Microbial-induced phase transition of GeO$_2$ and its study by XRD and Raman spectrum

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Abstract. In this paper, we report the formation of germanium dioxide nanoparticles obtained from the action of certain microbes on Germanium crystal under low magnetic field at ambient temperature. The atomic oxygen is chemisorbed in the presence of catalyst by forming GeO$_2$. The evolution of the Germanium dioxide from Germanium and microbes-induced phase transitions in GeO$_2$ is studied by the means of X-ray diffraction method and Raman spectroscopy. The formation of GeO$_2$ from Germanium is also prone to surface oxidation which may compromise surface sensitive measurements. The X-ray diffraction method is not sensitive to anharmonicity-induced dynamical effects due to which there would be a lack of clarity about the phases and transitions intervening in the phase transition of GeO$_2$. The detection of phase transition of GeO$_2$ was being studied by broadening and shifts of diffraction angle in X-ray diffraction. Raman scattering establish the microbial induced phase transitions and identify phases of germanium oxide. The detection of phase transition was being studied by substantial broadening and softening of Raman modes as to identify the transition regions and possible intermediate phases.

1. Introduction

Germanium dioxide (GeO$_2$) is a versatile, wide band gap material having unique thermal, optical and electrical properties, such as high thermal stability, high dielectric constant, and refractive index. Due to these properties, GeO$_2$ is a promising candidate for different applications, such as vacuum technology, solar cells, catalysis, Li-ion batteries, especially in optoelectronic devices; core of optical fibers [1, 2]. It is found in crystalline, liquid and amorphous phases.

At ambient temperatures, crystalline GeO$_2$ occurs in three stable polymorphs, i.e., (i) $\alpha$-quartz like trigonal or hexagonal structure with tetrahedral coordination, (ii) Tetragonal or Rutile structure with octahedral coordination, (iii) Amorphous or Vitreous (Glassy). $\alpha$-quartz and rutile forms exhibit similarity in hardness, transparency, and colourlessness but show considerable difference in chemical and optical properties, such as solubility, density and indices of refraction [3-6].

Tetragonal structure of GeO$_2$ has denser and stable phase at ambient conditions but transforms to hexagonal phase at 1306 K with less density [7]. The tetragonal structure is insoluble in water and hexagonal phase is slightly soluble in water (0.4 g/100 g H$_2$O at 300 K). These differing structural
properties induce physical and chemical properties of the GeO$_2$ and in turn also affect possible applications of both modifications. Interdisciplinary studies on GeO$_2$ are necessary to bridge the gap between its research applications and commercialization. The structural analogy of GeO$_2$ is close to SiO$_2$ and the study of the transformation of different quartz phases occurring during reactions is important. Polymorphism of GeO$_2$ influences the material characteristics and hence utilized for different applications.

The primary aim of this research work is to study the phase transitions related to GeO$_2$ nanoparticles (NPs) which is biologically synthesized by germanium crystal. GeO$_2$ NPs exhibit unique physical and chemical properties as compared with the bulk material. X-ray diffraction (XRD) and Raman spectroscopy was employed to study the phase transition of the GeO$_2$. In the present research, germanium dioxide NPs was fabricated biologically from Ge crystal by using different bacteria in presence of magnetic field at ambient temperature. The phase of GeO$_2$ NPs was studied by analyzing X-ray diffraction patterns. The spectral properties could also be used to identify the α-quartz, rutile and amorphous forms of GeO$_2$, which were recorded by Raman spectroscopy.

2. Methodology

Germanium dioxide nanocrystals were fabricated in the presence of culture of bacteria Pseudomonas putida and low magnetic field of about 0.1 Gauss at ambient temperature. The exposure time for the reaction was kept at 6 hrs. The formation of germanium dioxide nanocrystals occurs due to the interaction of bacteria with the Ge crystal. Bacteria are well known natural living organism for synthesis of NPs as well as they can control and modify various reaction parameters, such as pH, temperature and chemical potential of the reaction etc., to catalyze the oxidation of germanium for the formation of germanium dioxide nanocrystals [8]. Magnetic field induces directional movement of microbes and show unique characteristics [9].

The newly reported magnetically induced direct method of biosynthesis may be more effective than currently employed physical and chemical methods for synthesis of GeO$_2$. In this mechanism, pre- and post- physical/chemical/biological treatments like preparation of metal salt solution, filtration, sonication, etc. for the synthesis and retrieval of nanoparticles are not required. It is a faster and more economical than other methods. More research is required to explore this new route of biogenesis.

3. Experimental results and Discussions

The characterization of biologically prepared sample of GeO$_2$ is performed by X-ray diffraction [PANalytical, operated at 40 kV, 30 mA, Cu-K$_\alpha$ radiation ($\lambda$ = 1.5405Å)] and Raman spectroscopy.

3.1. X-ray diffraction of pure Germanium crystal (Ge) and biologically synthesized GeO$_2$

XRD of pure Ge shows an intense peak at 45.5° which matches with standard data as shown in figure 1. X-ray diffraction data gives all the structural information of GeO$_2$ due to difference in chemical sensitivity of Ge-O and Ge-Ge pairs. The structural information of GeO$_2$ can be resolved better with X-ray diffraction [10,11]. The germanium dioxide nanoparticles were studied using XRD with series of intensive peaks at 20.5°, 26.1°, 27.6°, 36.1°, 37.9°, 38.0°, 39.0°, 40.5°, 43.3°, 45.5°, 56.5°, 57.3°, 65.6°, 76.4° corresponding to germanium dioxide lattice reflections as shown in figure 2. The Ge atoms in GeO$_2$ are arranged in basic tetrahedral units with quartz like polymorph. X-ray diffraction shows that the O − Ge − O intratetrahedral angle is more distorted in vitreous GeO$_2$. 


From the XRD data, the lattice planes (100, 101, 110, 102, 111, 201, 210 and 203) of the quartz GeO$_2$ are found at 20.5°, 26.1°, 36.1°, 38.0°, 39.0°, 45.5°, 56.5° and 65.6° respectively. The lattice planes (110, 101, 200, 111 and 002) of the rutile GeO$_2$ are found at 27.6°, 37.9°, 40.5°, 43.03°, and 57.3° respectively. The lattice planes (100 and 102) of the vitreous GeO$_2$ is found at 36.1° and 56.5° respectively.
3.2. Raman Spectra

The structure of GeO₂ as depicted by Raman spectra at room temperature occurs in α-quartz, rutile and amorphous forms [12]. In quartz structure, Ge atoms are arranged at the center of the corner linked GeO₄ tetrahedra. The structure is trigonal with three Ge atoms per unit-cell. For quartz structure, there are low, mid and high frequency vibrational modes for GeO₂. The high frequency region ranges from 857 to 970 cm⁻¹ which are assigned to Ge-O stretching motions within the GeO₄ tetrahedra groups as shown in figure 3. In this range, there are four weak bands ranging from 886 to 958 cm⁻¹. The mid-frequency region ranges from 442 to 595 cm⁻¹ which are assigned for Ge-Ge stretching motions (figure 4). The low frequency region ranges from 122 to 327 cm⁻¹ which are assigned to Ge-O bending modes as shown in figure 5[13].

In rutile structure, Ge atoms are arranged at the center of the edge linked GeO₄ tetrahedra. The structure is tetragonal with two Ge atoms per unit cell. For rutile structure, the highest frequency corresponds to 700 cm⁻¹ which is assigned to Ge-O stretching modes within GeO₆ octahedral group [14].

Figure 3. High frequency range Raman spectra.

Figure 4. Mid-frequency range Raman spectra.
The Raman spectra of vitreous GeO$_2$ exhibit similar spectrum as that of quartz form. This similarity between vitreous and quartz form implies that germanium is four coordinated in the vitreous GeO$_2$.

\[ \text{Figure 5. Low frequency range Raman spectra} \]

4. Conclusions
In this paper, we have reported the formation of GeO$_2$ nanoparticles through microbial route using bacteria and low magnetic field at normal temperature and pressure. We also discussed the experimental results on formation of different phases, and phase transformations in GeO$_2$.

Investigation of phase transformation of GeO$_2$ nanocrystals have been done with the help of XRD and Raman spectra. The results demonstrated that most Ge atoms were transformed into GeO$_2$ after the oxidation of Germanium under microbial and magnetic environment. During the formation of GeO$_2$ from germanium, the polymorphs of GeO$_2$ were found with dominance of $\alpha$-quartz as compared to rutile and vitreous structure. Raman scattering spectroscopy of biologically fabricated germanium dioxide successfully detected and identified all the Raman active modes which confirm the formation of $\alpha$-quartz, rutile and vitreous phases. It was seen that Raman spectroscopy is better for phase transition analysis than XRD method.

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