CHAPTER 2

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In this chapter, the synthesis of the compounds selected for the present work and the experimental techniques employed to characterize the specimens, are briefly discussed. The details about each of the instrument, its model number, working and operating conditions have been given. This chapter sums up the whole scheme of events leading to successful completion of experimental work.

2.1 SYNTHESIS

Ceramic and glass-ceramic materials are technologically very important because of their wide variety of applications in day to day life. Thus the preparation of novel ceramic materials is of great significance in the advancement of Material Science. There are numerous methods of fabrication such as mechanical method, which include solid-state reaction, and ball-milling etc., and the chemical method, which includes sol-gel, wet-dry and polymer-sol-gel etc. To attain a quality product with respect to purity, homogeneity, reactivity, particle size etc. each method has its own advantages and disadvantages. In this context, the solid-state reaction is found to be simpler, expedient and economical method among other available techniques in terms of performance, reliability, reproducibility and economy. This makes it a very versatile route.

2.1.1 Solid state reaction

Lithium silicate (LS) ceramics were prepared via solid state reaction technique. The various steps in solid-state reaction process are represented as a flow chart shown in Figure 2.1. In the present work, high purity (AR grade) raw chemicals are used for the preparation of samples. The constituents of the required specimen are taken in stoichiometric ratio and dry
mixed followed by wet mixing in acetone medium. The mixing is done using agate mortar and pestle. The mixture was then calcined at a certain temperature depending upon the composition. The calcined powder are again ground and are mixed with poly vinyl alcohol (PVA) (which acts as a binder) to give the dry shape sufficient strength and to have better compactness amongst the granules of the materials. The green pellets of dimension 12 mm diameter and 2-3 mm thickness are made using hydraulic press with a stainless steel dye.

The pellets are kept at 450 °C for 4 h. to remove the binder and the process of heating should be slow enough to avoid the formation of cracks and blistering in the ceramics.

**Fig. 2.1** Flow chart describing various steps involved in solid-state reaction
These pellets were then sintered with predetermined optimized temperature and time in an air atmosphere to increase the density and toughness of the sample.

To synthesize Magnesium aluminum silicate (MAS) glass-ceramics, sintering route was adopted, using three-stage heating schedules involving calcination, nucleation and crystallization processes. General steps followed in the preparation of glass-ceramics are:

1. Grinding and mixing of initial charge
2. Calcination
3. Grinding
4. Controlled crystallization
5. Sintering

In the present case calcination and sintering were done within a high temperature furnace.

2.2 CHARACTERIZATION

2.2.1 X-ray diffraction

X-ray diffraction is a powerful technique that reveals detailed information about the chemical composition and crystallographic structure of the materials. Powder XRD is one of the most widely used technique to characterize ceramics. In the present case, the x-ray powder diffraction patterns were recorded at room temperature by Philips Xpert-pro X-ray powder diffractometer (Model PW 1710) using:

(a) CuKα radiation (λ = 1.5405 Å) in a wide range of the Bragg angles 2θ (10° ≤ 2θ ≤ 70°) at a scanning rate of 2° per minute for MAS glass-ceramics and

(b) Co (λ = 1.78897 Å) radiation in a wide range of the Bragg angles 2θ (10° ≤ 2θ ≤ 90°) at a scanning rate of 2° per minute for LS ceramics.

The crystallite size (D) of the powdered LS ceramic samples were roughly estimated from broadening of reflection peaks using Scherrer’s equation [62],

\[ D = \frac{0.89\lambda}{\beta_{1/2}\cos\theta} \]

where \( \lambda = 1.78897 \) Å and \( \beta_{1/2} \) = half peak width of reflections.

The data obtained from XRD is indexed by standard powder diffraction files provided by International Centre for Diffraction Data – ICDD (formerly known as JCPDS).
2.2.2 Scanning electron microscopy

The SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons. It is a useful technique to study the topography, morphology and composition of the materials with excellent resolution. When a very narrow beam of high energy electrons strikes the sample, the secondary electrons (SEs), characteristic x-rays and back-scattered electrons (BSEs) are ejected from the sample. These electrons are then collected by specialized detectors for detection and convert into signal that displays on a screen. In the present study, the FE-SEM micrograph was taken on the fractured surface of the LS ceramic samples using field emission scanning electron microscope (FESEM: SUPRA-40 field emission scanning electron microscope) and SEM micrograph was taken on the fractured surface of the MAS glass-ceramic samples using scanning electron microscope (SEM: JSM-5800 scanning microscope JEOL). As the samples are non-conducting, a thin layer of gold is coated using a sputter coater.

2.2.3 Differential Thermal Analysis (DTA)

Measurement of physical and chemical properties of the materials as a function of temperature is called thermal analysis. Differential Thermal Analysis (DTA) is a thermoanalytic technique, similar to differential scanning calorimetry. In this technique, the sample under study and the inert reference material are heated (or cooled) under identical conditions, while recording any temperature difference between sample and reference. The extra heat input required to maintain the temperature during any thermal event in the sample is measured and plotted against temperature or time (DTA curve). During this thermal event, the sample temperature either lags behind or leads the temperature of the reference depending on the change whether it is endothermic or exothermic. Thus, a DTA curve provides data on the transformations that have occurred, such as glass transitions, crystallization and melting. In the present work differential thermal analysis of the powdered samples was performed using a differential thermal analysis (Model Perkin Elmer Pyris Diamond TG-DTA). All the measurements were done at a heating rate of 10 °C/min in O2 atmosphere using alumina as reference.
2.2.4 Dielectric Spectroscopy

When a dielectric material is subjected to an applied electric field, polarization of charge takes place within the material due to induced dipole moment or due to rotation of permanent electric dipoles present in the material. The polarizability, $\alpha$ of the dielectric is defined by

$$P = \alpha E$$

where $P$ is the induced dipole moment by the local electric field, $E$. In dielectric materials, the possible polarizations are electronic polarization, ionic polarization, dipolar or orientation polarization and Space charge polarization. Electronic polarization is caused by a slight displacement of the negatively charged electron cloud in an atom relative to the positively charged nucleus, which induces dipole moment under the influence of local electric field. In ionic polarization, the net induced dipole moment is due to the slight relative displacement or separation of anions and cations from their equilibrium position. Dipolar or Orientation polarization describes the alignment of permanent dipoles. These dipoles may change their orientation and they tend to align themselves with an applied electric field and contribute to the total polarizability. Interfacial polarization or space charge polarization arises as a result of accumulation of charges locally at the material interfaces as they drift through the material. The macroscopic behavior of a dielectric can be understood by considering the dielectric in between a parallel plate capacitor. The capacitance ($C$) of a capacitor with the dielectric is

$$C = \varepsilon_r \varepsilon_o A/h$$

where $\varepsilon_r = \varepsilon / \varepsilon_o$ is the dielectric constant or relative permittivity of the dielectric. $\varepsilon$ is called the permittivity of the dielectric, $\varepsilon_o$ ($8.85 \times 10^{-12}$ F/m) is the permittivity of free space, $A$ and $h$ correspond to the area and thickness of the conducting plates respectively.

When an alternative potential $U = U_0 \exp (j \omega t)$ is applied, the total current in the dielectric is given by

$$I = j \omega \varepsilon_r \varepsilon_o C_0 U$$

As $\varepsilon_r \varepsilon_o$ is complex quantity i.e. $\varepsilon_r \varepsilon_o = \varepsilon'_r - j \varepsilon''_r$, where $\varepsilon'_r$ and $\varepsilon''_r$ are respectively the real and imaginary parts of relative permittivity.

It follows that
The value of $\varepsilon'_r$ determines the out-of-phase component of the current (capacitive and lossless) and the value of $\varepsilon''_r$ determines the in-phase component of the current (lossy), as indicated in Figure 2.2(b).

It can be seen from the figure that

$$\tan\delta = \frac{\varepsilon''_r}{\varepsilon'_r}$$

where $\tan\delta$ is called either the loss tangent or the dissipation factor. The ac conductivity can be determined by the relation

$$\sigma_{ac} = \varepsilon_0\varepsilon''_r\omega = \varepsilon_0\varepsilon'_r\omega \tan\delta$$

In the present study, all the measurements are carried out using a laboratory made sample holder. The sintered pellets were coated with a thin layer of silver paint and fired at 150 °C for 2 hours. The capacitance and $\tan\delta$ was measured using an impedance analyzer (HIOKI 3532 LCR Hi-TESTER) in the frequency range (100 Hz–5 MHz) at room temperature and temperature (30 °C–500 °C) at 1 kHz, 10 kHz, 100 kHz and 1 MHz. The data was recorded for every five-degree.
2.2.5 Impedance spectroscopy

The complex impedance spectroscopy (CIS) is a powerful technique used to obtain information about the electrical properties (i.e., transport properties) of the samples. The main advantages of the techniques are that i) it involves relatively simple electrical measurements that can readily be automated ii) the measurements can be implemented by using arbitrary conducting electrodes iii) the results can be often correlated with the properties such as composition, microstructure, defects, dielectric properties, chemical reaction etc. of the sample iv) the resistance of the grain boundaries and that of the grains can be easily measured in most of the polycrystalline samples. AC measurements are often made with a Wheatstone bridge type of apparatus (Impedance analyzer or LCZ meter) in which the resistance R and capacitance C of the sample are measured and balanced against variable resistors and capacitors. Impedance spectroscopy consists of the measurement of impedance Z and the phase angle (θ) between the voltage and current as a function of frequency over a wide frequency range. Analysis of the data is carried out by plotting the imaginary part of the impedance \( Z'' = |Z| \cos(\theta) \) against the real part \( Z' = |Z| \sin(\theta) \) on a complex plane called the impedance plot. An impedance plot with linear scale is used to analyze the equivalent circuit as follows. Impedance plot of a pure resistor is a point on real axis and that of pure capacitor is a straight line coinciding with the imaginary axis. The impedance of a simple RC parallel circuit is given by

\[
Z^* = Z' - j Z'' = R \left( 1 - j \omega RC \right) / \left( 1 + \omega^2 R^2 C^2 \right)
\]

so that the real and imaginary components are

\[
Z' = R / \left( 1 + \omega^2 R^2 C^2 \right)
\]

and

\[
- Z'' = \omega R^2 C / \left( 1 + \omega^2 R^2 C^2 \right)
\]

After simplification, one gets

\[
(Z' - R/2)^2 + Z''^2 = (R/2)^2
\]

which represents the equation of a circle with centre at \((R/2, 0)\) and radius \(R/2\). Thus, a plot of \(Z'\) vs \(Z''\) (as parametric function of \(\omega\)) will result in a semicircle (Fig. 2.3) of radius \(R/2\). This plot is often called a complex plane plot (Nyquist diagram). Since the time constant of the simple circuit is \(\tau = RC = 1/\omega_0\) the equations can be written as
\[ Z' = \frac{R}{1 + \omega^2 \tau^2} \quad 2.11 \]

and

\[- Z'' = \frac{R \omega \tau}{1 + \omega^2 \tau^2} \quad 2.12 \]

This corresponds to the relaxation time of the sample and the characteristic frequency lies at the peak of the semi-circle. Two such circuits having different relaxation time constants and connected in series lead to two semicircles as shown in Fig. 2.4. The frequency response of an ideal polycrystalline ceramic carrying metallic electrodes exhibits an arc at high frequency corresponding to the polarization processes associated with the interior of the grains (bulk property), an arc at low frequency corresponds to the grain boundary regions and a spike at the lowest frequency corresponds to the electrode-ceramic interfacial region. Fig. 2.5(a) shows typical impedance plot for a polycrystalline sample and Fig. 2.5(b) represented the equivalent circuit. In the present work, impedance measurements have been performed using HIOKI 3532 LCR Hi-TESTER impedance analyzer in the frequency range (100 Hz–5 MHz) at different temperatures.

**Fig. 2.3** Nyquist plot of a resistor and capacitor in parallel and the corresponding equivalent circuit
Fig. 2.4 Schematic of dual arc impedance plot

Fig. 2.5 (a) The impedance plot for an ideal polycrystalline sample and (b) the corresponding equivalent circuit