Synthesis and Characterization of $CaGeO_3$ Nanoparticles by Ecofriendly Method

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ABSTRACT

In present study eco-friendly synthesis of calcium germanate by solid state mechanochemical method. The synthesis of $CaGeO_3$ *from CaO and* GeO_2 *was investigated at 1000* ^{O}C *for the period of 12 hr. The structural and micro structural properties of material were characterized by various techniques like Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction analysis (XRD), Energy dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA) and surface area determination (BET). The synthesized material show crystal planes which indicates the formation of triclinic* $CaGeO_3$ *with the space group [P1(2)] and d-line pattern matches well with reported JCPDS data card no.21-0142. Average particle size of the synthesized material was below 100 nm and band gap energy 3.28 eV. The electric properties of material exhibit semiconductor in nature.*

Keywords: *Calcium Germanate, Mechanochemical method, Electrical properties*.

INTRODUCTION

In the present communication the study of pervoskite system, synthesis and their characterization was investigated. Many researchers have been conducted with a view to rationalizing the design of perovskites, that is, to control the relationship between catalytic activity and chemical composition of crystalline ceramics known as perovskite type mixed oxides. The arche type perovskite is a mineral having the composition ABO_3. It was first described in the 1830s by the geologist Gustav Rose, who named it after the Russian mineralogist Count Lev Alekserich von Perovski[1]. One of the conditions for obtaining the peroviskite structure is that electroneutrality must be maintained. The cation in the A-site might be Mono-, di-, or trivalent, while that in the B-site might be tri-, tetra-, or pentavalent. The catalytic activity of such mixed oxide perovskites can be greatly improved by partial substitution of the cations in the A- and/or B-sites. Moreover, the B-site cations may be partially reduced to form finely dispersed metallic species supported on the A-site cation oxide, which makes these materials ideal catalyst precursors for a range of reactions involving metals as active sides [2-5].

Mineralization of organic water pollutants using interaction between ultraviolet radiation and semi-conductor catalysts has a strong potential as it has been widely demonstrated in the recent years[6]. Visible light-responsive photocatalysts have received considerable attention because visible light occupies the main part of solar light. The development of the future generation of photocatalytic materials is important for the efficient use of solar light. The past two decades have witnessed intensive studies within light induced mineralization of hazardous organic pollutant with use of TiO_2 photocatalyst[7]. The literature survey shows that lot of work is available on synthesis of homogeneous photocatalyst of the type TiO_2, ZnO, ZrO_2 and SnO_2 but little attention is given on synthesis of $MGeO_3$ perovskite and their applications.

Metastable nanostructure and ultra fine grained materials are produced by a large variety of methods. Besides the incipient crystallization of amorphous solids[8-11], mechanochemical alloying is nowadays one of the widely used preparation techniques to obtain nanocrystalline structures. Mechanochemical alloying techniques involve the synthesis of materials by high-energy milling in which elemental blends (or ore-alloyed powders, oxides, nitrates etc) are milled to achieve alloys or composite materials [12-14]. High energy mechanochemical method offers indeed supplementary degree of freedom in the choice of possible routes for synthesizing new materials and found further as an attractive method of synthesis in view of its potential for large scale production. The products obtained by this method may be amorphous alloys, metastable crystalline phase, nanocrystalline materials and quasi crystals[15-18].

Germanium oxide (GeO_2) is an important semiconductor material that has attracted much interest owing to its unique optical property and silica analogue. Moreover, nanostructured GeO_2 possesses the superior physical and chemical properties compared with its bulk counterparts. Nowadays, it is being widely used in optoelectronic devices, vacuum technology, and catalysis. For example, GeO_2 nanowires were used in one-dimensional luminescence nanodevices by Sahnoun et al., and GeO_2 nanotubes and nanorods as an important optical fibre material have been used in thermal vacuum test successfully by Jiang et al. It is well known that GeO_2 forms in two stable crystalline structures at an ambient temperature, the α-quartz trigonal structure and the rutile tetragonal structure.

In the present study we focus on the synthesis of $CaGeO_3$ by green chemistry approach such as solid state mechanochemical method. Synthesized material were characterized by various, namely: Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction analysis (XRD), Energy dispersive X-ray spectroscopy (EDS) coupled with scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA) and surface area determination (BET).

EXPERIMENTAL

The starting material used for the synthesis of calcium garmanate, Calcium oxide (CaO) and Germanium oxide (GeO_2) used were analytical grade. $CaGeO_3$ nanocrystalline powder was prepared by using stoichiometric mixture of CaO and GeO_2, this mixture was subjected to stepwise calcinations by heating till terminal temperature. The increase in temperature of muffle furnace was programmed at the rate 10 °C/ min from one temperature to the subsequent temperature for 12 hours. After heating at 600 °C the material was cooled and grounded with a gap of 3 hours using mortar and pestle. Later on the ground material was further heated at 1000 °C for another 12 hours. Finally nanocrystalline powders of $CaGeO_3$ obtained were used for further characterization.

The vibrational frequency of the synthesized material was studied by Fourier Transform Infrared Spectroscopy (FT-IR), Shimadzu -8400S, in the range of 400-4000 cm^{-1}. The optical property of synthesized product was studied by using Perkin Elmer- λ -950, UV-visible spectrophotometer over the range 200-800 nm. The phase compositions and structure properties of the material was studied using X-ray diffractometer (XRD), Rikagu-DMAX-250 with Cu Kα radiation, having λ= 1.5406 Å. The surface morphology and chemical compositions of synthesized catalyst was analyzed using a scanning Electron Microscope-JED-2300LA coupled with an Energy Dispersive Spectrometer-JED-23000La. Transmission Electron Microscopic images were recorded on Philips, CM-200. The effect of temperature on stability was evaluated by thermogravimetry on Shimadzu TG-DTA 60M analyzer. Further, electrical conductivity was measured as a function of temperature.

RESULTS AND DISCUSSION

IR spectroscopy:

The infrared spectra are depicted in Figure 1 confirm the formation of $CaGeO_3$ nanocrystalline after mechanochemical milling of CaO and GeO_2. As can be seen, the spectra of the product obtained by mechanochemical synthesis for 12 hours exhibit the vibration frequency band below 700 cm^{-1} and confirm the presence of Ca-O bonds. IR shows peaks between 750 cm^{-1} to 1000 cm^{-1} assigned to the stretching vibrations of Ge-O.

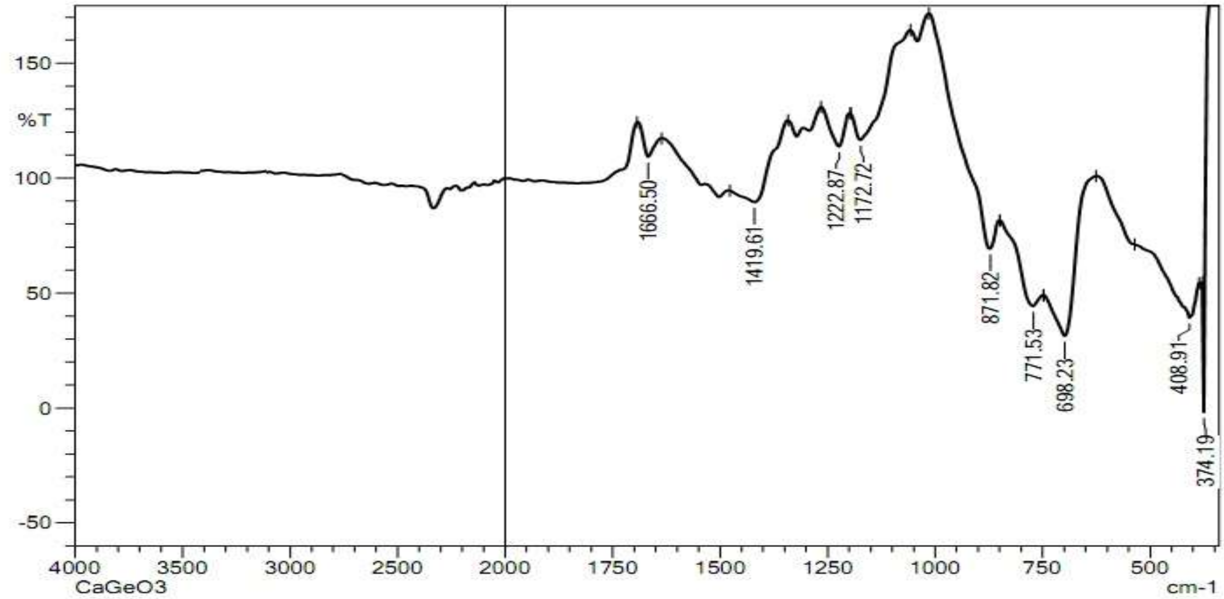

Fig.1: FT-IR spectra of $CaGeO_3$

Photophysical properties:

The photo-absorption of the photocatalyst depends on the mobility of electron-hole pairs, which determines the probability of electron and holes to reach reaction sites on the surface of the photocatalyst. Figure 2 represent the UV-visible diffused reflectance spectra of synthesized $CaGeO_3$ nanocrystalline material. The synthesized material shows the absorption shifts towards UV-visible region. The diffused reflectance spectra of $CaGeO_3$ shows corresponding adsorption edge cut off at 390 nm. These wavelengths are used to evaluate the band gap energies by the equation.

$$Eg = h\upsilon = hc/\lambda = hc\ddot{\upsilon}$$

Thesynthesized nanocrystalline $CaGeO_3$ shows the band gap energy 3.28 eV.

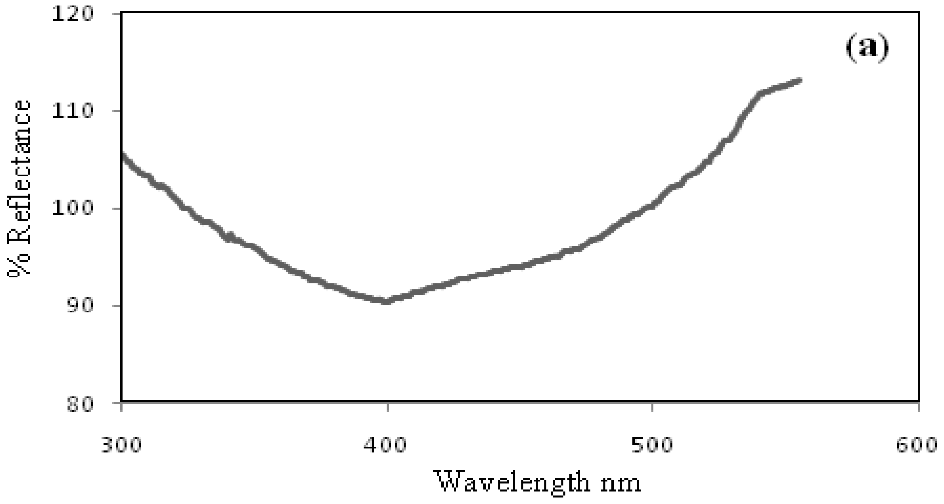

Fig. 2: UV- DRS spectra of $CaGeO_3$,

X-ray diffraction:

Figure 3 shows the XRD patterns of mechanochemically synthesized nanocrystalline mixed metal oxide $CaGeO_3$. The presences of strong and sharp diffraction peaks at 2θ are located at 24.7, 27.1, 28.1, 29.2 and 48.6 which corresponds to (201), (121), (210), (120) and (303) crystal planes for $CaGeO_3$. The crystal planes indicates the formation of triclinic $CaGeO_3$ with the space group P1(2) and d-line pattern matches well with reported JCPDS data card no.21-0142 for $CaGeO_3$.

The average particle sizes were calculated using Debye-Scherrer formula.

$$D_{(hkl)} = k\,\lambda/\beta\cos\theta$$

The average crystalline size of $CaGeO_3$ is 83 nm. The observed particle size may be due to specific surface area.

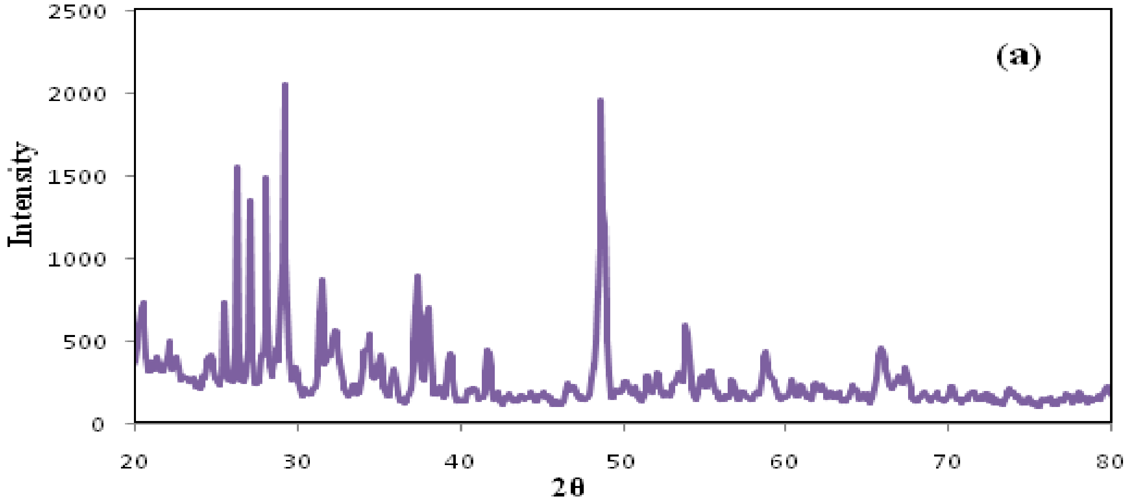

Fig.3: XRD pattern of $CaGeO_3$

SEM analysis:

Figure 4 shows the SEM morphology of the synthesized nanocrystalline metal germanate ($CaGeO_3$) powders prepared at 1000 °C for 12 hours using mechanochemical method. The powders obtained contain a large portion of agglomerates with a small particulate size and some of shows multilayer deposition. Since the agglomeration was sufficiently large and soft. It could be clearly observed that the agglomerates are actually formed very small particles in nanometric range size. Although the agglomerates are of irregular size the fine nanometric particles are mostly below 100 nm in size.

The EDS analysis was employed to determine the composition of pure $CaGeO_3$ nanocrystalline. The results obtained matches well with the reaction stoichiometry.

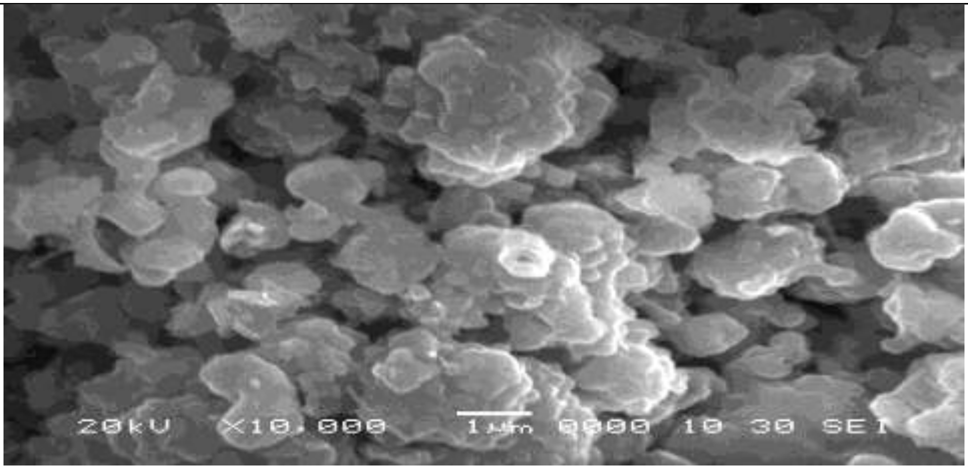

Fig.4: SEM images of $CaGeO_3$

TEM analysis:

The TEM images along with the selected area of electron diffraction pattern (SAED) recorded corresponding to $CaGeO_3$ is shown in Figure 5. The TEM's reveals that, the nanoparticles are elliptical and linked to each other. The dark spot in the TEM micrograph can be alluded to $CaGeO_3$ nanoparticles as SAED pattern associated with such spots reveals occurence of triclinic structures and are in good agreement with the XRD data. The average size of the $CaGeO_3$ nanocrystals was found in the range of 70 to 80 nm.

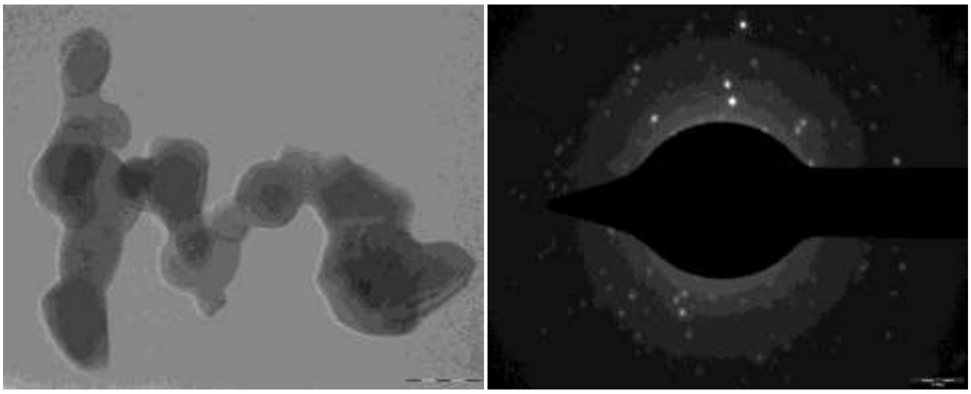

Fig. 5: TEM and SAED images of $CaGeO_3$

BET Surface area analysis:

The N_2 adsorption isotherm of synthesized CaGeO3 is shown in Figure 6. It reveals that all the synthesized metal germinate have typical IV N_2 adsorption-desorption isotherms with H_1 hysteresis which indicates that the samples preserve the cylindrical mesopores. The BJH pore size distribution demonstrates that all the samples have a narrow pore diameter range. Pore volume (single point total pore volume of pores at P/P^o), pore size (determined from BJH desorption isotherm) and BET specific surface area of the material is given in Table 1.

Table 1: N_2 adsorption-desorption results for the metal germanate photocatalyst

Catalyst	BET area (m^2/gm)	Pore volume (cc/g)	Pore size(Å)
$CaGeO_3$	3.117	0.034	438.6

TG-DTA analysis:

The TG curve in Figure 7 shows no weight loss observed upto 900 °C. The clear plateau formed on TG curve indicates the stability of the product formed. On the DTA curve a main endothermic effect was observed at 390 to 450 °C with a minimum at about 420 °C for $CaGeO_3$ endothermic effect was observed at 500 to 700 °C with a minimum at about 600 °C. No further weight loss and no thermal effect observed in both indicating the stability of the product formed.

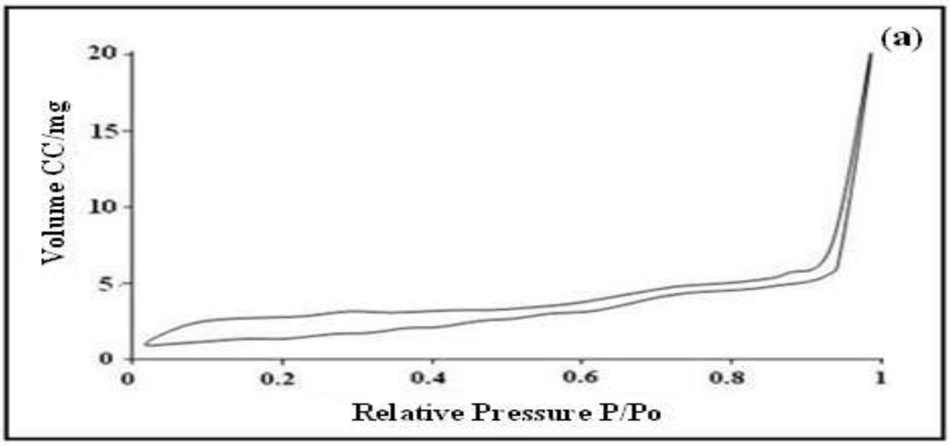

Fig. 6: N_2 adsorption-desorption isotherms of synthesized $CaGeO_3$

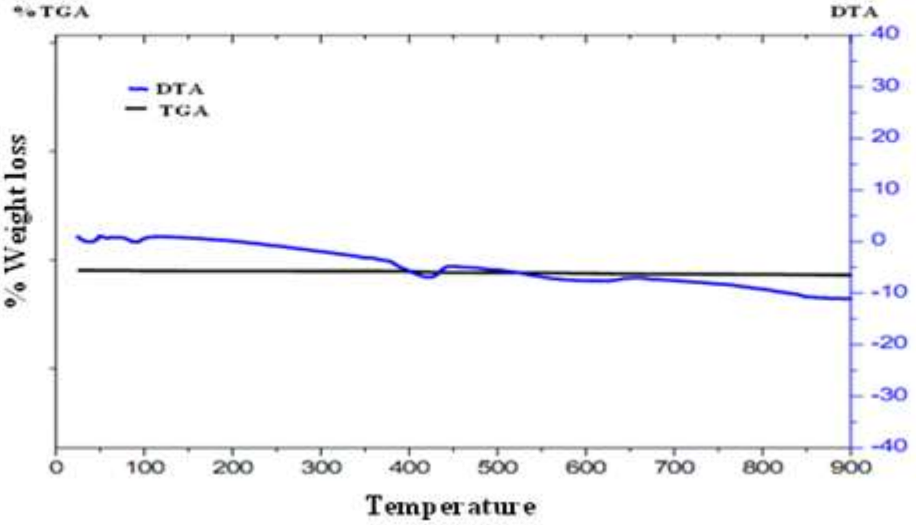

Fig. 7: TG-DTA of $CaGeO_3$

Electrical properties:

The thin films were prepared for the I-V characteristic and electrical conductivity studies. Ethyl cellulose used as solid binder for making of films. First ethyl cellulose is added in mortar and few drop of organic binder (Organic binder contains organic solvent and is evaporated at 500 °C) was added after 20 min, then add sample (ethyl cellulose: sample ratio is 1:10) and make a paste. This material is used for making films by using the screen printing. These films were heated at 550 °C for 1 hour to evaporate the organic binder. These films were used for the determination of I-V characteristic and electrical conductivity.

Fig.8 shows the I-V characteristic of films of $CaGeO_3$ at room temperature. Here voltage was continuously varied with constant room temperature and change in conductance was recorded. I-V characteristics are observed to be symmetrical in nature, indicating the ohmic nature of nanocrystalline materials. Electrical conductivities for synthesized nano $CaGeO_3$ are shown in Fig.8. Electrical performance of the material was studied by measuring change in conductance with temperature. The dependence of conductivity of metal germanate films in air ambience. The conductivity of the film goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the materials.

Fig.9 depicts the variation of electrical conductivity as a function of temperature. Activation energies were estimated from the slope of log σ versus 1/T curve. Activation energies obtained for $CaGeO_3$ is found to be 0.52 kJ / mole. The observed trend is explained on the basis of ionic size of Ca.

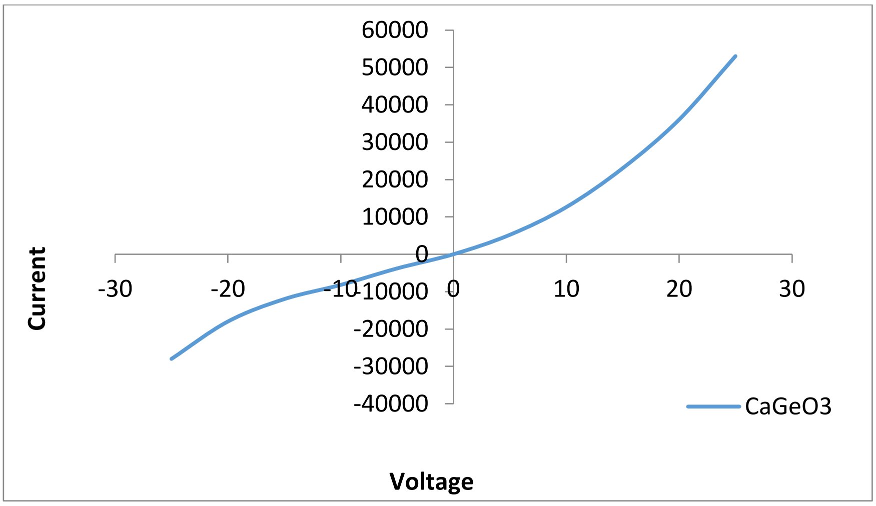

Fig.8: IV Characteristic of $CaGeO_3$

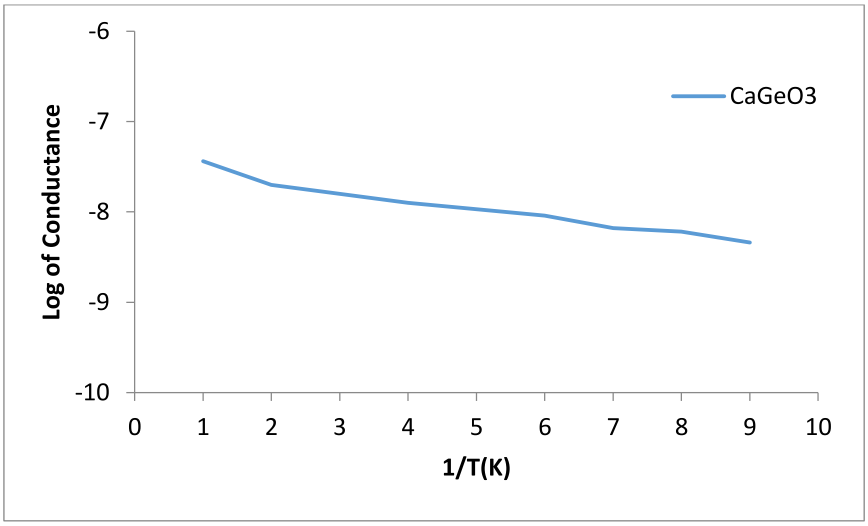

Fig.9: Electrical conductivity of $CaGeO_3$.

CONCLUSIONS

Nanocrystalline $CaGeO_3$ material was successfully synthesized by green chemistry approach solid state Mechanochemical method. XRD analysis confirmed the prepared material was pure $CaGeO_3$ with the crystallite size varying from 70 – 80 nm. The band gap energy of material was 3.28 eV . The size of the nanocrystalline $CaGeO_3$ was measured both by TEM and SEM and the results were in good agreement with each other. The morphology of the nanoparticle was formation of triclinic. Electrical properties confirmed that the semiconducting nature of synthesized nanocrystalline $CaGeO_3$.

ACKNOWLEDGEMENTS

Author is thankful to B.C.U.D., Savitribai Phule Pune University, Pune for financial support and Principal K.T.H.M. College, Nashik for providing laboratory facilities and a valuable guidance for this work.

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