} - \text{V}_{\text{O}}^{\bullet\bullet})$, $(2\text{La}_{\text{Ca}}^{\bullet} - \text{V}_{\text{Ca}}^{\prime\prime})$ or $(4\text{La}_{\text{Ca}}^{\bullet} - \text{V}_{\text{Ti}}^{\prime\prime\prime})$ due to Coulombic attraction. At lower frequencies, the dipoles which are formed due to the formation of vacancies are able to follow the frequency of the applied field and result in high dielectric constant. But as frequency increases, the dipoles are not able to follow the frequency of the applied field so the dielectric constant remains independent of frequency and lower values of ϵ' occur at higher frequencies.

The higher values of ϵ' , which are observed at lower frequencies, may also be explained on the basis of space charge polarization due to inhomogeneous structure, where individual high conducting grains are separated by either air gaps or low conducting grain boundaries. The inhomogeneities in the present system may also arise as a result of

impurities, porosity, oxygen vacancies and grain structure or defects in the grain boundary [23]. Another reason for the high values of ϵ' at lower frequencies and the decrease of ϵ' with the increase in frequency may be attributed to the multi component (*i.e.* electronic, ionic, orientation and space charge) mechanism of polarizability, contributing to the total polarization in the material at lower frequencies. But, as the frequency becomes higher and higher, some of the above mentioned mechanisms of polarizability may cease to contribute to ϵ' .

Loss tangent or loss factor ($\tan \delta$) represents the energy dissipation in the dielectric system. Fig. 5(b) shows the variation of $\tan \delta$ with frequency at room temperature. It is observed that $\tan \delta$ remains almost constant up to a certain frequency and thereafter it increases with the increase in frequency for all the compositions, which may be ascribed to the fact that the ionic conductivity caused by conduction involves some movement of vacancies. With an increase in frequency, retardation in polarization caused by ionic conductivity is enhanced, leading to an increase in $\tan \delta$.

3.4. Composition dependence of dielectric properties

Fig. 6 shows the variation of ϵ' and $\tan \delta$ with La content at different frequencies. It is observed from Fig. 6(a) that the value of ϵ' reduces with increasing La content. This can be explained on the basis of the Maxwell-Wagner theory of extrinsic factors as the dielectric constant is sensitive to grain size and is extrinsically influenced. According to this theory, the dielectric constant is directly proportional to the grain size of the samples [24–26]. In the present study, it is observed that the average grain sizes of the samples decrease with the increase of La content (Fig. 4). The decrease in grain size leads to the decrease in polarizability of atoms in the structure, which results in a decrease of ϵ' .

The variation of $\tan \delta$ with La content at different frequencies is shown in Fig. 6(b). It is realized that the $\tan \delta$ reduces with increasing La concentration. In general, oxygen vacancies are responsible for the dielectric loss in ferroelectrics [27]. Here the oxygen vacancies (discussed earlier) are reduced

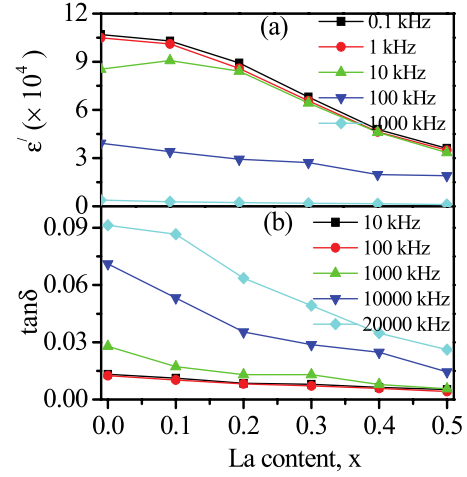


Fig. 6. Composition dependence of (a) dielectric constant (ϵ') and (b) dielectric loss ($\tan \delta$) of various $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ sintered at 1573 K.

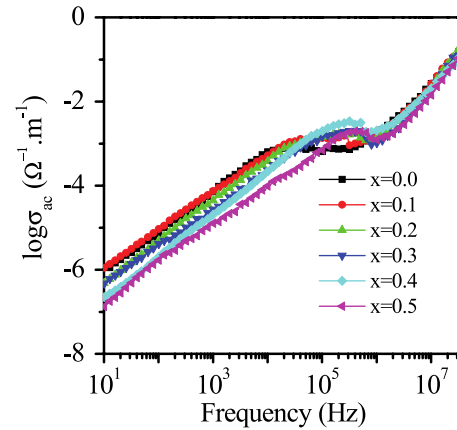


Fig. 7. Frequency dependence of ac conductivity of various $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ sintered at 1573 K.

with the increase of La content, which in turn decreases the $\tan \delta$. Relative density also plays an important role in controlling the dielectric loss of the samples [28]. Here, the density increases with La content (Fig. 3), so the $\tan \delta$ decreases with increasing La content.

3.5. Frequency dependence of ac conductivity

In order to understand the conduction mechanism and the type of polarons responsible for conduction, calculations of ac conductivity (σ_{ac}) were carried out at room temperature in the frequency

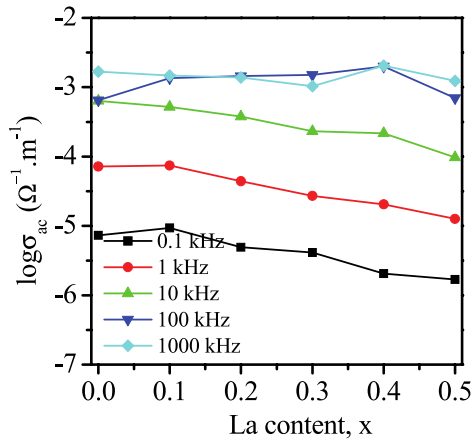


Fig. 8. Composition dependence of ac conductivity of various $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ sintered at 1573 K.

range from 10 Hz to 32 MHz. It is well known that there are two types of polarons viz. small polarons and large polarons. In the small polarons model the conductivity increases linearly with an increase in frequency and in case of large polarons the conductivity decreases with the increase in frequency [29]. Fig. 7 shows the frequency dependent σ_{ac} plot. It is observed from Fig. 7 that the σ_{ac} increases linearly with the increase in frequency indicating small polarons type of conduction. However, a slight decrease in σ_{ac} at certain frequency may be attributed to mixed polarons.

3.6. Composition dependence of ac conductivity

The σ_{ac} for various La content at different frequencies is shown in Fig. 8. The σ_{ac} is found to decrease with the increase of La content. The decrease in σ_{ac} may be primarily due to the decrease in loss because of La substitution as stated earlier. The decrease in σ_{ac} with La content may also be explained on the basis of average grain sizes as the areas of grain boundaries are highly resistive in oxide ceramics. Here, the average grain sizes decrease with increasing La content, as seen from the optical micrograph (Fig. 4). The decreased grain size causes and increase in the grain boundary areas or in resistance as in the case of smaller grains, the number of grain boundaries per unit thickness is higher than that of large grain ceramics. Hence, the

resistivity of the composition increases, which in turn causes a decrease in σ_{ac} of the composition with La content.

4. Conclusions

Polycrystalline $\text{Ca}_{1-x}\text{La}_x(\text{Ti}_{0.5}\text{Fe}_{0.5})\text{O}_3$ have been successfully synthesized by the standard solid state reaction technique. The XRD studies of the compositions revealed the formation of a single phase perovskite structure with orthorhombic phase. The lattice parameters increased but the average grain sizes decreased with the increase of La content. The dielectric constant decreased while the dielectric loss and ac conductivity increased as the frequency increased for all the compositions. The compositional dependence indicated that both ϵ' and $\tan \delta$ decreased with increasing La content. The calculation of ac conductivity indicated mixed polarons hopping type conduction.

Acknowledgements

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