

Research Article

Effect of γ -Irradiation on the Dielectric and Conductivity Properties of Nano-Wollastonite

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Nanocrystalline porous CaSiO_3 ceramic powders have been synthesized by a novel low-temperature initiated self-propagating, gas-producing solution combustion method. Single phase β - CaSiO_3 (Wollastonite) is formed by calcination at 900°C for 3 h. The crystallization and phase formation temperatures in this method are found to be lower compared to the powder obtained via solid state reaction method. The powder is characterized by powder XRD (X-Ray Diffraction), and crystallite sizes are evaluated using Scherrer's formula as well as from TEM (Transmission Electron Microscopy). The Wollastonite powder is exposed to ^{60}Co γ -radiation to accumulated doses of 1, 3, and 5 KGy and low-frequency (10^2 – 10^6 Hz) dielectric measurements are carried out before and after irradiation. The dielectric conductivity is estimated from the dielectric constant and loss tangent. Exposure to γ -radiation results in substantial modification in the properties of the ceramic powder due to changes in the porosity of the material. The correlation between dielectric and conductivity properties is discussed in relation to porosity effect.

1. Introduction

Materials with porous architecture and high surface area are known to have numerous potential applications in nanotechnology. Several attempts are being made to develop these materials for specific applications such as catalysis and separation science, molecular sieves, zeolites, hybrid optics, bioceramics and many more. Ceramic materials with porous structure like silicates of calcium can combine the advantages of both porous materials and ceramics as they have a combination of thermal, electrical, and dielectric properties which make them useful for technological applications. CaSiO_3 is one such material that can be used for the production of special radio ceramics, sanitary components, porcelain materials, lining bricks, glaze, and flux [1]. CaSiO_3 ceramics are also used as a biomaterial in medical industry [2]. CaSiO_3 in different phases have been synthesized by different routes and characterized earlier [3]. However, a complete

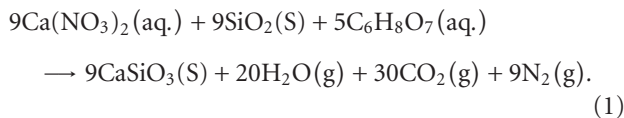
understanding of the dielectric and electrical properties of these materials has not yet emerged. An understanding of the dielectric and electrical properties is important from the point of applications. Many times these materials are used for applications in radiation rich environments such as space, nuclear reactors and nuclear waste containers. Exposure to radiation can bring in modification in their physical properties due to structural changes. Thus, it is important to understand the effect of ionizing radiation on the properties of these materials.

Enhanced dielectric properties of CaSiO_3 ceramics at microwave frequency range have been reported earlier by Cai et al., Wang et al., and Sun et al. [4–6]. Cai et al. [4] have reported that CaSiO_3 ceramics possess excellent dielectric properties with relative dielectric constant $\epsilon_r = 7.0$ – 9.0 and loss tangent $\tan \delta = (1.0$ – $5.0) \times 10^{-4}$. Wang et al. [5] have showed that, at the sintering temperature of 1320°C , the CaSiO_3 nanopowders prepared by sol-gel

method exhibit excellent dielectric properties with $\epsilon = 6.69$ and quality factor $Qf = 25398$ GHz. Sun et al. [6] have investigated a low-permittivity microwave dielectric ceramic system $(Ca_{1-x}Mg_x)SiO_3$. Substitution in the A-site occurred in the composition range of $0.1 \leq x \leq 0.9$. When $x = 0.1$, the specimen sintered at 1290°C for 2 h exhibits excellent dielectric properties with $\epsilon = 6.49$ and $Qf = 62420$ GHz. Although dielectric properties of $CaSiO_3$ at microwave frequencies have been investigated earlier, there appears to be hardly any studies on low-frequency dielectric and conductivity properties of $CaSiO_3$ ceramics and their structural modification upon exposure to ionizing radiation. The present investigation was carried out in an attempt to understand the effect of ionizing radiation (γ -radiation) on the structural and low-frequency (10^2 – 10^6 Hz) dielectric and conductivity properties. To the best of our knowledge, this is the first ever attempt made to study the γ -irradiation effects on dielectric and conductivity properties of porous nano- β - $CaSiO_3$ at low frequencies (audio-radio frequencies).

2. Experimental

The $CaSiO_3$ ceramic powder is prepared by dissolving stoichiometric quantities of Analar grade calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$), fumed silica (SiO_2 of 99.9% purity and surface area of $200\text{ m}^2/\text{gm}$), and citric acid ($C_6H_8O_7$, which acts as a fuel for redox reaction) in a minimum quantity of water and dispersed well using magnetic stirrer for half an hour. The stoichiometry of the redox mixture used for combustion process was calculated using total oxidizing and reducing valencies of the ingredients which serve as numerical coefficients for the stoichiometric balance so that the equivalence ratio is unity and the energy released by the combustion is maximum [7]. The heterogeneous redox mixture was rapidly heated in a muffle furnace maintained at $500 \pm 10^\circ\text{C}$. The redox mixture when heated at 500°C boils and thermally dehydrates forming a honeycomb-like gel, which ignites to yield voluminous $CaSiO_3$ powder. Assuming complete combustion of the mixture used, the synthesis of $CaSiO_3$ may be represented by reaction equation



X-ray powder diffractometer (Phillips X'pert) using CuK_α radiation with a Ni-filter was used to record diffractograms of the ceramic powders. The surface morphology, size distribution of the grains were examined by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM photographs were taken with a Philips (XL30-ESEM) instrument. A JEM 2000 Ex instrument was used to take TEM photographs. The combustion product of "as formed" $CaSiO_3$ is ground well to form a fine powder. The calcined powder (at 900°C , where it has attained the single phase of β - $CaSiO_3$) is ground well, and it is pressed into pellets of 2 mm thickness and 5 mm diameter. The ceramic samples were irradiated at room temperature by γ -radiation

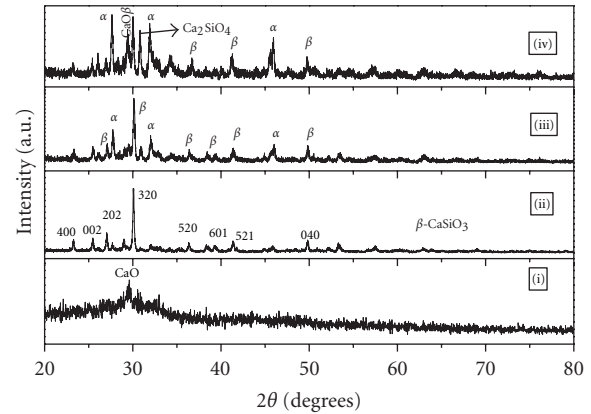


FIGURE 1: XRD patterns of $CaSiO_3$ (i) as formed, (ii) calcined at 900°C (β - $CaSiO_3$), (iii) exposed to γ -radiation to an accumulated dose of 1 KGy, and (iv) exposed to 5 KGy.

using ^{60}Co γ -irradiator (Blood Irradiator-2000) to three different accumulated doses of 1, 3, and 5 KGy. The dielectric measurements were carried out using Hioki impedance analyzer 3532-50 (Japan) in the frequency range 10^2 – 10^6 Hz at room temperature. AC conductivity as a function of frequency is estimated from the dielectric measurement data.

3. Results and Discussion

3.1. Powder XRD Studies. The XRD patterns of "as formed", sintered (at 900°C for 3 hours), and γ -irradiated $CaSiO_3$ powders are shown in Figure 1. The XRD patterns reveal that "as formed" $CaSiO_3$ powder exhibits amorphous phase. The powder gives rise to a single β - $CaSiO_3$ phase when calcined at 900°C for 3 h. The peak positions of β - $CaSiO_3$ phase and their hkl values are in good agreement with JCPDS file no. 84-0655. It is found that the crystal system of single phase β - $CaSiO_3$ is monoclinic with space group $P2_1/a$. The particle size of the ceramic powders is calculated from the full width at half maximum (FWHM) of the diffraction peaks and line broadening Scherrer's formula $D = k\lambda/\text{FWHM} \cdot \cos\theta$, where λ is the wavelength of X-ray, θ is the Bragg angle, and k is the constant which depends on the grain shape (0.89 \AA for circular grains). It was found that the average particle size of the single phase β - $CaSiO_3$ powder is in the range of 20–30 nm. After γ -irradiation to an accumulated dose of 1 KGy, extra peaks are observed in the diffractogram. Further, for higher dose of 5 KGy, still more peaks are observed. This observation appears to be unusual. It is normally believed that exposure of ceramic powders to ionizing radiation would result in decrease in crystallinity and increase in amorphous content as a result of disorder introduced due to generation of defects. In the present case, additional peaks are observed after γ -irradiation. This may be attributed to the sample going into a mixed phase (α - and β - $CaSiO_3$) after irradiation.

3.2. Transmission Electron Microscopy. Figure 2 shows the TEM image of β - $CaSiO_3$. It can be seen that the particles are agglomerated. The mean particle size is observed to be

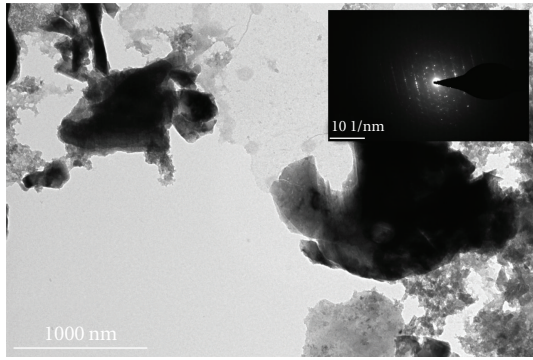


FIGURE 2: TEM image of β -CaSiO₃ calcined at 900°C with SAED inset.

about 30 nm in agreement with the estimation from XRD measurements. The SAED (Selected Area Electron Diffraction) pattern showed in the inset displays bright spots. This shows single crystal nature of β -CaSiO₃.

3.3. Scanning Electron Microscopy. The morphology and size distribution of calcined β -CaSiO₃ before γ -irradiation and β -CaSiO₃ exposed to 5 KGy dose were examined using SEM images and are shown in Figure 3. The image shows that the sintered sample before irradiation is porous. On the other hand, the irradiated sample exhibits sheet morphology consisting of regularly arranged nanorods due to chain like structure of (SiO₄)⁻⁴ ions increasing the porosity [8]. Similar type of sheet morphology in SEM image of CaSiO₃ has been reported earlier by Zhou and Yan [9].

3.4. Dielectric Measurements. Ceramic materials possess high values for static dielectric constant (ϵ) and are widely used in technological applications. When used for making electronic components, the value of ϵ determines the degree of miniaturization of electronic circuits. The dielectric constant of a material is related to the polarizability α , in particular to the dipole polarizability, which arises from structures with a permanent electric dipole that can change orientation in an applied electric field. In metals, the electronic charge is delocalized and $\epsilon \ll 0$. In insulators, the charge is localized and $\epsilon > 0$. Materials with a dielectric constant greater than that of silicon nitride ($\epsilon > 7$) are classified as high dielectric constant materials [10]. In general, polarization of a dielectric in the presence of an electric field comprises two factors: relaxation polarization and resonance polarization. The former plays a major role at lower frequencies and responds to the message of the sample structure. The latter plays an important part at higher frequencies. Microstructure difference, morphotropic phase boundary, pores, defects, and so forth are the main sources of the relaxation polarization, but they do not work at higher frequencies [11].

The static dielectric constant is taken as $\epsilon = \epsilon'(\omega \rightarrow 0)$, where the frequency dependent complex dielectric function is $\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are the real and imaginary parts, respectively. The dissipation factor is referred to as the loss tangent $\tan \delta = \epsilon''/\epsilon'$, where the

angle δ is the phase difference between the applied electric field and the induced current. The dielectric loss is a measure of the imaginary part (ϵ'') of the complex dielectric function [12].

Figure 4 shows the variation of relative or static dielectric constant with frequency for β -CaSiO₃ powders before and after γ -irradiation. Dielectric measurements (in the frequency range 10²–10⁶ Hz) before irradiation of β -CaSiO₃ reveal that the dielectric constant decreases sharply in the KHz region and more slowly in the MHz region with increasing frequency. This suggests that at low frequencies the electronic, ionic, dipolar, and space charge (surface charge) polarizations contribute to the dielectric constant. However, in the MHz frequency range, the contribution from the space charge polarization is minimized and the dielectric constant almost remain constant. This feature is similar to those observed in some dielectric oxides, such as Ba₄LaMnNb₃O₁₅ (M = Ti and Sn) [13]. For an accumulated dose of 1 KGy, the dielectric constant increases, while for higher doses, it decreases. The variation of loss tangent with frequency shown in Figure 5 also behaves similar to dielectric constant. Increase in dielectric constant and loss tangent after exposure to a dose of 1 KGy γ -radiation may be attributed to atomic displacements. The γ -radiation is known to interact with atoms of the solids by first generating secondary electrons which in turn produce atomic displacements. Atomic displacements produce various types of lattice defects. The defects influence macroscopic physical properties. In the present case, the off-centre displacement of Ca and Si ions from normal sites would lead to distortion of the structure. This may result in increase in polarization and hence increase in dielectric constant and loss tangent. Similar effects have been observed previously by Darwish et al. in crystalline Co-Zn ferrites [14]. However, the decrease in dielectric constant and loss tangent after exposure to higher doses appears to be due to a different mechanism. Higher doses of γ -radiation may cause rearrangement of atoms and primary defects. The rearrangement would produce stable defects due to redistribution of γ -radiation energy over the sample. This would suppress the polarization properties and migration of defects. Such effects are more pronounced in binary (such as CaSiO₃) and ternary ceramic materials as proposed by Mektieva [15]. However, the γ -radiation effects on the dielectric properties of ceramics would depend strongly not only on the γ -dose but also on the prior history of the material.

3.5. Electrical Conductivity Measurements. Electrical conductivity should be low for dielectrics to show a good response. In general, the defect centers and impurities that could contribute to the conductivity are randomly distributed in dielectrics. Conduction is basically due to a hopping of electrons in the dielectric materials. In the case of ionic solid such as CaSiO₃, the excess electrons in a narrow conduction band (or excess holes in a narrow valence band) due to their interaction with lattice ions can distort the surroundings in such a way that a potential well generated is deep

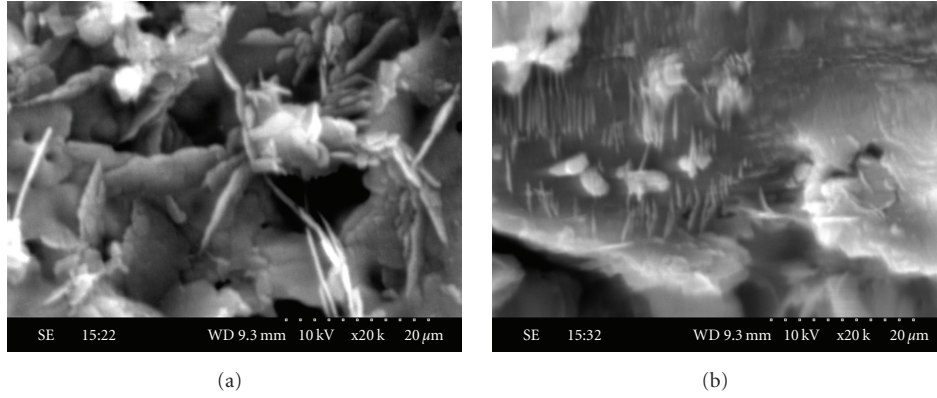


FIGURE 3: SEM photographs of β -CaSiO₃ (a) before γ -irradiation and (b) after γ -irradiation to an accumulated dose of 5 KGy.

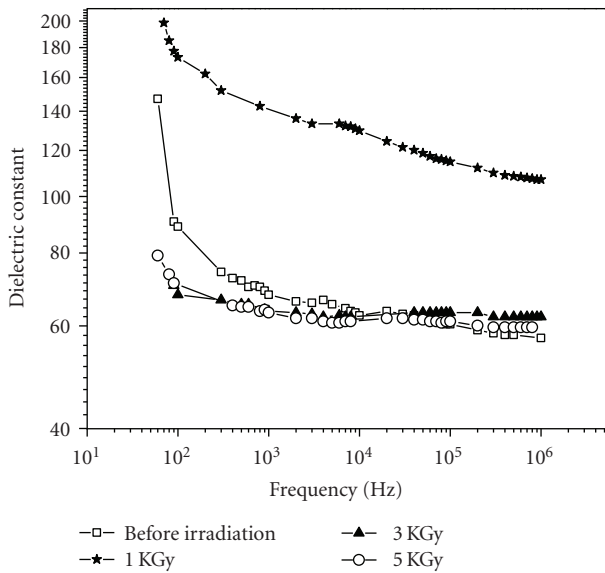


FIGURE 4: Variation of dielectric constant with frequency for β -CaSiO₃.

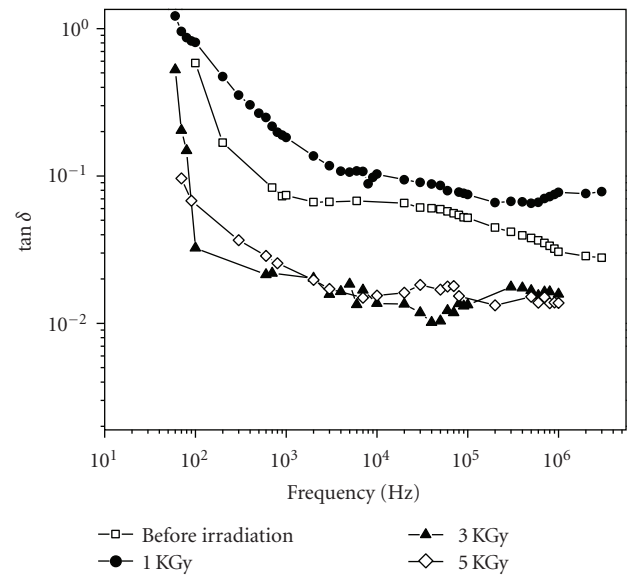


FIGURE 5: Variation of loss tangent with frequency for β -CaSiO₃.

enough to introduce localization leading to the conductivity. Although conduction does occur in dielectrics, it is rather low. The dielectric conductivity (σ) can be obtained from the dielectric constant and loss tangent using the relation [16]

$$\sigma = \epsilon' \epsilon_0 \omega \tan \delta = \epsilon'' \epsilon_0 \omega, \quad (2)$$

where " ϵ_0 " is the dielectric constant of free space, and $\omega = 2\pi f$ is the angular velocity. Figure 6 shows the variation of conductivity as a function of frequency for β -CaSiO₃ before and after γ -irradiation. Both unirradiated and irradiated samples exhibit the same behavior, that is, high frequency dispersion and flat frequency insensitive conductivities at low frequencies. The nature of conductivity behavior can be explained using Almond-West type power law using single exponent [17]

$$\sigma(\omega) = \sigma(0) + A \omega^s, \quad (3)$$

where $\sigma(0)$ is the DC conductivity which is the frequency independent part of σ versus ω plot, A is a constant, and " s "

is the power law exponent. The data were computer-fitted to the above equation. The value of exponent lies in the range 0.7 to 0.9. Figure 6 shows the fit of the conductivity data to power law. The DC conductivity (frequency independent plateau in the low frequency region) evaluated from the fit for the unirradiated sample is of the order of 10^{-9} mho cm^{-1} . The frequency dependent conductivity can be explained as follows: in a hopping model, it is possible to distinguish different characteristic regions of frequency. In the low frequency region where the conductivity almost remains constant, the transport would take place on infinite paths. In the region of frequencies where the conductivity increases with frequency, the transport is dominated by contributions from hopping of infinite clusters [18]. The DC conductivity increases by a factor of 3 after exposure to 1 KGy, while for higher doses of exposure, the conductivity decreases. Since the dielectric constant and dielectric conductivity are directly related, both exhibit similar variation after exposure to γ -radiation. Similarly, the decrease in dielectric constant

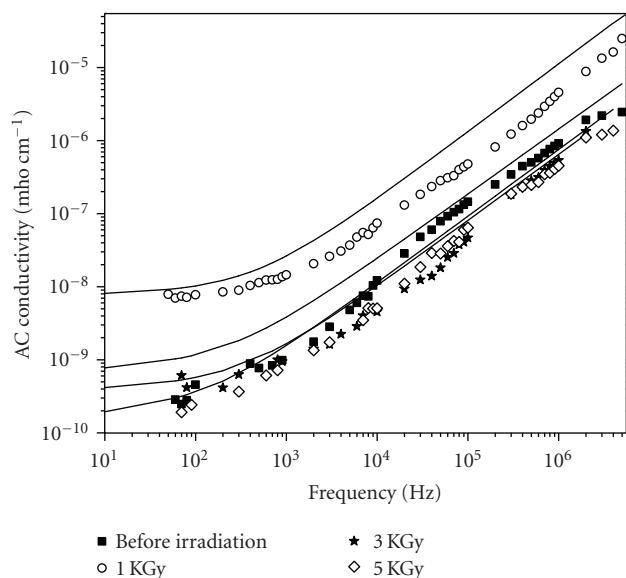


FIGURE 6: Variation of conductivity with frequency for β -CaSiO₃. The solid lines are fit to power law equation.

and hence dielectric conductivity at higher dose may be attributed to the porosity of the CaSiO₃ powder. However, the effect of porosity on the dielectric conductivity needs further investigation. In semiconducting SrTiO₃ doped with Y₂O₃, it is reported that increase in porosity has resulted in decrease in conductivity [19]. However, in polycrystalline NaNbO₃ ceramic, porous counterpart is known to exhibit higher bulk conductivity than dense ones [20]. In any case, exposure of ceramic powders to γ -radiation has resulted in modifications in the dielectric and electrical properties of nano- β -CaSiO₃. The investigation thus reveals the possibility of employing γ -radiation in controlling the properties of ceramic powders for specific technological applications.

4. Conclusion

Crystalline CaSiO₃ ceramic powder synthesized by solution combustion route exhibits a single β -phase when calcined at 900°C in the nanoregime with a particle size of the order of 20–30 nm. The powder exhibits a quite high dielectric constant as well as dielectric conductivity at low frequency. Exposure of the nanopowder to γ -radiation results in substantial changes in the dielectric and conductivity perhaps due to increase in porosity of the material. However, detailed investigation would be required to ascertain the effect of porosity on the properties of the material. The investigation reveals the possibility of employing the ionizing radiation to tailor the dielectric and electrical properties of the Wollastonite.

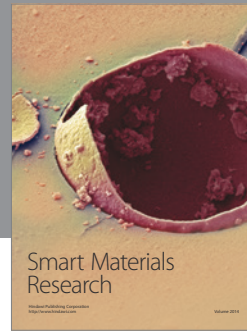
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