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Structural characterization and temperature-dependent luminescence of $CaF_2:Tb^{3+}/Eu^{3+}$ glass ceramics

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Abstract: Tb^{3+}/Eu^{3+} co-doped transparent glass ceramics containing CaF_2 nanocrystals were successfully synthesized by high temperature melt-quenching method and subsequent heating. The structure and morphology of the samples were investigated by X-ray diffraction (XRD), transmittance electron microscopy (TEM), high resolution TEM (HRTEM) and selected area electron diffraction (SAED). The photoluminescence properties and energy transfer process from Tb^{3+} to Eu^{3+} of $CaF_2:Tb^{3+},Eu^{3+}$ phosphors were also investigated through excitation spectra and decay curves. In addition, the emission spectra of the glass ceramics in a wide temperature range from 21 to 320 K were recorded under the excitation of 485 nm. It was found that the fluorescence intensity ratios of Tb^{3+} at 545 nm ($^5D_4\rightarrow{}^7F_5$) to Eu^{3+} at 615 nm ($^5D_0\rightarrow{}^7F_2$) was highly temperature-dependent with an approximate linear relationship, and the temperature sensitivity was about 0.4%/K. It is expected that the investigated Tb^{3+}/Eu^{3+} co-doped CaF_2 glass ceramics may have prospective application in optical thermometry.

Keywords: $CaF_2:Tb^{3+}/Eu^{3+}$; glass ceramics; structural characterization; optical thermometry; rare earths

Temperature is one of the most important fundamental physical parameters, and the accuracy measurement of temperature is crucial in many fields of science, engineering and industry. Recently, optical thermometry based on luminescent materials has been extensively investigated for its non-invasive operating mode, high-spatial resolution and quick response[1–12]. To achieve high detection sensitivity, many optical temperature sensing techniques have been developed, such as the spectral shift of emission bands, absolute fluorescent intensity, fluorescence lifetime, and the fluorescence intensity ratio[13–16]. Furthermore, sensing temperature with intensity ratio of dual emission bands rather than individual emission peak is regarded as a very promising approach, because it can reduce dependence on measurement conditions and improve sensing accuracy.

The Tb^{3+} and Eu^{3+} co-doped materials have recently received considerable interests for possible applications in temperature sensing, owing to the temperature-dependent energy transfer from Tb^{3+} to Eu^{3+}. Self-reference temperature determination based on the intensity ratio of emission bands from different ions rather than a single ion is therefore much preferred, which has been demonstrated with e.g. Eu^{3+} and Tb^{3+} co-doped metal organic frameworks and nanomaterials[17–21]. As the $^5D_4$ state (20500 cm^{-1}) of Tb^{3+} is located near the center of $^5D_2$ (21500 cm^{-1}) and $^5D_1$ (19000 cm^{-1}) states of Eu^{3+}, the energy mismatch between these excited states of Tb^{3+} and Eu^{3+} is much closer to the maximal phonon energy of the host, resulting in a strong interaction between Tb^{3+} and Eu^{3+} [22]. With the participation of several phonons, the multi-phonon-assisted energy transfer from Tb^{3+} to Eu^{3+} ions is efficient in co-doped samples and its possibility increases rapidly with temperature. Consequently, the intensity ratio between $^5D_4\rightarrow{}^7F_2$ (Tb^{3+} at 545 nm) and $^5D_0\rightarrow{}^7F_2$ (Eu^{3+} at 615 nm) was temperature dependent, giving high sensitivity to a temperature change.

Oxyfluoride glass ceramics have been widely investigated as host materials for rare earth ions recently because they have the advantages of not only fluorides with comparatively low phonon energies, but also oxide materials with high chemical and mechanical stabilities[23]. On the other hand, CaF_2 is a promising candidate for desired host materials due to its high solubility of both sensitizer and activator rare-earth ions, wide transparent spectral region (about from 0.125 to 10 μm), good chemical stability, low phonon energy, friendliness to environment, and gives a good match of refractive index with the alumino-silicate glass[24–28].

In this paper, transparent glass ceramics containing CaF_2:5%Tb^{3+}/1%Eu^{3+} nanocrystals were successfully prepared by melt-quenching and subsequent heating. The

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fluorescence intensity ratio between the Tb^{3+}:$^5D_4 \rightarrow {}^7F_5$ transition and the Eu^{3+}:$^5D_0 \rightarrow {}^7F_2$ one in the glass ceramics was found to be highly temperature-dependent.

1 Experimental

The samples were prepared with nominal composition (in mol.%) 45SiO_2-20Al_2O_3-10CaO-25[(1–x–y)CaF_2-x TbF_3-y EuF_3](x=0.05, y=0; x=0, y=0.01, 0; x=0.05, y=0.01) by melt-quenching method. The raw materials of SiO_2 (AR), Al_2O_3 (AR), $CaCO_3$ (AR) and CaF_2 (AR) and high purity TbF_3 (99.99%), EuF_3 (99.99%) were completely mixed and crashed in an agate mortar. The well ground stoichiometric chemicals were put into an alumina crucible and melted at 1400 ℃ for an hour. The melt was poured into a preheated hot copper mold and then was pressed by another plate to form transparent precursor glass (labeled as PG). The PG was followed by annealing at 450 ℃ for 10 h to release internal stress. Subsequently, PG glass was heat-treated at 700 ℃ for 2 h to form glass ceramics sample, which was labeled as GC700.

Differential scanning calorimetry (DSC) measurement was carried out in a simultaneous thermal analyzer (NETZSCH STA 449F3) at a heating rate of 10 K/min under N_2 atmosphere to determine the glass transition (T_g) and crystallization (T_x) temperatures. The phase structures and the mean crystallite size of samples were identified via the XRD measurement (MAC Science Co. Ltd. Mxp18. AHF, Tokyo, Japan) with nickel-filter Cu Kα radiation in the range of 2θ=10°−80°. The accelerating voltage was 40.0 kV and the tube current was 100.0 mA. The microstructure of glass ceramics was analyzed by a HRTEM (FEI Talos F200X, FEI Ltd., Hillsboro, Oregon, United States). The excitation spectra of the samples were recorded with a JY Fluorolog-3-Tou fluorescence spectrophotometer (JobinYvon Ltd., France) using a 450 W Xenon lamp as the excitation light source. The emission spectra were obtained by a Jobin-Yvon HRD-1 double monochromator equipped with a Hamamatsu R928 photomultiplier. The signals were analyzed by an EG&G 7265 DSP lock-in amplifier and stored into computer memories. For the measurements at low temperature, the powder sample was pressed into a round tablet with thickness of 0.8 mm and diameter of 8.0 mm. And the tablet was glued to a copper pedestal with cryogenic glue, then fixed in a closed-cycle cryostat fed by a WC50 helium compressor. Temperature of the sample was controlled over the range of 21–300 K by a Lake Shore Model 321 temperature controller.

2 Results and discussion

Fig. 1 shows the DSC curve of the glass with (x, y)=(0.05, 0.01) composition. The glass transition temperature T_g, the CaF_2 crystallization temperature T_x, and the

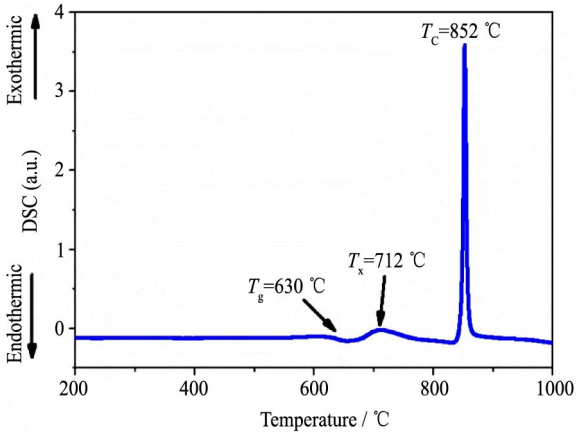

Fig. 1 Differential thermal analysis curve of 45SiO_2-0Al_2O_3-10CaO-25[(1–x–y)CaF_2-$x$$TbF_3$-$y$$EuF_3$] ($x$=0.05, y=0.01) glass

crystallization temperature of oxide matrix T_c were estimated to be 630, 712, and 852 ℃, respectively. Fig. 2 shows the XRD patterns of as-synthesized 5 mol.% Tb^{3+}, 1 mol.% Eu^{3+}, and 5 mol.% Tb^{3+}/1 mol.% Eu^{3+} co-doped CaF_2 PG and GC700. PG is determined to be structurally amorphous, characterized by two diffuse humps without any sharp peaks. After heat treatment at 700 ℃ for 2 h, four strong diffraction peaks unambiguously indexed to cubic CaF_2 phase (JCPDS No. 35-816) with space group Fm-3m (No. 225) emerge in the XRD pattern for GC700, suggesting that the CaF_2-based glass ceramics have been successfully synthesized. Based on the diffraction peak widths, the mean crystalline size of 5% Tb^{3+}/1% Eu^{3+} GC700 nanocrystals were estimated to be 15 nm with Scherrer equation:[29]

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where D is the crystal size, k=0.89, λ (0.154056 nm) represents the wavelength of Cu Kα radiation, θ is the Bragg angle of XRD peak, and β is the full-width at half-maximum of the diffraction peak.

For investigating the morphology of GC700 sample with 5 mol.% Tb^{3+}/1 mol.% Eu^{3+} co-doped CaF_2, TEM,

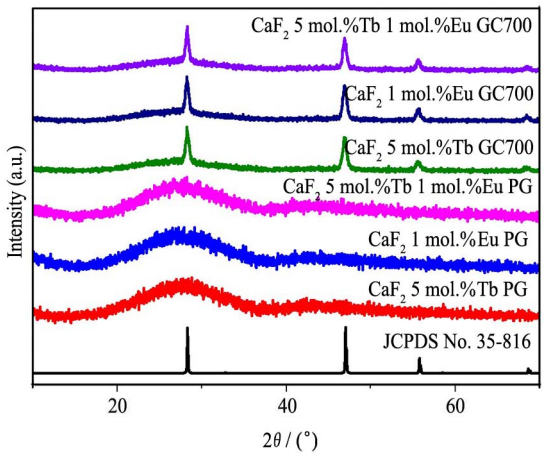

Fig. 2 XRD patterns of PG and GC700 with 5 mol.%Tb^{3+}, 1 mol.%Eu^{3+}, and 5 mol.% Tb^{3+}/1 mol.% Eu^{3+} co-doped CaF_2