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Experimental Techniques

2.1. Introduction

Nowadays, there is great interest in the synthesis of nanocrystalline materials, which show an improved electrochemical performance due to their unusual physiochemical properties compared to the bulk [1-7]. Also, nano science is considered as input for the next industrial revolution. The nanocrystalline metal oxide compounds have the small grain size, which lead to the increase of ionic conductivity and also stabilize the crystal structure at high-temperature. Synthesis and stabilization of nanocrystalline structures with required properties are the challenging task, since nano scale materials have large surface area and high reactivity, which tend to react themselves to form necking and hence, agglomerated into large secondary particles [8]. Hence, the synthesis process plays an important tool for the design of nanostructures with required properties such as crystallite size, size distribution, shape, homogeneity, etc., in order to meet the requirement for desired specific applications [9-12]. Various wet chemical techniques such as, hydrothermal, co-precipitation, polyol, microemulsion, sonochemical, microwave heating, spray pyrolysis, sol-gel, combustion, etc., have been used for synthesis of wide range of the multicomponent nanocrystalline oxide powders.
2.2. Synthesis processes for the preparation of nanocrystalline metal oxides

2.2.1. Sol-gel process

Sol–gel is the wet chemical technique to prepare glass, glass ceramic and crystalline materials relatively at low temperature. By definition, a sol is a dispersion of colloidal (nanosize solid) particles in a liquid, and a gel is a pseudo-solid, where the solvent is dispersed in a solid polymeric network. The sol-gel process involves the evolution of inorganic polymeric networks through the formation of a colloidal suspension (sol) and gelation of the sol is the formation of a network in a continuous liquid phase (gel). Through the sol-gel process, homogeneous inorganic oxide materials with desirable properties of hardness, optical transparence, chemical durability, tailored porosity, and thermal resistance, can be produced at room temperature. According to the chemical mechanism, sol-gel process can be divided into two distinct routes [13,14].

1. Colloidal route

2. Chemical polymerization route

2.2.1.1. Colloidal route

A colloid is a suspension in which the dispersed phase is in nano size. Here, the gravitational forces are negligible and interactions are due to short-range forces. The inertia of the dispersed phase is so small that it exhibits Brownian motion. A sol is a colloidal suspension of solid particles in a liquid. This route involves dispersion of colloidal particles in a liquid to form a sol. Then, this sol is destabilized to form a gel. The aqueous solution of silicic acid is used as the
source of SiO$_2$ network to synthesis SiO$_2$ glass using the colloidal process. Other components like metal salts and glass formers are also added in the form of the aqueous solutions and then, it is formed as a sol. The polymerization of monomer silicic acid leads to the formation of branched chains in three dimensions, which resulted the formation of gel and can be converted into amorphous or polycrystalline or nanocrystalline solids by one of the following ways.

Heat-treated at the temperature below the glass transition temperature (T$_g$) to obtain glass through the polymerization.

Sintering the gel well above the T$_g$ but within the melting point range and fusing the gel particulate to form glass.

Similarly, the dried gel is heat treated at higher temperature (above T$_c$) to form polycrystalline or nanocrystalline solids.

2.2.1.2. Chemical polymerization route

An appropriate chemical is added to the solution of organometallic compounds or metallic salts to obtain sol. Further, the sol transforms into gel at low temperature. Aging and drying of gels at low temperature produce glass. There are seven steps involved in this process to synthesis materials and they are mixing, casting, gelation, aging, drying, dehydration and densification. Different stages involved in the sol-gel process are represented pictorially and it is shown in fig. 2.1. and 2.2.
Fig. 2.1 Schematic diagram of various stages involved in sol-gel process

- Alkoxide Solution
- Sol
- Wet gel
- Xerogel
- Dense ceramics

Fig. 2.1 Schematic diagram of various stages involved in sol-gel process
Mixing

In colloidal route, the mixing of colloidal particles in water forms sol. The gel is obtained by adjusting a particular pH. In chemical polymerization route, mixing involves hydrolysis and condensation. The liquid alkoxide precursor \( \text{Si(OR)}_4 \), \((\text{R}= \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{etc})\) is hydrolyzed with water. Metal alkoxide are popular precursors, because they react readily with water and it is called hydrolysis with the following reactions.

\[
\text{Si (OR)}_4 + \text{H}_2\text{O} \rightarrow \text{HO – Si (OR)}_3 + \text{ROH}
\]

(or)

\[
\begin{array}{c}
\text{OR} \\
\text{HO – Si – OR} \\
\text{OR}
\end{array}
\rightarrow
\begin{array}{c}
\text{OH} \\
\text{HO – Si – OH} \\
\text{OH}
\end{array}
\]

\[
\text{RO – Si – OR} + 4\text{H}_2\text{O} \rightarrow \text{RO – Si – O – Si – OR} + 4\text{ROH}
\]

Depending upon the amount of water and catalyst, the hydrolysis may go up to completion or stop while particularly hydrolyzed. The hydrolyzed molecule can link together in a condensation reaction. During condensation reaction, alcohol or water is liberated.

\[
\begin{array}{c}
\text{OR} \\
\text{RO – Si - OR} + \text{HO – Si – OR} \\
\text{OR}
\end{array}
\rightarrow
\begin{array}{c}
\text{OR} \\
\text{RO – Si – O – Si - OR} + \text{ROH} \\
\text{OR}
\end{array}
\]
Casting
The prepared condensed sol can be cast into a mould. The mould must be selected to avoid adhesion of the sol.

Gelation
The condensation reaction builds up larger and larger by the process of polymerization to form three-dimensional network of macro particle. When sol becomes a gel it can support a stress elastically and this is defined as the gelation point or gelation time. The gelation time will depend upon the temperature, solvent, pH condition and also the removal of the solvent.

Aging
During aging, the casted object is maintained for a period of time. The polycondensation continues and the liquids are expelled from the pores. This increases the thickness of the particle necks and decreases the porosity. By aging, strength of the gel increases.

Drying
The existing liquid in the interconnected pore network is removed during drying. Thus, there is a decrease in the volume of the gel, which is equal to the volume of the liquid lost by evaporation. After drying, the pores of the gel are emptied.
**Dehydration**

During dehydration, chemically stable solid is obtained. This is due to the removal of unwanted surface elements like H and R from Si-OH and Si-OR bonds.

**Densification**

Densification is the last treatment process in the sol gel process. By heating the gel at higher temperature, the pores can be eliminated and densified glass/polycrystalline solids can be obtained equivalent to fused quartz or fused silica. The densification temperature depends on the dimensions of the pore network, the connectivity of the pores, surface area, etc.

---

**Fig 2.2.** Various steps of sol-gel process with respect to time and temperature.
2.2.1.3 Advantages of sol-gel process

- The chemicals are in solution form. The reaction is in the atomic level. Better homogeneity and better purity are possible.
- It is a low temperature preparation technique. This leads to saving of energy, minimum evaporation losses, minimum air pollution, no reaction with the container, no phase separation.
- New non-crystalline solids outside the range of normal glass formation can be prepared. Better glass products can be formed from the special properties of gels. New crystalline phases are formed from new non-crystalline solids at lower temperature.
- Special products like films and fibers can be formed. Mixing of organic and inorganic compounds is possible.

2.2.1.4. Disadvantages of sol-gel process

- High cost of raw materials
- Large shrinkage during processing
- Micro porosity, residual hydroxyl group
- Long processing time
- Difficulty in producing large pieces and health hazards of organic solutions.

In the present investigation, La$_{9.33}$Si$_6$O$_{26}$, La$_{10}$Si$_6$O$_{27}$ and the various composition of Ba doped La$_{10}$Si$_6$O$_{27}$ are taken to synthesize by tailor made sol gel process. The
synthesis procedures of the lanthanum silicates by sol gel process are given in their respective chapters.

2.2.2. Combustion Process

Combustion processes are attracting attention for synthesis of crystalline materials because of the many advantages over other wet chemical syntheses such as direct fabrication of nano structures, low cost precursors, better maintenance of stoichiometry, etc. In addition, these combustion processes can scale up to bulk synthesis, which may extend for industrial applications.

Combustion is a kind of chemical reaction, which releases heat through an exothermic reaction between a fuel and oxidants. The chemical reaction of combustion results from a rearrangement of the atoms of the constituent elements into a new combination of molecules. Such reactions occur in accordance with stiochiometric relationships with the fuel and oxidant as well as the characteristics of the elements involved. Also, the resulting volumetric changes in the starting materials based upon the number of molecules reacted and produced during the combustion. Hence, it is necessary to quantify the amount of fuel as well as oxidant in order to achieve complete combustion.

Each fuel substances have its own temperature to react with the oxidant and it is referred to its ignition temperature. Below this ignition temperature, combination will not take place. The heat of combustion of a fuel is always depends on the elements and compounds of fuel as well as oxidant. Based on the fuels and their combinations with the metal ion sources (commonly metal nitrates, acetates,
hydroxides), combustion process has been classified into two categories such as fuel-oxidant and polymeric intermediate process [15-16].

2.2.2.1. Combustion fuel-oxidant

Fuel-oxidant combustion technique involves an exothermic decomposition of fuel-oxidant precursors such as urea-nitrate, acrylamide – nitrate, glycine-nitrate, DHF-nitrate, etc, relatively at lower temperature [17-19]. During the combustion process, large volume of gases will evolve, which prevent the agglomeration and lead to the formation of fine powders with nano structures. Release of heat during the combustion reaction depends on the fuel-oxidant stoichiometry in the precursor composition. The fuel-oxidant stoichiometry is used to calculate, based on the thermodynamical concepts used in the field of propellants and explosives, for the required nature of combustion process [20].

2.2.2.2. Polymeric intermediate combustion

The polymeric precursor route is known to be simple cost effective and versatile low temperature route for the synthesis of multicomponent metal oxides relatively at lower temperatures [21]. The general idea of this process is to distribute the metal ions atomistically throughout the polymeric structure and to inhibit their segregation and precipitation from the solution [22]. Further heating of polymeric intermediates yields ultra fine nano crystalline metal oxides. Generally, hydroxyl carboxylic acids such as citric acid, tartaric acid, etc., are used as a polymerizing as well as chelating agents in this process [23]. The physiochemical properties of the synthesized powders are critically depend on the properties of polymeric intermediates, which influence on the combustion parameters such as ignition
temperature, heat evolution, combustion duration etc. Hence, two mixed carboxylic acids (citric acid and acrylamide) have been used in order to control the structural properties of final products.

2.2.2.3. Advantages of combustion process

Gel combustion show the advantages over the other processes mainly due to the following component facts,

1. Low cost and low temperature process (compared to alkoxide based sol gel process).
2. Better control of stoichiometry.
3. Crystalline size of final oxide products, produced by these methods is invariably in the nanometer range.
4. Exothermic reaction makes product almost instantaneously.
5. Possibility of multicomponent oxides with single phase and high surface area.

2.2.2.4. Disadvantages of Combustion process

1. Contamination due to carbonaceous residue, particle agglomeration, poor control on particle morphology.
2. Understanding of the combustion behavior is needed to perform the controlled combustion in order to get final products with desire properties.
3. Possibility of violent combustion reaction, which needs special production.

In the present investigation, BaMoO₄, SrMoO₄ and the various composition of La doped BaMoO₄, La doped SrMoO₄ are taken to synthesis by gel combustion
process. The synthesis procedures of the La doped molybdates by gel combustion process are given in their respective chapters.

2.3. Characterization Techniques

In the combustion process, the mechanism of combustion reaction plays a major role in the physiochemical properties of final products, which are mainly depend on the microstructure, structural coordination, porosity etc., of the polymeric intermediates. The heat generation during combustion reaction lead to the formation of nanocrystalline powders relatively at lower temperatures. To identify the correlation between dried gels or the nature of polymeric intermediates and the final product, it is necessary to monitor the various steps involved in the synthesis process. Hence, in the present investigations, the characterization techniques like FTIR, XRD, TG/DTA and SEM are used to identify the structural coordination, phase, thermal behavior and microstructures of the synthesized nanocrystalline compounds, which are briefly described in this chapter.

2.3.1. Thermal analysis (TG/DTA)

In thermal analysis, during the heating process, the substance may undergo phase transition or chemical decompositions. Phase transitions involve heat effects such as exothermic or endothermic. If gaseous products are formed during a chemical decomposition, the process would be accompanied by mass loss in addition to the
effects. In this work, simultaneously TG/DTA experiments were carried out to investigate the thermal behavior of polymeric intermediates [24-25].

(a) **Thermo gravimetric Analysis (TGA)**

In thermogravimetry process, mass of the sample is precisely measured while it is subjected to a predetermined heating. Sample may also be maintained isothermally at a fixed temperature. Thermo-balance having sensitivity of µg is available in the present thermogravimetric system.

(b) **Differential Thermal Analysis (DTA)**

In DTA, it measures the difference in temperature between the sample cell (Ts) and the thermally inert reference (Tr) and record this difference (Ts-Tr) as the function of temperature, which give the information about thermal behavior of the sample such as exothermic (heat emission during the reaction) or endothermic (heat absorption during the reaction). An exothermic process is plotted with upward deflection, while, an endothermic process is plotted with a downward deflection in the DTA curve.

Polymeric intermediates were characterized by thermal analysis to study their thermal behavior. This thermal analysis was used to identify the ignition temperature of the precursors. For this purpose, both thermogravimetric (TG) and differential thermal analysis (DTA) techniques were employed to characterize thermal and mass loss events on heating the samples using a simultaneous TG/DTA system of Labsys M/s. Setaram., France or TA instrument of SDT Q600 V20.5. Approximately 3 - 6 mg dried gel or polymeric intermediate was used as sample and a heating rate of 10 °C/min was employed from room temperature to
900°C. Thermal behaviors (TG/DTA curves) of the samples were recorded under nitrogen atmosphere.

2.3.2. Fourier transform infrared spectroscopy (FTIR)

FTIR is a powerful technique for identifying the structural coordination in the substances such as solids, liquids and gases. It is based on the interaction of IR radiation with the substance and the nature of interaction, which reveals the properties of the substance [26].

When infrared radiation passes through a sample (solid, liquid or gas), certain frequencies of the radiation are absorbed by the molecules of the substance leading to the molecular vibrations. The frequencies of absorbed radiation are unique for each molecule, which provides the characteristics of a substance [27].

Samples preparation for FTIR analysis are given below,

(a) For liquid samples, the easiest is to place one drop of sample between two plates of single crystal sodium chloride. The drop forms a thin film between the plates.

(b) Solid samples can be mixed with potassium bromide (KBr) as diluter to form a very fine powder. The powder is then compressed into a thin transparent pellet, which is used for taking FTIR spectrum.

(c) Polymer samples can be dissolved in a solvent such as methylene chloride and the solution placed onto plates of single crystal sodium chloride. Further evaporation lead to the formation of thin film of the original material on the plate, which is frequently used for polymer samples.
Solid samples also can be examined as a mull, which is prepared by thorough grinding (to avoid the scattering of IR radiation) of few mg sample with mulling oil (Nujol-liquid paraffin is commonly used as a mulling agent). The mull is examined as a thin film between flat sodium chloride single crystal plates.

The dried gel, fine powdered polymeric intermediate as well as calcined dried gel / polymeric intermediate at different temperatures mixed with spectral pure KBr powder in 1:20 ratio, thin transparent pellets were made using KBr press and used for the FTIR spectral measurements using Schimadzu FTIR/8300/8700 spectrophotometer or thermo Nicolet FTIR-6700 spectrometer in the range of wavenumber 4000 – 400 cm\(^{-1}\) with 2 cm\(^{-1}\) resolution for 20 scans.

2.3.3. X-ray powder diffraction (XRD)

X-ray powder diffraction is one of the most important techniques to characterize the powder samples. It is effectively used for deduction of an order/disorder phenomenon, structural determination, phase analysis and also determination of crystallite size of the powder samples [28]. The positions and the intensities of the peaks are used to identify the structure, phase, etc., of the material [29].

Consider two parallel monochromatic X-ray beams with the wave length of \(\lambda\) falling on the successive planes of the crystal at an angle of \(\theta\). Constructive interference of the reflected rays from two successive planes occurs, only the path difference between the two rays fulfils the Bragg’s condition, \(n\lambda = 2d\sin\theta\), where \(n\) is integer and \(d\) is an inter planar distance [28-29].
The crystallite size of the particles can be calculated by suitable analysis of X-ray line broadening. Generally, in XRD pattern, diffracted lines are not always sharp and may be broadened due to the instrumental factors or the nature of the specimen (mainly crystallite size). If the particles are very small, the lines are broader than usual. The broadening increases with decreasing crystallite size. The crystallite size of the sample could be determined using Scherrer’s formula [30-31].

\[
L = \frac{0.9\lambda}{\beta_{1/2}\cos\theta}
\]

Where, \( \lambda \) – wavelength of the radiation used in Å, \( \theta_B \) – Bragg’s angle in degrees, \( \beta_{1/2} \) – Full width at half maxima (FWHM) in radians, \( \beta_{1/2} \) is calculated using the following expression,

\[
\beta_{1/2} = (\beta_{M}^2 - \beta_{S}^2)
\]

Where, \( \beta_M \) – measured FWHM of the sample and \( \beta_S \) – measured FWHM of the Si standard. Peak corresponds to the (111) plane of the standard was used as standard for the estimation of the instrumental broadening.

The prepared nanocrystalline powders were finely grounded and filled in the sample holder and mounted on the X-ray diffractometer. The X-ray diffraction patterns were recorded between 10° to 80° with scanning rate of 0.05 per second using a X’ Pert PRO MPD, PANalytical (Philips) X-ray powder diffractometer using graphite monochromator employing Cu Kα radiation. The obtained patterns were compared with ICDD data.
2.3.4. Scanning electron microscope (SEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid sample. The schematic diagram of SEM instrument is shown in fig. 2.3. The signals that derive from electron-sample interactions reveal information about the sample including external morphology, chemical composition, crystalline structure and orientation of materials. Accelerated electrons in SEM have significant amounts of kinetic energy, and this energy is dissipated in different forms of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (SE), backscattered electrons (BSE), diffracted backscattered electrons, photons, visible light, and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples [32]. The electron beam causes various excitations in the sample, which are characteristic of the elements present in the material. Characteristic X-rays emitted by the sample can be used for elemental identification. The intensity of the signal can be used for quantitative analysis. When a fast moving electron approaches the atom, it gets decelerated due to the coulombic field. This results in a loss of energy for the electron and that energy appears as photon, referred to as breaking radiation. The characteristic X-rays emitted by the atoms will appear as spikes over this smoothly varying photon intensity.
There are several characteristic X-ray lines with which an atom can be identified. The intensities of these lines can be related to the concentrations of the emitting species in the sample.

Small amount of the prepared crystalline metal oxide powder sample is sprayed on the carbon tape. Small broken piece of the sintered metal oxide crystalline pellet is pasted on the carbon tape and carbon tape is pasted over the aluminum stub. Thin Gold layer is coated over the powder or pellet sample using
sputter coater for good conduction. The SEM images and SEM-EDX spectrum were taken using Hitachi - SN – 3400N model SEM instrument.

2.3.5. Transmission electron microscope (TEM)

In TEM, the transmitted electrons are used to create an image of the sample. The schematic diagram of TEM instrument is shown in fig. 2.4. The transmission electron microscope uses a high energy electron beam transmitted through a very thin sample to image and analyze the microstructure of materials with atomic scale resolution. The electrons are focused with electromagnetic lenses and the image is observed on a fluorescent screen, or recorded on film or digital camera. The electrons are accelerated at several hundred kV, giving wavelengths much smaller than that of light: 200kV electrons have a wavelength of 0.025Å. However, whereas the resolution of the optical microscope is limited by the wavelength of light, that of the electron microscope is limited by aberrations inherent in electromagnetic lenses, to about 1-2 Å.

High resolution imaging mode of the microscope images the crystal lattice of a material as an interference pattern between the transmitted and diffracted beams. This allows one to observe planar and line defects, grain boundaries, interfaces, etc. with atomic scale resolution [33]. The bright field/dark field imaging modes of the microscope, which operate at intermediate magnification, combined with electron diffraction, are also invaluable for giving information about the morphology, crystal phases, and defects in a material.
Transmission electron micrographs (TEM) were taken in a JEOL 200 FX microscope operating an accelerating voltage of 200 kV. The samples were
dispersed in acetone and drops of the dispersion were transferred to a carbon coated copper grid. Dried copper grid was further used for the TEM analysis.

2.3.6. X-ray fluorescence spectrometry (XRF)

X-ray fluorescence spectrometry (XRF) is an analytical technique used to identify and determine the concentrations of elements present in solid and liquid samples. When a high energy X-ray collides with an atom, an electron is ejected from a low energy level (e.g. K shell) and a vacancy is created. As a result, an electron from a higher energy level (e.g. L shell) falls into this vacancy. The difference in energy produced as the electron moves between these levels is released as secondary X-rays, which are characteristic of the element. This process is called X-ray fluorescence. By measuring the energy of the secondary X-ray, the identity of the element can be determined. By counting the number of X-rays emitted at each energy, the concentration of the element can be determined.

The prepared nanocrystalline metal oxide powders were finely ground and it is filled with mixing of boric acid in the sample holder and mounted on the X-ray fluorescence spectrometry. The presence of elemental composition of metal oxide samples are observed using Bruker S4-Pioneer model X-ray fluorescence spectrometry instrument.
2.4. Electrical Conductivity studies

The measurement of the electrical conductivity of a superionic substance gives the information about the extent of the ionic transport in it. One of the electrical characterization techniques for those fast ionic conductors is the application of a D.C bias via two standard metal electrodes, polarization occurs at the electrodes due to the inability of mobile ions to cross the electrolyte/electrode interface and ionic current falls to zero. In principle, this problem may be solved in a variety of ways including the use of D.C. techniques with either a four electrode configuration or two reversible electrodes, which will allow ionic transport from electrolyte to electrode or A.C. techniques (impedance spectroscopy). Although they may be very successful under particular circumstances, the D.C. methods are often more difficult to carry out experimentally, are less versatile and give less detailed results than their A.C counterparts.

2.4.1. Impedance Spectroscopy

Impedance spectroscopy is a perturbation technique used for electrical characterization of materials. The response of a system to an applied sinusoidally varying alternating voltage is recorded as a function of wide range of frequencies. Impedance is opposition to the flow of current, which is given by the ratio of the applied voltage to the resultant current. The locus of impedance as a function of angular frequency is called an impedance spectrum. The measured impedance is correlated to elementary processes occurring in a material. Impedance analysis of ionic solids identifies the elementary process such as bulk conduction, grain
boundary conduction and electrode/electrolytes interface processes from the impedance - frequency domain.

2.4.2. Basic a.c. theory

A small amplitude of ac signal is used in impedance measurement to perturb the system.

The applied potential $E(\omega)$ is given by,

$$E(\omega) = E_0 \exp (j\omega t)$$

$\omega$ ($2\pi f$) is the angular frequency, $t$ is time. The output current of the system is also a sinusoidal and represented by,

$$I = I_0 \exp (j\omega t + \varphi)$$

According to Ohm’s law, impedance ($Z$) of the system at any angular frequency $\omega$ can be represented by,

$$Z = E/I = (E_0/I_0)\exp (-j\phi)$$

$$= Z_0 \exp (-j\phi)$$

$$= Z \cos \phi - jZ \sin \phi$$

$$Z = Z_r - jZ_i$$

Where $j$ is the imaginary number having the value of $\sqrt{-1}$, $Z_r$ and $Z_i$ are real and imaginary parts of the impedance respectively. The phase angle $\phi$ is represented by
\[ \phi = \tan^{-1}(\frac{Z_i}{Z_r}) \]

For pure resistor (R), capacitor (C) and inductor (L), the impedance is given by the following representations:

\[ Z = R + 0 \ j \]
\[ Z = 0 - j \frac{1}{\omega C} \]
\[ Z = 0 + j \omega L \]

From the above equations, it has been observed that the impedance due to capacitor and inductor depends on the frequency of the input signal. The plot of real and imaginary parts of impedance for a particular range of frequency is known as impedance spectrum and it appears as semicircles or straight lines depending on the combinations of resistance and capacitance.

Apart from the impedance, three other important representations are used in complex plane analysis, and they are given below.

Admittance

\[ Y = Z^{-1} = Y_r + j \ Y_i \]

Permittivity

\[ \varepsilon = \frac{A}{j \omega C_o} = \varepsilon_r - j \varepsilon_i \]

Modulus

\[ M = \varepsilon^{-1} = M_r + j M_i \]

Where \( C_o = \varepsilon_o \ (A/l) \), \( \varepsilon_o = 8.854 \times 10^{-12} \text{F/m} \) and A/L is the cell constant.
The complex permittivity and modulus representations are used for analyzing the dielectric response of the system.

The electrical behavior of any sample can be represented in the form of equivalent circuit, which represents the various current conducting elements in the sample. If resistance and capacitance are connected in series or parallel, the impedance of the circuits is given as follows.

2.4.3. Series combination of R and C

A circuit containing a resistance and a capacitance in series is shown in fig 2.5.a. The total impedance (Z) of the circuit is given by

\[ Z = R + \left( \frac{1}{j \omega C} \right) = R - \left( \frac{j}{\omega C} \right) \]

The above equation contains real \( (Z') \) and imaginary \( (Z'') \) terms as indicated below:

\[ Z' = R \quad \text{and} \quad Z'' = \frac{1}{\omega C} \]

Fig 2.5. a also shows the complex impedance plot \( (Z'' \text{ vs } Z') \) for the circuit containing a resistance and a capacitance in series. From fig 2.5. a, the complex impedance plot gives a vertical spike, because \( Z' \) is of fixed value and \( Z'' \) decrease with increasing \( \omega \). The point at which the vertical spike is touch in the real axis gives the resistance value of the circuit as shown in fig.2.5.a.
2.4.4. Parallel combination of R and C

A circuit containing a resistance and a capacitance in parallel is shown in fig 2.5.b. The total impedance \( Z \) is given by,

\[
Z = \left( \frac{1}{R + j\omega C} \right)^{-1}
\]

\[
= \left\{ \frac{R}{(1 + (\omega RC)^2)} \right\} - \left\{ Rj\omega RC / (1+(\omega RC)^2) \right\}
\]

Therefore,

\[
Z' = \frac{R}{(1 + (\omega RC)^2)} \quad \text{and} \quad Z'' = R\omega RC / (1+(\omega RC)^2)
\]

Fig. 2.5. b also shows the complex impedance plot \( (Z'' \text{ vs } Z') \) for the circuit containing a resistance and a capacitance in parallel. From the Fig. 2.5. b, the complex impedance plot gives a semicircle. The point at which the semicircle is touch in the lower frequency of real axis gives the resistance value of the circuit as shown in fig.2.5.b.
2.4.5. Complex plane analysis

In solid electrolytes, the ionic conductivity effects complicated mainly because of the migration of the charge carrying species through grains and across grain boundaries. $Z^*$ the contribution of various process such as electrode reactions at the electrode/ electrolyte interface can also be in the frequency domain. Complex plane analysis, a mathematical technique, which allows determination of the individual component values from reduced data obtained over a range of frequencies. It involves simply the plotting one against the other of the real and imaginary parts of the complex electrical quantities described above, i.e. $Z^*$, $Y^*$, $\varepsilon^*$ and $M^*$ as a frequency dispersion. The subsequent plots are characteristic of particular equivalents circuits and it consists ideally of a combination of semicircles and straight lines. Intercept with the real axis and frequency values at maximum or minimum position lead to the single component values. The technique requires the minimum of raw data manipulation. Since the plotted parameters are very simply related to the measurable quantities $R_s$, $C_s$, $R_p$ and $C_p$.

Any system under test can be defined in terms of an equivalent R, C, L network by a comparison of experimentally derived complex plane plots with standard forms. In effect, one is modeling an observed A.C response in terms of an equivalent circuit [34, 35].

2.4.6. Preparation of pellets for impedance measurements

Prepared nanocrystalline metal oxide pellets sintered at 800 °C, with 10 mm diameter and 2-2.5 mm thickness were made under a pressure of 5 tons using
spectralab make pelletizer. Silver paste as electrodes was painted on both side of each sintered pellet and heated at 200 °C for half an hour to ensure maximum contact and adherence. The real ($Z'$) and imaginary ($Z''$) parts of the impedance data were measured for the pellets using Novocontrol Alpha A High performance frequency analyzer in the frequency range 0.1Hz - 1MHz at different temperature. The measured impedance data were analyzed using the Win fit software to obtain the bulk resistance and also its electrical behavior in terms of equivalent circuits. Also, the conductivities of nanocrystalline metal oxide samples were calculated using the pellets dimension and the bulk resistance obtained from the analysis of the measured impedance data at different temperatures. Activation energies were calculated from the temperature dependent conductivity plots of the nanocrystalline metal oxide samples.

2.4.7. Brick layer model

Bauerle et al. is credited with the development of an equivalent circuit model for conducting ceramics with resistive grain boundaries [36]. Beekmans and heyne et al. reported the microstructures including the second phase grain boundary layers and the corresponding frequency dependent impedance behavior consistent with this impedance to overall transport [37]. Their rough model was further qualified by Van Dijk and Burgraaf and it is known as brick layer model [38, 39]. The brick layer model is routinely employed to describe the frequency dependent electrical behavior of polycrystalline electroceramics, including ionic conductors and electronic conductors [40, 41]. More recently, Maier and Neif
have taken into account the parallel grain boundary contributions in materials with conductive grain boundaries [42, 43].

A 3-D array of monosized cubic grains (“bricks”) is constructed with uniform grain boundary layers (“mortar”) separating them as shown fig. 2.6. A single grain and its surrounding grain boundary layers are represented in figure. In its simplest form, the brick layer model assumes 1) a primitive cubic lattice of cubic grains of constant grain size, 2) laterally and vertically homogeneous electrical properties of single grain boundaries and 3) no variation of electrical properties from boundary to boundary.

Figs. 2.6. a and b. Schematic three dimensional representation of grain and grain boundaries in the polycrystalline materials and impedance spectrum based on brick layer model.

Based on the brick layer model, the polycrystalline material consists of the grain and grain boundary effects. The bulk or grain interior conductivity ($\sigma_g$) and grain
boundary conductivity ($\sigma_{gb}$) were calculated using the following equations [44 - 46]

$$\sigma_{gi} = \frac{1}{R_{gi}} \frac{ND}{A} = \frac{1}{R_{gi}} \frac{t}{A}$$

$$\sigma_{gb} = \frac{1}{R_{gb}} \frac{N\delta_{gb}}{A} = \frac{1}{R_{gb}} \frac{t \delta_{gb}}{A}$$

where $R_{gi}$ and $R_{gb}$ are resistances of bulk (or grain interior) and grain boundary respectively, $t$ is the thickness of the sintered pellet and $A$ is the area of the sintered pellet. $N$ is the number of the grain boundary planes parallel to the electrodes.

If the grain boundary conductivity is much smaller than that of the grain interiors of the electroceramics, the grain boundary width is negligibly small than the grain size. The applied electric field in the vertical direction of the electrode (i.e. ionic transport contribution of parallel grain boundaries) can be neglected. Transport is dominated by the contribution of series path (top and bottom grain boundary layers and grain cores), resulting in the equivalent circuit consisting of series of two parallel RC circuits in which one for the grain core and another for grain boundary core. With this model a simple interpretation of the impedance spectra is possible as shown in fig 2.6 b. The parallel combination of the higher frequency semicircle represents the bulk (grain interior) values. The lower frequency semicircle is caused solely by the grain boundaries.

2.4.8. Space charge layer model

In the typical polycrystalline materials, the grain boundary conductivity is smaller than the grain interior conductivity. To achieve the equal conductance,
grain boundary conductivity must be increased. For nanocrystalline materials, the dimensions of the grain boundaries become comparable to those of the grains. Hence, a significant fraction of the atoms will be in the disordered grain boundary regions and it can be expected to contribute to the conductivity enhancement. Thus, an enhancement of several orders of magnitude in the grain boundary conductivity will translate into a similar enhancement in the overall ionic conductivity of the sample [47, 48].

From the structural point of view, a grain boundary is a crystallographic mismatch zone. At thermodynamic equilibrium, the grain boundary core of an ionic crystal carries an electric charge due to the presence of excess ions of a given sign. This charge is compensated by adjacent space charge of opposite sign. Owing to the charged grain boundary core, the concentration of charged point defects in the space charge layer deviate from their bulk values. As demonstrated by Maier and Waser, the accumulation or depletion of charge carrier in the space charge layer significantly influences the electrical properties of polycrystalline ionic and mixed conductors [49-52]. Xin Guo et al, elaborately explained Schottky barrier model and experimental evidence support the model [53]. Guo et al also reported that the oxygen vacancy depletion in the space charge layer was suggested for very low grain boundary conductivity in Y₂O₃ – CeO₂ [54]. Grain boundary blocking effects very similar to those in CeO₂ have also been observed for acceptor doped ZrO₂ and SrTiO₃ and successfully explained by the depletion of charge carriers, viz., oxygen vacancies in ZrO₂ and oxygen vacancies and electron holes in SrTiO₃ in the space charge layers [55-58]. Structurally, a space
charge layer is part of bulk, but electrically, a space charge layer is part of the grain boundary. Thus, the grain boundary consists of grain boundary core and two adjacent space charge layers. The thickness of the electrical grain boundary $\delta_{gb} = 2\lambda^* + b$. Here $\lambda^*$ is the width of the space charge layer and $b$ is the thickness of the grain boundary core. Fig 2.7. a shows the model of polycrystalline solid electrolyte using space charge layer and Fig 2.7. b shows the defects concentration plot in the space charge layer model.

![Diagram](image)

Fig 2.7. a) Model of the polycrystalline solid electrolyte using space charge layer model. b) Defect concentration plot in the space charge layer model.

An additional explanation for enhanced conduction is related to the formation of space charge regions in the close vicinity of the grains. Charged species, impurities, and defects tend to segregate to the grain boundaries in order to minimize strain and lower electrostatic energies in the system. These boundary charges are compensated by the formation of space charge close to the adjoining
grains. Thus, bulk ionic defects with equal charge to that of the boundary will be depleted while those with opposite charge will accumulate in the space charge region.

In the present work, the enhanced electrical conductivities of the prepared La$_{9.33}$Si$_6$O$_{26}$, Ba doped La$_{10}$Si$_6$O$_{27}$, La doped BaMoO$_4$ and La doped SrMoO$_4$ are studied by analyzing the measured impedance data at different temperatures, in terms of bulk and grain boundary conductivities using the brick layer model. Also, attempts are made to calculate space charge potential, concentration of oxygen vacancies as well as the activation energy using the space charge layer model to account the observed grain interior conductivity and grain boundary conductivity of the nanocrystalline Ba doped La$_{10}$Si$_6$O$_{27}$ sample.
References


