Research Article

Preparation and Electrical Properties of $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ and 0.2) Ferroelectric Ceramics

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Polycrystalline ceramic samples of pure and germanium (Ge^{4+}) doped fresnoite of general formula $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ and 0.2) have been prepared by solid state reaction technique. The formation of the single phase compound was confirmed by X-ray diffraction and the structural parameters were refined by the Rietveld refinement technique. The dc conductivity of both the materials has been measured as a function of temperature from room temperature to 753 K and activation energy was calculated using the relation $\sigma = \sigma_0 \exp(-E_a/kt)$. The activation energy 4.74 eV obtained for the pure compound is very high in comparison with 1.47 eV of Ge^{4+} -substituted compound. The frequency and temperature dependent dielectric behavior of both the compounds have been studied. The real and imaginary parts of the dielectric constant increase with the increase of temperature.

1. Introduction

Fresnoite, a rare barium titanium silicate mineral, $\text{Ba}_2\text{TiOSi}_2\text{O}_7$, was discovered during the geological investigation of the sanbornite deposits at Fresno County, California [1]. The mineral shows a noncentrosymmetric tetragonal crystal structure with space group $P4bm$ [2]. Due to its non-centrosymmetry, the material shows good ferroelectric, piezoelectric, pyroelectric, optical, and other physical properties useful for different practical devices [3–8]. The single crystal data of fresnoite shows a broad peak in dielectric permittivity at ~ 433 K but the same peak is absent in dielectric loss curve. It is surprising that the ceramic samples fail to reveal the dielectric anomaly shown in case of single crystal at 433 K [3]. Not only that, but a small reproducible dielectric anomaly has also been reported in the frequency range 0.1–100 kHz at 805 K. However, the single crystal X-ray data taken at 297 K and 573 K revealed no change in symmetry except small changes in atomic position, the largest of which were less than $0.02 \text{ \AA}$ [8]. Recent studies on oriented crystallization using thermal gradient, crystallization kinetics, and electrical properties through impedance spectroscopy were also carried out on fresnoite and fresnoite like glassy materials

[9–11]. The ceramic sample also showed good hysteresis loop at room temperature but the shape of the loop remained unchanged when temperature increased to 875 K. It is surprising that the high temperature X-ray, DTA, and specific heat measurements gave no indication of phase transition.

The present paper reports on the synthesis, X-ray diffraction, dc conductivity, and dielectric properties of pure and 10% Ge-doped fresnoite compounds.

2. Materials and Method

The Polycrystalline ceramic samples of pure and Ge-substituted fresnoite compounds of general formula $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ and 0.2) were prepared by conventional solid state reaction technique using high purity (99.9%) carbonates and oxides (BaCO_3 , TiO_2 , GeO_2 and SiO_2). Stoichiometric mixture of these oxides and carbonates was thoroughly mixed and grinded for several hours and then calcined at $800\text{--}900^\circ\text{C}$ in silica crucible in air atmosphere. The process of mixing and calcination was repeated until a fine homogeneous powder of the material was obtained. The resulting mixture was compressed into pellet form and sintered at desired temperature. The complete synthesis

FIGURE 1: RT X-ray diffraction patterns of $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ & 0.2).

process of both the compounds was reported in our earlier paper [12]. The formation of the single phase compound was checked by X-ray diffraction pattern using the Rigaku X-ray diffractometer with $\text{CuK}\alpha$ radiation and nickel filter in a wide range of 2θ from 10 to 70° with a scanning rate of 2° per minute. The dc electrical conductivity as a function of temperature was measured by laboratory made setup. The dielectric constant and dissipation factor as a function of frequencies (100 Hz to 2 MHz) and temperature (300 K–673 K) were measured by Hioki 3532-50 LCR HiTester. The dc conductivity and dielectric measurements were performed on the circular dish-shaped samples with silver paint coated on two sides as the electrodes.

3. Results and Discussion

The room temperature (RT) X-ray diffraction patterns of the samples $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ and 0.2) are shown in Figure 1. From the X-ray diffraction pattern it is observed that there is a small shift in some of the peaks positions and intensities for the substituted compound with respect to the pure compound. The detailed Rietveld refinement of X-ray diffraction data for both the compounds was reported in our earlier paper [12]. The lattice parameters and some other structural parameters are summarized in Table 1.

The temperature dependence of dc electrical conductivity (σ_{dc}) for both the compositions has been evaluated by taking the steady-state values of current and results are plotted for elevated temperature range from 643 to 753 K shown in Figure 2. The resistivities of these samples are so high that they are almost temperature independent from RT to 643 K and hence the results are plotted for an elevated temperature range from 643 to 753 K. The high resistivity of

FIGURE 2: $\log \sigma$ versus $1000/T$ curves of $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ & 0.2).

the samples reveals the insulating property of ferroelectrics. Not only this, when an electric field is applied to the samples, there is the known reorientation of the dipoles, but also the displacement of the charge carriers. Therefore, the electrical conductivity behavior should be considered for ferroelectricity. After 643 K, the conductivity of both the samples increases up to the measured temperature range. The increase in conductivity may be explained by the fact that it is a consequence of thermally activated processes, which can be described by the Arrhenius relation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right), \quad (1)$$

where σ_0 is the preexponential factor, E_a is the activation energy, and k is the Boltzmann constant having the value $k = 8.6 \times 10^{-5} \text{ eV/K}$. The Arrhenius equation is an accurate formula for the temperature dependence of reaction rates. In the natural logarithm form, the Arrhenius equation has the same form as an equation for a straight line; hence, we fit the data as a straight line and calculate the activation energy by measuring the slope of this straight line. The activation energies of both the samples ($x = 0.0$ and 0.2) were calculated from $\log \sigma$ versus $1000/T$ curve and tabulated in Table 1. It is well known that oxide materials need high temperature for their processing; at temperature above 1000°C , the oxygen present in the compound is expected to escape from the sample lattice and create oxygen vacancies in the lattice. During the cooling process, oxygen again enters in the lattice but these oxygen ions cannot totally compensate the loss of oxygen. This is the case with titanates and other layered structure compounds including present compounds [13, 14]. The high value of activation energy of the pure fresnoite compound and the decrease in E_a of Ge-substituted compound can be explained on the basis of energy band gap (E_g) of silicon (Si) and germanium (Ge). The energy band gap for Ge (0.67 eV) is smaller than energy band gap

TABLE I: Structural and electrical parameters of $\text{Ba}_2(\text{TiO})\text{Si}_{1-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ and 0.2).

Composition	$a = b$ (Å)	c (Å)	V (Å ³)	Tetragonality (c/a)	E_a (eV)
$x = 0.0$	8.542	5.220	381.083	0.61	4.74
$x = 0.2$	8.551	5.222	383.437	0.61	1.47

FIGURE 3: Dielectric constant versus $\log f$ curves of $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ & 0.2) at room temperature. FIGURE 4: Dielectric constant versus temperature curves of $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ & 0.2) at 100 kHz.

for Si (1.11 eV); hence, with the substitution of Ge on Si site the activation energy decreases and conductivity increases. This increase in conductivity can also be explained on the basis of dissociation bond energy of Si–O bond and Si–Ge bond. When the Ge-ion is substituted in Si-site, the Si–O bond of high bond energy 452 kJ/mol breaks and makes a new bond Si–Ge of low bond energy 297 kJ/mol hence bond strength reduce and increases the conductivity of substituted compound. The detailed description of the high activation energy value of the pure fersite compound has been given on the basis of energy band model in our earlier paper [15]. Although there is a difference in conductivity of both samples, their small but finite conductivities have been taken into account to explain the ferroelectricity in the samples.

Figure 3 shows the variation of dielectric constant (ϵ') as a function of frequencies (100 Hz to 2 MHz) at RT. From the figure, it is clear that dielectric constant decreases with the increase of frequency. At lower frequencies, the dielectric constant decreases rapidly but it remains almost constant (relaxation behavior) or frequency independent at higher frequencies. This variation of dielectric constant and dissipation factor at lower frequencies is attributed not to the electronic and ionic contribution of polarization, but to the space charge contribution. While with the increase of frequency, the ionic and electronic contribution become dominant and space charge contribution diminishes gradually and hence dielectric constant decreases with the increase of frequency.

The temperature variation of dielectric constant of $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ and 0.2) at a frequency of 100 kHz is shown in Figure 4. From the figure it is observed that dielectric constant of pure compound is almost temperature independent up to 600 K and then increases up to the measured temperature range. When the Ge^{4+} ions are substituted on Si^{4+} ions site, dielectric constant increases rapidly and continuously after a temperature of 400 K. The plot reveals that at lower temperature the magnitude of dielectric constant of the $x = 0.2$ compound is lower than the dielectric constant of pure ($x = 0.0$) compound. But, at higher temperature the dielectric constant increases with respect to the dielectric constant of the $x = 0.0$ compound. This increase in dielectric constant for substituted compound implies that this substitution produces more and more dipole moments in the lattice at higher temperature and hence increases the dielectric constant. But, no dielectric anomaly occurs up to the measured temperature range in both the compounds. Figure 5 shows the variation of dissipation factor (ϵ'') of both the compounds as a function of temperature at a frequency of 100 kHz. The dissipation factor shows almost similar behavior as the dielectric constant. The decrease in magnitude of dissipation factor for the $x = 0.2$ compound at higher temperature supports the nature of dielectric constant as shown in Figure 4. Not only this, but no dielectric anomalies have also been observed in any case up to the measured temperature range.

FIGURE 5: Dissipation factor versus temperature curves of $\text{Ba}_2\text{TiOSi}_{2-x}\text{Ge}_x\text{O}_7$ ($x = 0.0$ & 0.2) at 100 kHz.

4. Conclusion

Analyzing the X-ray results, it is concluded that the Rietveld refinement with a structural model of Pseudo-Voigt function using noncentrosymmetric space group $P4bm$ confirmed the tetragonal structure of both the compounds. The dependence of dielectric constant and dielectric loss on temperature could be discussed with the effect of Ge^{4+} concentration on both conductivity and dielectric behaviour. The high resistivity and moderate dielectric constant of both the samples tends to ferroelectricity and responsible for good dielectric and ferroelectric behavior useful for different practical devices. Because of low dielectric constant, both the materials are useful for low frequency resonator.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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