Dielectric properties of fluormica glass-ceramics

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We report here measurement of the real (ε') and imaginary (ε'') parts of the relative complex permittivity of fluormica type glass-ceramics. The measurements were made in the temperature range of 298–673 K and frequency range of 100 Hz to 5 MHz. The two distinct absorption peaks were observed near 0.1 MHz and 5 MHz. These peaks are interpreted as due to the dipole motion in crystalline and residual glass phase in glass-ceramic.

RECENTLY, considerable attention has been focused on the development of new glass-ceramics (GC)[1]. The GC is an important system both from the scientific and technological point of view. The separation of crystalline phase from the glass phase under regulated heat treatment is interesting, both from a physical aspect as well as the resulting modification of glass properties. In fact, one can design the GC by proper selection of composition and heat-treatment cycle to suit end-use in mind. Through these treatments, one can realize very fine-grained uniform structure free from porosity, low thermal expansion, desired dielectric constant and good resistance to thermal shock. Considerable efforts have been made[2–4] in the development of machinable GC through the controlled crystallization of two-dimensional or layered silicates in the flusilicate GC. Among these, fluormica exhibits unusual combination of properties like machinability, resistance to withstand high temperatures, high dielectric constant with low loss and high dc resistivities. With the advent of integrated circuit designs and consequent miniaturization of circuits, there is a need to develop suitable substrates for electronic packaging with good electrical, thermal and mechanical properties. Although ceramics is widely used for electronic packaging, their dielectric constant is quite high (> 10 at 1 MHz) and hence it is useful for high-power packages[5]. The fluormica GC appears to be a likely candidate for electronic packaging substrate and this demands a careful study of its properties. The system chosen in the present work for the investigation of dielectric behaviour is fluormica GC. In the fluormica system, the word mica is a generic name given to the family of minerals with layered structure and general molecular formula:

$$X_{(0.5-1.0)}Y_{2-3}(Z_4O_{10})(OH)_2,$$
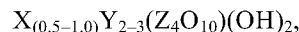
where X is a cation of co-ordination number 12, alkali (Na, K, etc.) or alkali earth (Ca, Sr, etc.) Y is Mg, Al, or Li, and Z is Al, B or Si. These compounds are commonly called fluormica and are structural analogues of natural mica in which fluorine ions replace hydroxyl ions[6–8]. We have considered the fluormica with the molecular formula close to $K_2Mg_2Al_2Si_6O_{20}F_4$ for investigation of the dielectric properties.

Glass and GC were prepared through the melt-quenching technique[3,4]. The starting raw materials were oxides and carbonates of analar grade. A homogeneous glass of composition K_2O 4.2 mol%, MgO 47.13 mol%, Al_2O_3 14.91 mol%, MgF_2 21.09 mol%, B_2O_3 18.24 mol% and SiO_2 78.26 mol% was obtained by melting in an open hearth furnace in the temperature range 1723–1873 K in a platinum crucible for about 2 h (to ensure homogeneity of the melt), and then quenched at 300 K on a graphite block. The glass samples were annealed at 873 K for about 2 h and cooled to 300 K. The X-ray diffraction of these samples confirms the amorphous nature of glass, as shown in Figure 1. In order to transform this glass to GC, controlled nucleation and crystallization were carried out in a programmable vertical tubular furnace using different heating schedules. For nucleation, the temperature of the sample was kept at about 873 K for 4 h and was raised to 1123 K for crystallization, based on the experience with sintering process and DTA data.

The frequency-dependent capacitance (C) and dissipation loss (tan δ) of the samples of glass and GC were measured using HP 4192 A LF Impedance Analyser in the frequency range of 100 Hz–5 MHz and temperature range of 298–673 K. Using these data, the real (ε') and imaginary (ε'') parts of the dielectric constant were evaluated using the relations
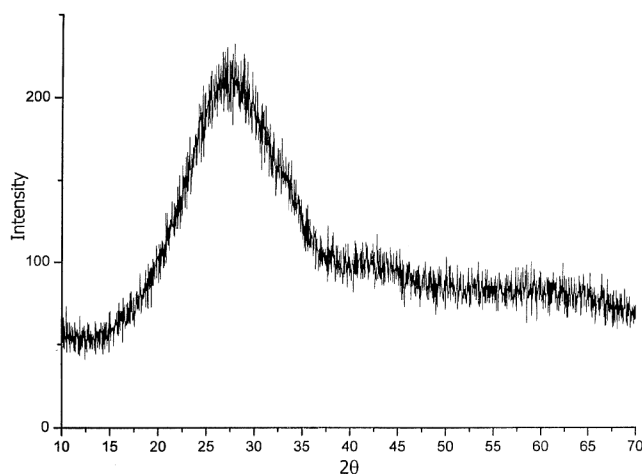
Figure 1. XRD pattern for fluormica glass at room temperature.

$$\varepsilon' = Cl/\varepsilon_0 A, \tag{1}$$

$$\varepsilon'' = \varepsilon' \tan \delta, \tag{2}$$

where l is the thickness of the sample, A the effective area between the electrode and ε_0 the free-space permittivity.

Figure 2 shows the XRD pattern with peak-marked d-spacing for the GC sample. The well-formed diffraction pattern and d values confirm that the predominant phase formed is fluorophlogopite[6–8], with unidentified peaks due to some impurities in the sample. The results of various studies on heating rates and maximum growth tem-
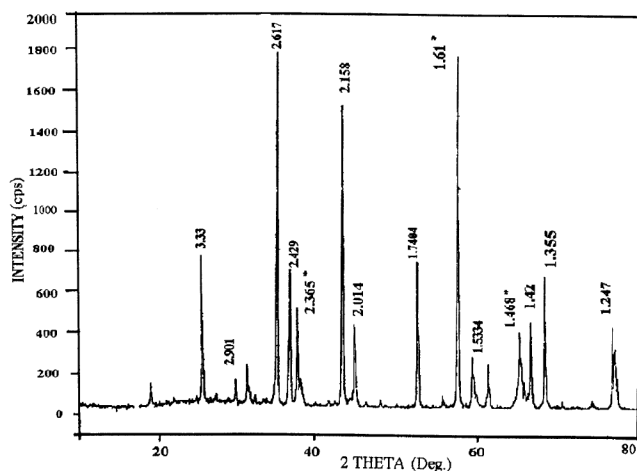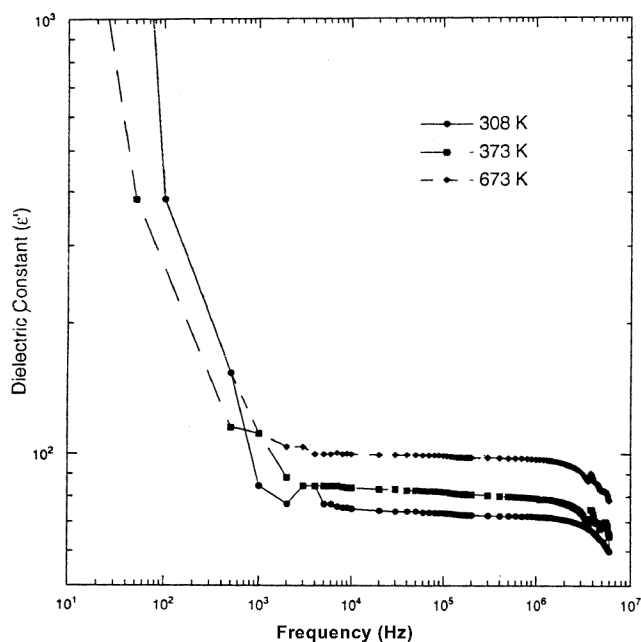

Figure 2. XRD pattern for fluormica glass-ceramic prepared by glass route.
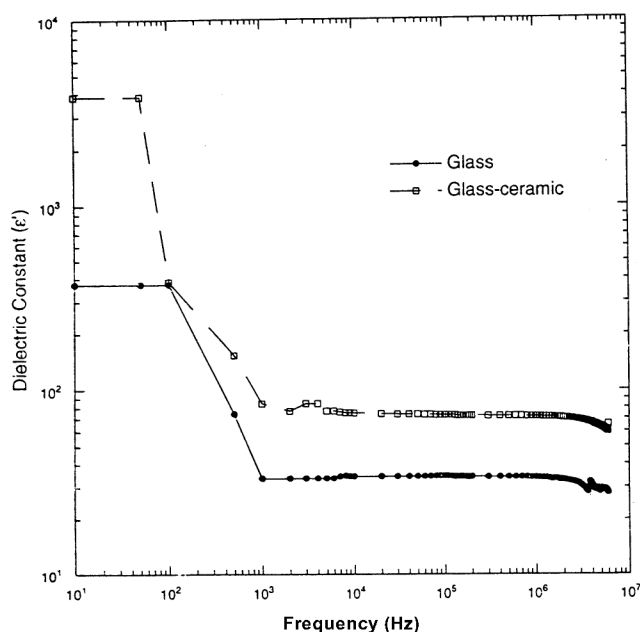
perature pointed out that the temperature of nucleation around 873 K and the crystallization temperature around 1123 K along with lower heating rates of 15–20 K/h were conducive for the development of desired microstructure. The samples obtained after annealing showed a smooth surface with practically zero porosity, and a density of 2.72 g/cc as expected. Figures 3 and 4 show the variation of dielectric constant (ε') as a function of frequency for glass and GC samples at constant temperature and glass-ceramic sample at different temperatures respectively. Dielectric constants are found to decrease with increase in frequency, in the 100 Hz to 5 MHz range, for both glass and GC samples. It is interesting to note that as the temperature increases, the dielectric constant increases at all frequencies. Further, the GC sample showed higher dielectric constant than that of glass, suggesting that the dielectric constant is dependent on the crystallite size, porosity, and density[8,9]. Figures 5 and 6 show the variation of dielectric loss (tan δ) with frequency for glass and GC samples at constant temperature, and for GC sample at different temperatures. They show two 'absorption maxima' at two different high frequencies. These curves reveal the presence of relaxational effects in the samples. Similar to relative loss factor (ε''; Figure 7), the loss tangent also exhibits a maximum value.

The change in dielectric constant from low to high frequencies (above 10^3 Hz) implies that there is appreciable contribution of space charge (Figures 4 and 6). At frequencies greater than 10^4 Hz, space charge cannot shift orientation direction with the applied field[11,12]. Thus between 2×10^6 and 7×10^6 Hz, we should only have dipolar, ionic, atomic, or electronic polarization. The
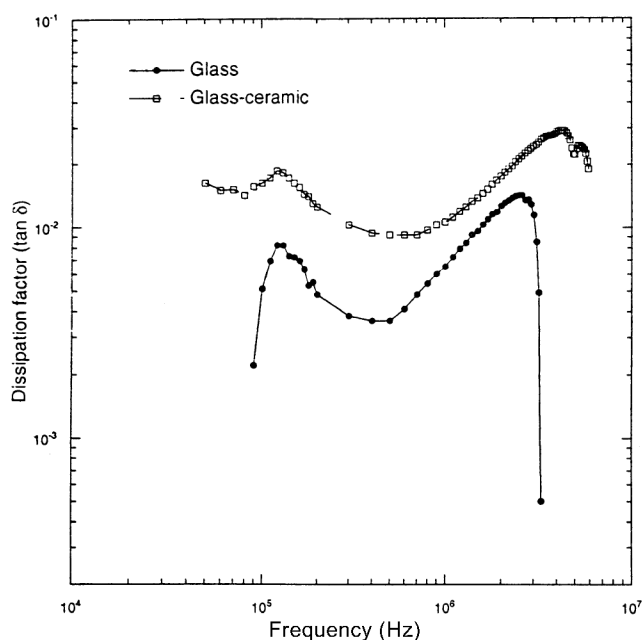

Figure 3. Variation of dielectric constant (ε') with frequency for a fluormica glass and fluormica glass-ceramic sample at 308 K.

Figure 4. Variation of dielectric constant (ε') with frequency for a fluormica glass-ceramic sample at different temperatures.

contribution of ionic polarization to the relative dielectric constant of glass and GC samples is expected to be negligible because the bond character is predominantly covalent[13]. The two main mechanisms expected to contribute to the relative dielectric constant are dipolar and electronic polarization. Electronic polarization always contributes to the total polarization, as it is always present and active up to 10^{17} Hz. It is not possible to sepa-

rate the electronic polarization in the frequency range 0.1 kHz–5 MHz used in our measurement. We propose that there is dipolar polarization in these structures, similar to those in α-SiC that contribute to the dielectric constant of glass and GC samples between 10^4 and 10^7 Hz.

Dielectric constant decreases with increase in frequency in the 100 Hz to 5 MHz range. Dielectric constant also increases with increase in temperature. The rise in ε' at high temperatures and at low frequencies is ascribed to the dc conductivity effect; at higher frequencies such effects are negligible. The observed two peaks attribute the multiple relaxation peaks for different phases in the material as is evident from d-spacing values of XRD (Figure 2)[6–8]. The increase in ε' at higher temperatures/frequencies may be due to weakening of binding force between the ions leading to mobile ion contribution. The increase in ε'' at high frequencies, peaking near 10^6 and 3×10^6 Hz, is likely due to resonant loss of the dipoles. This is also evident in the decrease of ε' at frequencies greater than 10^4 Hz; space charge cannot shift dipole orientation direction with the applied field. This can be attributed to structural rearrangement of the molecule, the α-relaxation process connected with dipole motion. The α-process is the dynamics of the structural rearrangement of the molecules constituting glass[14]. Besides the α-peak, further relaxation process leads to additional peaks usually located in the kHz–MHz region. They are termed β-relaxation (or γ, δ, . . . relaxation, if there are more than one peak) processes and are related to the internal change of molecular conformation and depend on the thermal history of the sample[14,15]. The α and β peaks are observed as evident from Figures 6 and 7. The strong

Figure 5. Variation of dissipation factor (tan δ) with frequency for a fluormica glass and fluormica glass-ceramic sample at 308 K.
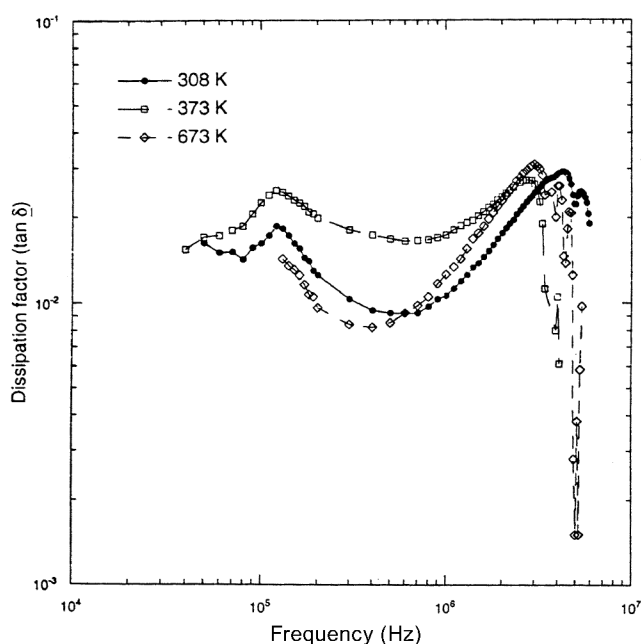
Figure 6. Variation of dissipation factor (tan δ) with frequency for fluormica glass-ceramic sample at different temperatures.
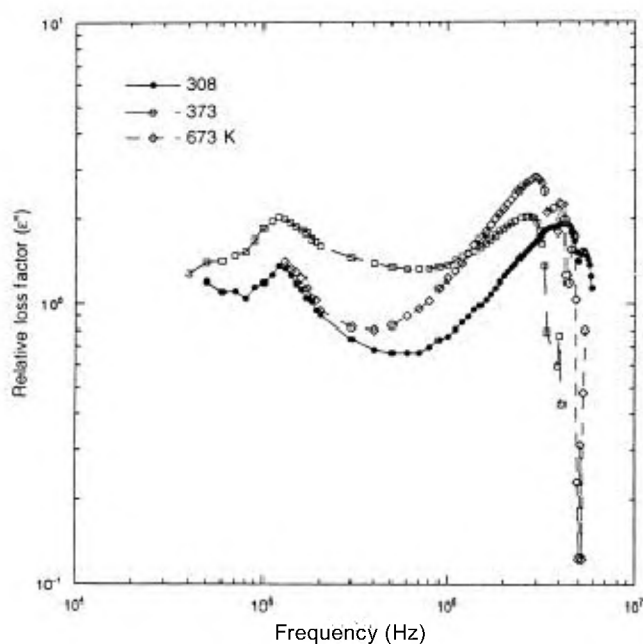
Figure 7. Variation of relative loss factor (ε'') with frequency for glass-ceramic sample at different temperatures.

effect of the crystalline phase on the complex dielectric constant is further evidence that the relaxation is likely related mainly to the cooperative orientation movement of the existing dipoles. The magnitude of the peak increases with temperature. This is expected due to increase in K^+ conducting ion available. Figure 6 shows two relaxation processes near 0.1 MHz and 3 MHz. This is attributed to crystalline and residual glass phases in GC. As the temperature increases, the relaxation at low frequency becomes indistinguishable.

Two distinct relaxation peaks were observed in the frequency dependence of dielectric loss. The absorption appears to be related to dipole motion in the crystalline and residual glass phases of GC.

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Gamma-ray spectroscopic analysis of biotite granites

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Samples collected at various altitudes of the Rajapalayam hills, Western Ghats, Tamil Nadu (lat. 9°19′ and long. 77°32′) were subjected to radioactive analysis using gamma-ray spectrometric technique. The activities of naturally occurring radioactive elements ^{232}Th, ^{238}U and ^{40}K have been determined and compared with in situ measurements using an environmental radiation dosimeter. The linear correlation coefficient has been obtained. The high values found in the activities for ^{232}Th, ^{238}U and ^{40}K are attributed to upward motion of uranium due to metamorphism. The ratio of Th to U exhibits a close agreement with universal value for crustal rock.

INDIA is one of the countries in the world having the highest background radiation levels[1]. These areas are the coastal plains of the south Indian peninsula. The background radiation levels are due to the presence of monazite sand[2]. The monazite deposits in the coastal areas of Tamil Nadu and Kerala are due to the weathering of rocks in the Nilgiri hills and the Western Ghats[3]. Rajapalayam hills (Muthulingapuram) occupy a portion of the Western Ghats (lat. 9°19′ and long. 77°32′). We measured the background radiation levels at different altitudes (sites) in biotite-granites of Rajapalayam hills and identified naturally occurring radionuclides. Calcium carbonate deposits are largely found in the adjoining areas of Rajapalayam. There are a number of cement factories in and around this place, which make use of these deposits[3] for the cement manufacture. As the River Arjuna migrates, minerals containing radionuclides from the Rajapalayam hills can get mixed with the calcium deposits and thereby occur in the calcium products such as white limestone used for wall painting and cement manufacture. Hence the study of minerals with special reference to radionuclides gain importance.

The site, Muthulingapuram hills, is situated about 6 miles southeast of Rajapalayam and about 15 miles south of Srivilliputhur, Tamil Nadu, India. According to the Survey of India toposheet No. 58 G/11/1, it lies between latitudes 9°19′ and 9°25′ and longitudes 77°32′ and 77°45′ (Figure 1). The samples analysed in the present investigation were collected both on the southern and northern side of the hills.

Determination of radioactivity involves measurements of either alpha, beta or gamma radiations from the sam-

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