2.1 Synthesis of the Materials

We have synthesized two types of heterovalent complex perovskite oxides using solid state reaction technique.

(i) \(A(B_{1/2}B''_{1/2})O_3\) having 1:1 ratio.
Here \(A=\text{Ba, Sr, Ca}; \ B' = \text{Fe, Al}; \ B'' = \text{Nb, Sb}\) giving

- \(\text{Ba(Fe}_{1/2}\text{Sb}_{1/2})O_3\) (BFS);
- \(\text{Sr(Fe}_{1/2}\text{Sb}_{1/2})O_3\) (SFS);
- \(\text{Ca(Fe}_{1/2}\text{Sb}_{1/2})O_3\) (CFS);
- \(\text{Ba(Al}_{1/2}\text{Nb}_{1/2})O_3\) (BAN);
- \(\text{Sr(Al}_{1/2}\text{Nb}_{1/2})O_3\) (SAN);
- \(\text{Ca(Al}_{1/2}\text{Nb}_{1/2})O_3\) (CAN)

and

(ii) \(A(B'_{1/3}B''_{2/3})O_3\) having 1:2 ratio.
Here \(A=\text{Ba, Sr, Ca}; \ B' = \text{Mg}; \ B'' = \text{Nb}\) giving

- \(\text{Ba(Mg}_{1/3}\text{Nb}_{2/3})O_3\) (BMN);
- \(\text{Sr(Mg}_{1/3}\text{Nb}_{2/3})O_3\) (SMN);
- \(\text{Ca(Mg}_{1/3}\text{Nb}_{2/3})O_3\) (CMN).

For \(A(\text{Fe}_{1/2}\text{Sb}_{1/2})O_3\) (where \(A = \text{Ba, Sr, Ca}\)), powders of \(\text{ACO}_3\) (reagent grade), \(\text{Fe}_2\text{O}_3\) of purity 99.99 % and \(\text{Sb}_2\text{O}_5\) (reagent grade); for \(A(\text{Al}_{1/2}\text{Nb}_{1/2})O_3\), reagent grade powders of \(\text{ACO}_3\), \(\text{Al}_2\text{O}_3\) and \(\text{Nb}_2\text{O}_5\); and for \(A(\text{Mg}_{1/3}\text{Nb}_{2/3})O_3\), powder of \(\text{ACO}_3\) (reagent grade), \(\text{MgO}\) of purity 99.99 % and \(\text{Nb}_2\text{O}_5\) (reagent grade) are used. All these powders are taken in stoichiometric ratio and mixed in presence of acetone for 10 h. The mixture are calcined in between 1200 to 1300 °C in air and brought to room temperature under controlled cooling with a cooling rate of 100 °C per hour. The calcination and sintering temperatures schedule for these materials are given in the following table:
<table>
<thead>
<tr>
<th>Materials</th>
<th>Calcination temperature (°C)</th>
<th>Calcination time (Hour)</th>
<th>Sintering temperature (°C)</th>
<th>Sintering time (Hour)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFS</td>
<td>1250</td>
<td>9</td>
<td>1300</td>
<td>4</td>
</tr>
<tr>
<td>SFS</td>
<td>1250</td>
<td>10</td>
<td>1300</td>
<td>6</td>
</tr>
<tr>
<td>CFS</td>
<td>1200</td>
<td>9</td>
<td>1250</td>
<td>4</td>
</tr>
<tr>
<td>BAN</td>
<td>1300</td>
<td>9</td>
<td>1350</td>
<td>4</td>
</tr>
<tr>
<td>SAN</td>
<td>1350</td>
<td>12</td>
<td>1400</td>
<td>6</td>
</tr>
<tr>
<td>CAN</td>
<td>1300</td>
<td>9</td>
<td>1350</td>
<td>6</td>
</tr>
<tr>
<td>BMN</td>
<td>1300</td>
<td>10</td>
<td>1350</td>
<td>6</td>
</tr>
<tr>
<td>SMN</td>
<td>1300</td>
<td>9</td>
<td>1350</td>
<td>4</td>
</tr>
<tr>
<td>CMN</td>
<td>1300</td>
<td>9</td>
<td>1350</td>
<td>6</td>
</tr>
</tbody>
</table>

The calcined samples are pelletized into discs using polyvinyl alcohol as binder. Finally, the discs are sintered at the temperature 50 °C above the calcination temperature for the corresponding material and cooled down to room temperature by adjusting the cooling rate. The sintering temperature was kept 50 °C higher than the calcination temperature to register the proper grain growth. We had checked the grain growth and the porosity of the pellet using scanning electron micrograph and hence optimized this temperature for these samples.

2.2 Structural Study by X-ray Diffraction (XRD)

X-ray diffraction (XRD) technique is a powerful tool for material characterization as well as for detailed structural elucidation. Since the physical properties of solids (e.g., electrical, optical, magnetic etc.) depend on atomic arrangements of materials, determination of the crystal structure is an indispensable part of the characterization of materials, mainly the identification of the chemical species. If a crystalline specimen is visualized as being made up of tiny fragments of completely random arrangement, it is called a fine crystalline powder. XRD patterns are used to establish the atomic arrangement or structure of the materials because the $d$-spacing of diffraction planes is of
the order of x-ray wavelength. For a crystal with a given $d$-spacing (interplanar spacing) and for a given wavelength $\lambda$, the various orders $n$ of reflection occur only at the precise values of angle $\theta$, which satisfies the Bragg equation given by $n\lambda = 2d \sin\theta$. The powder profile of a substance, even without further interpretation, can be used for identification of materials. The simplicity and advantages of x-ray powder diffraction method can be given as follows: (a) The powder diffraction pattern is the characteristic of a substance, (b) Each substance in a mixture produces its pattern independent to others, (c) It describes the state of chemical combination of elements in the material, (d) The method is capable to develop quantitative and qualitative analysis of a substance. The accurate determination of lattice parameters provides an important basis in understanding various properties of the materials. The calculation of lattice constants from the line positions or $d$-spacing can be done from a general formula:

$$\frac{1}{d_{\text{hkl}}^2} = V^2 \left[ h^2b^2c^2\sin^2\alpha + k^2c^2a^2\sin^2\beta + l^2a^2b^2\sin^2\gamma \right]$$ (2.1)

where $V$ = volume of the unit cell = $abc(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma + \cos\alpha\cos\beta\cos\gamma)^{1/2}$, here $a$, $b$, $c$, $\alpha$, $\beta$ and $\gamma$ are lattice parameters and $h$, $k$, $l$ are the Miller indices.

The kinematic theory of x-ray diffraction describes that for a perfect crystal, intensities are concentrated at the reciprocal lattice points. As the lattice defect causes the spread in the intensity distribution curves, the nature and extent of the intensity spread is an obvious measure of crystal imperfection present in the sample under study. Since the different types of defects may be co-existent in crystalline materials, the problems which arise are of separation of these types of defects and identification and quantitative estimation of the extent and distribution of each type of defects. The different factors affecting the diffraction intensities can be grouped into single expression for use in calculating the relative intensities of reflections. For powder method, the intensity is [116]:

$$I = J \frac{1 + \cos^22\theta}{4\sin^2\theta\cos\theta} F^2 A(\theta)$$ (2.2)

where $J$ is multiplicity factor, $F$ is structure factor, which can be written as
\[ F = \sum_{n} f_n \exp 2\pi i (hx_n + ky_n + lz_n) \]  

2.3 Microstructural Analysis by Scanning Electron Micrograph (SEM)

In modern materials science research, scanning electron microscope (SEM) is widely used powerful tool. SEM produces an image with marked three-dimensional appearance. It produces micrographs by scanning the surface of a specimen with a small
electron probe (a beam of electron) synchronous with an electron beam from a source. The contrast is due to the topographical variations and atomic number differences in the specimen. The SEM is capable of examining a relatively large field of view, thus giving sufficient information of the structure and its uniformity, topographical details of a surface with clarity and detail, the particle aspect ratio and the regularity of pattern arrays [117-119]. The basic units of SEM are: (a) electron-optical columns together with appropriate electronics, (b) the vacuum system, which includes the specimen chamber and stage, (c) signal detection and display systems. The electron column contains magnetic lenses whose function is to demagnify the electron beam. Two sets of scanning coils are incorporated in the SEM. The scanning coils are coupled with appropriate scan generator to cause the beam to be deflected over the specimen surface in a roster like pattern. The specimen chamber is designed such that specimen orientation is rapid and provides many movements. The normally attained orientations in the specimen stages are translation, 360° rotation and provision for tilting the specimen. The detection system used in SEM depends on the interaction of primary electron beam with the specimen. The different effects are secondary electron emission, reflected or back-scattered electron current, x-ray production and cathodoluminescence. All of the signals can be detected, amplified and used to control the brightness of a cathode ray tube (CRT). The deflection of the electron beam in the CRT is controlled by the same scan generator, which determines the position of the electron beam on the sample. For microscopic study, the scanning electron micrographs of the samples under investigation are taken by a FEI Quanta 200 scanning electron microscope. Grain size of the samples was estimated by measuring more than 50 grains of different regions in each sample and taking their root mean square diameter.

2.4 Dielectric Study Using Alternating Current Impedance Spectroscopy

Alternating current impedance spectroscopy (ACIS) is used to study the dielectric properties of the materials. ACIS allows to measure the capacitance (C) and loss tangent
(tanδ) in a wide frequency range at various temperatures. From the measured capacitance and loss tangent, one can calculate the four basic dielectric functions as mentioned in section 1.4.4. The real and imaginary parts of dielectric constant are obtained from the relation \( \varepsilon' = \frac{C}{C_0} \) and \( \varepsilon'' = \varepsilon' \tan\delta \) respectively. From these two parameters, other dielectric functions are calculated using the various relations as mentioned in section 1.4.4.

For the dielectric measurement, the sintered pellets are well polished and electroded. After electroding the pellet is connected to a LCR meter (Hioki, Japan) for the measurement of capacitance and loss tangent in the frequency range from 50 Hz to 1 MHz as a function of temperature. The Eurotherm 2216 temperature controller is used to control the temperature of the sample. All the dielectric data are collected while heating at a rate of 0.5 °C min\(^{-1}\).

It is to be mentioned here that various relaxation processes seem to coexist in real perovskite oxides, which contain a number of different energy barriers due to point defects appearing during the technological process. Therefore, the departure of the response from the ideal Debye model in solid-state samples, resulting from the interaction between dipoles, cannot be disregarded [120]. The situation in solid solutions or compounds is complex, leading to ambiguity of analyses based on particular models with formulae having many parameters [70].

The dielectric relaxation of insulating or semiconducting condensed matter system can be analyzed in terms of (1) dipolar relaxation mechanism and (2) conductivity relaxation mechanism. For dipolar relaxation originating from dipole motion, the dielectric response can be described as a direct relationship between the dielectric constant and admittance and can be expressed by the Debye or Cole-Cole or Davidson-Cole or Havriliak-Negami equations as mentioned earlier in section 1.4.4 of chapter 1.

For conductivity relaxation, a sublinear frequency dispersive ac conductivity has been observed at high frequencies, such that the real part of the conductivity \( \sigma(\omega) \) can be expressed by the Jonscher’s power law [74]:

\[ \sigma(\omega) = \sigma_0 + \sigma_1 \omega^{\alpha} \]
\[ \sigma(\omega) = \sigma_{dc} \left[ 1 + \left( \frac{\omega}{\omega_H} \right)^n \right] ; \quad 0 < n \leq 1 \]  

(2.4)

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

### 2.5 X-ray Photoemission Spectroscopy (XPS)

X-ray photoemission spectroscopy is one of the powerful modern physical methods for the investigation of electronic structure of materials [121-124]. It is highly surface-sensitive technique. In XPS the photon of energy \( \hbar \nu \) (\( \hbar \) - Planck constant, \( \nu \) = frequency of the radiation of monochromatic sources for photoelectron) is absorbed by an atom in a molecule or solid, leading to ionization and the emission of a core (inner shell) electron as shown in Figure 2.1. Thus, from the conservation of energy one can write:

\[ E(A) + \hbar \nu = E(A^+) + E(e^-), \]

(2.5)

where \( E(e^-) \) is the energy of the emitted core electron and \( E(A) \) and \( E(A^+) \) are the energies of atom of molecules under investigation and the ionized atom respectively. Since the electron's energy is present solely as kinetic energy (KE), the above expression can be rearranged to give the following expression for the KE of the photoelectron:

\[ KE = \hbar \nu - \left[ E(A^+) - E(A) \right]. \]

(2.6)

The final term in brackets, representing the difference in energy between the ionized and neutral atoms, is generally called the binding energy (BE) of the electron which then leads to the following equation:

\[ KE = \hbar \nu - BE. \]

(2.7)

The kinetic energy distribution of the emitted photoelectrons (i.e. the number of emitted photoelectrons as a function of their kinetic energy) can be measured using any appropriate electron energy analyser and a photoelectron spectrum can thus be recorded.
Figure 2.1: Diagram of energy absorption by the atom and emission of core electron in XPS study.

The basic instrumental setup for XPS study is shown in Figure 2.2. In this setup, an X-ray source of fixed-energy radiation is used as incident energy source, an electron energy analyzer is used to disperse the emitted electrons according to their kinetic energy, and thereby measure the flux of emitted electrons of a particular energy. A high vacuum environment is created to overcome interference effect of the emitted photoelectrons from gas phase collisions.

For each and every element, there will be a characteristic binding energy associated with each core atomic orbital, i.e., each element will give rise to a characteristic set of peaks in the photoelectron spectrum at kinetic energies determined by the photon energy and the respective binding energies. The presence of peaks at particular energies therefore indicates the presence of a specific element in the sample under study and the intensity of the peaks is related to the concentration of the element within the sampled region. Thus, XPS has wide range of applications (e.g., to get an information about valence states, environment of ions, structure of crystal, the binding state of atoms in chemical compounds). In XPS, the excitation by low energies gives direct access to the band structure of the compounds. The ability of XPS method to
distinguish between the different oxidation states allows an efficient study of these changes with most of such studies concerning the core levels. The qualitative interpretation of core level XPS study has led to a greater understanding of their electronic structure.

**Figure 2.2: Basic Instrumental setup of XPS study.**

The X-ray photoemission spectra of the materials are taken by X-ray photoemission spectroscopy (XPS) (VG ESCALAB 2201-XL Imaging System, England). XPS profiles of the samples are obtained using Al-Kα source (1486.6 eV). The C1s peak is used as the reference standard. The spectra are normalized to the maximum intensity after a constant background subtraction.

### 2.6 Theoretical Electronic Structure Calculations

The electrical properties of perovskite oxides containing transition metal are dominated by the interaction between transition metal cations and oxygen anions. Thus to have a clear information about the transport properties, the study of electronic structure of these materials in terms of spectral density function and density of states is required.

The density of states (DOS) of the materials are obtained by first principles calculation based on density functional theory (DFT) under generalized gradient
approximation (GGA) employing full-potential linearized augmented plane wave plane
wave method (FLAPW) as implemented in WIEN 2k code [55]. The basis set as well as
the potential and the charge density in FLAPW method consists of spherical harmonics
inside non-overlapping spherical muffin-tins around each atomic site and in a Fourier
series in the interstitial region. The basis functions inside each muffin-tin consist of the
energy as obtained from the solution of Schrodinger equation for each angular
momentum and the derivatives of the solutions with respect to this energy. In our
calculation no shape approximation corresponding to either potential or the charge
density in the interstitial is taken into account. The product of muffin-tin radius R and
K_{max} (maximum reciprocal space K for the plane-wave expansion in the interstitial)
governed the convergence of basis set and the basis set can be systematically converged
by increasing this product as well as the maximum angular momentum. In the calculation
of DOS, RK_{max} is taken to be 8 and 47 number of k points in the irreducible wedge of the
Brillouin zone have been used. The iteration process have been repeated until the
calculated total energy converged to less than (0.1) mRy.