REPRINTS OF PUBLICATIONS
EFFECT OF SINTERING TEMPERATURE ON THE DIELECTRIC PROPERTIES OF Li$_2$SiO$_3$ CERAMIC

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Lithium silicate (Li$_2$SiO$_3$) ceramic was prepared via solid-state reaction technique using high purity ingredients: Lithium Carbonate (Li$_2$CO$_3$) (99.5%) and Silicon Dioxide (SiO$_2$) (99.5%) in the following molar ratio: Li$_2$CO$_3$:SiO$_2$ (1:1)

In the first stage, the initial charge was thoroughly mixed in agate mortar for 2 h, including wet mixing in acetone media for 1 h. The mixture was then calcined at 900 °C for 3 h. The calcined powder was then cold pressed into cylindrical pellets of 12 mm diameter and 2 - 3 mm of thickness at a pressure of 80 MPa using a hydraulic press. PVA (poly vinyl alcohol) was used as a binding agent.

Keywords: Ceramics; Dielectrics; Sintering

1. Introduction

Lithium silicate ceramic systems belong to technologically important class of ceramic materials for various applications. Thus, for example, there has been research in recent years on their application as electronic devices, as CO$_2$ captors and as breeder materials for nuclear fusion reactors, in addition to other more well-known applications such as in batteries and in low thermal expansion glass ceramics used in ceramic hobs [1-10]. Various properties of Lithium silicate ceramics such as dielectric, conductivity and other properties depend on the composition and microstructure. In this study, the investigation is concerned with the preparation of Lithium Silicate (Li$_2$SiO$_3$) ceramic and the effect of sintering temperature on the dielectric properties of Lithium silicate ceramic are also investigated. This study also presents the influence of temperature and frequency on the dielectric properties of Lithium silicate ceramic.

2. Experimental

Lithium silicate (Li$_2$SiO$_3$) ceramic was prepared via solid-state reaction technique using high purity ingredients: Lithium Carbonate (Li$_2$CO$_3$) (99.5%) and Silicon Dioxide (SiO$_2$) (99.5%) in the following molar ratio:

Li$_2$CO$_3$:SiO$_2$ (1:1)

In the first stage, the initial charge was thoroughly mixed in agate mortar for 2 h, including wet mixing in acetone media for 1 h. The mixture was then calcined at 900 °C for 3 h. The calcined powder was then cold pressed into cylindrical pellets of 12 mm diameter and 2 - 3 mm of thickness at a pressure of 80 MPa using a hydraulic press. PVA (poly vinyl alcohol) was used as a binding agent.

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binder for preparing pellets. These pellets were then sintered at 800 °C, 850 °C, 900 °C and 950 °C for 2 h in an air atmosphere.

The compound formation was confirmed by X-ray diffraction (XRD) using Philips Xpert-pro X-ray powder diffractometer in a wide range of the Bragg angles $2\theta (10^\circ \leq 2\theta \leq 90^\circ)$ being irradiated by Co ($\lambda = 1.78897$ Å). The surface morphology was recorded using Field emission scanning electron microscope JEOL (model: JSM – 5800F). In order to study the dielectric properties of the compound, both the flat surfaces of the samples were polished and electroded with air-drying conducting silver paint. After electroding, the pellets were dried at 150 °C for 2 h to remove moisture, if any, and then cooled to room temperature before taking any electrical measurement. The dielectric permittivity ($\varepsilon_r$) and loss tangent (tanδ) of the sample was measured using an impedance analyzer (HIOKI 3532 LCR Hi-TESTER) in the frequency range (100 Hz – 5 MHz) at some selected temperatures (35 °C, 50 °C, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C & 350 °C).

3. Results and discussion

3.1. Structural

Fig.1 shows the bulk densities of the Li$_2$SiO$_3$ ceramic sintered at various temperatures for 2 h. The density of the Li$_2$SiO$_3$ ceramic was initially increased with sintering temperature up to 900 °C but decreases at 950 °C. We can draw the conclusion that Li$_2$SiO$_3$ ceramic could be well-sintered at 900 °C.

![Fig. 1. Variation of bulk density of Li$_2$SiO$_3$ ceramic with sintering temperature.](image)

XRD pattern of Lithium silicate (Li$_2$SiO$_3$) ceramic sintered at 900 °C is shown in Fig. 2. Detailed structural analysis in different crystal structure and cell constants exhibit that the sample has an orthorhombic structure with lattice parameters: $a = 9.396$ Å, $b = 5.396$ Å, $c = 4.661$ Å, which is in well agreement with the phase given in JCPDS card number 83 – 1517. The crystallite size of the powder sample was roughly estimated from broadening of reflection peaks using Scherrer’s equation [11], $D = \frac{0.89\lambda}{(\beta_{1/2}\cos \theta)}$, where $\lambda = 1.78897$ Å and $\beta_{1/2}$ = half peak width of reflections. The average crystallite size was found to be ~ 30 nm. Other effects of the broadening were ignored.
Fig. 2. Room temperature XRD pattern of Lithium silicate (Li$_2$SiO$_3$) ceramic sintered at 900 °C.

The FE-SEM micrograph was taken on the fractured surface of the sample using scanning electron microscope. The highly distinctive, more or less uniform and compact grain distributions (with less voids) are observed. It shows the polycrystalline texture of the material. The average grain size of the sample sintered at 900 °C was found to be 2.4 μm. There are a few islands and holes in SEM, which suggests that the pellet sample was of high density. Fig. 3 shows dense and homogeneous microstructure of Lithium silicate (Li$_2$SiO$_3$) ceramic sintered at 900 °C.

Fig. 3. FE-SEM of lithium silicate (Li$_2$SiO$_3$) ceramic sintered at 900 °C.

3.2. Dielectric properties

Fig. 4 show the variation of dielectric constant ($\varepsilon_r$) and loss tangent (tanδ) with frequency for Li$_2$SiO$_3$ ceramic sintered at three different temperatures. In all cases both the parameters decrease on increasing frequency indicating a normal behavior of dielectric materials having mobile charge carriers (i.e., ions and electrons). The fall in dielectric constant arises from the fact that the polarization does not occur instantaneously with the application of the applied electric field as charges possess inertia. The delay in response towards the impressed alternating electric field leads to loss and hence decline in dielectric constant. The loss tangent (tanδ) also decreases with increasing frequency. It is observed that at higher frequency, these parameters became almost frequency independent. It is also observed that at high temperatures (> 250 °C), width of the plateau region decreases with the increase of sintering temperature. The sample sintered at 900 °C has a low dielectric loss at high temperatures. The frequency dependence of loss
tangent exhibits interesting results. It is evident from Fig. 4 that at high temperatures (>300 °C), the loss tangent reaches the instrumental saturation value (\(\tan\delta = 10\)) in the low frequency region but at high frequency (i.e. 1 MHz) the value of \(\tan\delta\) drops down from this saturation drastically. It shows the possibility of using the material for high frequency applications with low dissipation factor.

![Graph showing variation in dielectric constant (\(\varepsilon_r\)) and loss tangent (\(\tan\delta\)) with frequency for samples sintered at different temperatures.](image)

*Fig. 4. Variation of dielectric constant (\(\varepsilon_r\)) and loss tangent (\(\tan\delta\)) with frequency for the samples sintered at (a)800 °C (b)850 °C and (c)900 °C.*
Table 1 shows the room temperature $\varepsilon_r$ and tan$\delta$ values of the samples measured at 1 MHz. The dielectric constant of the samples is in the range of 15.13 – 18.51.

**Table 1: Physical properties of Li$_2$SiO$_3$ ceramic sintered at different temperatures.**

<table>
<thead>
<tr>
<th>Sintering temperature ($^\circ$C)</th>
<th>$\varepsilon_r$ at 1 MHz at 35$^\circ$C</th>
<th>tan$\delta$ at 1 MHz at 35$^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>15.13</td>
<td>0.069</td>
</tr>
<tr>
<td>850</td>
<td>18.19</td>
<td>0.066</td>
</tr>
<tr>
<td>900</td>
<td>18.51</td>
<td>0.070</td>
</tr>
<tr>
<td>950</td>
<td>17.82</td>
<td>1.565</td>
</tr>
</tbody>
</table>

Fig. 5 (a) variation of dielectric constant ($\varepsilon_r$) of all the samples with frequency at room temperature (35$^\circ$C) (b) variation of loss tangent (tan$\delta$) with sintering temperature at 3 MHz.

The sample sintered at 900 $^\circ$C for 2 h have the lowest dielectric loss at 3 MHz (Fig. 5 (b)) and high dielectric constant (Fig. 5 (a)) at room temperature. It is clear that the sample sintered at 900 $^\circ$C has the best dielectric property.

**4. Conclusions**

The Li$_2$SiO$_3$ ceramic was prepared by a solid-state reaction technique. X-ray structural study reveals an orthorhombic crystal structure of the material. The optimum sintering temperature for Li$_2$SiO$_3$ ceramic was found to be 900 $^\circ$C. The surface morphology of the compound is studied through FE-SEM, which shows the uniform distribution of well compacted grains throughout the sample. Dielectric constant and dissipation factor decrease with the increase in frequency. The sample sintered at 900 $^\circ$C has the best dielectric property.
References

IMPEDANCE AND CONDUCTIVITY ANALYSIS OF Li₂SiO₃ CERAMIC

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Lithium metasilicate (Li₂SiO₃) ceramic was prepared via solid-state reaction technique. The formation of the compound in an orthorhombic crystal structure was confirmed by an X-ray diffraction (XRD) technique. Surface morphology of the compound was studied by field emission scanning electron microscopy (FE-SEM). Detailed studies on the electrical behavior (complex impedance [Z*], electrical conductivity and relaxation mechanism) of the Li₂SiO₃ ceramic have been carried out at various temperatures. The Nyquist plots suggest that the grains and grain boundaries are responsible in the conduction mechanism of the material at high temperature. The frequency dependent conductivity and dielectric relaxation of Li₂SiO₃ ceramic are investigated over a frequency range from 100 Hz to 5 MHz and in a temperature range from 35 °C to 350 °C by using alternating current impedance spectroscopy. The conductivity isotherms show a transition from frequency independent dc region to dispersive region where the conductivity continuously increases with the increasing frequencies.

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Keywords: Ceramics; Grain boundaries; Impedance properties; Sintering

1. Introduction

Lithium ceramics are of research interest because of their technological applications. Thus, for example, there has been research in recent years on their application as electronic devices, as CO₂ captors and as breeder materials for nuclear fusion reactors, in addition to other more well-known applications such as in batteries and in low thermal expansion glass ceramics used in ceramic hobs [1–10]. Various properties of Lithium silicate ceramics such as dielectric, conductivity and other properties depend on the composition and microstructure. In this paper, we present a systematic study of Lithium metasilicate (Li₂SiO₃) ceramic prepared by solid state reaction technique and the influence of temperature and frequency on impedance properties.

2. Experimental

2.1. Material preparation

Lithium metasilicate (Li₂SiO₃) ceramic was prepared using a high-temperature solid-state reaction technique. Li₂CO₃ and SiO₂ of analytical grade were thoroughly mixed in agate mortar for 2 h, including wet mixing in acetone media for 1 h. The mixture was then calcined at 900 °C for 4 h. The calcined powder was then cold pressed into cylindrical pellets of 12 mm diameter and 2 - 3 mm of thickness at a pressure of 80 MPa using a hydraulic press. PVA (poly vinyl alcohol) was used as a binder for preparing pellets. These pellets were then sintered with optimized temperature and time (900 °C, 2 h) in an air atmosphere.

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2.2. Material characterization

The formation of the single phase compound was confirmed by X-ray diffraction (XRD) in a wide range of Bragg angles $2\theta$ ($10^\circ \leq 2\theta \leq 90^\circ$) with Co radiation (1.78897 Å). The surface morphology was recorded using field emission scanning electron microscope. The electrical parameters were measured using an impedance analyzer (HIOKI LCR HI Tester, Model: 3532) as a function of temperature over a wide range of frequencies (100 Hz – 5 MHz) after drying the silver coated sample at 150 °C for 2 h.

3. Results and discussion

3.1. Structural

The XRD pattern of the sintered sample is shown in Fig. 1. Detailed analysis of the pattern exhibits the formation of new compound in orthorhombic crystal system with lattice parameters: $a=9.396$ Å, $b=5.396$ Å, $c=4.661$ Å, which is in well agreement with the structure given in JCPDS file number 83-1517. The crystallite size ($D$) of the compound was determined using the broadening of a few XRD peaks using the Scherrer’s equation [11], 

$$D = \frac{0.89\lambda}{(\beta_{1/2}\cos \theta)},$$

where $\lambda = 1.78897$ Å and $\beta_{1/2}$ is the peak width of the reflection at half intensity. The average crystallite size was found to be ~ 30 nm. Other effects of the broadening were ignored. Fig. 1 (inset) shows the field emission scanning electron micrograph of the sample at room temperature. The FESEM micrograph was taken on the fractured surface of the sample using scanning electron microscope. The highly distinctive, more or less uniform and compact grain distributions (with less voids) are observed. It shows the polycrystalline texture of the material. The average grain size was found to be 1 – 3 µm.

![Fig. 1. Room temperature XRD pattern and FE-SEM micrograph (inset) of Li$_2$SiO$_3$ ceramic.](image)
3.2. Impedance analysis

Fig. 2(a) exhibits the variation of real part of impedance ($Z'$) with frequency at different temperature. The decrease in the magnitude of $Z'$ with the increase in both frequency as well as temperature indicates the increase in a.c. conductivity. The values of $Z'$ merge at higher frequency ($\geq 25$ kHz) which indicates the release of space charges. Fig. 2(b) represents the impedance loss spectrum (i.e. variation of imaginary part of impedance [$Z''$] with frequency). The nature of the pattern is characterized by (1) decreasing the height of the peaks with rising temperature (2) significant broadening of the peaks with the rising temperature and (3) marked asymmetry in the peak pattern. The curves show that the value of $Z''$ reaches maximum value of $Z''_{\text{max}}$ for temperature $\geq 250$ °C.

The relaxation time ($\tau$) was calculated from the frequency maxima ($f_{\text{max}}$) at $Z''_{\text{max}}$. At the peak, the relaxation is defined by the condition:

$$\omega_m \tau_m = 2\pi f_{\text{max}} \tau_m = 1$$
where, $\tau_m$ is the relaxation time and $f_{\text{max}}$ is the relaxation frequency. It is independent of the sample geometrical factors and depends basically on the intrinsic property of the material only. Relaxation time of the sample decreases with the increase in temperature (Table 1). This result suggests the presence of temperature-dependent electrical relaxation phenomenon in the material possibly due to migration of immobile species/defects.

**Table 1: Relaxation time ($\tau$), Bulk Resistance ($R_b$) and Relaxation Frequency ($f_b$) of Li$_2$SiO$_3$ ceramic.**

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Relaxation time ($\tau$) (in ms)</th>
<th>Bulk Resistance ($R_b$) (in kΩ)</th>
<th>Relaxation frequency ($f_b$) (in kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>$5.831 \times 10^{-1}$</td>
<td>6967.33</td>
<td>0.4</td>
</tr>
<tr>
<td>300</td>
<td>$2.915 \times 10^{-2}$</td>
<td>608.42</td>
<td>5</td>
</tr>
<tr>
<td>350</td>
<td>$2.915 \times 10^{-3}$</td>
<td>114.64</td>
<td>50</td>
</tr>
</tbody>
</table>

The Nyquist diagram ($Z''$ vs. $Z'$) obtained at different temperature over a wide range of frequencies (100 Hz - 5 MHz) has been displayed in the figure 3(a). The effect of temperature on the impedance parameter of the material becomes clearly visible with rising temperature. The straight lines with large slopes at lower temperature indicate the insulating behavior of the material. However, on increasing temperature, the slope of the lines decreases, and hence they bend towards $Z'$ - axis by which semicircle could be formed. The intercept of the semicircle on the real axis is the bulk resistance ($R_b$) (given in Table 1) of the sample. The resistance is obtained from the intersection of the semicircle and the $Z'$ axis. It is clear from the figure that the resistance decreases on increasing temperature. At much higher temperature (i.e. at 350 $^\circ$C); It was possible to trace two semicircles (i.e. figure inset). The appearance of two semicircles suggests the presence of both bulk as well as grain boundary effects in the polycrystalline sample. Each semicircle is a representative of RC circuit that corresponds to individual component of the material (Fig. 3(b) [inset]).
3.2. ac conductivity analysis

The electrical conductivity (ac) of the material has been investigated at different temperatures over a wide range of frequency. The ac electrical conductivity of the sample was calculated from the conductivity relation \( \sigma = \omega \varepsilon_0 \varepsilon \tan \delta \) where \( \varepsilon_0 \) is the vacuum dielectric permittivity and \( \omega \) is the angular frequency. Fig. 4 shows the frequency dependence of ac conductivity, \( \sigma (\omega) \) at various temperatures. It is evident from the figure that at low frequencies, conductivity shows frequency independent nature of the sample which gives rise to dc conductivity. However, at the higher frequencies, \( \sigma \) exhibits frequency dispersion. At higher temperatures (i.e. \( \geq 300 ^\circ \text{C} \)), \( \sigma \) exhibits frequency dispersion in low as well as in high frequency
regions. The temperature, at which grain resistance dominates over grain boundary resistance, is marked by a change in slope of ac conductivity with frequency. The frequency at which the change of slope takes place is known as the hopping frequency. The a.c. conductivity of the sample increases with the increase of temperature.

Fig. 4. Frequency dependence of a.c. conductivity ($\sigma_{ac}$) at various temperatures for Li$_2$SiO$_3$ ceramic sintered at 900°C for 2 h.

4. Conclusions

The Li$_2$SiO$_3$ ceramic was prepared by a solid-state reaction technique. X-ray structural study reveals an orthorhombic crystal structure of the material. The surface morphology of the compound is studied through FE-SEM, which shows the uniform distribution of well compacted grains throughout the sample. The electrical parameters such as the real and imaginary parts of impedance and ac electrical conductivity as a function of frequency at different temperature have been studied through complex impedance spectroscopy. Nyquist plots show the presence of bulk and grain boundary effects in the system. The nature of variation of (ac) conductivity with temperature exhibits the NTCR behavior of the sample like that of a semiconductor.

References

Structural and dielectric studies of Li$_2$SiO$_3$ ceramic

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1. Introduction

Lithium silicate ceramic systems belong to technologically important class of ceramic materials for various applications. Thus, for example, there has been research in recent years on their application as electronic devices, as CO$_2$ captors and as breeder materials for nuclear fusion reactors, in addition to other more well-known applications such as in batteries and in low thermal expansion glass ceramics used in ceramic hobs [1–9]. Various properties of Lithium silicate ceramics such as dielectric, conductivity and other properties depend on the composition and microstructure. In this paper, we present a systematic study of Lithium metasilicate (Li$_2$SiO$_3$) ceramic prepared by solid state reaction technique and the influence of temperature and frequency on dielectric properties.

2. Experimental

Lithium metasilicate (Li$_2$SiO$_3$) ceramic sample was prepared via solid-state reaction technique. Li$_2$CO$_3$ and SiO$_2$ of analytical grade were thoroughly mixed in agate mortar for 2 h, including wet mixing in acetone media for 1 h. The mixture was calcined at 900 °C for 4 h. The calcined powder was then cold pressed into cylindrical pellets of 12 mm diameter and 2–3 mm of thickness at a pressure of 80 MPa using a hydraulic press. PVA (poly vinyl alcohol) was used as a binder for preparing pellets. These pellets were then sintered at 900 °C for 2 h. The compound formation was confirmed by X-ray diffraction (XRD) in a wide range of the Bragg angles 2θ (10° ≤ 2θ ≤ 90°) using Cu (λ = 1.78897 Å) radiation. FE-SEM was used to study the surface morphology of the ceramic. The dielectric permittivity ($\varepsilon_r$) and loss tangent (tanδ) of the sample was measured using an impedance analyzer (HIOKI 3532 LCR Hi-TESTER) in the frequency range (5 kHz–5 MHz) at room temperature and temperature (35 °C–400 °C) at 1 kHz, 10 kHz, 100 kHz and 1 MHz.

3. Results and discussion

3.1. Structural

The XRD pattern of the sintered sample is shown in Fig. 1. All of the reflection peaks of XRD pattern were indexed in different crystal systems and unit cell configurations. Detailed analysis of the pattern exhibits that the sample has an orthorhombic structure with lattice parameters: a = 9.396 Å, b = 5.396 Å, c = 4.661 Å, which is in well agreement with the orthorhombic structure given in JCPDS card number 83-1517. The crystallite size of the powder sample was roughly estimated from broadening of reflection peaks using Scherrer’s equation [10],

$$D = \frac{0.9\lambda}{B_{1/2} \cos \theta},$$

where $\lambda = 1.78897$ Å and $\theta_{1/2}$ = half peak width of reflections. The average crystallite size was found to be ~30 nm.

Fig. 1 (inset) shows the field emission scanning electron micrograph of the sample at room temperature. The FE-SEM micrograph was taken on the fractured surface of the sample using scanning electron microscope. The highly distinctive, more or less uniform and compact grain distributions (with less voids) are observed. It shows the polycrystalline texture of the material. The average grain size was found to be 1–3 μm.

3.2. Dielectric properties

Fig. 2(a) shows the variation of dielectric permittivity ($\varepsilon_r$) and loss tangent (tanδ) of Li$_2$SiO$_3$ ceramic with frequency at room temperature.
Both the parameters decrease on increasing frequency indicating a normal behavior of dielectric materials having mobile charge carriers (i.e., ions and electrons) [11]. The fall in dielectric permittivity arises from the fact that the polarization does not occur instantaneously with the application of the electric field as charges possess inertia. The delay in response towards the impressed alternating electric field leads to loss and hence decline in dielectric permittivity. The loss tangent (tanδ) also decreases with increasing frequency. It is observed that at higher frequency, these parameters became almost frequency independent. The dielectric permittivity and dielectric loss of the sample at 5 MHz are 25.66 and 0.033 at room temperature.

Fig. 2(b) shows the variation of dielectric permittivity (εr) of Li2SiO3 ceramic with temperature at selected frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz). From these curves, it can be seen that dielectric permittivity increases almost linearly with increasing temperature (i.e. from 35 °C to 140 °C) and then starts decreasing slowly. The broadening of dielectric peaks may be attributed to the disorder present in the system. For higher temperatures (>200 °C), the charge carriers are free to move through the crystal causing a polarization and hence εr increases. The charge accumulation at the grain boundaries is responsible for higher values of dielectric permittivity at low frequencies [12,13]. At high frequency εr results from the grains which have a small dielectric permittivity.

Fig. 1. Room temperature XRD pattern and FE-SEM micrograph (inset) of Li2SiO3 ceramic.

Fig. 2. Variation of (a) dielectric permittivity (εr) and dielectric loss (tanδ) with frequency at room temperature, (b) variation of dielectric permittivity (εr) and tanδ (c) with temperature for Li2SiO3 ceramic and (d) variation of ac conductivity (lnσac) as a function of inverse of absolute temperature (10^3/T) at three different frequencies for Li2SiO3 ceramic.
The variation of dielectric loss ($\tan \delta$) with temperature for the sample is shown in Fig. 2(c). The loss tangent increases slowly with rise of temperature. This increase in $\tan \delta$ may be due to enhancement in conductivity of the material. The rapid increase of dielectric loss at higher temperature in low frequency region may be due to space charge polarization. It is also interesting to observe that the dielectric loss at high frequencies is much lower compared to those at low frequencies. It shows the possibility of using the material for high frequency applications with low dissipation factor.

3.3. Conductivity study

Fig. 2(d) shows the variation of ac conductivity ($\sigma_{ac}$) as a function of inverse of absolute temperature ($10^3/T$) at three different frequencies. The ac conductivity ($\sigma_{ac}$) and activation energy ($E_a$) of the sample were calculated using the relation $\sigma = \sigma_0 \exp(-E_a/k_B T)$, where $\varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$ is the vacuum permittivity, $\omega$ is the angular frequency, $K_B$ is the Boltzmann constant and $\sigma_0$ is the pre-exponential factor. Conductivity of the sample at higher temperature is higher, which is very common behavior in most of the dielectric ceramics [14]. In the lower temperature region (I), there is linear variation in conductivity with temperature with strong frequency dependence. In the higher temperature range (II), conductivity varies exponentially with the temperature but with relatively weak frequency dependence. The nature of variation of $\sigma_{ac}$ over a wide temperature range supports the thermally activated transport properties of the material. The activation energy ($E_a$) of the sample was calculated from the slope of $\ln \sigma$ vs. $1/T$ curves. The value of activation energy of the compound at 10 kHz, 100 kHz and 1 MHz is found to be 0.059, 0.053 and 0.070 eV (region I) and 1.19, 0.81 and 0.50 eV (region II), respectively. The activation energy was found to increase on increasing temperature. This behavior suggests that the conduction mechanism in Li$_2$SiO$_3$ ceramic may be due to the hopping of charge carriers. The value of activation energy of the sample in the region (I) is found to be very low. The smaller activation energy of the compound ($\ll 1$ eV) within moderate temperature range suggests the presence of singly ionized oxygen vacancies in the conduction process.

4. Conclusions

Lithium metasilicate (Li$_2$SiO$_3$) ceramic have been prepared via solid state reaction technique. Dielectric permittivity and dissipation factor decrease with the increase in frequency. The values of dielectric permittivity at relatively low frequency were very high and are attributed to the existence of interfacial polarization that arises due to the inhomogeneous structure of the material ensuring the presence of secondary phases at the grain boundaries. The loss tangent as a function of frequency shows an interesting result. The activation energies at higher temperatures were found to be less than 1 eV. This suggests the presence of singly ionized oxygen vacancies in the conduction process.

References

A comparative study on the dielectric and ac conductivity of ionically conducting lithium silicate ceramics

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Abstract Lithium silicate ceramics were prepared via solid-state reaction technique. Two ceramics with different molar ratios of Li$_2$CO$_3$/SiO$_2$ (designed as L$_1$S and L$_2$S) were prepared for dielectric studies. X-ray diffraction pattern showed that L$_1$S ceramic is obtained as single-phase composition, whereas L$_2$S ceramic exhibit multiphase with Li$_4$SiO$_4$ as a major phase. Dielectric studies of the compounds shows a strong frequency dispersion of permittivity in the low frequency region followed by a nearly frequency independent behavior in the high frequency region. Dielectric loss (tan δ) seems to be reduced at higher frequencies after reaching the instrumental saturation. The present study reveals that high dielectric compositions can be realized by Li$_2$O-rich system (i.e., L$_2$S ceramic). From the dielectric studies, we can prescribe L$_1$S ceramic as a good dielectric material since it possesses low dielectric loss. The values of activation energies suggest the presence of singly ionized oxygen vacancies in the conduction process.

Keywords AC conductivities · Batteries · Li$^+$ conductors · XRD

Introduction

Lithium silicate (LS) ceramic systems belong to technologically important class of ceramic materials for various applications. Thus, for example, there has been research in recent years on their application as electronic devices, as CO$_2$ captors and as breeder materials for nuclear fusion reactors, in addition to other more well-known applications such as in batteries and in low thermal expansion glass ceramics used in ceramic hobs [1–10]. Among these ceramics, LSs (Li$_2$SiO$_3$ and Li$_4$SiO$_4$) seem to present very good properties as materials in nuclear research as tritium ($^3$T) breeding materials and as materials to absorb carbon dioxide [11–16]. Various properties of LS ceramics such as dielectric, conductivity and other properties depend on the composition. Keeping in view of these facts, we have carried out detailed comparative studies of the effect of Li$_2$O on the structural, dielectric and ac conductivity properties of LS ceramic prepared by solid state reaction method.

Experimental

Material preparation

LS ceramic sample was prepared via solid-state reaction technique. Two samples were prepared by taking AR grade chemicals in the following molar ratios:

Li$_2$CO$_3$/SiO$_2$ (1 : 1) designed as L$_1$S and

Li$_2$CO$_3$/SiO$_2$ (2 : 1) designed as L$_2$S

In the first stage, the powder was thoroughly mixed in agate mortar for 2 h, including wet mixing in acetone media for 1 h. The mixture was then calcined at 900°C for 4 h. Cylindrical pellets of 12-mm diameter and 2–3 mm thickness were prepared in a hydraulic press using 80 MPa pressure. PVA was used as a binder for preparing pellets. These pellets were then sintered with optimized temperature and time (900°C, 2 h) in an air atmosphere. The sintered pellets were polished with zero grain emery paper, and coated with high purity silver paste and then dried for 2 h at 150°C.
Material characterization

The sintered samples were crushed and the phase constitution was studied by X-ray diffraction (XRD) in a wide range of the Bragg angles $2\theta$ (10° $\leq 2\theta \leq$ 90°) using Co ($\lambda=1.78897$ Å) radiation. The dielectric permittivity ($\varepsilon_r$) and dielectric loss (tan $\delta$) of the samples were measured using an impedance analyzer (HIOKI 3532 LCR Hi-TESTER) in the frequency range (5 kHz to 5 MHz) at room temperature and temperature (30–400°C) at frequency (1 kHz, 10 kHz, 100 kHz and 1 MHz).

Results and discussion

Structural study

The XRD pattern of the sintered samples is shown in Fig. 1a [17]. The sharp and single reflection peaks of $L_1$S ceramic can be readily indexed to the orthorhombic $Li_2SiO_3$ structure with lattice parameters: $a=9.396$ Å, $b=5.396$ Å, $c=4.661$ Å, which is in good agreement with JCPDS file number 83-1517. Sharp and single peaks of $L_1$S ceramic confirmed the formation of single-phase compound with a minor trace of $Li_2SiO_3$ phase. For $L_2$S ceramic (Fig. 1b), it is clearly observed that the main crystal phase is $Li_4SiO_4$ (JCPDS file No. 76-1085) accompanied by $Li_2SiO_3$ phase (JCPDS file No. 83-1517), $Li_2Si_2O_5$ phase (JCPDS file No. 80-1470) and $SiO_2$ phase (JCPDS file No. 86-0681).

Dielectric properties

The frequency dependence of the dielectric parameters (i.e., $\varepsilon_r$ and tan $\delta$) of $L_1$S [17], and $L_2$S at room temperature is compared in Fig. 2. Both the parameters decrease on increasing frequency indicating a normal behavior of dielectric materials having mobile charge carriers (i.e., ions and electrons) [18]. Table 1 shows the room temperature $\varepsilon_r$ and tan $\delta$ values of the samples measured at 1 and 5 MHz, respectively. The fall in dielectric constant arises from the fact that the polarization does not occur instantaneously with the application of the electric field as charges possess inertia. The delay in response towards the impressed alternating electric field leads to loss and hence decline in dielectric constant [17]. The value of dielectric loss (tan $\delta$) of $L_1$S is smaller than that of its counterpart (i.e., $L_2$S). The dielectric loss (tan $\delta$) also decreases with increasing frequency. It is observed that at higher frequency, these parameters became almost frequency-independent.

Figure 3 shows comparison of relative dielectric constant ($\varepsilon_r$) of $L_1$S [17], and $L_2$S ceramics with temperature at four different frequencies. The value of dielectric constant of $L_2$S is higher than that of its counterpart (i.e., $L_1$S). For higher
temperatures, the charge carriers are free to move through the crystal causing a polarization, and hence $\varepsilon_r$ increases. The charge accumulation at the grain boundaries is responsible for higher values of dielectric constant at low frequencies [19, 20]. At high frequency, $\varepsilon_r$ results from the grains which have a small dielectric constant. The Li$_2$O-rich system (i.e., L$_2$S) is expected to have a higher dielectric constant, due to the polarizability of the Li$^+$ ions (1.20 Å$^3$), which are higher than those of Si$^{4+}$ ions (0.87 Å$^3$). Increasing Li$_2$O content will increase the polarization of ion shift and thus raise the dielectric constant. In Li$_2$O-rich system (i.e., L$_2$S), the maximum dielectric constant ($\varepsilon_{\text{max}}$) of 5,000 at 400°C fell down to 38 as frequency increases from 1 kHz to 1 MHz. This shows that the dielectric relaxation behavior in the material is complicated [20]. Attempts are being made to analyze these new results.

Figure 4 shows comparison of dielectric loss (tan $\delta$) of L$_1$S and L$_2$S ceramics with temperature at four different frequencies. The dielectric loss of both the samples reaches the instrumental saturation value (tan $\delta=10$) at low frequencies and drops down from this saturation at high frequencies. This shows the possibility of using the material for high frequency applications with low dissipation factor.

Table 1 Physical properties of LS ceramics sintered at 900°C

<table>
<thead>
<tr>
<th>Physical parameters</th>
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<td>at 5 MHz</td>
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Fig. 3 Variation of dielectric constant ($\varepsilon_r$) of a L$_1$S and b L$_2$S with temperature at different frequencies (1 kHz–1 MHz)

Fig. 4 Comparison of variation of dielectric loss (tan $\delta$) of a L$_1$S and b L$_2$S ceramics with temperature at different frequencies
Dielectric loss (tan δ) of ceramic is dependent on a variety of factors. At least two types of dielectric losses for ceramics have been distinguished: migration losses caused by the movement of mobile ion (Li⁺), and deformation losses by defect or deformation of the basic silicon dioxide network. The higher concentration of alkali ions (Li⁺) in L₂S ceramics results in higher losses. L₁S ceramic is best in terms of dielectric loss.

Conductivity study

Figure 5 compares the variation of ac conductivity (ln σ_{ac}) with inverse of absolute temperature (10^3/T) for L₁S and L₂S ceramics at 1 MHz. The ac conductivity (σ_{ac}) and activation energy (E_a) of both the samples were calculated using the relation σ = ε₀κ₀ when tan δ and σ = σ₀exp(-E_a/K_B T), where ε₀ is the vacuum permittivity, ω is the angular frequency, K_B is Boltzmann constant and σ₀ is the pre-exponential factor. An anomaly or slope change was observed in our dielectric studies of the samples. The corresponding temperature of the anomaly (as observed in ac conductivity plot, Fig. 5) reflects the transition point where the bulk conduction ceased and grain boundary conduction starts up. It is well known that grain boundary conduction in polycrystalline ceramics takes place at higher temperatures [21] though the temperature varies from material to material depending on the grain growth as it is nicely depicted in Fig. 5 by appearance of their anomaly at different temperatures. With a further increase in temperature after the bend, a linear increase in ac conductivity is observed which corroborates the grain boundary conduction in the materials. Conductivity of L₂S ceramic is higher than that of its counterpart (i.e., L₁S). L₂S ceramic consists of Li₄SiO₄ phase, which are known as an important class of fast Li-ion conducting materials. These materials usually accommodate Li vacancies which allow fast Li-ion conduction. Conductivity of both the samples (i.e., L₁S and L₂S) at higher temperature is higher, which is very common behavior in most of the dielectric ceramics [22]. In the lower temperature region, there is linear variation in conductivity with temperature for both the samples. The nature of variation of σ_{ac} over a wide temperature range supports the thermally activated transport properties of the material. The activation energy (E_a) of both the samples was calculated from the slope of ln σ vs. 1/T curves. The value of activation energy of the samples in the low temperature region is found to be very low. The smaller activation energy of the samples (<<1 eV) within moderate temperature range suggests the presence of singly ionized oxygen vacancies in the conduction process.

Conclusions

LS ceramics have been prepared via solid state reaction technique. Dielectric constant and dissipation factor decrease with the increase in frequency for both the samples. The values of dielectric constant at relatively low frequency were very high and are attributed to the existence of interfacial polarization. The dielectric loss as a function of frequency shows an interesting result. The higher concentration of alkali ions (Li⁺) in L₂S ceramics results in higher dielectric constant and higher losses. From the dielectric studies, we can prescribe L₁S ceramic as a good dielectric material compared to L₂S ceramic since it possesses low dielectric loss. The activation energy increases with the increase of temperature for both the ceramics. The activation energies for both the samples were found to be less than 1 eV. This suggests the presence of singly ionized oxygen vacancies in the conduction process.
References

Structural, dielectric and electrical properties of lithium silicate ceramics: a comparative study

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Abstract Lithium silicate (LS) ceramics were prepared via a solid-state reaction technique. Two ceramics with different molar ratios of \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) (1:1 and 1:2) were prepared for dielectric studies. X-ray diffraction pattern showed that \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) (1:1) ceramic is obtained as single phase composition whereas \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) (1:2) ceramic exhibit a multiphase structure with \( \text{Li}_2\text{SiO}_3 \) as a major phase. Microstructural analysis shows that the compounds have well defined grains separated by grain boundaries. Dielectric and electrical properties of the samples were studied in a wide temperature (30–400 °C) and frequency ranges (100 Hz–5 MHz). From the dielectric studies, we can prescribe \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) (1:2) ceramic as a good dielectric material since it possesses low dielectric loss. Detailed analysis of the impedance data suggests that the conduction of \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) (1:2) ceramic is mainly due to the bulk effects whereas the complex impedance plots of \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) (1:1) ceramic suggests the presence of both bulk as well as grain boundary contributions. The bulk resistance of the samples has been observed to decrease with rise in temperature showing a typical negative temperature coefficient of resistance behavior. The low activation energies of the samples suggest the presence of singly ionized oxygen vacancies in the conduction process.

1 Introduction

Lithium silicate (LS) ceramic systems belong to technologically important class of ceramic materials for various applications. Thus, for example, there has been research in recent years on their application as electronic devices, as \( \text{CO}_2 \) capsors and as breeder materials for nuclear fusion reactors, in addition to other more well-known applications such as in batteries and in low thermal expansion glass ceramics used in ceramic hobs [1–10]. Various properties of LS ceramics such as dielectric, conductivity, impedance and other properties depend on the composition and microstructure. In the present work, we have carried out detailed comparative studies on the structural, dielectric, ac conductivity and electrical properties of LS ceramics.

2 Experimental

2.1 Material preparation

Lithium silicate ceramics were prepared via solid-state reaction technique. Two samples were prepared by taking AR grade chemicals in the following molar ratios:

- \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) (1:1) designed as LS-1 and
- \( \text{Li}_2\text{CO}_3/\text{SiO}_2 \) (1:2) designed as LS-2

In the first stage, the powder was thoroughly mixed in agate mortar for 2 h, including wet mixing in acetone media for 1 h. The mixture was then calcined at 900 °C for 4 h. The calcined powder was ground thoroughly for about 2 h. The finely ground powder is then mixed with 5-wt% PVA, as binder. The mixture was dried and then ground to get fine powder. Cylindrical disks of about 2–3 mm height and 12 mm diameter were made by applying a pressure of 80 MPa. These pellets were then sintered at 900 °C for 2 h in an air atmosphere. The sintered pellets were polished with zero grain emery paper, and coated with high purity silver paste and then dried for 2 h at 150 °C.
2.2 Material characterization

The sintered samples were crushed and the phase constitution was studied by X-ray diffraction (XRD) in a wide range of the Bragg angles $2\theta$ ($10^\circ \leq 2\theta \leq 90^\circ$) using Co ($\lambda = 1.78897$ Å) radiation. FE-SEM was used to study the surface morphology of the samples. Dielectric and impedance parameters of the samples were measured using an impedance analyzer (HIOKI 3532 LCR Hi-TESTER) over a wide temperature (30–400 °C) and frequency ranges (100 Hz–5 MHz).

3 Results and discussion

3.1 Structural study

The XRD pattern of the sintered samples is shown in Fig. 1. The sharp and single reflection peaks of LS-1 ceramic (Fig. 1a) [11], can be readily indexed to the orthorhombic Li$_2$SiO$_3$ structure with lattice parameters of $a = 9.396$ Å, $b = 5.396$ Å, $c = 4.661$ Å, which is in well agreement with JCPDS card number 83-1517. For LS-2 ceramic (Fig. 1b), it’s clearly observed that the main crystal phase is Li$_2$SiO$_3$ (JCPDS card number 83-1517), accompanied by Li$_2$Si$_2$O$_5$ phase (JCPDS card number 04-0436) and crystalline Quartz low (SiO$_2$) phase (JCPDS card number 86-1629).

The FE-SEM micrograph was taken on the fractured surface of the pellets using field emission scanning electron microscope. The average grain size of LS-1 and LS-2 ceramics was found to be 1–3 μm [11] and 2–4 μm respectively. It shows the polycrystalline texture of the material. LS-1 sample developed more irregular grain boundaries with a large number of small grains present at grain junctions and grain boundaries, indicating that the grain growth of large grains was inhibited by the small grains during sintering. The highly distinctive, more or less uniform and compact grain distributions (with less voids) are observed. Figure 2 shows dense microstructure of the samples with different magnifications at room temperature.

3.2 Dielectric properties

Properties such as dielectric constant, dielectric loss and electrical conductivity are closely related to microstructure as well as to composition. The frequency dependence of the dielectric parameters (i.e., $\varepsilon_r$ and $\tan\delta$) of LS-1 [11] and LS-2 at room temperature is compared in Fig. 3. Both the parameters decrease on increasing frequency indicating a normal behavior of dielectric materials having mobile charge carriers (i.e., ions and electrons) [12]. The fall in dielectric constant arises from the fact that the polarization does not occur instantaneously with the application of the electric field as charges possess inertia. The delay in response towards the impressed alternating electric field leads to loss and hence decline in dielectric constant [11]. Table 1 shows the room temperature $\varepsilon_r$ and $\tan\delta$ values of the samples measured at 1 MHz. LS-1 ceramic has the highest dielectric constant at room temperature. LS-2 ceramic has the lowest dielectric constant, since SiO$_2$-rich ceramic is expected to possess a lower dielectric constant. The low dielectric constant provides an attractive feature for minimizing cross-talk and increasing signal transmission speeds. The dielectric loss (tan$\delta$) also decreases with increasing frequency.

Figure 4 shows comparison of relative dielectric constant ($\varepsilon_r$) of LS-1 [11] and LS-2 ceramics with temperature at 100 kHz and 1 MHz. The value of dielectric constant of LS-1 is higher than that of its counterpart (i.e., LS-2). The value of $\varepsilon_r$ starts increasing almost linearly with temperature and then starts decreasing slowly in both the samples. The broadening of dielectric peaks may be attributed to the disorder present in the system. For higher temperatures, the charge carriers are free to move through the crystal causing a polarization and hence $\varepsilon_r$ increases [11]. The peak value of the dielectric constant (i.e., $\varepsilon_{r\text{max}}$) at different frequencies for both the samples is shown in Table 1. The charge accumulation at the grain boundaries is responsible for higher values of dielectric constant at low frequencies [13, 14]. At high frequency, $\varepsilon_r$ results from the grains which have a small dielectric constant [11]. The SiO$_2$-rich ceramic, i.e., LS-2 is expected to possess lower dielectric constant since the dielectric constant of SiO$_2$ is the lowest among the ceramics.

Figure 5 shows comparison of dielectric loss (tan$\delta$) of the LS-1 [11] and LS-2 ceramics with temperature at 100 kHz and 1 MHz respectively. Dielectric loss (tan$\delta$) of ceramic is dependent on a variety of factors. At least two
types of dielectric losses for ceramics have been distinguished: migration losses caused by the movement of mobile ion (Li$^+$), and deformation losses by defect or deformation of the basic silicon dioxide network [15]. Among the ceramics, silica ceramic has the lowest tanδ in the high frequency region. LS-2 ceramic is best in terms of dielectric loss, since LS-2 is rich in SiO$_2$ content. Dielectric loss of ceramic is also dependent on microstructure. The increase in the grain size of LS-2 ceramic deteriorates the dielectric loss. Decrease of grain boundaries per unit volume result in a material (i.e., LS-2) with a lower dielectric loss (tanδ) and better polarisability.

3.3 Conductivity study

Figure 6 compares the variation of ac conductivity ($\ln\sigma_{ac}$) with inverse of absolute temperature ($10^3/T$) for LS-1 [11] and LS-2 ceramics at two different frequencies. The ac conductivity ($\sigma_{ac}$) and activation energy ($E_a$) of both the samples were calculated using the relation $\sigma = \omega\varepsilon_0\tan\delta$ and $\sigma = \sigma_0\exp\left(-E_a/K_BT\right)$, where $\varepsilon_0$ is the vacuum permittivity, $\omega$ is the angular frequency, $K_B$ is the Boltzmann constant and $\sigma_0$ is the pre-exponential factor. An anomaly or slope change was observed in our dielectric studies of the samples. The corresponding temperature of the anomaly (as observed in ac conductivity plot, Fig. 6) reflects the transition point where the bulk conduction ceased of and grain boundary conduction starts up. It is well known that grain boundary conduction in polycrystalline ceramics takes place at higher temperatures [16] though the temperature varies from material to material depending on the grain growth as it is nicely depicted in Fig. 6 by appearance of their anomaly at different temperatures. With a further increase in temperature after the bend, a linear increase in ac conductivity is observed which corroborates the grain boundary conduction in the materials. Conductivity of both the samples (i.e. LS-1 and LS-2) at higher temperature (region II) is higher, which is very common.

![Fig. 2](image-url)
behavior in most of the dielectric ceramics [17]. In the lower temperature region (region I), there is linear variation in conductivity with temperature with strong frequency dependence for both the samples. The nature of variation of $\sigma_{ac}$ over a wide temperature range supports the thermally activated transport properties of the materials. The activation energy ($E_a$) of both the samples was calculated from the slope of $\ln \sigma$ versus $1/T$ curves. The values of ($E_a$) at different frequency are given in Table 2.

The activation energy was found to increase on increasing temperature. This behavior suggests that the conduction mechanism in LS ceramic may be due to the hopping of charge carriers. The value of activation energy ($E_a$) of LS-1 is higher than that of its counterpart (i.e., LS-2). The value of activation energy of both the samples in the low temperature region (region I) is found to be very low. The smaller activation energy ($\ll 1$ eV) of the samples within moderate temperature range suggests the presence of singly ionized oxygen vacancies in the conduction process.

### 3.4 Impedance analysis

The electrical behavior of the system was studied over a wide range of frequency and temperature using a complex impedance spectroscopy technique (CIS). This technique
enables us to separate the real and imaginary components of the complex impedance parameters, and hence provides information of the structure–property relationship of the sample. A polycrystalline material usually has grain and grain boundary properties with different time constants at high temperature leading to two successive semicircles. It can conventionally be displayed in a complex plane plot (Nyquist diagram) in terms of the following formalism:

Complex impedance, \( Z^* (\omega) = Z' - jZ'' \)  \( \tag{1} \)

where \( Z = |Z| \cos \theta \) and \( Z'' = |Z| \sin \theta \).

Figures 7 and 8 show a set of Nyquist plots (\( Z' \) vs. \( Z'' \)) of LS-1 and LS-2 ceramic over a wide range of frequency (100 Hz–5 MHz) at different temperatures. The effect of temperature on impedance parameter of the materials becomes clearly visible with rise in temperature. A single semicircular arc has been observed in a wide temperature range \( (\leq 250 \, ^\circ \text{C}) \) (Fig. 7a) for LS-1 ceramic whereas LS-2 ceramic shows a single semicircular arc at all temperatures (Fig. 8). This indicates that the electrical properties of LS-2 ceramic arise mainly due to the bulk effects. It also indicates that as the temperature increases intercept point on the real axis shifts towards the origin indicating the

![Fig. 5 Temperature variation of loss tangent (tanδ) of LS-1 and LS-2 ceramics at a 100 kHz and b 1 MHz](image)

![Fig. 6 Variation of ac conductivity (lnσac) as a function of inverse of absolute temperature (10^3/\( T \)) at a 100 kHz and b 1 MHz](image)

<table>
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<tr>
<th>Compositions</th>
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<th>(Region I) ( E_a ) (in eV)</th>
<th>(Region II) ( E_a ) (in eV)</th>
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<td></td>
<td>1 MHz</td>
<td>0.070</td>
<td>0.50</td>
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<tr>
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<td></td>
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<td>0.058</td>
<td>0.13</td>
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</table>

Table 2 Comparison of activation energies \( E_a \) (in eV) of LS-1 and LS-2 ceramics at 10, 100 kHz and 1 MHz
decrease in the resistive property of the materials. The intercept of the semicircle on the real axis is the bulk resistance \((R_b)\) of the samples. The values of bulk resistance \((R_b)\) and bulk capacitance \((C_b)\) of LS-1 and LS-2 ceramics are compared in Table 3. This type of electrical behavior can be explained in terms of an equivalent circuit comprising of a parallel combination of \(RC\) circuits (Figs. 7a, 8b). At much higher temperatures \((\geq 300 \, ^\circ C)\), it was possible to trace two semicircles (Fig. 7b) for LS-1 ceramic. The appearance of two semicircles in the studied temperature range suggests the presence of both bulk as well as grain boundary effects in the polycrystalline LS-1 ceramic sample. Each semicircle is a representative of an \(RC\) circuit that corresponds to individual component of the material (Fig. 7b, inset).

Figure 9 exhibits the variation of real part of impedance \((Z')\) with frequency at different temperatures for LS-1 and LS-2 ceramic. The decrease in the magnitude of \(Z'\) with increase in both frequency as well as temperature indicates the increase in ac conductivity for both the samples. The values of \(Z'\) merge at higher frequencies \((\geq 100 \, kHz)\) which

<table>
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<th>(f_r) (kHz)</th>
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Fig. 7 a Nyquist plot of LS-1 ceramic at 250 °C with equivalent circuit. b Nyquist plots of LS-1 ceramic at three different temperatures with equivalent circuit (inset)

Fig. 8 a Nyquist plots of LS-2 ceramic at two different temperatures. b Nyquist plots of LS-2 ceramic at two different temperatures with equivalent circuit

Table 3 Values of bulk resistance \((R_b)\), relaxation frequency \((f_r)\), and bulk capacitance \((C_b)\) of LS-1 and LS-2 ceramics at different temperatures
indicates the release of space charges. Figure 10 represents the impedance loss spectrum (i.e., variation of imaginary part of impedance \( z'' \) with frequency) of LS-1 and LS-2 ceramics. Figure 10a shows that the value of \( z'' \) for LS-1 ceramic reaches maximum value of \( z''_{\text{max}} \) for temperatures \((\geq 250 \, ^{\circ}\text{C})\) whereas the value of \( z'' \) for LS-2 ceramic reaches maximum for much higher temperatures \((\geq 350 \, ^{\circ}\text{C})\) (Fig. 10b). The average peak position regularly changes towards the higher frequency side on increasing temperature. Furthermore, as the temperature increases the magnitude of \( z'' \) decreases, the effect being more pronounced at the peak position. The shift of the peak towards higher frequency on increasing the temperature is due to the reduction in the bulk resistivity of the samples. The relaxation time \( \tau \) of both the samples was calculated from the frequency maxima \( f_{\text{max}} \) at \( z''_{\text{max}} \). At the peak, the relaxation is defined by the condition:

\[
\omega_{\text{m}} \tau = 2\pi f_{\text{max}} \tau = 1
\]

(2)

where \( \tau \) is the relaxation time at \( f_{\text{max}} \) and \( f_{\text{max}} \) is the relaxation frequency. It is independent of the sample geometrical factors and depends basically on the intrinsic properties (i.e., microstructure) of the material only. The \( \tau \)-value for both the samples is found to be decreasing on increasing temperature, which is a typical semiconductor behavior. The nature of variation of \( \tau \) with temperature shows that the relaxation process is temperature dependent. The variation of \( \tau \) as a function of inverse of absolute temperature for both the samples is shown in Fig. 11.

The activation energy evaluated from the slope of the curve, using the relation \( \tau = \tau_0 e^{-E_a/\kappa T} \) (where \( \tau_0 \) pre-exponential factor, \( E_a \) activation energy, \( k \) Boltzmann constant and \( T \) absolute temperature) is found to be 1.28 eV and 1.37 eV for LS-1 and LS-2 ceramics respectively.
Lithium silicate ceramics have been prepared via solid state reaction technique. The microstructure of the materials shows the formation of uniformly distributed grains throughout the surface. Dielectric constant and dissipation factor decrease with the increase in frequency for both the samples. The values of dielectric constant at relatively low frequency were very high and are attributed to the existence of interfacial polarization that arises due to the inhomogeneous structure of the material ensuring the presence of secondary phases at the grain boundaries. From the dielectric studies, we can prescribe LS-2 sample as a good dielectric material compared to LS-1 ceramic since it possesses low dielectric loss at higher temperatures. LS-2 ceramic may be used for straight forward insulation purposes owing to its low dielectric constant and low dielectric loss at higher temperatures. The low values of dielectric loss at higher frequencies also suggest application of these materials for microwave filters and infrared devices. CIS enables us to separate the grain and grain boundary contributions in the material. Both the grain and grain boundary resistances decrease with a rise in temperature. We used an equivalent circuit to explain electrical phenomena occurring inside the material. The nature of variation of ac conductivity with temperature exhibits the NTCR behavior of the sample like that of a semiconductor. The activation energy increases with the increase of temperature for both the samples. The activation energies at higher temperatures were found to be less than 1 eV. This suggests the presence of singly ionized oxygen vacancies in the conduction process.

References

Dielectric and impedance properties of sintered magnesium aluminum silicate glass-ceramic

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Abstract: Magnesium aluminum silicate (MgO–Al₂O₃–SiO₂, MAS) glass-ceramic was prepared via sintering route. X-ray diffraction (XRD) analysis indicates the formation of multiphase compound with magnesium silicate fluoride and cordierite as major phases. Dielectric studies of the compound shows a strong frequency dispersion of permittivity in the low frequency region followed by a nearly frequency-independent behavior in the high frequency region. The presence of alkali ions (K⁺) in MAS glass-ceramic results in higher dielectric constant and higher losses. Dielectric loss (tanδ) seems to be reduced at higher frequencies after reaching the instrumental saturation at 1 kHz. Electrical properties of the material have been studied using a complex impedance spectroscopy (CIS) technique in a wide temperature (30–500 °C) and frequency (100 Hz–5 MHz) ranges. The complex impedance plots reveal the contribution of bulk as well as grain boundary effects in it. The bulk resistance, evaluated from complex impedance spectrum, has been observed to decrease with the rise in temperature, showing a typical negative temperature coefficient of resistance (NTCR) behavior. The smaller activation energy (E_a) of the compound within moderate temperature range suggests the presence of ions (K⁺ and F⁻) and singly ionized oxygen vacancies in the conduction process. The nature of variation of the electrical conductivity, and the values of activation energy of different temperature regions, suggest that the conduction process is of mixed type.

Keywords: glass-ceramic; conductivity; dielectric properties; electrical properties

1 Introduction

Magnesium aluminum silicate (MgO–Al₂O₃–SiO₂, MAS) glass-ceramic systems belong to a special class of technologically important advanced ceramics, having applications in the areas related to ultrahigh vacuum, high temperature, high voltage, etc. They have high thermal stability, low thermal conductivity, good mechanical strength and very high electrical insulation and are also vacuum compatible [1–6]. The properties of MAS glass-ceramic such as hardness, machinability, conductivity and other properties depend on the composition and microstructure.

Complex impedance spectroscopy (CIS) is a well-known and powerful technique for investigating polycrystalline materials, where the contribution of different processes, such as bulk conduction, grain boundary conduction and transport across electrode–sample interface, can be resolved in the frequency domain. The results can be often correlated with the properties such as composition, microstructure, defects and dielectric properties of the sample. This technique has the advantage over DC techniques of being able to separate the electrical responses (i.e.,
transport properties) of different regions of a material (i.e., the resistance of the grain boundaries and that of grains can be easily separated in most of the polycrystalline materials), provided their electrical responses are within the measuring range of the instrumentation. In this paper, we present a systematic study of MAS glass-ceramic prepared by sintering route and the influence of temperature and frequency on dielectric and impedance properties with a view of understanding the conduction mechanism involved.

2 Experimental procedures

MAS glass-ceramic sample was prepared via sintering route, using three-stage heating schedule involving calcination, nucleation and crystallization processes. The initial charge was prepared by taking analytical reagent (AR) grade chemicals in proper weight percentages of SiO$_2$ 47.5%, Al$_2$O$_3$ 16.5%, MgO 18.5%, K$_2$O 9.5%, B$_2$O$_3$ 8%. In the first stage, the initial charge was thoroughly mixed in agate mortar for 2 h, including wet mixing in acetone media for 1 h. The mixture was then calcined at 950 °C for 6 h. 7 wt% MgF$_2$ was added to the calcined charge and was pulverized using agate mortar and pestle for 2 h. Finely milled charge was seasoned in 5% H$_3$PO$_4$ acid solution in acetone medium for a period up to 72 h. Cylindrical pellets of 12 mm diameter and 3 mm thickness were prepared in a hydraulic press using 80 MPa pressure. They were then sintered using a two-step heating program. In the first step, the compact was heated up to 670–700 °C for 2–4 h to ensure good nucleation and initiate crystal growth. These pellets were then sintered with optimized temperature and time (1000 °C, 3 h) in air atmosphere. Approximately 15 mg of crushed fine powders of the sintered pellets were used for differential thermal analysis (Model Pyris Diamond TG-DTA), which was heated up to 905 °C at the rate of 10 °C/min in O$_2$ atmosphere using alumina as reference. The sintered sample was crushed and the phase constitution was studied by X-ray diffraction (XRD) using Philips Xepro X-ray Powder Diffractometer in a wide range of Bragg angles 2θ (10° ≤ 2θ ≤ 70°) being irradiated by Cu Kα (λ = 1.5405 Å). The bulk density for the sintered sample was measured by Archimedes method (i.e., immersion in distilled water). Scanning electron microscopy (SEM) was used to study the surface morphology of the ceramic. For dielectric measurements, the sintered pellets were polished with zero-grain emery paper, and coated with high-purity silver paste and then dried for 2 h at 150 °C. Dielectric and impedance parameters were measured using an impedance analyzer (HIOKI LCR HI Tester, Model 3532) as a function of temperature over a wide range of frequencies (100 Hz–5 MHz).

3 Results and discussion

3.1 Structural study

The differential thermal analysis (DTA) curve for MAS glass-ceramic is shown in Fig. 1. A broad endothermic peak in the DTA curve around 260 °C is due to the dehydration, reduction and some decomposition reactions taking place. The observed exothermic peak around 700 °C is indicative of the crystallization process. Bulk density of the sample measured at room temperature is found to be 1.72 g/ml.

![Fig. 1 DTA curve for MAS glass-ceramic prepared by sintering route.](image)

The room-temperature XRD pattern of the sintered sample is shown in Fig. 2. The XRD analysis of the sample reveals that magnesium silicate fluoride (JCPDS 76-0638), cordierite (JCPDS 85-1722), together with minor traces of phlogopite (JCPDS 16-0352) and sapphirine (JCPDS 21-0549), were developed. The predominant crystalline phases are found to be magnesium silicate fluoride and cordierite. SEM micrographs of the sample with different magnifications at room temperature are shown in Fig. 3. Figure 3(a) shows a highly densified microstructure with large amount of molten glass phases for MAS glass-ceramic. The photograph also shows the presence of plate-like microstructure (Fig. 3(b)).
Fig. 2 Room-temperature XRD pattern of MAS glass-ceramic.

Fig. 3 SEM micrographs of fresh fractured surface of MAS glass-ceramic with different magnifications at room temperature.

3.2 Dielectric properties

Figure 4 shows the variation of relative dielectric constant ($\varepsilon_r$) and loss tangent (tan$\delta$) of MAS glass-ceramic with frequency at room temperature. Both the parameters decrease with the increasing frequency, indicating a normal behavior of dielectric materials having mobile charge carriers (i.e., ions and electrons) [7]. Table 1 shows the room-temperature $\varepsilon_r$ and tan$\delta$ values of the sample measured at different frequencies. The fall in dielectric constant arises from the fact that the polarization does not occur instantaneously with the application of the electric field as charges possess inertia. The delay in response towards the impressed alternating electric field leads to loss and hence decline in dielectric constant [8]. The loss tangent (tan$\delta$) also decreases with the increasing frequency. It is observed that at higher frequency, these parameters become almost frequency-independent. The dielectric constant and dielectric loss of the sample at 5 MHz are 26.14 and 0.033 at room temperature, respectively.

![Figure 4](image)

Fig. 4 Variation of dielectric constant ($\varepsilon_r$) and loss tangent (tan$\delta$) with frequency at room temperature.

<table>
<thead>
<tr>
<th>Physical parameters (at room temperature)</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 kHz</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>94.44</td>
</tr>
<tr>
<td>tan$\delta$</td>
<td>0.527</td>
</tr>
</tbody>
</table>

Table 1 Physical relative properties of MAS glass-ceramic sintered at 1000 °C

The variation of relative dielectric constant ($\varepsilon_r$) with temperature at selected frequencies (1 kHz, 10 kHz, 100 kHz and 1 MHz) is shown in Fig. 5(a). From these curves, it can be seen that dielectric constant increases almost linearly with the increasing temperature (i.e., 30–150 °C) and then starts decreasing slowly. The broadening of dielectric peaks may be attributed to the disorder or defects presented in the system [8]. Since there is no anomaly at 150 °C in the DTA curve, the permittivity peak at 150 °C does not correspond to a phase transition. In general, a structural phase-transition temperature depends strongly on the chemical composition, and in this case, the anomaly was not observed in the cooling regime (not shown here) as it should be in a reversible process, so it is concluded that this experimental feature does not correspond to a structural phase transition. It is well accepted that the presence of Mg$^{2+}$ cations could give
rise to defects such as oxygen vacancies. The presence of K$^+$ cations must also be considered with the consequent generation of oxygen vacancies in the structure. All these features lead us to conclude that this anomaly is not intrinsic in character and may be induced by point defects. For higher temperatures (> 230 °C), the charge carriers are free to move through the crystal causing a polarization and hence $\varepsilon_r$ increases. The increase in permittivity at higher temperatures is possibly due to the polarizability of K$^+$ ions (3.83 Å$^3$), which is higher than that of Mg$^{2+}$ ions (1.32 Å$^3$). Polycrystalline aggregates such as MAS glass-ceramics exhibit interfacial or space charge polarization arising from the differences amongst the conductivity of two phases (magnesium silicate fluoride and cordierite), which are present in the material. If phases of different conductivity present, the motion of charge carriers occurs readily through one phase, but it is interrupted when it reaches a phase boundary of other phases. This causes a build-up of charge at the interface, which corresponds to a large polarization and high value of effective dielectric constant. The charge accumulation at the grain boundaries is responsible for higher values of dielectric constant at low frequencies [9,10]. At high frequency, $\varepsilon_r$ results from the grains which have a small dielectric constant [8]. It is interesting to note that as the temperature increases, the dielectric constant increases at all frequencies.

The variation of loss tangent (tan$\delta$) with temperature for the sample is shown in Fig. 5(b). This increase in tan$\delta$ may be due to the enhancement in conductivity of the material. The rapid increase of loss tangent at higher temperature in low frequency region may be due to space charge polarization. In addition, the high loss factor of MAS glass-ceramic at higher temperatures is due to the large glass content and the high mobility of alkali ions (K$^+$). It is observed that, even at high frequency (1 MHz) and temperature (450 °C), the dielectric loss (tan$\delta$) remains relatively low (0.46), an important fact from the point of view of technological applications.

### 3.3 Conductivity study

Figure 6 shows the variation of AC conductivity (ln$\sigma_{AC}$) as a function of the inverse of absolute temperature ($10^3/T$) at four different frequencies. The AC conductivity ($\sigma_{AC}$) and activation energy ($E_a$) of the sample was calculated using the relation $\sigma = \omega\varepsilon_0\varepsilon_{\infty}\tan\delta$ and $\sigma = \sigma_0\exp(-E_a/k_BT)$, where $\varepsilon_0$ is the vacuum permittivity; $\omega$ is the angular frequency; $k_B$ is Boltzmann constant, and $\sigma_0$ is the pre-exponential factor. Conductivity of the compound at higher temperature is higher, which is a very common behavior in most of dielectric ceramics [11]. Because alkali metal ions (such as Na$^+$, Li$^+$ and K$^+$) are source of conductive carriers in glass-ceramic, the composition and content are closely related with the electrical conductivity of glass-ceramic. In this ceramic, K$^+$ ions are mobile and contribute to the conductivity. The higher values of conductivity at higher temperatures are possibly due to the movement of mobile K$^+$ and F$^-$ ions. In the lower temperature region (Region I), there is linear variation in conductivity with temperature with strong frequency dependence. The region which lies in the temperature range from 150 °C to around 230 °C does not obey the conductivity relation and its trend seems as a metallic behavior. In the higher temperature range (Region II), conductivity varies exponentially with temperature but with relatively weak frequency dependence. The nature of variation of $\sigma_{AC}$ over a wide temperature range supports the thermally activated transport properties of
the material. The activation energy \((E_a)\) of the compound was calculated from the slope of \(\ln \sigma\) vs. \(1/T\) curves. The values of \(E_a\) at different frequencies are given in Table 2.

![Figure 6](image.png)

**Fig. 6** Variation of AC conductivity \((\ln \sigma_{AC})\) as a function of the inverse of absolute temperature \((10^3/T)\) at four different frequencies for MAS glass-ceramic.

**Table 2** Activation energy of MAS glass-ceramic sintered at 1000 °C

<table>
<thead>
<tr>
<th>Activation energy ((E_a, eV))</th>
<th>Region I</th>
<th>Region II</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 1 kHz</td>
<td>0.09</td>
<td>0.76</td>
</tr>
<tr>
<td>at 10 kHz</td>
<td>0.06</td>
<td>0.51</td>
</tr>
<tr>
<td>at 100 kHz</td>
<td>0.06</td>
<td>0.30</td>
</tr>
<tr>
<td>at 1 MHz</td>
<td>0.07</td>
<td>0.19</td>
</tr>
</tbody>
</table>

The activation energy is found to increase with increasing temperature. This behavior suggests that the conduction mechanism in MAS glass-ceramic may be due to the hopping of charge carriers between different localized states. The value of activation energy in Region I is found to be very low. The small values of activation energy in Region II may be due to the singly ionized oxygen vacancies. Therefore, the conductivity may be of mixed type (i.e., ionic-polaronic and space charge) [12,13].

### 3.4 Impedance analysis

The electrical behavior of the system was studied over a wide range of frequency and temperature using a complex impedance spectroscopy (CIS) technique. This technique enables us to separate the real and imaginary components of the complex impedance parameters, and hence provides information of the structure–property relationship of the sample. A polycrystalline material usually has grain and grain boundary properties with different time constants at high temperature leading to two successive semicircles. It can conventionally be displayed in a complex plane plot (Nyquist diagram) in terms of the following formalism:

\[
Z'(\omega) = Z' - jZ''
\]

where \(Z' = |Z| \cos \theta\) and \(Z'' = |Z| \sin \theta\).

Figure 7(a) shows a set of Nyquist plots \((Z' vs. \ Z'')\) over a wide range of frequency (100 Hz–5 MHz) at different temperatures. The effect of temperature on impedance parameter of the material becomes clearly visible with the rise in temperature. A single semicircular arc has been observed in a wide temperature range \((< 400 °C)\). This indicates that the electrical properties of the material arise mainly due to the bulk effects. As temperature increases, the intercept point on the real axis shifts towards the origin.

![Figure 7](image.png)

**Fig. 7** (a) Nyquist plots of MAS glass-ceramic at different temperatures; (b) Nyquist plots of MAS glass-ceramic with equivalent circuit (inset).
indicating the decrease in the resistive property of the material. The intercept of the semicircle on the real axis is the bulk resistance ($R_b$) of the sample. The values of bulk resistance ($R_b$) and bulk capacitance ($C_b$) are shown in Table 3. This type of electrical behavior can be explained in terms of an equivalent circuit comprising of a parallel combination of $RC$ circuits. At much higher temperatures ($\geq 450^\circ$C), it was possible to trace two semicircles (Fig. 7(b)). The appearance of two semicircles suggests the presence of both bulk as well as grain boundary effects in the polycrystalline sample. Each semicircle is a representative of an $RC$ circuit that corresponds to individual component of the material (Fig. 7(b) inset). The presence of pores modifies the complex impedance plots by changing the diameters of the grain interior or grain boundary arc without introducing a new arc or other characteristic in the impedance spectrum. Thus, it is not possible to quantify the degree or nature of porosity using impedance spectrum.

### Table 3 Values of bulk resistance ($R_b$), relaxation frequency ($f_r$), and bulk capacitance ($C_b$) of MAS glass-ceramic at different temperatures

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$R_b$ (kΩ)</th>
<th>$f_r$ (kHz)</th>
<th>$C_b$ (pF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>3059.17</td>
<td>0.65</td>
<td>80</td>
</tr>
<tr>
<td>350</td>
<td>569.38</td>
<td>5</td>
<td>56</td>
</tr>
<tr>
<td>400</td>
<td>165.25</td>
<td>25</td>
<td>38</td>
</tr>
<tr>
<td>450</td>
<td>75.07</td>
<td>75</td>
<td>28</td>
</tr>
<tr>
<td>500</td>
<td>27.19</td>
<td>250</td>
<td>23</td>
</tr>
</tbody>
</table>

Figure 8 exhibits the variation of the real part of impedance ($Z'$) with frequency at different temperatures. The decrease in the magnitude of $Z'$ with increase in both frequency as well as temperature indicates the increase in AC conductivity. The values of $Z'$ merge at higher frequencies ($\geq 100$ kHz), which indicates the release of space charges. Figure 9 represents the impedance loss spectra (i.e., the variation of the imaginary part of impedance ($Z''$) with frequency). The curves show that the value of $Z''$ reaches maximum value, $Z''_{\text{max}}$, at all temperatures. The average peak position regularly changes towards the higher frequency side on increasing temperature. Furthermore, as the temperature increases, the magnitude of $Z''$ decreases and the effect is more pronounced at the peak position. The shift of the peaks towards higher frequency on increasing temperature is due to the reduction in the bulk resistivity. The relaxation time ($\tau$) was calculated from the frequency maxima ($f_{\text{max}}$) at $Z''_{\text{max}}$. At the peak, the relaxation is defined by the condition:

$$\omega_{\text{max}}\tau = 2\pi f_{\text{max}}\tau = 1$$

where $\tau$ is the relaxation time at $f_{\text{max}}$ and $f_{\text{max}}$ is the relaxation frequency. It is independent of the sample’s geometrical factors and depends basically on the intrinsic properties (i.e., microstructure) of the material only. The $\tau$ value is found to be decreasing on increasing temperature, which is a typical semiconductor behavior. The nature of variation of $\tau$ with temperature shows that the relaxation process is temperature dependent. The variation of $\tau$ as a function of the inverse of absolute temperature is shown in Fig. 10.

The activation energy evaluated from the slope of the curve, using the relation $\tau = \tau_0 \exp(-E_a / kT)$ (where $\tau_0$ is the pre-exponential factor; $E_a$ is the activation energy; $k$ is Boltzmann constant, and $T$ is absolute temperature), is found to be 0.48 eV.
3.5 Modulus studies

Impedance spectroscopy is a powerful technique for characterization of grain boundaries in ceramic materials. The advantage of adopting complex electric modulus formalism is that it can discriminate electrode polarization from grain boundary conduction process. In polycrystalline materials, impedance formalism might emphasize grain boundary conduction process, while bulk effects on frequency domain would dominate in the electric modulus formalism. The use of modulus spectroscopy plot is particularly useful for separating components with similar resistance but different capacitance. The other advantage of electric modulus formalism is that the electrode effect is suppressed. Due to the above reasons, the complex electric modulus ($M'$) have been calculated from the impedance data using the following relation:

$$M'(\omega) = 1/\varepsilon(\omega) = M' + jM^*$$

$$M' = \omega C_o Z'$$ and $$M^* = \omega C_o Z'^*$$

where $\omega$ is the angular frequency ($2\pi f$); $C_o = \varepsilon_o (A/t)$ is the geometrical capacitance; $\varepsilon_o$ is the permittivity of free space; $A$ is the area of the electroded surface and $t$ is the thickness.

Figure 11(a) shows the variation of $M'$ with frequency for MAS glass-ceramic at selected temperatures. A very low value (~ zero) of $M'$ in the low frequency region is observed. Continuous increases in the dispersion on increasing frequency for all the temperatures are observed. Such observations could possibly be related to a lack of restoring force governing the mobility of the charge carriers under the action of an induced electric field. This confirms the elimination of electrode effect in the material. The value of $M'$ decreases with the rise in temperature in the high frequency region. Figure 11(b) shows the variation of $M^*$ with frequency over a wide temperature range and frequencies ascribing correlation between motions of mobile ions [14]. A well-defined relaxation mechanism is observed in temperature range 300–500 °C. The relaxation peaks shift towards higher frequency side with the rise in temperature. At frequencies lying to the left of the peaks, the charge carriers ($K^+$ and $F^-$ ions) may be considered as mobile over long distances whereas in the region to the right of the peaks, charge carrier motion is generally confined in their potential well. The nature of modulus spectrum suggests the existence of hopping mechanism of electrical conduction in the material. The value of $M^*$ increases as a function of temperature.

4 Conclusions

MAS sample was prepared via sintering route. XRD
analysis reveals several crystalline phases formed in this material: magnesium silicate fluoride, cordierite, together with minor traces of phlogopite and sapphirine. The predominant crystalline phases are found to be magnesium silicate fluoride and cordierite. Dielectric constant and dissipation factor decrease with the increase in frequency. The increase of $\varepsilon_r$ at higher temperatures may be due to the weakening of binding force between the ions leading to mobile ions ($K^+$ and $F^-$) contribution. CIS enables us to separate the grain and grain boundary contributions in the material. Both the grain and grain boundary resistances decrease with the rise in temperature. We used an equivalent circuit to explain electrical phenomena occurring inside the material. The nature of variation of AC conductivity with temperature exhibits NTCR behavior of the sample like that of a semiconductor. The activation energies at higher temperatures are found to be less than 1 eV. This suggests that polarons at lower temperatures, singly ionized oxygen vacancies and long range conductivity associated with extrinsic mechanisms due to the presence of $K^+$ and $F^-$ ions at higher temperatures contribute to the conduction process in the material.

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References