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Synthesis of Glass Nanocomposite Powders: Structure, Thermal, and Antibacterial Study

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The aim of the present study is to synthesize $CaO \bullet GeO_2$ glass nanocomposite powders. The samples are prepared at 1450°C, and to investigate the structure of the samples, differential thermal analysis (DTA), X-ray diffraction, and Fourier Transform Infrared (FTIR) spectroscopy are used. The main crystallizing phase is found to be $CaGe_2O_5$ crystals. Furthermore, the potential antibacterial properties of the materials towards the Gram-negative bacteria, *Escherichia coli*, are preliminarily studied.

1. Introduction

Over the past decade, metal oxide nanocomposites have been attracting significant attention due to their various potential applications in catalysis, electronics, photonics, and sensors.[1–5] In addition to alumina, silica, and titania, germania has been gaining tremendous importance mainly due to its enhanced reactivity and optical properties.[6,7] Germania–silica hybrid materials, Nd^{3+}doped germania glasses, and erbium-doped germania have been prepared for optical device fabrications.[8–10] Most methods employed for the synthesis of germanium oxide-based materials, however, involve the use of high-temperature conditions, which sometimes may lead to the sintering. Thus, milder methods for the synthesis of such nanomaterials would be beneficial. Recently, germanium oxide was synthesized under mild conditions using bioinspired methods. These methods involved the use of specific peptide sequences derived from the combinatorial phage-library or amino acids that helped in the efficient mineralization of the materials. Nanocomposite powders of germanium oxide integrating gold, palladium, tin oxide nanoparticles have also been prepared using biomimetic methods. Although the catalytic and optical applications of germanium oxide nanocomposite powders are well known, research related to the antimicrobial activities of germanium oxide nanocomposite powders is relatively sparse. Even though over the past years great efforts have been made in engineering biomedical devices, using different kinds of materials, as well as experimental [11] and theoretical [12–14] analyses, in this work, we have explored the development of a new material, by preparing nanocomposite powders of calcium oxide–germania. Recently, the antimicrobial properties of CaO nanoparticles were studied and they were found to be highly effective against bacteria. They have also been found to be potent in toxic waste remediation.[15–17] The biological approach used in the current research is a mild method of preparation of such nanocomposite powders, which upon calcination lead to highly crystalline materials. Further, we analyzed the antibacterial effects of nanocomposites of calcium oxide–germania against Gram-negative bacteria.

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2. Results and Discussion

The FT-IR transmittance spectra of the glass nanocomposite powders show the highest frequency band at 878 cm^{-1} of theGeO_2 glass, due to the Ge-O-Ge bond stretching. The coordination of Ge in GeO_2 glass closely resembles that of Ge in hexagonal GeO_2, in which Ge is tetrahedrally coordinated by GeO_2.[18–20] This shift can be related as in alkali germanate glasses to the change in the coordinating number of Ge from 4 to 6. This interpretation is in agreement to the general knowledge that an increase in the coordination number from XO_4 to XO_6 lead to a decrease in X-O-X stretching frequency. The DTA curves recorded on the bulk sample of the as-quenched investigated glass nanocomposite powders exhibit a slope change followed by two exothermic peaks. The slope change may be attributed to the glass transition, while the exothermic effects can be related to crystallization processes. When the glass is heated, its heat capacity together with other properties, changes abruptly in a narrow temperature range, called glass transition; this is the

transformation temperature range at which the glass network acquires mobility, changing from a rigid to a viscous structure. The inflection point at the slope-change temperature of the DTA curves was taken as the glass transition temperature (T_g) and was recorded at 698°C for $CaO{\bullet}GeO_2$. The presence of two exothermic peaks during the crystallization of these glasses suggests the formation of more than one crystalline phase during the devitrification process or a two-step crystallization mechanism. To clarify this point, XRD measurements were carried out on heated in the DTA furnace up to the temperature of the first and the second exothermic peaks. The XRD pattern of di-germanate glass heated to the temperature of the first DTA exo-peak shows several reflections that could not be ascribed to any known crystalline phase. The XRD pattern of the glass heated up the temperature of the second DTA exo-peak shows the same reflections but the XRD peaks are higher and sharper. The reflections of the same unknown phase were detected on the XRD pattern of germanate glass heated to the temperature of the first DTA exo-peak. In addition to these reflections, the main reflections of $CaGe_2O_5$ crystals were also found. These results suggest that the investigated glass a devitrification process in two step, microcrystals are initially formed and are then converted at higher temperatures into well shaped crystals. This hypothesis was confirmed by recording DTA curves at different heating rates. Taking into account that the higher the DTA heating rate, the higher is the temperature of the first crystallization peak, the size of the crystals formed in this step should be also increased with a consequent decrease of the recrystallization amount. The activation energy E for crystal growth was evaluated from the DTA curves using the equation [21]

$$\ln_{\beta} = -(\mathrm{E}/\mathrm{R})\left(l/T_p\right) + \mathrm{const} \quad (1)$$

This equation is based on the temperature shift of the DTA peak T_p, as the DTA heating rate β is changed. Multiple DTA runs were recorded in air at different heating rates on the bulk samples. Plots of ln $_{\beta}$ versus l/T_p, give straight lines in both cases. From their slopes an E values of 657 KJ mol^{-1} was calculated for $CaO{\bullet}GeO_2$ glass nanocomposite powders. In order to evaluate the effect of the sample on the microbial growth, the materials were grinded in a mortar to obtain powders, and *E. coli* bacteria were inoculated in absence and in presence of the 100 mg of powders.[22–25] The zones of inhibition formed by the materials without $CaO{\bullet}GeO_2$ and containing $CaO{\bullet}GeO_2$ against *E. coli* is shown in **Figure 1**. It is possible to observe that the materials exhibited mild activity against *E. coli*, glass nanocomposite powders induce an inhibition halo around the synthesized hybrid.

3. Conclusion

Based on the experimental results, the following conclusions can be drawn:

- The structure of germanate glass contains a GeO_6/GeO_4 molar ratio.
- The investigated internal crystal of the glass nanocomposite powder exhibits nucleation without the addition of any nucleating agent as well as a two-step crystallization process.

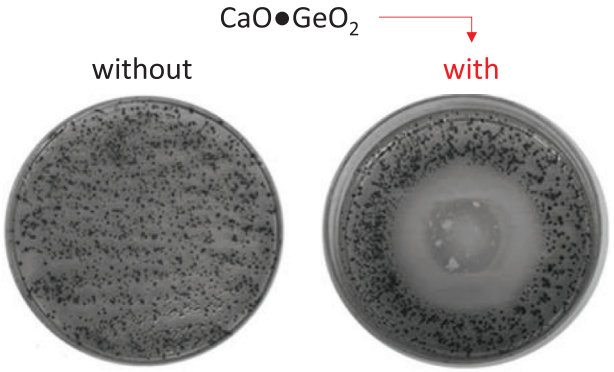

Figure 1. Representative images of *E. coli* bacteria plates treated without or with pure $CaO{\bullet}GeO_2$.

- Crystals are initially formed in the glassy matrix and then converted at higher temperatures into well shaped crystals.
- The $CaO{\bullet}GeO_2$ as preliminary study show antibacterial activity against *E. coli*, suggesting the need to further investigate this materials' behavior and hypothesize their use as antibacterial biomedical implants.

4. Experimental Section

$CaO{\bullet}GeO_2$ glass nanocomposite powders prepared by mixing appropriate amount of ultra pure calcium carbonate (Aldrich), and germanium oxide (Heraeus) in batches of a size suitable to yield 2 g of glasses. The sample was melted in an uncovered Pt crucible in an electric oven at 1450°C. The melt was quenched by plunging the bottom of the crucible into cold water. Although this resulted in fracture of the sample, pieces of transparent glass of size adequate for the experimental measurements were obtained by such technique. Differential thermal analysis (DTA) curves were recorded in air at different heating rates (5–20°C min^{-1}) on bulk and powdered specimens (< 45 pm) of about 60 mg from room temperature to 1200°C. Powdered Al_2O_3 was added to improve heat transfer between bulk sample and sample holder. A Netzsch thermoanalyser high temperature DSC 404 was used with Al_2O_3 as reference material. The DTA curves were elaborated by Netzsch software. The sample was chemically characterized by FT IR spectroscopy using a Prestige 21 (Shimadzu, Japan) system in the 400–4000 cm^{-1} region. The Prestige software (IR solution) was used to analyze the FTIR spectra. To investigate the amorphous nature of the as-quenched glasses and to identify the crystalline phases grown during the DTA runs, the thermally processed sample was finely ground and the crystalline phases have been identified by XRD analysis using a Philips diffractometer (Philips, Amsterdam, The Netherlands) equipped with a PW 1830 generator, tungsten lamp, and Cu anode, where the source of X-ray is given by a Cu-Kα radiation (λ = 0.15 418 nm). To identify the crystallizing phases, the X-ray diffraction (XRD) patterns were matched to the JCPDS data.

The antibacterial activity of the nanocomposite powders versus the Gram-negative *Escherichia coli* (ATCC 25 922) was evaluated. The sample was washed, centrifuged, before testing for antibacterial activity. A bacterial cell suspension of 10×10^5 CFU mL^{-1} was produced by diluting the bacterial culture in distilled water. *E. coli* was inoculated in TBX Medium (Tryptone Bile X-Gluc) (Liofilchem, Italy), and then incubated with the different composites for 24°C. The release of the drug was evaluated by observing the different bacterial growth and by measuring the diameter of the inhibition halo (ID). The obtained values are the mean standard (SD) deviation of measurements on samples analyzed three times.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

antibacterial, glass-ceramics, thermal properties

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