

ELECTRICAL AND DIELECTRIC PROPERTIES OF MgO–Y₂O₃–Si₃N₄ SINTERED CERAMICS

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We discussed the effect of composition of Silicon Nitride/yttrium oxide with Magnesium oxide on the electrical and dielectric properties of sintered ceramics. A constant amount of MgO was added to different concentrations of Si₃N₄ and Y₂O₃. It is found that the dc conductivity is thermal activated process in the high temperature range and the activation energy is composition dependent. The variation of dc conductivity with the concentration of Si₃N₄/Y₂O₃ is explained. The permittivity and conductivity representation has also been employed to study temperature and frequency dependence of the ac response. Microstructure, compositional porosity and morphology were also investigated by Scanning Electron Microscope (SEM) and X-rd. As the Si₃N₄/Y₂O₃ concentrations increases the sintered ceramics based composite becomes denser. These types of samples can be used as a high temperature semiconducting materials.

INTRODUCTION

Over the past twenty years, studies on Silicon Nitride (Si₃N₄) ceramics have contributed to the sound knowledge of the relationship between its in situ toughening behavior and micro structural parameters, such as size, shape, and grain-boundary phases. The industrial use of Si₃N₄ ceramics has been partially inhibited by both difficulty and cost of manufacturing complex shape components. Limitations in size, geometry, and cost can be partially overcome by the use of suitable joining technologies [1]. However, silicon nitride is intrinsically difficult to sinter because of the covalent character of the Si–N bonds and the extremely low self-diffusion coefficients of silicon and nitrogen. By oxidizing silicon nitride above 1100°C and addition of magnesium ion as a sintering aid, oxidation products such as Mg₂SiO₄ and MgSiO₃ are formed and bonding between Si₃N₄ and MgSiO₃ could be achieved [2]. Thus, in practice, to achieve nearly complete densification of powder compacts, sintering aids which promote liquid-phase assisted sintering are required for such ceramics. Silicon nitride is a material for the high temperature structural composite with its high hardness, high fracture toughness, good oxidation and corrosion resistance, and light weight etc. The electrical behaviors of silicon nitride prepared by chemical vapor deposition, spark

plasma sintering and sputtering technique have also been reported [3-5]. Three types (ohmic, SCLC and F-P conduction mechanism) of electrical conduction have also been found [6]. A. Kikkawa et al. [7] investigated the electrical properties of Cat-CVD SiN_x films prepared by the incorporation of a catalytic nitridation layer which provide high quality gate dielectric films at low temperature. Takashi Goto et al. [8] reported dielectric properties of chemically deposited silicon nitride. The observed result shows that the a.c. conduction is caused by hopping carriers. The value of loss tangent (tan δ) increases with increasing the temperature. The value of tanδ for amorphous Si₃N₄ is smaller than that of the crystalline CVD Si₃N₄. Dielectric properties also depend on the microstructure of silicon nitride. It shows dielectric constant of 8.1-8.6 and dielectric loss 1.1×10^{-3} - 5.6×10^{-3} at microwave frequency range. Nowadays most silicon nitride ceramics are prepared using α-Si₃N₄ powders. In silicon nitride ceramics, the microstructure is similar to whisker-reinforced ceramic composites, with large rod like β-Si₃N₄ grains as the reinforcing agents [9]. The effect of microstructure or grain size on dielectric properties are also already discussed [10]. In earlier studies on the microstructural characterization of silicon nitrides ceramics, it is noted that all of them are conducted at relatively low TEM/SEM magnifications and therefore are limited to the

examination of the general microstructure [11-13]. M. Liu et al. [14] reported that the pressureless sintered silicon nitride with Y_2O_3 , AlN and TiO_2 shows good densification and high hardness. The material consists of large acicular β grains and small equiaxed α -grains. And an amorphous phase containing the sintering aids is found at the two-grain boundaries and at the grain pockets. Yttrium shows good sensor application due to high operating temperature, which makes these oxide sensors suitable for automotive applications. AC electrical properties of composites and theoretical high-frequency behaviour of multi layer films have been studied by Lee et al. [15]. The survey of literature reveals that the detailed conductivity studies of Y_2O_3 based composites are scarce. The frequency dependent A.C. conductivity reveals that the Y_2O_3 concentration is responsible for the variation of conductivity of the composites. Frequency dependent dielectric constant for different composites is due to interfacial space charge polarization leading to the large value of dielectric constant. Frequency dependent dielectric loss, as well as variation of dielectric loss as a function of mass percentage of Y_2O_3/Si_3N_4 already reported [16]. The dielectric studies are important to understand the nature of dielectric losses and the transport mechanisms. The aim of this work is to characterize the dielectric behavior and the electrical conductivity of the investigated ceramics based composites and determines the influence of composition on the dielectric and electrical properties.

EXPERIMENTAL PROCEDURE

The materials under study are sintered silicon-nitride ceramics with MgO and Y_2O_3 . The samples were prepared by grinding 99.999 % pure Silicon Nitride (Alfa Aesar, Johnson Matthey company USA) with constant concentration of MgO (CDH, New Delhi) and different concentration of Y_2O_3 (CDH, New Delhi). The chemical composition of the samples are given in Table 1. The grinding was carried out for 30 min for each samples in an appropriate mortar. The obtained powders were made into pellets by means of a hydraulic press at a pressure of 100 MPa. Sintering was carried out under normal atmospheric pressure in a silica crucible heated by a graphite heating element in furnace. The temperature was raised from room temperature to $900^\circ C$ at a rate of $15^\circ C$ per min and kept around that temperature for 8 hrs.

Table 1. Composition of Samples ($Si_3N_4 + MgO + Y_2O_3$).

Sample	A	B	C	D	E	F
Si_3N_4 (%)	0	10	20	30	40	50
MgO (%)	50	50	50	50	50	50
Y_2O_3 (%)	50	40	30	20	10	0

Then the samples were sintered for 2h at $950^\circ C$ after rising the temperature from $900^\circ C$ to $950^\circ C$ at the same heating rate. The cooling rate controlled $40^\circ C/min$. up to $700^\circ C$ and $25^\circ C/min$ upto room temperature.

For DC conductivity measurement, the samples were mounted in a specially designed sample holder where a vacuum of about 10^{-3} Torr could be maintained throughout the measurement. The thickness of samples was 1.0-1.5 mm and diameter ~ 10 mm. A DC voltage 30 volt was applied across the samples and resulting current was measured by a digital electrometer (Keithley, model 617). The temperature is measured by mounting a Chromel-Alumel thermocouple near the sample. Before the I-V characteristics measurement, the samples were annealed at $100^\circ C$ in vacuum to avoid the effect of moisture. Dielectric measurements were performed by an L-C-R-Q bridge (Scientific, model no. 6018) at two fix frequencies (100 Hz and 1 KHz). The microstructure of the fracture surface of the post-sintered samples was observed using a Scanning Electron Microscope (SEM) (JEOL, 3300, Tokyo, Japan) and XRD (PANalytical X-Ray Diffractometer with PW1830 Generator) on the powder samples.

RESULTS AND DISCUSSION

Microstructural Characterization

In Figure 1 the microstructures of the sintered samples are shown in the SEM images of fractured surface of the samples. It can be seen that the volume of pores and grain size decreased remarkably from A to E. However, variation of composition has insignificant effect on the grain shape. During sintering, oxides react with the silica on the surface of Si_3N_4 and some of the nitride forms an oxynitride at a high temperature, which promotes the densification of the material. The surface of this particular elongated grain shows distinct evidence of crack growth along the surface of the grain. Such a growth mode helps to produce a tortuous crack path, which in turn contributes to crack deflection and bridging, thereby improving the toughness of these ceramics. Since more space was available, so the growth of β - Si_3N_4 grains is promoted. The large grains surrounding fine grains can form closed pores [17-18]. This effect results in the rearrangement stage and rapid initial densification. So desired ceramics become denser with the increasing the ratio of Si_3N_4/Y_2O_3 with constant MgO content and confirm certain electrical and dielectric properties of the sintered samples. The identified phases for all compositions of sintered sample are presented in figure 1b, which are α - Si_3N_4 , β - Si_3N_4 , Y_2O_3 and $MgSiO_4$. The XRD indicates that the major phase is α - Si_3N_4 , and that the sintered samples basically preserve the characters of the starting powders.

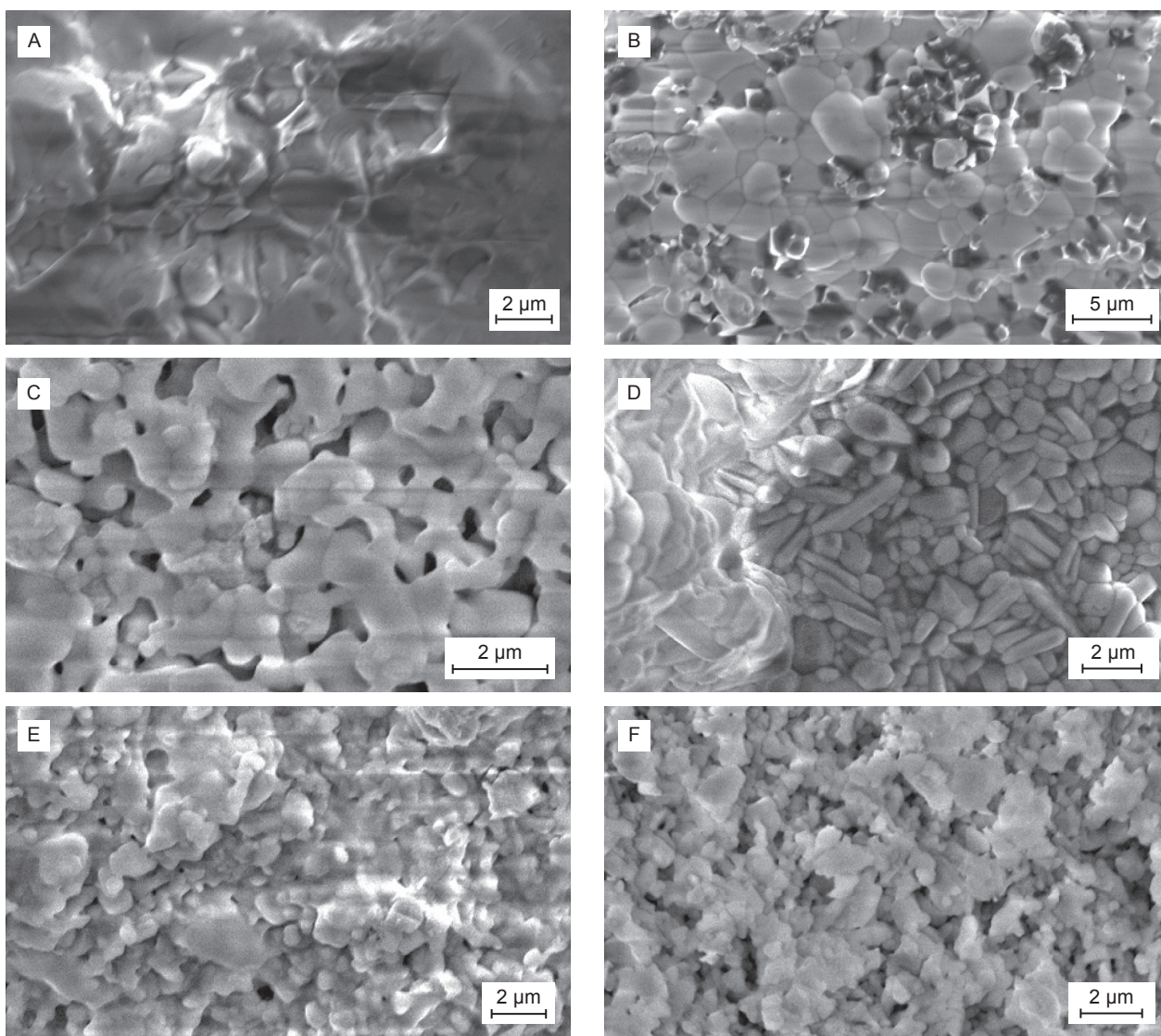


Figure 1a. SEM micrographs showing the grain size and grain boundaries in all samples.

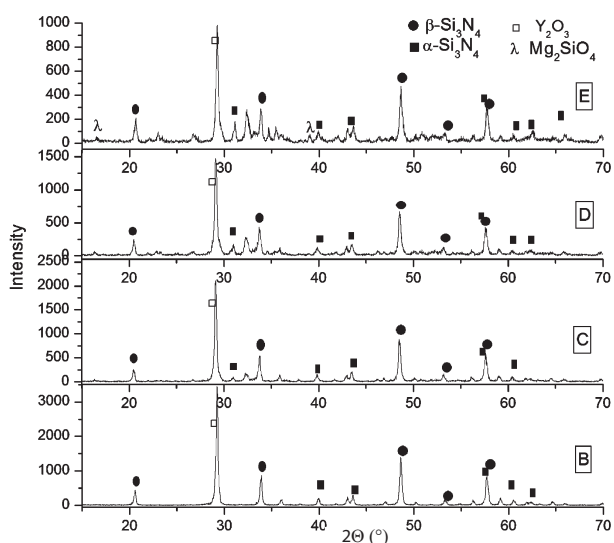


Figure 1b. X-Ray diffraction patterns showing the different phases.

DC Conductivity

In Figure 2 the DC conductivity for all samples under study has been plotted as a function of reciprocal temperature. Initially, in the lower temperatures region ($T < 800$ K), the conductivity is nearly temperature independent and varies with composition of Si_3N_4/Y_2O_3 . In the high temperatures region ($T > 800$ K), the DC conductivity increases exponentially with temperature for all of the investigated samples. As it can be seen in Figure 2, all of the samples show double slope and the high temperature regimes are well fitted to Arrhenius relation. The Arrhenius behavior of the DC conductivity can be expressed by the usual relation

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{\Delta E_{dc}}{kT}\right) \quad (1)$$

where σ_0 is the pre-exponential factor, ΔE_{DC} is the activation energy for DC conductivity and k is Boltzmann

constant. The electrical parameters calculated from the least- square straight-line fits using Equation (1) are given in Table 2.

The lower temperature behavior of DC conductivity suggests that the incorporation of Y_2O_3 result in decreasing the conductivity of the investigated ceramics composites. Moreover, with the exception of sample *F* which exhibit gradual transition temperature, the transition temperature decreases with decreasing the Si_3N_4/Y_2O_3 ratio. The lower temperature behavior of dc conductivity suggests that the few amount of trapping levels result in decreasing the conductivity of the investigated ceramics. And in thermal activated conduction region, formation of large number of trapping levels within the energy gap; start to participate in the conduction mechanism. The composition dependence of the activations energy, inset of Figure 2, shows that ΔE_{DC} increases with Si_3N_4 content and reaches maximum at 30 % then decreases further. The pre-exponential factor, σ_0 , exhibits similar trend. Since σ_0 depends on the mobility and concentration of charge carriers i.e. improvement in conductivity can be attributed to an increase in the mobility of the charge carriers.

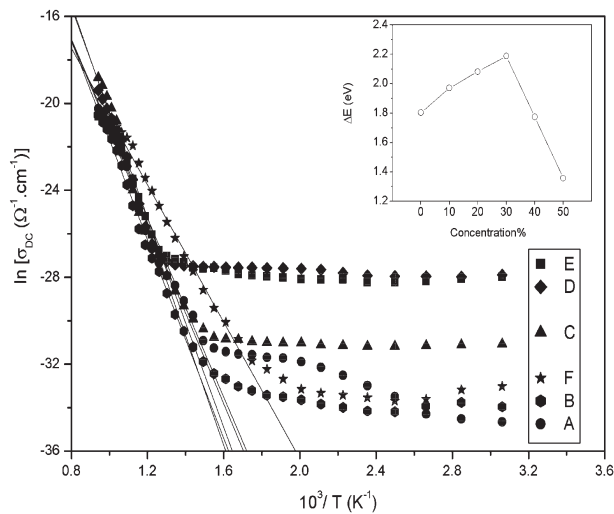


Figure 2. Temperature dependence of DC conductivity at various concentrations of Y_2O_3/Si_3N_4 in the sample. The inset shows the corresponding activation energy for high temperatures region.

It is known that the refractory oxides MgO and Y_2O_3 are used as activators for sintering silicon nitride. When they react, silicates are formed and the higher the melting points of the silicate, the higher the strength characteristics of the material [19]. Replacement of oxides makes it possible to improve the properties of a silicon nitride ceramics. The electrical characteristics of the materials suggest a significant increment in the electrical conductivity compared with silicon nitride or materials based on it.

Predominantly, silicon nitrides have electrical conductivity which is electronic in nature and, hence, may be used as high temperature semiconducting materials. Upon sintering of a mix containing Si_3N_4 , MgO and Y_2O_3 , formation of Mg_2SiO_4 and $MgSiO_3$ is possible, having electronic conductivity and affecting the electrical properties of the samples obtained [2]. Due to formation of new phases the electrical conductivity increases in the sample D and sample E. The electrical conductivity of the sintered samples may form the basis for designing a new class of semiconductors based on yttrium-containing oxynitride systems for chemical current sources, sensors, and fuel cells applications with elevated operating characteristics.

Dielectric Properties

The AC response of the silicon nitride ceramics were investigated in the temperature range 310-1070 K for chosen frequencies (100 and 1 kHz). Permittivity and conductivity representation are employed in the analysis of experimental data (Figures 3 and 4). In Figure 3 the dielectric constant (ϵ'), dielectric loss (ϵ'') and the normalized dielectric loss ($\epsilon'/\epsilon''_{DC}$) of all compositions under study are represented as a function of temperature.

As a general feature of the results represented in Figure 3a,b, ϵ' and ϵ'' remain almost independent of temperature up to 800 K. As the temperature is increased further, ϵ' and ϵ'' increase quite appreciably with temperature. It is observed that in all the investigated samples ϵ' decreased with frequency due to the fact that beyond a certain frequency of the applied electric field the particle exchange does not follow the alternating field.

Table 2. Electrical and dielectric parameters at particular choice of temperatures and frequency.

Sample	ΔE_{DC} (eV) ($T < 800$ K)	σ_{DC} ($\Omega^{-1} cm^{-1}$) ($T = 425$ K)	σ_0 ($\Omega^{-1} cm^{-1}$)	ϵ' at ($T = 900$ K) ($f = 100$ Hz)	$\epsilon''/\epsilon''_{DC}$ at ($T = 500$ K) ($f = 100$ Hz)	ΔE_{AC} (eV)
A	1.32	4.7×10^{-15}	7.1×10^{-1}	66.8	6.1×10^{19}	1.01
B	1.70	1.5×10^{-15}	3.3×10^1	65.1	3.7×10^{22}	1.29
C	1.64	2.9×10^{-14}	4.3×10^1	100.4	4.2×10^{21}	0.64
D	1.83	7.5×10^{-13}	1.3×10^2	87.5	1.9×10^{20}	1.87
E	1.97	5.4×10^{-13}	5.8×10^{-1}	90.1	4.0×10^{20}	1.12
F	1.33	2.7×10^{-15}	7.9×10^{-3}	49.9	2.9×10^{22}	1.28

Moreover, the results show that the dielectric constant (ϵ') and dielectric loss (ϵ'') increase with increasing Si_3N_4/Y_2O_3 ratio.

The dielectric loss (ϵ'') consists of two contributions, one from the dielectric polarization processes, and the other from DC conduction. To study the origin of the dielectric loss in the operating temperature range, the DC contribution was calculated using the relation $\epsilon''_{DC} = \sigma_{DC}/\epsilon_0\omega$. The results represented in Figure 3c shows insignificant conductive loss (ϵ''_{DC}) over the entire temperature range. However, the temperature dependence of the normalized dielectric loss for high temperatures region ($T > 800$ K) shows that the apparent increase in ϵ'' with increasing Si_3N_4/Y_2O_3 ratio is due to DC contribution. As a conclusion, the dielectric loss cannot be attributed to DC conduction in the entire temperature range. In this case the excess of electrons in a narrow conduction band is due to their interaction with lattice ions and distorted by the surroundings. In the case of dielectrics, it is deep enough to introduce localization leading to the existence of conduction although it is very little.

The total AC conductivity $\sigma'(\omega)$ is evaluated using the relation $\sigma' = \epsilon_0\epsilon''\omega$. The results for all compositions under study are shown in Figure 4. It can be noted that AC conductivity shows initially weak temperature dependence but strong frequency dependence as shown in the inset of Figure 4 for sample B. By increasing the temperature

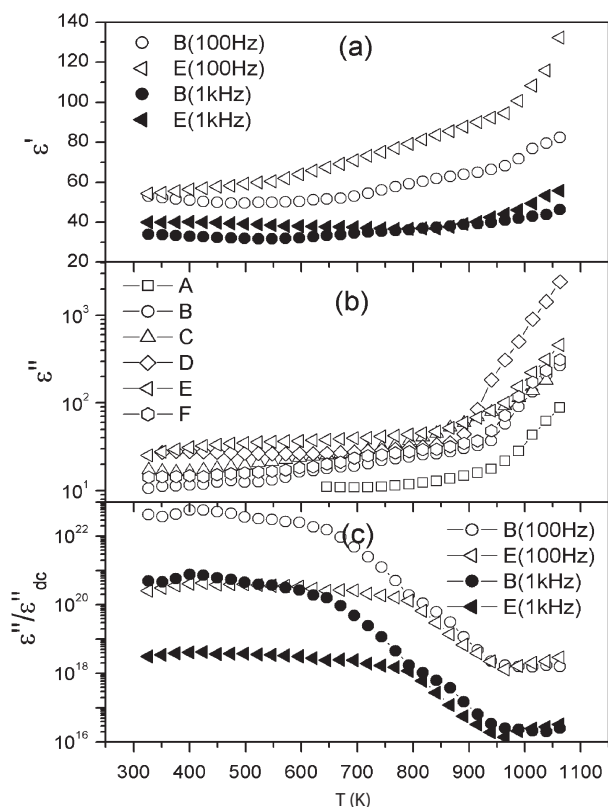


Figure 3. Temperature dependence of (a) dielectric constant (b) dielectric loss (c) normalized dielectric loss.

the frequency dependence becomes insignificant. The other compositions also show similar trend. The results reflect common feature of the temperature dependence of AC conductivity for amorphous materials. I.e. the AC conductivity shows weak temperature dependence at low temperatures but strong frequency dependence. By increasing temperature, the AC conductivity shows strong temperature dependence and all curves converge at higher temperatures.

It can be noted that the temperature dependence of AC conductivity exhibits two relaxation processes with different activation energies. For the high temperature region, the values of ΔE_{AC} calculated from the least square fitting to Arrhenius relation are listed in Table 2 ($f = 100$ Hz). It can be noted that ΔE_{AC} is lower than the calculated activation energy for DC conductivity (ΔE_{DC}) for all compositions except for D. Hence it can be concluded that the dc and AC contributions arise from completely separate mechanisms.

It is well known [17-18] that dielectric properties are strongly dependent on the dielectric polarizability, porosity and the grain sizes. The dielectric constant decreases with increasing porosity, and the geometrical nature of the pores is also a factor that affects the dielectric constant. In order to eliminate the effect of pores on the dielectric properties, Si_3N_4 ceramic was sintered at different temperatures [20]. The presence of these macro pores can decrease the dielectric constant (ϵ') and the dielectric loss (ϵ'') of the samples. As it is confirmed in Figure 1, the evident suppression in ϵ' and ϵ'' can be attributed to the apparent increase in the porosity.

The variation in ϵ' and σ_{AC} with temperature and frequency may therefore, be attributed to space charge polarization whose possibilities is quite large in the present case. We have established that the dielectric properties of the materials are significantly affected with

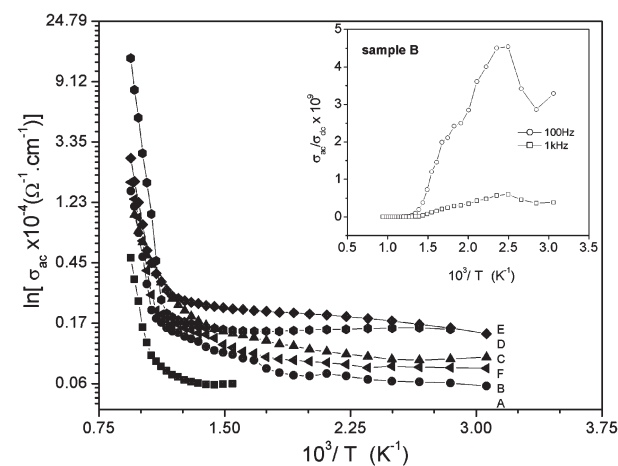


Figure 4. AC conductivity versus temperature measured on various concentrations of Y_2O_3/Si_3N_4 in the sample at 1 kHz. The inset shows the frequency dependence of AC conductivity for sample B.

temperature as well as frequency. Due to different region of conductivity the charge may be accumulated which may result into large polarization at high temperature. The dielectric dispersion observed in the present case may, therefore, be understood in terms of space charge polarization.

CONCLUSION

The ceramics prepared using MgO and $\text{Si}_3\text{N}_4/\text{Y}_2\text{O}_3$ having uniform structure and relative porosity was obtained in a two-step sintering technique. On cooling new phase will form glass which provides a continuous network through the whole microstructure, so the composites became denser in sample D and E. And the conductivity increases exponentially with temperature greater than 800 K. The dielectric dispersion observed in this study may, therefore, be understood in terms of space charge polarization. The result shows that the dielectric constant (ϵ') and dielectric loss (ϵ'') vary with $\text{Si}_3\text{N}_4/\text{Y}_2\text{O}_3$ ratio and the dielectric loss cannot be attributed to dc conduction in the entire temperature range.

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