Chapter 3
Structural and Dielectric Study of A(Fe$_{1/2}$Sb$_{1/2}$)O$_3$

[A = Ba, Sr, Ca]

Structural Study

(a) X-ray Diffraction Study (XRD)

The x-ray diffraction patterns of the powdered samples of Ba(Fe$_{1/2}$Sb$_{1/2}$)O$_3$ (BFS), Sr(Fe$_{1/2}$Sb$_{1/2}$)O$_3$ (SFS) and Ca(Fe$_{1/2}$Sb$_{1/2}$)O$_3$ (CFS) at room temperature are shown in Figures 3.1.1, 3.1.2 and 3.1.3 respectively. The diffraction peaks detected within the measured 2θ range of 10 - 80° are indexed and lattice parameters are determined using a least-squares method with the help of a standard computer programme (POWD-MULT).

Tables 3.1.1, 3.1.2 and 3.1.3 show the comparison between the observed and calculated interplaner spacings along with the $hkl$ values for these materials. A good agreement between the observed and calculated interplaner spacings (d-values) suggests that the BFS is having monoclinic structure at room temperature with lattice parameter $a = 4.0956$ Å, $b = 2.8960$ Å, $c = 4.4270$ Å and $\beta = 91.79°$ [125], SFS is having a cubic structure with $a = 7.9041$ Å [126] and CFS is having monoclinic structure with $a = 5.9565$ Å, $b = 6.9847$ Å, $c = 5.8047$ Å and $\beta = 97.53°$ [127]. X-ray diffraction confirms the formation of single phase of these materials.
Figure 3.1.1: XRD pattern of BFS at room temperature.

Table 3.1.1: Comparison of $d_{\text{observed}}$ and $d_{\text{calculated}}$ for BFS.

<table>
<thead>
<tr>
<th>20 (in degrees)</th>
<th>h k l</th>
<th>$d_{\text{observed}}$ (Å)</th>
<th>$d_{\text{calculated}}$ (Å)</th>
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Figure 3.1.2: XRD pattern of SFS at room temperature.

Table 3.1.2: Comparison of $d_{\text{observed}}$ and $d_{\text{calculated}}$ for SFS.

<table>
<thead>
<tr>
<th>20 (in degrees)</th>
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<th>$d_{\text{observed}}$ (Å)</th>
<th>$d_{\text{calculated}}$ (Å)</th>
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<td>76.120</td>
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Figure 3.1.3: XRD pattern of CFS at room temperature.

Table 3.1.3: Comparison of $d_{\text{observed}}$ and $d_{\text{calculated}}$ for CFS.

<table>
<thead>
<tr>
<th>$2\theta$ (in degrees)</th>
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<th>$d_{\text{calculated}}$ (Å)</th>
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<tr>
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<td>1.9374</td>
<td>1.9376</td>
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Using the XRD-results, the crystallite sizes of BFS, SFS and CFS are calculated by the Debye – Scherrer formula [124a]:

\[ L = \frac{0.9 \lambda}{B \cos \theta}. \]  

(3.1.1)

where \( L \) is the average size of the particle, \( \lambda \) is the wavelength of X-ray radiation, \( B \) is the full width at half maximum (FWHM) and \( \theta \) is the diffraction angle. According to the data in figures 3.1.1, 3.1.2, 3.1.3 (the highest intensity peaks of the histograms) and formula (3.1.1), the average particle size of the BFS, SFS and CFS are found to be 2.58 \( \mu \text{m} \), 3.2 \( \mu \text{m} \) and 1.77 \( \mu \text{m} \) respectively.

(b) Scanning Electron Micrograph (SEM)

The SEM micrographs of the sintered pellets of BFS, SFS and CFS are shown in Figure 3.1.4. The compactness of the samples with the regular arrangement of the grains is observed in these micrographs. The average size of the grain is found to be 7 \( \mu \text{m} \) for BFS, 1.5 \( \mu \text{m} \) for SFS and 1 \( \mu \text{m} \) for CFS respectively. Comparing these results with the crystallite sizes obtained from XRD-data, one can conclude that the degree of agglomeration for BFS is higher than those of SFS and CFS.
Dielectric Study

The logarithmic angular frequency $\omega (= 2\pi v)$ dependent plots of the dielectric constant $\varepsilon'$ and dielectric loss $\tan\delta (= \varepsilon''/\varepsilon')$ of BFS, SFS and CFS at various temperatures are shown in Figure 3.2.1, 3.2.2 and 3.2.3 respectively. The high value of $\varepsilon'$ which increases with decreasing frequency and increasing temperature corresponds to bulk effect of the systems. The peak in the $\tan\delta$ vs $\ln\omega$ curve indicates the dielectric relaxation. The relaxation phenomena in BFS, SFS and CFS are associated with a frequency dependent orientational polarization. At low frequency, the permanent dipoles align themselves along the field direction and contribute fully to the total polarization of the dielectric. At higher frequency, the variation in the field is too rapid for the dipoles to align themselves, so their contribution to the polarization and hence, to dielectric permittivity can become negligible. Therefore, the dielectric constant, $\varepsilon'$ ($\omega$) decreases with increasing frequency (Figure 3.2.1(a)). The increase in peak value of $\tan\delta$ with the increase of temperature and frequency as shown in Figure 3.2.1(b) indicates that the number of charge carriers increases by thermal activation. The fast rising trend of $\tan\delta$ at low frequencies is a representative of the presence of d.c. conductivity in these materials. The observed peaks in $\tan\delta$ can be explained according to the fact that a strong correlation between the conduction mechanism and the dielectric behaviour exists in BFS [125], SFS [126] and CFS [127]. Accordingly, a peak is expected when the hopping
frequency of the charge carriers is approximately equal to that of the external applied field and in this case, $\omega \tau = 1$, where $\tau$ is the relaxation time of the hopping process.

**Figure 3.2.1:** Frequency dependence of $\varepsilon'$ (a) and $\tan \delta$ (b) at various temperatures for BFS.

**Figure 3.2.2:** Frequency dependence of $\varepsilon'$ (a) and $\tan \delta$ (b) at various temperatures for SFS.
Figure 3.2.3: Frequency dependence of $\varepsilon'$ (a) and $\tan \delta$ (b) at various temperatures for CFS.

In Fig. 3.2.1, $\tan \delta$ decreases as $\omega$ increases, reaches a minimum and then increases. The same behaviour of $\tan \delta$ is also observed in other two oxides in Figs. 3.2.2 and 3.2.3, but the rising trend at low frequencies are not so clear in these cases as in Fig. 3.2.1. The intensive monotonous increase in $\tan \delta$ at low frequency in BFS is probably due to the contribution of the dc conductivity. At low frequency, the ac conductivity is similar to the dc conductivity, so $\sigma_{dc}$ has an observable influence to the loss component of the dielectric response. With increasing frequency, the influence of the dc conductivity would be ignorable. It is to be noted that the Gibb's free energy for BaO, SrO and CaO are 477.7 KJ/mole, 511.1 KJ/mole, 551.6 KJ/mole respectively [127a]. Therefore, the Ba-O bond is much weaker than that of Sr-O and Ca-O bond and hence one may expect a higher dc conductivity in the Ba-compounds.
For a thermally activated relaxation process, the relaxation time \( t \) has the form 
\[ \tau_0 \exp\left(\frac{Q}{k_B T}\right) \]
where \( Q \) and \( k_B \) are the activation energy for the relaxation process and the Boltzmann's constant, respectively. Then, the resonant condition is
\[ \omega_m \tau_0 \exp\left(\frac{Q}{k_B T}\right) = 1, \tag{3.2.1} \]
where \( \omega_m \) is the frequency at which tan\( \delta \) peaks. Figure 3.2.4 plots the temperature dependence of the most probable relaxation frequency (\( \omega_m \)), i.e., the Arrhenius relation for the loss curve for these materials. A straight line is obtained with \( Q = 0.81 \) eV for BFS, 0.74 eV for SFS and 0.60 eV for CFS.

**Figure 3.2.4:** Temperature dependence of the most probable relaxation frequency obtained from the frequency dependent peak of loss tangent for BFS (a), SFS (b) and CFS (c). The symbols are the experimental points and the solid line is the least squares straight-line fit.

**Figure 3.2.5:** Cole-Cole plot between \( \varepsilon'' \) and \( \varepsilon' \) for BFS at 363 K. Solid line is the fitting of Cole-Cole equation.

**Figure 3.2.6:** Cole-Cole plots between \( \varepsilon'' \) and \( \varepsilon' \) for SFS at 323 K and 403 K.

**Figure 3.2.7:** Cole-Cole plots between \( \varepsilon'' \) and \( \varepsilon' \) for CFS at 243 K and 323 K.
It seems clear that the widths of loss peaks in Figures 3.2.1, 3.2.2 and 3.2.3 cannot be accounted for in terms of a monodispersive relaxation process, but point towards the possibility of distribution of relaxation times. One of the most convenient ways of checking the polydispersive nature of dielectric relaxation in BFS, SFS and CFS is through complex Argand plane plots between $\varepsilon''$ and $\varepsilon'$, usually called Cole-Cole plots [58]. For a pure monodispersive Debye process, one expects semicircular plots with a centre located on the $\varepsilon'$ axis whereas, for polydisperse relaxation, these Argand plane plots are close to circular arcs with end points on the axis of reals and a centre below this axis. The complex dielectric constant in such situations is known to be described by the empirical relation [58]:

$$
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau_0)^\alpha}
$$

(3.2.2)

where $\varepsilon_s$ and $\varepsilon_\infty$ are the low- and high-frequency values of $\varepsilon'$ respectively, and $\alpha$ is a measure of the distribution of relaxation times.

Figure 3.2.8: Comparison of measured $\varepsilon''$ for SFS (a) CFS (b) with that calculated using the Cole-Cole equation. The symbols represent the experimental points and solid lines represent the calculated points.

Figures 3.2.5, 3.2.6 and 3.2.7 show the Cole-Cole plots between $\varepsilon'$ and $\varepsilon''$ for BFS, SFS and CFS respectively. It is evident from these plots that the relaxation process differs from the monodispersive Debye process (for which $\alpha = 0$). The Cole-Cole plots confirm the polydisperse nature of dielectric relaxation of BFS, SFS and CFS. The
parameter $\alpha$ as determined from the fitting of the equation (3.2.2) (solid line) with the experimental points (symbols) in Figure 3.2.5 for BFS is found to be 0.6 at 363 K.

The experimental data of SFS and CFS are also fitted with the Cole-Cole expression 3.2.2. The solid lines in Figures 3.2.8(a) and 3.2.8(b) are the fitting of Cole-Cole function corresponding to $\varepsilon''$ for SFS and CFS respectively. The values of $\alpha$ as obtained from the fitting are found to be in between 0.29 and 0.26 for the temperature range from 263 to 383 K for SFS and in between 0.102 and 0.12 for the temperature range from 263 to 303 K for CFS. A good agreement between the directly measured values of $\varepsilon''$ and those calculated using Cole-Cole model suggests that the relaxation mechanism in BFS, SFS and CFS is polydispersive in nature for which $0<\alpha<1$.

If we plot the $\tan\delta$ ($\omega$, $T$) data in scaled coordinates, i.e., $\tan\delta$ ($\omega$, $T$)/$\tan\delta_m$ and $\log(\omega/\omega_m)$, where $\tan\delta_m$ corresponds to the peak value of loss tangent, the entire dielectric loss data can be collapsed into one master curve as shown in Figure 3.2.9. The scaling behaviour of $\tan\delta$ ($\omega$, $T$) clearly indicates that the relaxation describes the same mechanism at different temperatures for BFS, SFS and CFS.

![Figure 3.2.9](image)

**Figure 3.2.9**: Scaling behaviour of $\tan\delta$ at various temperatures for BFS (a), SFS (b) and CFS (c).
3.3. Impedance Study

If an alternating potential is applied across the sample, a phase shift $\theta$ between the current and the voltage is induced due to the time dependence of the polarisation processes. If the current $I$ and the voltage $V$ are considered to have a time variation of $e^{j\omega t}$, the quantity $V/I$ is a complex number with no time dependence and is called the complex impedance $Z^*$, the real part of which ($Z'$) may be interpreted as resistance and the imaginary part ($Z''$) may be interpreted as capacitance ($C$). Here $1/Z^* = G + j\omega C$, where $G$ is the conductance and $\omega$ is the frequency of the a.c. field.

In conductivity relaxation, the dielectric response can be described as a relationship between the electric modulus and the impedance. The angular frequency dependence plots of real ($Z'$) and imaginary ($Z''$) parts of complex impedance at various temperatures for BFS, SFS and CFS are shown in Figures 3.3.1, 3.3.2 and 3.3.3 respectively. It is observed that $Z'$ decreases with increasing frequency as well as with increasing temperature which indicates the semiconducting behaviour of the materials. The frequency dispersion behaviour of $Z''$ shows the similar nature as $Z'$.

It is to be mentioned that the low frequency dispersion of impedance in BFS, SFS and CFS indicates the absence of any inhomogeneties arising owing to Maxwell-Wagner polarization [130]. Also, the set of peaks of dielectric loss spectra cannot be attributed to the space-charge polarization at the grain boundaries and interfacial polarization at the electrodes because this relaxation is characteristic of ionic motion and they may not be affected by the type of electrodes. To elucidate this point, we have shown the complex impedance plots [$Z''$ against $Z'$ data, so called $Z$-plots] in Figures 3.3.1(c), 3.3.2(c) and 3.3.3(c) for BFS, SFS and CFS respectively, where we expect a separation of the bulk phenomenon from the surface phenomenon. For a polycrystalline dielectric material having interfacial boundary layers (grain-boundary), two semicircular arcs or depressed circular arcs may be obtained in the complex plane plot. At each temperature, the absence of any second arc confirms that the polarization mechanism in these materials
corresponds to bulk effect arising in semiconductive grains. No residual semicircle at low frequencies attributed to contact or electrode effects has been noticed, probably due to the fact that sample was well polished and electroded by sputtering.

**Figure 3.3.1:** Frequency dependence of $Z'$ (a) and $Z''$ (b) at various temperatures for BFS. The Cole-Cole plots between $Z'$ and $Z''$ are shown in (c) at 223 K and 263 K.

**Figure 3.3.2:** Frequency dependence of $Z'$ (a) and $Z''$ (b) at various temperatures for SFS. The Cole-Cole plots between $Z'$ and $Z''$ are shown in (c) at 343 K and 423 K.
3.4 Admittance Study

The frequency dispersion behaviours of real ($Y'$) and imaginary ($Y''$) parts of admittance $Y^*$ of BFS, SFS and CFS are shown in Figures 3.4.1, 3.4.2 and 3.4.3 respectively as a function of temperature. It is observed that $Y'$ exhibits an asymmetric maximum ($Y'_m$). It may be noted that the position of peak $Y'_m$ shifts to higher frequencies with the increase of temperature as well as the value of $Y'$ increases with increasing temperature. It is depicted from Figures 3.4.1(b), 3.4.2(b) and 3.4.3(b) that $Y''$ decreases with decreasing frequency and becomes constant at lower frequency region. The Cole-Cole plots between $Y''$ and $Y'$ are shown in Figures 3.4.1(c), 3.4.2(c) and 3.4.3(c) for BFS, SFS and CFS respectively.
Figure 3.4.1: Frequency dependence of $Y'$ (a) and $Y''$ (b) at various temperatures for BFS. Cole-Cole plot between $Y''$ and $Y'$ at 423 K is shown in (c).

Figure 3.4.2: Frequency dependence of $Y'$ (a) and $Y''$ (b) at various temperatures for SFS. Cole-Cole plots between $Y''$ and $Y'$ are shown in (c) at 383 K and 423 K.
Alternating current impedance spectroscopy is a useful method for characterizing materials, which have been adopted for BFS, SFS and CFS. Alternating current impedance spectroscopy allows measurement of the capacitance and loss tangent (tanδ) or, real and imaginary impedance over a frequency range. From the measured capacitance and tanδ, four complex dielectric functions can be computed. They are impedance (Z*), permittivity (ε*), electric modulus (M*), and admittance (Y*). Since these functions are interrelated (see equations 1.7 to 1.10), only one set of measurements is needed to calculate all of them. Admittance and impedance are two sides of the same coin. It only makes a difference for visualization of the results, not for physical understanding. Hence a detail explanation of the same data will just be a repetition of the earlier explanation.

3.5 Electric Modulus Study

From the physical point of view, the electric modulus corresponds to the relaxation of the electric field in the materials when the electric displacement remains
constant. Therefore, the modulus represents the real dielectric relaxation process [131]. In
the modulus formalism, an electric modulus \( M'(\omega) \) is defined in terms of the complex
dielectric permittivity \( \varepsilon^*(\omega) \) by

\[
M'(\omega) = \frac{\varepsilon'(\omega)}{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2} \quad \text{and} \\
M''(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2}.
\]

Based on Equation (3.5.1) we have changed the form of presentation of the
dielectric data from \( \varepsilon'(\omega) \) and \( \varepsilon''(\omega) \) to \( M'(\omega) \) and \( M''(\omega) \). The angular frequency
dependence plots of real part and imaginary parts of electric modulus for BFS, SFS and
CFS at various temperatures are shown in Figures 3.5.1, 3.5.2 and 3.5.3 respectively.
\( M'(\omega) \) shows a dispersion tending towards \( M'_\infty \) (the asymptotic value of \( M'(\omega) \) at higher
frequencies), while \( M''(\omega) \) exhibits a maximum (\( M''_m \)) centered at the dispersion region
of \( M'(\omega) \). It may be noted that the position of the peak (\( M''_m \)) shifts to higher frequencies
as the temperature is increased. The frequency region below peak maximum \( M''_m \)
determines the range in which charge carriers are mobile on long distances. At frequency
above peak maximum \( M''_m \), the carriers are confined to potential wells, being mobile on
short distances.
The frequency $\omega_m$ (corresponding to $M''_m$) gives the most probable relaxation time $\tau_m$ from the condition $\omega_m \tau_m = 1$. Figure 3.5.4 shows that the most probable relaxation time obeys the Arrhenius relation defined as:

$$\omega_m = \omega_0 \exp \left[ \frac{-E_a}{k_B T} \right] ,$$

(3.5.2)

where $\omega_0$ is the pre-exponential factor and $E_a$ is the activation energy. The activation energy $E_a = 0.75$ eV for BFS, 0.73 eV for SFS and 0.61 eV for CFS are obtained from the least squares fitting of the experimental data points. The activation energy is found to be close to the activation energy of loss tangent of the corresponding materials.
Figure 3.5.2: Frequency dependence of $M'$ (a) and $M''$ (b) at various temperatures for SFS.
Figure 3.5.3: Frequency dependence of $M'$ (a) and $M''$ (b) at various temperatures for CFS.

Figure 3.5.4: Temperature dependence of the most probable relaxation frequency obtained from the frequency dependent peak of $M''$ for BFS (a), SFS (b) and CFS (c). The crosses are the experimental points and the solid line is the least squares straight-line fit.

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Figure 3.5.5: Scaling behaviour of $M''$ at various temperatures for BFS (a), SFS (b) and CFS (c).

Figure 3.5.6: Cole-Cole plots between $M''$ and $M'$ for BFS (a), SFS (b) and CFS (c).

We have scaled each $M''$ by $M''_m$ and each frequency by $\omega_m$ for different temperatures in Figure 3.5.5. The overlap of the curves for all the temperatures indicates that the relaxation describes the same mechanism at various temperatures. Figure 3.5.6 shows the Cole-Cole plots between $M''$ and $M'$ at two different temperatures for these materials.
3.6 A.c. Conductivity Study

We have also adopted the conductivity formalisms to study the relaxation mechanism in BFS, SFS and CFS. If one assumes that the total loss in the dielectric is due to the conduction of charge carriers, the real part of a.c. conductivity ($\sigma$) can be obtained from the relation $\sigma = \omega \varepsilon_0 \tan \delta$. The frequency spectra of the conductivity for BFS, SFS and CFS are shown in Figures 3.6.1, 3.6.2 and 3.6.3 respectively at different measuring temperatures. The conductivity shows a dispersion which shifts to higher frequency side with the increase of temperature. It is observed that the values of $\sigma$ increases with increasing frequency indicating the semiconducting behaviour of the materials. It is seen that $\sigma$ decreases with decreasing frequency and tends to become independent of frequency after a certain value. Extrapolation of this part towards lower frequency will give $\sigma_{dc}$ [132]. The conductivity spectra follow the Jonscher’s power law defined as [70]:

$$\sigma(\omega) = \sigma_{dc} \left[ 1 + \left( \frac{\omega}{\omega_H} \right)^\alpha \right]^\beta,$$

(3.6.1)

where $\sigma_{dc}$ is the dc value of conductivity and $\omega_H$ is the hopping frequency of charge carriers.

![Figure 3.6.1: log-log plot of frequency (angular) dependence of the conductivity ($\sigma$) of BFS at various temperatures. Solid lines are the best fitting of the Jonscher's power law.](image)
Figure 3.6.2: Log-log plot of frequency (angular) dependence of the conductivity ($\sigma$) of SFS at various temperatures. Solid line is the best fitting of the Jonscher's power law.

Figure 3.6.3: Log-log plot of frequency (angular) dependence of the conductivity ($\sigma$) of CFS at various temperatures. Solid line is the best fitting of the Jonscher's power law.
The experimental conductivity data are fitted to Equation (3.6.1) keeping in mind that the values of the exponent, $n$ are weakly temperature dependent. The best fit of conductivity spectra is exhibited by solid lines in the Figures 3.6.1, 3.6.2 and 3.6.3 for BFS, SFS and CFS respectively.

The very basic fact about AC conductivity in BFS or SFS or CFS is that $\sigma$ is an increasing function of frequency (any hopping model has this feature). In a hopping model, it is possible to distinguish different characteristic regions of frequency [133]. At low frequencies where the conductivity is constant, the transport takes place on infinite paths. For a region of frequencies where the conductivity increases strongly with frequency, the carriers can hop only between two sites and a total response is produced by the sum of the individual response of pairs of sites randomly distributed throughout the material.

It is to be noted that the frequency dependence of ac conductivity in BFS, SFS and CFS may arise due to bound charge carriers trapped in the samples. Hopping of charge carriers among the trap levels situated in the band gap of the materials may give to a frequency dependent ac conductivity with frequency dependence $\sim \omega^n$, where $n$ is $<1$. More precisely the relation is expressed by the Jonscher’s power law. The power law dependence of conductivity on frequency is of a universal nature and corresponds to the short range hopping of charged carriers through trap sites separated by energy barriers of varied heights. If a single charge species is presumed to move along an infinite lattice of identical potential wells, the conductivity is expected to be independent of frequency (in the absence of long range interaction). In the case of single particle hopping backward and forward in a double well with infinite barriers on other side, conductivity will increase and saturate at high frequency which is observed in the frequency dependence of ac conductivity in these materials.
3.7 Comparison

Finally, it can be concluded that the crystalline structures of BFS and CFS are found to be monoclinic whereas for SFS it is cubic. Due to the change of the ionic-radii of the A-site cations and hence the tolerance factor, the crystalline structures as well as the electrical properties of these double perovskites are found to be different.

Since the dielectric constant of a material is different at different temperatures and frequencies, to present a comparison of the entire dielectric data in language appears cumbersome, however, if interested, one can easily make a comparison using the various figures. From the application point of view, one requires the dielectric material with high dielectric constant and low loss, which varies with the change of the values of frequency and temperature. At room temperature (303 K) the values of dielectric constant ($\varepsilon'$) and loss tangent ($\tan\delta$) at 100 Hz are found to be 666 and 0.47 for BFS, 531 and 0.19 for SFS and 323.25 and 0.09 for CFS respectively.