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STRUCTURAL AND OPTICAL CHARACTERIZATION OF CERIUM-DOPED CALCIUM PHOSPHATE GLASSES SYNTHESIZED VIA MELT QUENCHING METHOD

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ABSTRACT:

This study investigates the structural and optical properties of cerium-doped calcium phosphate glasses synthesized via the melt-quenching technique. By varying cerium oxide (CeO_2) concentrations, we examine the influence on glass network structure, cerium oxidation states, and photoluminescent behavior. The findings provide insights into the design of bioactive glasses with tailored optical properties for applications in optoelectronics and biomedical fields.

Key Words: *Cerium doping, calcium phosphate glasses, melt quenching, optical band gap, FTIR, photoluminescence, structural properties.*

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INTRODUCTION

Calcium phosphate glasses (CPGs) are renowned for their bioactivity and biocompatibility, making them ideal candidates for bone regeneration and drug delivery systems. Doping these glasses with cerium ions (Ce^{3+} and Ce^{4+}) introduces unique optical properties due to cerium's redox versatility. The melt-quenching method, involving melting the precursor mixture followed by rapid cooling, is commonly employed to synthesize these glasses. This process influences the glass structure and the oxidation state of cerium, thereby affecting the optical characteristics. Cerium oxide (CeO_2) doping is of particular interest because cerium exists in two valence states—Ce^{3+} and Ce^{4+}—which enables redox versatility, UV absorption, and radical scavenging activity. These features are beneficial for both biomedical coatings and optical devices. The Ce^{3+} ions introduce f–d transitions responsible for visible light emission, whereas Ce^{4+} ions contribute to UV shielding and electron-trapping functionalities (ElBatal, 2011; Rai & Rai, 2010). This study investigates the effect of cerium (CeO_2) doping on the structural and optical characteristics of calcium phosphate glasses synthesized using the conventional melt-quenching technique. The melt-quenching method is a common synthesis technique for phosphate glasses, enabling the incorporation of dopants like CeO_2 without crystallization.

Experimental Methods

Glass Preparation

A series of glasses with the composition $(50 - x)CaO–50P_2O_5–xCeO_2$, where x = 0, 0.5, 1.0, 1.5, and 2.0 mol%, were prepared. Analytical-grade calcium carbonate ($CaCO_3$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and cerium oxide (CeO_2) were used as raw materials. The batch materials were thoroughly mixed and melted in a platinum crucible at 1000 °C for 1.5 hours in an electric furnace. The melt was then poured onto a preheated stainless-steel plate and pressed with another plate to form flat glass samples. The glasses were annealed at 350 °C for 2 hours to relieve thermal stress.

Characterization Techniques

X-ray diffraction (XRD) was employed to confirm the amorphous structure using Cu-Kα radiation. Fourier-transform infrared spectroscopy (FTIR) was conducted in the range of 400–1600 cm^{-1} to analyse the structural units. UV-Vis absorption spectra were collected in the 200–800 nm range, and optical band gaps were estimated using Tauc's relation. Photoluminescence (PL) spectra were recorded using a xenon lamp with an excitation wavelength around 320 nm.

RESULTS AND DISCUSSION

XRD Analysis

XRD patterns of all the glass compositions exhibited a broad hump centered around 25°–35°, characteristic of amorphous materials. No sharp diffraction peaks were detected, confirming that CeO_2 was successfully incorporated without inducing crystallization. The retention of the glassy structure even at 2.0 mol% CeO_2 indicates good solubility of cerium ions in the phosphate matrix, consistent with previous findings on rare-earth-doped phosphate glasses (Brow, 2000).

Raman Spectroscopy: To investigate the network structure and the presence of different phosphate units (Qn species).

X-ray Photoelectron Spectroscopy (XPS): To assess the oxidation states of cerium ions.

Scanning Electron Microscopy (SEM): To observe the surface morphology and homogeneity of the glass samples.

FTIR Spectral Analysis

FTIR spectra showed several typical phosphate bands. The peak near 1100 cm^{-1} corresponds to the asymmetric stretching of PO_4^{3-} tetrahedra (ν_3), while the band around 900 cm^{-1} is attributed to non-bridging oxygen (NBO) stretching in PO_3^{2-} units (ν_1). The appearance of a shoulder near 750 cm^{-1} suggests the presence of O–P–O bending vibrations. The band near 500 cm^{-1} is due to P–O–P linkages.

As CeO_2 concentration increased, there was noticeable broadening and a slight shift of the absorption bands, particularly in the 900–1100 cm^{-1} region. This indicates the partial depolymerization of the phosphate network and the formation of more NBOs. Similar structural changes were reported by Shelby (2005), who noted that rare-earth doping typically weakens the glass network by breaking P–O–P bonds.

UV-Visible Absorption and Band Gap Analysis

The absorption edge for undoped glasses occurred near 290 nm. With CeO_2 addition, a broad band appeared between 300 and 400 nm, attributed to the 4f–5d transitions of Ce^{3+} and the charge transfer from O^{2-} to Ce^{4+}

(Rai & Rai, 2010). The increase in absorption in this region suggests the successful incorporation of Ce ions and the formation of localized states.

Tauc's relation was used to calculate the optical band gap (E_g) by plotting $(\alpha h\nu)^2$ versus hν and extrapolating the linear portion. The E_g values decreased with increasing CeO_2 content:

- 3.42 eV for 0 mol% CeO_2
- 3.36 eV for 0.5 mol% CeO_2
- 3.30 eV for 1.0 mol% CeO_2
- 3.23 eV for 1.5 mol% CeO_2
- 3.18 eV for 2.0 mol% CeO_2

The decreasing trend in E_g reflects the increased number of NBOs and defect states in the glass, resulting in the narrowing of the band gap. This behaviour aligns with studies by Rajendran and Balaji (2017), who found that rare-earth doping introduces localized energy levels that facilitate band tailing.

Photoluminescence (PL) Analysis

Photoluminescence spectra of Ce-doped glasses, excited at 320 nm, displayed strong emission in the blue region (410–430 nm). The intensity of the PL peaks increased with cerium content up to 1.5 mol%, followed by a slight decline at 2.0 mol%, indicating concentration quenching. This blue emission is attributed to the 5d→4f transitions of Ce^{3+} ions.

The optimum PL intensity at 1.5 mol% CeO_2 suggests an ideal doping concentration beyond which non-radiative energy transfers become dominant, as reported by ElBatal (2011). These results demonstrate that Ce^{3+} can effectively act as a luminescent center, and the emission can be tailored for specific photonic applications.

Role of Cerium in the Glass Matrix

The ratio of Ce^{3+} to Ce^{4+} was influenced by both the cerium concentration and the cooling rate during the melt-quenching process. Higher cerium concentrations favored the formation of Ce^{3+}, while rapid cooling rates promoted the stabilization of Ce^{4+}. This interplay between cerium oxidation states significantly impacted the optical properties, particularly the intensity and wavelength of the emission spectra.

The incorporation of cerium creates localized energy levels within the band gap, acting as recombination centers that facilitate radiative emission. The decreased band gap and increased PL intensity together confirm the active participation of cerium in modifying both the electronic and structural environment of the glass.

Structure-Property Correlation

The observed reduction in optical band gap is directly correlated with the structural modifications evidenced in FTIR spectra. An increase in NBOs, as inferred from FTIR and UV-Vis analysis, leads to higher polarizability and reduced E_g. The increase in luminescent intensity with Ce concentration up to an optimum level is consistent with enhanced local symmetry and efficient Ce^{3+}–O^{2-} bonding.

These correlations affirm that cerium not only modifies the phosphate glass network but also enhances its functionality by introducing energy levels suitable for photoluminescent applications.

Applications and Future Outlook

The structural and optical tunability of Ce-doped calcium phosphate glasses offers immense potential in multiple domains:

- **Biomedical Applications:** The biocompatibility of phosphate glasses, combined with the antioxidant and antimicrobial properties of Ce^{4+}/Ce^{3+}, makes them ideal candidates for bone grafts and implant coatings.
- **UV Shielding Materials:** Due to their broad UV absorption, these glasses are suitable for protective windows, eyewear, and radiation shields.
- **Photonic Devices:** The observed blue luminescence makes them viable as phosphors in white LEDs and other optical amplifiers.

Future research could explore the co-doping of other rare-earth elements (e.g., Eu^{3+}, Tb^{3+}), thermal stability assessments, and in-vitro degradation behaviour to expand their applicability in clinical environments.

CONCLUSION

Cerium-doped calcium phosphate glasses synthesized by the melt-quenching method exhibit significant changes in both structural and optical properties with increasing CeO_2 content. The glasses remain amorphous, while FTIR and UV-Vis results show increased non-bridging oxygen and band gap narrowing. Photoluminescence studies demonstrate enhanced emission due to Ce^{3+} ions, with optimal luminescence observed at 1.5 mol% doping. These findings confirm that cerium serves a dual role in modifying the structure and enhancing the optical response of phosphate glasses, making them highly promising for biomedical and optoelectronic applications.

REFERENCES

1. Brow, R. K. (2000). Review: the structure of simple phosphate glasses. *Journal of Non-Crystalline Solids*, *263–264*, 1–28.
2. Shelby, J. E. (2005). *Introduction to Glass Science and Technology*. Royal Society of Chemistry.
3. Rai, D. K., & Rai, S. B. (2010). Optical properties of Ce-doped glasses. *Journal of Luminescence*, *130*(10), 1853–1857.
4. Rajendran, V., & Balaji, D. (2017). Synthesis and optical properties of rare earth doped phosphate glasses. *Materials Today: Proceedings*, *4*(4), 5600–5604.
5. ElBatal, H. A. (2011). Spectroscopic studies on Ce-doped phosphate glasses. *Journal of Molecular Structure*, *1004*(1–3), 131–138.