Octahedral distortion-driven electrical and vibrational properties of $A_2\text{ErTaO}_6$ ($A = \text{Sr}$ and Ca) double perovskite oxides

Rajesh Mukherjee^{*,§}, Alo Dutta[†] and T. P. Sinha[‡]

^{*}Department of Physics, Ramananda College
Bishnupur, Bankura 722122, West Bengal, India

[†]Department of Condensed Matter Physics and Material Sciences
S. N. Bose National Centre for Basic Sciences
Block-JD, Sector-III, Salt Lake, Kolkata 700098, West Bengal, India

[‡]Department of Physics, Bose Institute
93/1 Acharya Prafulla Chandra Road, Kolkata 700009, West Bengal, India
[§]rajeshxrd@gmail.com

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Rietveld refinement analysis indicates that $A_2\text{ErTaO}_6$ ($A = \text{Sr}^{+2}, \text{Ca}^{+2}$) ceramics prepared by a solid-state route are crystallized in monoclinic perovskite phase with space group $P2_1/n$. Raman scattering and infrared spectroscopy are used to investigate the structure and phonon modes of the samples. Using Lorentzian lines, we have fitted the Raman spectra and the major Raman modes are assigned. Phonon vibrational frequency is modulated with the A-site cationic change. Impedance spectra of the samples over the frequency range of 100 Hz–1.1 MHz are investigated at different temperatures from 303 K to 573 K. Cole–Cole relaxation of dielectric constant is modified with the electrical conduction parameter to describe the temperature dependence of dielectric constant. The frequency-dependent conductivity spectra follow the double power-law.

Keywords: Rare-earth double perovskite; dielectric relaxation; Raman spectroscopy; electrical conductivity.

1. Introduction

Double perovskite oxides (DPOs) with the chemical formula $A_2B'B''\text{O}_6$ are widely studied because of their interesting and potentially useful physical properties.^{1,2} $A_2B'B''\text{O}_6$ is obtained from the perovskite oxide ABO_3 when the octahedrally coordinated B-cation is occupied by two kinds of B' - and B'' -cations with an appreciable difference in charge or size. The B' - and B'' -cations in DPO are ordered in a rock-salt lattice having alternatively $B'\text{O}_6$ and $B''\text{O}_6$ octahedra. Rock-salt ordering of the octahedral site cations doubles the unit cell of the simple undistorted ABO_3 perovskite, changing the space symmetry from $Pm3m$ to $Fm3m$. The most common type of distortion involves cooperative tilts of the octahedra. Octahedral tilting distortions lead to lowering of symmetry. Mandal *et al.*³ have synthesized the $A_2\text{MnB}'\text{O}_6$ ($A = \text{Ca}, \text{Sr}; B = \text{Sb}, \text{Ta}$) double perovskites and investigated their structural and magnetic properties. Using Rietveld refinement, they showed the significant ordering of B-site cation only in the case of $\text{Sr}_2\text{MnSbO}_6$ compared to the near-complete disorder of Mn/Ta in $\text{Sr}_2\text{MnTaO}_6$ as the difference of effective ionic radii of $\text{Mn}^{3+} - \text{Sb}^{5+}$ is greater than that of $\text{Mn}^{3+} - \text{Ta}^{5+}$. The $\text{Sr}(\text{B}_{0.5}\text{Ta}_{0.5})\text{O}_3$ ceramics, where $B = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Y}, \text{Er}$ and Yb , have been prepared by the conventional solid-state ceramic route and

their microwave dielectric properties have been investigated.⁴ The relative permittivity (ϵ') varies linearly with B-site ionic radii except for La. Kanaiwa *et al.*⁵ have prepared a series of $\text{Sr}_2\text{LnTaO}_6$ ($\text{Ln} = \text{lanthanides except for La, Ce and Pr}$) by solid-state reaction method and studied their crystal structures by powder X-ray diffraction (XRD). They have reported that crystal symmetry of all the materials is monoclinic. Magnetic susceptibility measurement reveals that all the materials are paramagnetic down to 5 K. Raman and infrared spectroscopic investigations of $\text{Sr}_2\text{LnTaO}_6$ and $\text{Ca}_2\text{LnTaO}_6$ ($\text{Ln} = \text{lanthanides, Y and In}$) double perovskites have been carried out by Dias *et al.*^{6,7} The crystal structures and phonon mode features for different lanthanide series in Ca-based double perovskites were determined using the experimental data besides the group theoretical model. Barnes *et al.* have shown the room-temperature crystal structures of $A_2M^{3+}M^{5+}\text{O}_6$ ordered perovskites using neutron and X-ray powder diffraction data.⁸ To the best of our knowledge, there is no study on the dielectric properties of the erbium-based tantalate in the low-frequency range. The dielectric properties of the samples are studied in a wide range of temperatures and frequencies. The vibrational properties of the samples are investigated by Raman and infrared spectroscopies together with factor group analysis.

2. Experimental

The polycrystalline ceramic powders of $\text{Sr}_2\text{ErTaO}_6$ (SET) and $\text{Ca}_2\text{ErTaO}_6$ (CET) were prepared via the conventional solid-state reaction route using stoichiometric amounts of SrCO_3 (Loba Chemie; reagent grade), CaCO_3 (Loba Chemie; reagent grade), Er_2O_3 (Alfa Aesar; 99.99%) and Ta_2O_5 (Alfa Aesar; reagent grade). These raw materials were well mixed in acetone medium for half a day. The mixture was then calcined in an alumina crucible at 1300°C for 10 h and cooled down to room temperature at an average cooling rate of 20°C/h . The calcined powder was again grinded and heated at a higher temperature. Finally, the materials were calcined at 1500°C in air for 10 h after grinding and heating several times. The finally calcined powder was pressed into pellets using 2% polyvinyl alcohol as a binder. The pellets were sintered at 1550°C for 10 h and cooled down to room temperature at the rate of 15°C/h . Phase purity of the sintered materials was determined by the XRD data taken by Rigaku Miniflex2 diffractometer using $\text{Cu-K}\alpha$ radiation. The XRD data were collected by step scanning over a range of $20^\circ \leq 2\theta \leq 100^\circ$ with an increment of 0.02° per step. The Rietveld refinement of the XRD pattern was performed for structural analysis and to confirm the phase purity of the sample. For studying the surface morphology, the scanning electron micrograph of the sample was taken by an FEI Quanta 200 scanning electron microscope (SEM).

In order to study the vibrational properties of SET and CET at room temperature, Fourier transform infrared (FTIR) and Raman spectra were studied. The FTIR spectrum was recorded in the transmittance mode from 400 cm^{-1} to 4000 cm^{-1} with a Perkin Elmer Spectrum 1000 spectrometer using the KBr pellet technique. The Raman spectrum was collected at an excitation wavelength of 488 nm using a LabRAM HR800 (Jobin Yvon) Raman spectrometer.

For electrical measurements, the sintered pellets were polished to make both their faces parallel and electroded by high-purity ultrafine silver paste. The capacitance (C), impedance (Z), phase angle (φ) and conductance (G) of the sample were measured as a function of both frequency (100 Hz – 1.1 MHz) and temperature (30 – 300°C) using a computer-controlled LCR meter (HIOKI-3552). The measuring temperature was controlled by a Eurotherm 2216e programmable temperature controller connected with the oven.

3. Results and Discussion

3.1. Structural and microstructural analyses

The room-temperature XRD patterns of SET and CET are shown in Figs. 1(a) and 1(b), respectively. The possibility of formation and stability of the DPO materials are determined by the tolerance factor which is written as: $T_f = (r_A + r_O) / [\sqrt{2}(\langle r_B \rangle + r_O)]$, where r_A and r_O denote the ionic radii of A- and O-ions, respectively, and $\langle r_B \rangle$ represents the average ionic radius of the B-site cations.⁹ The value of T_f close to

Fig. 1. Rietveld refinement plots for (a) SET and (b) CET. The symbols and the lines represent the experimental points and simulated XRD data, respectively. The scanning electron micrographs and the crystal structures of the samples are shown in the respective insets.

unity indicates the cubic perovskite structure. For $T_f \neq 1$, a tilt and rotation of the oxygen octahedra is obtained, in order to accommodate A- and B-cations. Here, the values of T_f for SET and CET are found to be 0.93 and 0.90, respectively, indicating a lower crystal symmetry than cubic. These values of T_f suggest that the materials synthesized under the present investigation have a monoclinic crystal structure like other perovskite oxides having nearly the same T_f .⁸ Figures 1(a) and 1(b) represent the Rietveld refinements of the XRD profiles of the samples in the monoclinic phase with $P2_1/n$ space group, where the symbols represent the experimental data and the solid lines represent the simulated patterns obtained using the FullProf code. The vertical bar lines represent Bragg positions and the bottom most line in each figure indicates the difference between the observed and the simulated patterns. The lattice parameters, atomic positions,

Table 1. Structural parameters extracted from the Rietveld refinement of the XRD data for SET and CET at room temperature.

SET	Sr	0.0044(15)	−0.0203(11)	0.2312(6)
	Er	0.5	0	0
	Ta	0.5	0	0.5
	O1	0.3330(10)	0.4230(11)	0.0078(54)
	O2	0.2714(11)	−0.2993(13)	0.4970(69)
	O3	0.0387(16)	0.4783(83)	0.2100(82)
Lattice parameters (Å): $a = 5.8048(3)$, $b = 5.8023(3)$, $c = 8.2182(5)$; $\beta = 90.511(3)^\circ$; Reliability factors: $R_p = 4.83$, $R_{wp} = 6.53$, $R_{exp} = 3.79$; $\chi^2 = 2.97$; Bond lengths (Å): $\langle \text{Er-O1} \rangle = 2.64(6)$, $\langle \text{Er-O2} \rangle = 1.96(7)$, $\langle \text{Er-O3} \rangle = 2.40(7)$, $\langle \text{Ta-O1} \rangle = 1.98(6)$, $\langle \text{Ta-O2} \rangle = 2.19(6)$, $\langle \text{Ta-O3} \rangle = 1.74(7)$; Bond angles: $\langle \text{Er-O1-Ta} \rangle = 124(2)^\circ$, $\langle \text{Er-O2-Ta} \rangle = 164(3)^\circ$, $\langle \text{Er-O3-Ta} \rangle = 165(3)^\circ$; Grain size (μm) = 1.3; BVS values: Sr = 1.826, Er = 3.167, Ta = 5.880				
CET	Ca	0.0258(21)	0.0530(13)	0.25
	Er	0.5	0	0
	Sb	0.5	0	0.5
	O1	0.6172(43)	−0.0323(76)	0.2716(24)
	O2	0.1610(75)	−0.1581(82)	0.0815(69)
	O3	0.2203(96)	0.7680(96)	0.4455(61)
Lattice parameters (Å): $a = 5.5794(2)$, $b = 5.7859(2)$, $c = 8.0278(4)$; $\beta = 90.04(1)^\circ$; Reliability factors: $R_p = 6.59$, $R_{wp} = 9.47$, $R_{exp} = 4.77$; $\chi^2 = 3.94$; Bond lengths (Å): $\langle \text{Er-O1} \rangle = 2.13(8)$, $\langle \text{Er-O2} \rangle = 2.36(6)$, $\langle \text{Er-O1} \rangle = 2.27(5)$, $\langle \text{Ta-O1} \rangle = 2.13(8)$, $\langle \text{Ta-O2} \rangle = 2.08(5)$, $\langle \text{Ta-O3} \rangle = 1.94(5)$; Bond angles: $\langle \text{Er-O1-Ta} \rangle = 141(3)^\circ$, $\langle \text{Er-O2-Ta} \rangle = 129(2)^\circ$, $\langle \text{Er-O3-Ta} \rangle = 145(2)^\circ$; Grain size (μm) = 1.4; BVS values: Ca = 2.087, Er = 3.025, Ta = 4.341				

bond lengths, bond angles and goodness of fitting parameters are listed in Table 1. It is observed from Table 1 that as the ionic radius of A-site cation decreases from SET to CET, the Er–O–Ta bond angle deviates much more from 180° , which has a great impact on the other physical properties of the materials. The decrease of average Er–O bond length and the increase of average Ta–O bond length in CET with respect to SET imply that Er–O bond is stronger in CET whereas Ta–O bond is stronger in SET. From the bond valence sum (BVS) analysis, it is seen that in case of SET, Er and Ta are overbonded but Sr is less bonded; whereas in case of CET, Ca and Er are overbonded but Ta is less bonded. The unit cell diagrams of SET and CET are given in the insets of the corresponding XRD figures. The SEM micrographs of SET and CET are shown in the insets of Figs. 1(a) and 1(b), respectively. The compact distribution of grains of various sizes and shapes indicates the high density of the synthesized materials. Theoretical densities for SET and CET are 7.433 gm/cm^3 and 6.720 gm/cm^3 , whereas the experimental densities obtained from Archimedes' principle are 7.1 gm/cm^3 and 6.3 gm/cm^3 , respectively. The relative densities are nearly 96% and 94%, respectively. Grain size variations and the values of BVS of the SET and CET are given in Table 1.

3.2. Vibrational analysis

Figure 2 shows the FTIR spectra of SET and CET. The bands appearing from 350 cm^{-1} to 700 cm^{-1} are the characteristic

Fig. 2. FTIR spectra of SET and CET.

of the vibrational modes of ErO_6 and/or TaO_6 octahedra. The lower energy bands found in between 360 cm^{-1} and 500 cm^{-1} are related to the deformational (asymmetric or symmetric bending) mode of the BO_6 polyhedra. Due to the lighter weight of Er-ion than Ta-ion, all the bands for ErO_6 octahedra appear in the higher energy side with respect to TaO_6 octahedra.¹⁰ It is observed that all the bending modes of BO_6 polyhedra shift to the higher energy side for CET than

SET, which can be correlated with the decrease of Er–O–Ta angle from SET to CET. The dips/bands appear at 530–650 cm⁻¹ and 505–625 cm⁻¹ for SET and CET, respectively, as shown by the arrow marks in the diagram. This broad nature of the observed vibrational bands is due to the overlapping of absorption peaks of both ErO₆ and TaO₆ octahedra. The width of this band is larger for SET than CET. The large difference of Er–O and Ta–O bonds in SET well separates the ErO₆ and TaO₆ stretching modes though they are overlapped to some extent. The bands at 553 cm⁻¹ and 640 cm⁻¹ for SET can be assigned as the stretching of Er–O and Ta–O bonds, respectively, and the corresponding bands for CET appear at 556 cm⁻¹ and 607 cm⁻¹. All the peaks are the characteristics of the materials.^{11,12} The opposite shifts of these two bands in CET with respect to SET can be correlated with the change of Er–O and Ta–O bond lengths. The higher bond length of Ta–O in CET shifts the corresponding bond to lower energy side whereas the opposite effect is observed for Er–O bond. The weak band at around 830 cm⁻¹ can be assigned to the symmetric stretching mode of the TaO₆ octahedra.

Raman scattering helps us to identify the structural defects and measure the structural parameters as it is sensitive to the crystal symmetry. The room-temperature Raman spectra of SET and CET are shown in Fig. 3(a) which are found to be well matched with the spectra of Ca₂ErTaO₆ studied by Dias *et al.*⁷ It is observed from the XRD analysis that SET and CET are crystallized in monoclinic *P*2₁/*n* space group (*C*_{2h}⁵), where the Er- and Ta-ions occupy the 2*a* and 2*b* Wyckoff sites of *C*_i symmetry, and Ca- and O-ions are at the 4*e* sites of the general *C*₁ symmetry. Thus the zone-center Raman active modes¹³ for SET/CET having *C*_{2h}⁵ point group symmetry are 24 and are defined as

$$\Gamma = 6T(3A_g + 3B_g) + 6L(3A_g + 3B_g) + 2v_1(A_g + B_g) + 4v_2(2A_g + 2B_g) + 6v_5(3A_g + 3B_g).$$

Here, *L* and *T* represent the librational and translational phonon modes, respectively, *v*₁, *v*₂ and *v*₅ correspond to the totally symmetric stretching, antisymmetric stretching and symmetric bending of ErO₆ (weak) and/or TaO₆ (strong) octahedra. The Raman spectra of SET and CET are well fitted with the sum of 22 Lorentzian peaks [as shown by the solid lines in Figs. 3(b)–3(e)] instead of 24 peaks because very less intensity peaks are neglected during Lorentzian fitting. The values of peak position and full-width at half-maximum (FWHM) of the peaks are listed in Tables 2(a) and 2(b). The highest frequency mode corresponding to 815–820 cm⁻¹ is due to the totally symmetric stretching of TaO₆ octahedra or *v*₁ mode for a free octahedron. The modes appearing in the range of 520–600 cm⁻¹ are assigned as the *v*₂ modes. The bending modes of the free octahedra are assigned as *v*₅ modes which are centered in the frequency range from 320 cm⁻¹ to 480 cm⁻¹. The *L* and *T* modes are spread over the frequency range between 100 cm⁻¹ and 300 cm⁻¹.

Since these modes are related with the *A*-cation, a large spectral change is observed as Sr is replaced by Ca.

It is observed from the Raman spectra that the frequencies of *v*₁ and *v*₅ modes present an opposite behavior when Ca replaces Sr. The frequencies of the *v*₁ modes decrease, while the frequencies of the *v*₅ modes increase. It is known that the phonon frequencies of different modes are proportional to the bonding energies between the *B*-site cations and O. The shorter Ta–O bond length in SET increases the bonding energy and hence the *v*₁ mode shifts to the higher frequency side with respect to CET. On the other hand, the Er–O distance decreases in CET than SET which increases the Er–O bonding energy and leads to an increase of other phonon frequencies.

3.3. Dielectric relaxation study

The logarithmic angular frequency (ω) dependences of the real (ϵ') and imaginary (ϵ'') parts of complex dielectric constant at different temperatures for SET and CET are shown in Figs. 4(a) and 4(b), respectively. At low frequency, the induced dipoles follow the field and give the highest value of polarization but at higher frequencies, the dipole cannot follow the rapid alteration of the field. So their contribution to the polarization and consequently the dielectric permittivity become negligible. The relaxation maxima are observed in the frequency dependence of ϵ'' in the dispersion region of ϵ' . The maxima positions in the frequency dependence of ϵ'' shift to the higher frequency side with increasing temperature. This is because when the temperature is high, the rate of polarization formed is quick, and thus the relaxation occurs at high frequency. The sharp increasing values of ϵ' and ϵ'' at low frequency as observed from Fig. 5 indicate that electrical conductivity dominates in the low-frequency range. Thus to explain the relaxation mechanism in SET and CET, we have fitted our experimental data using Cole–Cole equation^{14,15} incorporating the conductivity term which is defined as

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}} - j \frac{\sigma^*}{\epsilon_0 \omega^s}, \quad (1)$$

where $\sigma^* (= \sigma_1 + j\sigma_2)$ is the complex conductivity. From the above relation, complex permittivity can be separated into real and imaginary parts as follows:

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)[1 + (\omega\tau)^{1-\alpha} \sin(\alpha\pi/2)]}{1 + 2(\omega\tau)^{1-\alpha} \sin(\alpha\pi/2) + (\omega\tau)^{2-2\alpha}} + \frac{\sigma_2}{\epsilon_0 \omega^s}, \quad (2)$$

$$\epsilon'' = \frac{(\epsilon_s - \epsilon_\infty)(\omega\tau)^{1-\alpha} \cos(\alpha\pi/2)}{1 + 2(\omega\tau)^{1-\alpha} \sin(\alpha\pi/2) + (\omega\tau)^{2-2\alpha}} + \frac{\sigma_1}{\epsilon_0 \omega^s}, \quad (3)$$

where σ_1 and σ_2 are the contributions of conductivities of the free charge carriers and the space charges or localized charges, respectively, and *s* is the dimensionless frequency exponent which varies from 0 to 1. The first term of Eq. (3) is the part of the losses associated with the dielectric relaxation

Fig. 3. (a) Comparative Raman spectra of SET and CET. Lorentzian fittings of SET Raman spectra: (b) first part and (c) second part. Lorentzian fittings of CET Raman spectra: (d) first part and (e) second part.

Table 2. (a) Observed Raman active phonon modes for SET. (b) Observed Raman active phonon modes for CET.

Wavenumber (cm ⁻¹)	FWHM (cm ⁻¹)	Wavenumber (cm ⁻¹)	FWHM (cm ⁻¹)
(a)			
91	20	457	21
114	32	498	25
133	12	541	39
151	22	581	22
176	30	622	52
218	58	633	28
271	87	672	59
344	113	724	33
348	12	780	18
425	57	819	22
430	14	831	32
(b)			
80	23	403	47
93	23	449	19
117	12	480	23
164	29	529	71
150	14	580	53
251	12	643	34
222	13	703	106
258	11	775	35
264	10	797	21
322	18	815	30
383	20	842	44

due to permanent dipole orientation whereas the second term is the part of the losses associated with long-range migration of carrier response. The best fitting of the experimental data is shown by the solid lines in Fig. 4. When the dipolar relaxation by defects¹⁶ occurs in the lattice, the relaxation strength ($\Delta\epsilon = \epsilon_s - \epsilon_\infty$) is expressed by the following equation:

$$\Delta\epsilon = N_d \mu^2 / 3K_B T, \quad (4)$$

where N_d is the number of defect dipoles, μ is the dipole moment, K_B is the Boltzmann constant and T denotes the absolute temperature. When the temperature is constant, the total number of dipoles is constant. But when the temperature varies, $\Delta\epsilon$ changes consequently σ changes. That is, the system also starts to contribute to the electrical conduction along with polarization. Table 3 shows that dielectric strength decreases with increasing temperature implying that carrier polarization mechanism is weakly dispersive at higher temperature.¹⁷

3.4. Conductivity analysis

In order to study the dynamics of the charge carriers and the possible conduction mechanism, the frequency dependence of AC conductivities is studied in the temperature range from 303 K to 423 K. Figures 5(a) and 5(b) show the log-log plots of the frequency dependences of the conductivities for SET

Fig. 4. Angular frequency dependences of dielectric constant (ϵ' and ϵ'') at different temperatures for (a) SET and (b) CET.

and CET, respectively. The two plateau regions are observed in conductivity spectra, one at low-frequency side and the other one at high-frequency side, which suggest that the two relaxation processes are contributing to the bulk conduction behavior of these materials. Extrapolation of the low-frequency plateau of conductivity curves to $\omega \rightarrow 0$ gives the DC conductivity. Usually, for single relaxation process, the total conductivity at a given temperature can be expressed by the power-law¹⁸

$$\sigma(\omega) = \sigma(0) + A\omega^s, \quad (5)$$

where $\sigma(0)$ is the DC conductivity, A depends on the temperature and the exponent n is temperature- and material-dependent. The term $A\omega^s$ denotes the frequency dependence

Fig. 5. (Color online) Angular frequency dependences of AC conductivity at different temperatures for (a) SET and (b) CET. Red lines show the fittings of the experimental data to Jonscher's power-law.

Table 3. Fitting parameters obtained using the modified Cole-Cole model for SET and CET.

	Temp. (K)	$\Delta\epsilon = (\epsilon_s - \epsilon_\infty)$	α	s	$\omega_m (\times 10^5 \text{ rad} \cdot \text{s}^{-1})$	$\sigma_1 (\times 10^{-8} \text{ S} \cdot \text{m}^{-1})$	$\sigma_2 (\times 10^{-8} \text{ S} \cdot \text{m}^{-1})$
SET	303	190	0.30	0.85	02.8	15	20
	373	185	0.29	0.86	12.0	20	25
	423	180	0.28	0.87	30.0	22	30
CET	303	210	0.20	0.90	0.1	10	12
	373	200	0.19	0.91	1.3	12	13
	423	190	0.18	0.92	9.0	15	15

and characterizes all dispersion phenomena. The exponent s has been found to behave in a variety of forms as a constant or decreasing and/or increasing with the temperature but always varying within $0 < s < 1$. For SET and CET, the frequency dependence of conductivity does not follow the single power-law as given above, but is well described by the double power-law defined as¹⁹

$$\sigma(\omega) = \sigma(0) + A_1\omega^{s_1} + A_2\omega^{s_2}. \quad (6)$$

The exponents s_1 and s_2 correspond to the low- and high-frequency regions which vary from 1 to 2 and from 0 to 1, respectively. The lower and higher frequency regions represent the nondiffusing and localized diffusing modes, respectively, and, based on this theory, Ishii *et al.*²⁰ have predicted that the exponent s is greater than 1 and tends to attain 2 with increasing temperature in the lower frequency region, whereas it is less than 1 in the higher frequency region. The best fits of the experimental spectra using Eq. (5) are shown in Figs. 5(a) and 5(b) by solid lines.

From the conductivity analysis we notice that the room-temperature conductivity of CET is less than that of SET. In an

ideal double perovskite, the oxygen atoms are situated on the connection line of the B' - and B'' -cations. This occurs for highly symmetrical cubic structure. With the decrease of the crystal symmetry, $B'-O-B''$ bond angles deviate more from 180° . This is octahedral distortion. This deviation is more prominent when A-cation is small. Average tilt angle of the octahedral is given by $\theta = (180^\circ - \Phi)/2$, where Φ is the average $B'-O-B''$ bond angle. When we move from Sr to Ca, distortion within the crystal increases as a result of the decreasing size of A-site cation. It is observed from XRD data that Ta-O bond is shorter in SET which indicates stronger O-2p-Ta-5d hybridization in SET with respect to CET. On the other hand, the Er-O bond is shorter in CET than SET. But the 4f states are less extended than 5d states, hence the hybridization between O-2p and Er-4f states is less effective for charge transport in these materials. Also, when we replace Sr by Ca the average bond angles (Er-O-Ta) become less (i.e., more deviation from ideal 180°). Hence, the hybridization between O-2p states and Ta-5d states arising from the electron-transfer interaction is weakened in CET than SET which may responsible for the decrease in conductivity in CET than SET.

4. Conclusions

$A_2\text{ErTaO}_6$ ($A = \text{Sr}^{+2}, \text{Ca}^{+2}$) ceramics are synthesized by solid-state reaction method and studied by XRD, Raman scattering and infrared spectroscopy techniques along with dielectric relaxation and electrical characterization. With the decreases in the ionic radii of A-site cation, there is shrinkage in the volume of the cubo-octahedral space leading to distortion in the crystal structure. In the Raman spectra, we see that when Ca replaces Sr in the monoclinic structure, the frequency of the $\nu_1(A_{1g})$ mode decreases, while the frequencies of both the ν_5 and T modes increase. Modified Cole–Cole equation is used to analyze the frequency dependences of the real and imaginary parts of dielectric constant. Frequency-dependent conductivity spectra are found to follow the power-law. The room-temperature conductivity of CET is less than that of SET.

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