Dielectric and impedance spectroscopy of aluminium oxide substituted fused silica samples

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Abstract

This paper shows a comparative study of sintered and thermally quenched Al_2O_3 substituted fused silica ceramics processed by colloidal suspension route. The structural analysis is performed using X-ray diffraction measurements. The natural surface micrographs present close packing of non-uniform shape of grains. The high permittivity and low loss are illustrated from frequency dependent permittivity. The impedance spectroscopy shows non-Debye type relaxation mechanism. The Nyquist plot shows the presence of only grain effect. The overlapping large Polaron tunnelling model is attributed from the conduction studies of both sintered and quenched samples.

Keywords XRD · Silica · Impedance · Conductivity

1 Introduction

Extensive research work is being carried out in the field of advance materials due to their potential in development and commercialization of electronic components [1]. The lead-based ceramics are often preferred by various electronics industry due to the superior properties. The strict regulations made by various world agencies have banned the lead-based products looking into its toxicity declining public health and environment [2]. Fused silica acts as an antenna window in spacecraft having low dielectric parameters, low thermal expansion and high melting point [3]. Alumina has various crystalline phases with high strength and stiffness. Al_2O_3 ceramics have low permittivity ($\epsilon_r \sim 10$) and quality factor $\sim 50,000$ GHz. Sriharan et al. [4] fabricated and characterize the Al_2O_3 doped TiO_2 composites derived from soft chemical route. Luo et al. [5] reported the electrical properties of Al_2O_3 doped ZnO . The structural and electrical properties of pure fused silica were reported by same authors [6]. The effect of alumina on mechanical properties of fused silica ceramics is

reported by Wan et al. [7]. The colloidal processing helps to generate uniform microstructural. It possibly combines various consolidate mechanisms to fabricate complex materials [8]. Some of the dopants like Al_2O_3 plays a vital role in reducing the sintering temperature and enhance the mechanical strength. The certain factors such as content of impurity, particle size, synthesis step effects the doping amount of Al_2O_3 .

Detailed studies of the reported literature show that no clear results regarding the electrical properties of Al_2O_3 substituted fused silica samples are reported so far. Therefore, in this paper, the motivation lies in (a) finding a correlation between the structure and physical properties, and (b) understanding of the electrical parameters using complex impedance spectroscopy as well as conduction mechanism in sintered and quenched samples of Al_2O_3 substituted fused silica.

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2 Sample processing and experimental techniques

2.1 Ceramic suspension processing

Fused silica powder (M/S Chettinad Fused quartz Pvt. Ltd, India) and alumina powder (CT3000-SG, Alcoa-USA) was used to fabricate the samples by colloidal processing route. Egg white (fresh eggs extract) and sucrose (Loba Chemie, India) acted as a binder for preparation of suspension. In order to achieve homogenization egg white was stirred employing magnetic stirrer for 2 h. Further various ratios distilled water (premix) was mixed along with egg white and/or sucrose. This premix helps to synthesize the Al_2O_3 doped fused silica suspensions. 55–70 vol% loading added suspensions were further subjected to roll milling the premix with Al_2O_3 and fused silica powders in polypropylene bottles employing 3 mm zirconia grinding media for 24 h. The bubble formation (i.e. arises due to egg white) during the suspension preparation was controlled by 1-octanol (5 mL/100 mL of egg white). The zirconia media are filtered out from suspensions after 24 h of milling, and different measurements were performed. The obtained suspensions were cast into petroleum jelly-coated rectangular aluminium molds and kept in hot oven at 60 °C for 24 h for drying purpose. The green parts were separated from mold after it reached room temperature, and further heated for 24 h in an oven. All samples were kept at 900 °C for 2 h to ensure complete burnout of the organics and achieve sufficient handling strength. Then the sintering is done at 1100 °C in a high temperature furnace with soaking period for 2 h. The as-sintered Al_2O_3 substituted fused silica samples were subjected to thermal cycling for 5 times. A single thermal cycle comprises of heating to 900 °C, a 30 min dwell at 900 °C followed by quenching in chilled water (5 °C).

2.2 Experimental techniques

The phase formation of sintered and quenched samples was evolved using Rigaku MiniflexII X-ray diffractometer at a scanning rate of 2°/min over Bragg's angle ($10 \leq 2\theta \leq 70$, radiation = $\text{CuK}\alpha$). The surface micrographs were obtained employing the FESEM (M/S FEI Nova NanoSEM 400). One of the pellets each from sintered and quenched samples were polished parallel both sides and silver-painted forming metal–insulator–metal arrangement before electrical measurements. The computer-interfaced LCR meter (UK made N4L PSM) detects the electrical properties of the samples (sintered and

quenched) as a function of frequency (10^3 – 10^6 Hz) and temperature (25–500 °C). Figure 1a shows systematic representation of the synthesis and characterization carried out.

3 Results and discussions

3.1 Structural and morphological analysis

Figure 1b shows the structural analysis of the sintered and quenched samples. It is well known that beyond the 1100 °C the crystallization starts forming dispersed cristobalite crystals during fused silica processing. Hence at 1100 °C, the formation of the prepared samples is confirmed. The surface morphology and densification are illustrated in Fig. 2 (a) sintered and (b) quenched. It suggests that the pattern of grains is irregular and non-uniform having varying sizes. It depicts maximum grains are packed closely throughout the surface without cracks. The density of the sintered sample is 1.7 gm/cc while a slight increase in density is seen for the quenched sample that is 1.9 gm/cc. Figure 3 shows the EDX spectra of (a) sintered and (b) quenched samples. It suggests that all the elements are presented similar to base composition without any trace of impurity.

3.2 Analysis of dielectric parameters

The dipoles of dielectrics rearrange in a particular direction as subjected to an electric field, and exhibit alignment of polar charges. The dielectric material tries to reorient and neutralize charges on the electrodes can express in terms of a transfer function coined as dielectric permittivity. The dielectric permittivity of most dielectric materials is frequency dependent. Figure 4 (a, b) presents the relative dielectric constant (ϵ_r) and loss tangent ($\tan \delta$) at different frequencies and temperatures for both as-sintered and quenched Al_2O_3 substituted fused silica samples. The ϵ_r and $\tan \delta$ value falls on enhancement of frequency, which is a common trend of oxide materials. The different polarizations (interfacial, dipole, atomic, ionic, and electronic) have been dominant in low-frequency region [9]. The polarization fades away with enhancement of frequency slowly; as a result, dielectric constant decreases for both samples. The loss factor is the estimate of how dissipative material is when subjected to an external electric field. Figure 4a, b inset shows the loss has a similar trend like dielectric constant. At lower frequency the spectra show dispersive nature and the trend coincides at higher frequency depend mainly on the contribution of space charge polarization. It is well known that the $\tan \delta$ has two parts: (1) relaxation part (Debye or non-Debye) and

Fig. 1 **a** The representation of synthesis and further characterization process of samples. **b** XRD pattern of sintered and quenched Al_2O_3 substituted fused silica samples at room temperature

(2) dc conductivity part. The relaxation peaks are absent in both sintered and quenched samples in the experimental temperature range. The loss factor value increases as the frequency rise due to charge carriers and unknown defects [10].

3.3 Complex impedance analysis and Nyquist plot

The complex impedance spectroscopy (CIS) tool was designed by Bauerle [11] to shed light upon the polarization process in the materials. CIS helps to get information about the electrical characterization of polycrystalline

materials [12]. It suggests about homogeneous (bulk) and inhomogeneous distribution of grains, grain-boundary, electrolyte–electrode interface process, porosity in the materials.

Figure 5a, b presents the change of Z' with frequency at a few temperatures. The low-frequency dispersion is depicted for all curves, form a plateau at higher frequency. The relaxation process is delayed due to space charges causing the low-frequency dispersion. It is noticed that the Z' value of all the temperatures merged at high-frequency. The presence of combined PTCR (positive temperature coefficient of resistance)/NTCR (negative temperature

Fig. 2 Surface micrographs of **a** sintered, **b** quenched Al_2O_3 substituted fused silica

Fig. 3 EDX spectra showing the chemical composition of **a** sintered and **b** quenched Al_2O_3 substituted fused silica samples

coefficient of resistance) behavior is suggested for both sintered and quenched samples as with temperature rise the value of Z' increases as well as decreases [13].

Figure 5a, b inset presents the change of Z'' with frequency at few temperatures for both sintered and

quenched samples. At a characteristic frequency ($\omega_{\max} = 2\pi f_{\max}$) peak appears, that is independent of sample geometry, temperature-dependent and correspond to strength of the electrical relaxation in the materials. The relaxation process occurs due to immobile charges at

Fig. 4 Frequency dependent dielectric constant and (inset) loss factor of **a** sintered and **b** quenched of Al_2O_3 substituted fused silica samples

Fig. 5 Frequency dependent real and imaginary part of impedance **a** sintered and **b** quenched Al_2O_3 substituted fused silica samples

lower temperatures and vacancies at higher temperatures [14]. The asymmetric relaxation peaks with a broad distribution of relaxation times, suggesting Non-Debye type behavior in both sintered and quenched samples [15].

Figure 6a, b presents the variation of Nyquist plot of both sintered and quenched samples at selected temperatures. It is well known that; the Debye or non-Debye type relaxation mechanisms can be resolved from the shape of the semi-circular arc depicted in the Nyquist plot. In general, a full or partial semicircle depends on the relaxation strength and experimental range of frequency. These experimental data are usually fitted with an equivalent circuit comprising of resistance (R), capacitance (C) and constant phase elements (Q) connected in a parallel configuration to analyze the transport properties of the material. The circuit model suggests the kind of impedances and their arrangement (series/parallel) in the sample and compares the temperature dependence of the resistance and capacitance values to that of the simulated one. For both sintered and quenched samples, depressed semicircle (i.e., non-Debye-type response) suggests a new circuit model is needed to fit it. The occurrence of asymmetric semi-circle shows non-Debye type of relaxation in both the sintered and quenched samples [16, 17]. The circuit model used for fitting the impedance data of sintered and quenched sample is RQC. This suggests only grain effect is present at all temperatures for both the sintered and quenched samples.

3.4 Conductivity analysis

The ac conductivity in bulk materials occurs due to (a) long-range ac conductivity and (b) localized transport oxygen vacancies. To shed light on electrical transport properties, the ac conductivity needed to be explored. The frequency dependence of ac conductivity is explained using Jonscher's power law [18], $\sigma_{ac}(\omega) = \sigma(o) + \sigma_1(\omega) = \sigma_{dc} + A\omega^n$; $0 < n < 1$, where symbols have similar meaning. The σ_{ac} rise on increasing frequency in the high-temperature region for sintered and quenched samples due to space charge polarization [19]. The n value lies between zero and one. The universal power

Fig. 6 Nyquist plot of **a** sintered and **b** quenched samples at selected temperatures

Fig. 7 Frequency dependent AC conductivity **a** sintered; **b** quenched Al_2O_3 substituted fused silica samples and (inset) illustrates the change of n value with temperature

law is obeyed by both plots depicted from the best fit of above equation to the experimental data (Fig. 7a, b), where solid line corresponds to fitted curve and symbols

are experimental data. The n value less than 1 showing hopping motion having translational motion with a sudden hopping whereas $n > 1$ means that the motion involves localized hopping without the species leaving the neighborhood [20]. The equation $\sigma_{AC} = A\omega^n$; where the constant dependent temperature is represented by A , ω shows the angular frequency and the power-law exponent is given by n , where n is between $0 < n < 1$ [21]. Here from (inset) it is depicted that the n value first decreases and thereby increases with rise in temperature depicting an overlapping large Polaron tunnel mechanism (OLPT) [22].

4 Conclusion

The lead-free Al_2O_3 doped fused silica is fabricated using colloidal processing technique. The XRD pattern illustrated that the fabricated material has formed. The SEM micrographs show a densely packed surface morphology for sintered and quenched samples. The frequency-dependent AC conductivity plot obeys Jonscher's universal power law for both the sintered and quenched samples. Comprehensive analysis of impedance characteristics illustrated the non-Debye type of relaxation phenomena, the subsistence of NTCR/PTCR type behavior in the sintered and quenched samples. The above results suggest that the prepared lead-free samples are low loss material suitable for advance filter applications.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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