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Gamma ray irradiation-induced variations in structure and optical properties of cerium/titanium-doped oxyfluoride transparent glass-ceramics

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ABSTRACT

CeO_2/TiO_2-doped oxyfluoride transparent glass ceramics with a composition of $45SiO_2$–$20Al_2O_3$–$10CaO$–$25CaF_2$ were synthesized and irradiated by gamma ray. The effects of CeO_2/TiO_2 on the structure and optical properties of the samples before and after irradiation were investigated. Doping with CeO_2 causes network depolymerization and conversion of $[AlO_6]$ to $[AlO_4]$, enlarging the percolation region and promoting CaF_2 crystallization. Co-doping with CeO_2/TiO_2 helps reduce the intrinsic coloring of transparent glass ceramics containing only CeO_2, and the addition of TiO_2 enhances network interconnectivity, suppressing CaF_2 crystallization. Doping with CeO_2 and/or TiO_2 improves the structural stability of transparent glass ceramics upon irradiation and maintains the optical band gap and Urbach energy constant due to the defect saturation over the irradiation dose. Doping solely with CeO_2 allows for a lower radiation-induced absorption coefficient than co-doping CeO_2/TiO_2 because of the enhanced crystallization induced by CeO_2 and balanceable light absorption of polyvalent cerium ions.

1. Introduction

Transparent glass ceramics (TGCs) are inorganic composite materials formed through the controlled nucleation and crystallization of optimally formulated glass with a nanocrystalline phase dispersed in the glass matrix [1]. TGCs have been successfully deployed in applications such as large telescope mirror blanks, liquid crystal displays, solar cells and photonic devices due to their desirable mechanical, thermal, electrical, magnetic and optical properties [2,3]. In recent years, rare-earth-doped oxyfluoride TGCs have attracted interest due to their chemical stability, combining the mechanical strength of oxide glass with the low phonon energy of fluoride crystals, which minimizes the non-irradiative decay rate and allows rare-earth energy level emissions with improved quantum efficiency [4,5].

The interaction between TGCs and gamma (γ) rays or other ionizing radiation causes structural defects and property variations that depend on glass type, composition and radiation dose. Radiation durability is widely recognized as a significant requirement for photonic devices, especially those applied in space or in harsh radioactive environments. The defects induced by ionizing radiation usually absorb visible light, thereby worsening the material's optical properties and influencing the irradiation sensitivity and efficiency. Investigations related to the interaction between oxyfluoride glass or TGCs and radiation have mainly focused on the application of materials containing rare-earth fluorides in emission spectrometry and development of corresponding optical materials. For example, subjecting oxyfluoride glass doped with EuF_3 and DyF_3 to high-dose gamma radiation results in point defects in the glass matrix. The irradiation effect depends more on the rare-earths' characteristics than on the glass composition [6]. A study of SiO_2–Al_2O_3–Li_2O–LaF_3 oxyfluoride glass and a glass ceramic containing CeO_2, TbF_3 and Eu_2O_3 after X-ray radiation shows that the creation of color centers occurs mainly in the oxide glass matrix, and the trap centers are created primarily in the fluoride crystallites and depend on the rare-earth activators [7]. Appropriate stabilizers, such as transition metals and rare-earth oxides are conventionally introduced into the glass matrix to improve its irradiation resistance [8,9]. CeO_2 is most commonly used for this purpose. The effects of doping with

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transition metals and/or rare-earth oxides on oxyfluoride TGCs for the purpose of modifying radiation resistance have been rarely studied and are worthy of further investigation. It had been proposed that co-doping with CeO_2/TiO_2 provides glass with more effective radiation resistance compared to doping solely with CeO_2 and allows adjustable glass coloration [10], but the influence of a similar modification on oxyfluoride glass ceramics remains unaddressed. In this study, the effects of gamma irradiation on CeO_2/TiO_2-doped oxyfluoride TGCs were investigated using vibrational spectrometry and spectrophotometry analysis in the context of synthesis and comparative characterizations of CeO_2/TiO_2-doped oxyfluoride TGCs.

2. Experimental

2.1. Preparation of glass and TGCs

The commonly studied system $45SiO_2$–$20Al_2O_3$–10CaO–$25CaF_2$ suitable for fabricating oxyfluoride TGCs [5,11] was used to synthesize precursor glass (G) by the conventional melting-quench method. Reagent-grade chemicals such as silica, calcium carbonate, alumina and calcium fluoride were used as the starting materials for preparing the batch of base glass, and the doped mixtures were prepared by adding various ratios of CeO_2 and/or TiO_2 powder to the appropriate amount of the base glass. The mixtures were balanced and ball milled for 2 h and then melted using a corundum crucible in an electric furnace at 1400 °C for 1 h. The glass melt was poured onto a stainless-steel plate and was pressed by another plate to form a disk. Next, the glass was annealed at 550 °C for 1 h to eliminate the internal stress. The prepared glass discs were polished with SiC papers up to 1200 grit, ultrasonically cleaned in acetone and anhydrous ethanol, and washed with distilled water for further irradiation tests and measurements. The TGCs were produced by isothermally heating the precursor glasses at 650 °C for 4 h. The notation *a*Ce*b*Ti is used to identify an individual sample, where *a* and *b* represent the batched extra-molar fractions of CeO_2 and TiO_2 over the base glass, respectively (keeping the relative ratio of base components constant).

2.2. Irradiation test

The gamma irradiation test was conducted in air at room temperature using a ^{60}Co source (1.2×10^6Ci) in a gamma chamber manufactured by the MDS NORDION Company. The glass and TGC discs were subjected to a ramped increasing dose of 9 kGy, 18 kGy and 27 kGy at a dose rate of 3 kGy/h.

2.3. Measurements before and after irradiation

The TGCs were pulverized using an agate mortar for powder XRD analysis to detect the crystalline phase of the TGCs. The XRD measurements were performed using a diffractometer (DX-2500, HAOYUAN China) with Cu kα radiation and a Bragg angle 2θ ranging from 10° to 80° at a scanning rate of 0.05°/s.

Raman spectra in the range of 200–2000 cm^{-1} were recorded at room temperature on a Labram HR800 micro-spectrometer using the 514.5 nm line of an Ar^+ laser with a measured power of 5 mW and a system resolution of less than 1 cm^{-1}. Spectroscopic analysis using a UV-visible spectrophotometer (PERSEE T6) was carried out to measure the transmittance of the prepared glass and TGCs as a function of wavelength from 190 to 1100 nm. Spectrometric and spectroscopic analysis for the post-irradiation specimens were conducted within 36 h to avoid the bleaching of the radiated samples.

3. Results and discussion

3.1. The effects of doping CeO_2/TiO_2 on the structure and properties of oxyfluoride TGCs

3.1.1. Raman spectrometry analysis

Fig. 1 presents the Raman spectra of the CeO_2/TiO_2-doped TGCs. Band 700–800 cm^{-1} is associated with the vibration of the [AlO_4] tetrahedral [12,13], and bands across 800–1200 cm^{-1} are associated with the stretching mode of groups of silicon–oxygen tetrahedrons Q^n (where n is the number of bridging oxygen atoms, either 0, 1, 2, 3 or 4) [14–17]. As this broad envelope comprises component peaks situated within 900–950 cm^{-1}, 950–1000 cm^{-1}, 1000–1050 cm^{-1}, 1050–1100 cm^{-1} and 1100–1150 cm^{-1} that represent the Si–O stretching of Q^0, Q^1,Q^2, Q^3 and Q^4, respectively, the spectra are normalized in Raman intensity and then processed through deconvolution using Gaussian functions. In the resolved spectra, the peak position of the Q^n envelope shifts to a lower frequency, with higher level Q^n (i.e., Q^3 and Q^4) transferring into lower level Q^n (Q^0, Q^1, and Q^2) as CeO_2 increases. In addition, the band situated at 700–800 cm^{-1} related to the [AlO_4] group intensifies, indicating that doping solely with CeO_2 promotes the formation of [AlO_4] tetrahedral amid depolymerization of the glass structure. Co-doping with CeO_2/TiO_2 results in a smaller fraction of Si–O structural units compared with doping solely with CeO_2. Additionally, a component peak emerging at 855 cm^{-1} can be ascribed to the characteristic vibration of Ti–O–Si or Ti–O–Ti as well as the deformation of O–Ti–O or O–(Si,Ti)–O in chain and/or sheet units [18]. Raising the TiO_2 content enables the bands associated with Ti–O–Si and [AlO_4] to intensify, but those associated with Q^n to attenuate, implying that [SiO_4] groups are partially replaced by [$Si(Ti)O_4$], making full use of NBOs for network interconnection and thus increasing network rigidity.

3.1.2. XRD analysis

Fig. 2 displays the XRD patterns of the TGCs containing various levels of CeO_2/TiO_2 prepared by reheating the precursor glass at 650 °C for 4 h. Pattern comparison reveals that samples containing

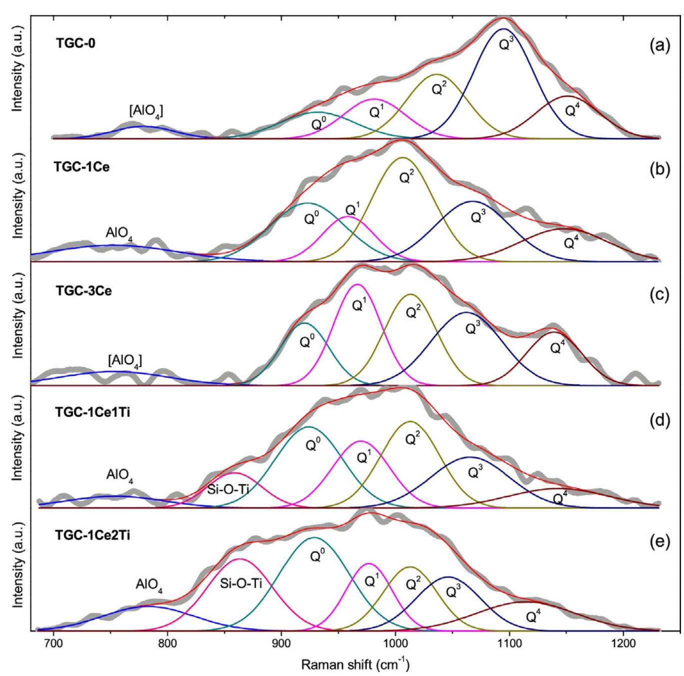

Fig. 1. Raman spectra of TGCs prepared by reheating precursor glass containing various levels of CeO_2/TiO_2 at 650 °C for 4 h.