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Structural characterization and temperature-dependent luminescence of CaF₂:Tb³⁺/Eu³⁺ 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 (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$) to Eu^{3+} at 615 nm (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) 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: CaF₂:Tb³⁺/Eu³⁺; 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, highspatial 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 intensitv 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 Tb³⁺ and Eu³⁺ co-doped materials have recently received considerable interests for possible applications in temperature sensing, owing to the temperature-dependent energy transfer from Tb³⁺ to Eu³⁺. 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. Eu³⁺ and Tb³⁺ co-doped metal organic frameworks and nanomaterials^[17–21]. As the ⁵D₄ state (20500 cm⁻¹) of Tb³⁺ is located near the cen-

ter of ${}^{5}D_{2}$ (21500 cm⁻¹) and ${}^{5}D_{1}$ (19000 cm⁻¹) states of Eu³⁺, the energy mismatch between these excited states of Tb³⁺ and Eu³⁺ is much closer to the maximal phonon energy of the host, resulting in a strong interaction between Tb³⁺ and Eu^{3+[22]}. With the participation of several phonons, the multi-phonon-assisted energy transfer from Tb³⁺ to Eu³⁺ ions is efficient in co-doped samples and its possibility increases rapidly with temperature. Consequently, the intensity ratio between ${}^{5}D_{4} \rightarrow {}^{7}F_{2}$ (Tb³⁺ at 545 nm) and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (Eu³⁺ 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, CaF₂ 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 μ m), 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 $Tb^{3+}: {}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition and the $Eu^{3+}: {}^{5}D_{0} \rightarrow {}^{7}F_{2}$ one in the glass ceramics was found to be highly temperature-dependent.

1 Experimental

The samples were prepared with nominal composition (in mol.%) $45SiO_2-20Al_2O_3-10CaO-25[(1-x-y)CaF_2-x$ TbF₃-y EuF₃](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 SiO₂ (AR), Al₂O₃ (AR), CaCO₃ (AR) and CaF₂ (AR) and high purity TbF₃ (99.99%), EuF₃ (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 °C 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 °C for 10 h to release internal stress. Subsequently, PG glass was heat-treated at 700 °C 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 Ka radiation in the range of $2\theta = 10^{\circ} - 80^{\circ}$. 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 CaF₂ crystallization temperature T_{x} , and the



Fig. 1 Differential thermal analysis curve of 45SiO₂-0Al₂O₃-10CaO-25[(1-x-y)CaF₂-xTbF₃-yEuF₃] (x=0.05, y=0.01) glass

crystallization temperature of oxide matrix T_c were estimated to be 630, 712, and 852 °C, respectively. Fig. 2 shows the XRD patterns of as-synthesized 5 mol.% Tb³⁺, 1 mol.% Eu³⁺, and 5 mol.% Tb³⁺/1 mol.% Eu³⁺ co-doped CaF₂ PG and GC700. PG is determined to be structurally amorphous, characterized by two diffuse humps without any sharp peaks. After heat treatment at 700 °C for 2 h, four strong diffraction peaks unambiguously indexed to cubic CaF₂ phase (JCPDS No. 35-816) with space group *Fm-3m* (No. 225) emerge in the XRD pattern for GC700, suggesting that the CaF₂-based glass ceramics have been successfully synthesized. Based on the diffraction peak widths, the mean crystalline size of 5% Tb³⁺/1% Eu³⁺ GC700 nanocrystals were estimated to be 15 nm with Scherrer equation:^[29]

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

where D is the crystal size, k=0.89, λ (0.154056 nm) represents the wavelength of Cu K α 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 CaF₂, TEM,



Fig. 2 XRD patterns of PG and GC700 with 5 mol.%Tb³⁺, 1 mol.%Eu³⁺, and 5 mol.% Tb³⁺/1 mol.% Eu³⁺ co-doped CaF₂

HRTEM and SAED of GC700 were performed, as shown in Fig. 3(a, b). The TEM bright-field images demonstrate that the well formed CaF₂ nanocrystals were homogeneously dispersed among glass matrix and the diameters of the nanocrystals were about 7–15 nm, in agreement with the average nanocrystal size calculated from XRD data. Further the HRTEM image is shown in Fig. 3(b) with their SAED rings well indexed to cubic CaF₂. The selected particle in Fig. 3(b) shows an inter planar spacing of 0.1908 nm, corresponding to the (220) lattice plane of CaF₂ (d_{220} =0.1930 nm). To summarize, the TEM, HRTEM and SAED images further confirm the formation of the cubic phase of CaF₂ glass ceramics.

In order to investigate the luminescent properties of PG and GC700 with 5 mol.% Tb³⁺,1 mol.% Eu³⁺, and 5 mol.% Tb³⁺/1 mol.% Eu³⁺ co-doped CaF₂, their excitation spectra (monitoring the emission of the Tb³⁺ ions at 541 nm and emission of the Eu^{3+} ions at 615 nm) were recorded and are depicted in Fig. 4. From the excitation spectra monitored with the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition of Tb³⁺ at 541 nm of the 5 mol.% Tb³⁺CaF₂ PG and GC700 samples in Fig. 4(a-b), the excitation peaks situated at 377 and 485 nm are ascribed to the ${}^{7}F_{6} \rightarrow {}^{5}L_{10}$ and ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ transition of Tb³⁺, respectively. In the excitation spectra of Eu³⁺ by monitoring the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition at 615 nm of 1 mol.% Eu³⁺ CaF₂ PG and GC700 in Fig. 4(a–b), the characteristic absorption peaks of Eu³⁺ at 394, 415, and 465 nm were observed, corresponding to the ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$, ${}^{7}F_{0} \rightarrow {}^{5}D_{3}$, and ${}^{7}F_{0} \rightarrow {}^{5}D_{2}$ transitions of Eu³⁺, respectively. (a)



Fig. 3 (a) TEM image of GC700 with 5 mol.%Tb³⁺/1 mol.% Eu³⁺ co- doped CaF₂; (b) HRTEM image of GC700 with 5 mol.%Tb³⁺/1 mol.%Eu³⁺ co-doped CaF₂ (the inset is the SAED)



Fig. 4 Excitation spectra of PG (a) and GC700 (b) containing 5 mol.%Tb³⁺, 1 mol.%Eu³⁺, and 5 mol.%Tb³⁺/1 mol.% Eu³⁺ co-doped CaF₂ by monitoring the ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ emission of the Tb³⁺ ions at 541 nm and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission of the Eu³⁺ ions at 615 nm, respectively

Aside from the characteristic absorption peaks of Eu^{3+} , the characteristic absorption peaks of Tb3+ are also observed in the excitation spectra of Eu³⁺ for 5 mol.% Tb³⁺/1 mol.% Eu³⁺ co-doped CaF₂PG and GC700, which is a clear evidence for the occurrence of the ET from Tb³⁺ to Eu³⁺. Moreover, the intensity ratio of 465 to 485 nm in PG decreases from 4.4 to 3.9 after crystallization. It can be deduced that the ET is more effective in GC700 than PG^[30]. Due to the thermo-sensitive luminescent properties of Tb³⁺/Eu³⁺ co-doped samples caused by the ET between Tb³⁺ and Eu³⁺ ions, it is better to choose the characteristic excitation band of Tb³⁺ for effective excitation. However, the strongest peak of Tb³⁺ at 377 nm was overlapped with the peak of Eu³⁺ at 394 nm. As a result, we selected the excitation band around 485 nm corresponding to the ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ of Tb³⁺ as the best choice.

Furthermore, the ET transfer of Tb^{3+} to Eu^{3+} was also investigated through decay curves of Tb^{3+} emission by monitoring ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ transition of Tb^{3+} under the 485 nm excitation in 5 mol.% Tb^{3+} and 5 mol.% $Tb^{3+}/1$ mol.% Eu^{3+} co-doped CaF₂PG and GC700 samples. It can be clearly seen that the fluorescence decay becomes quick after the Eu^{3+} ions co-doped as the acceptor of ET in Fig. 5. It is found that all decay curves can be well fitted by double exponential decay mode with the following equation^[31]:



Fig. 5 Decay curves of PG (a) and GC700 (b) containing 5 mol.%Tb³⁺, and 5 mol.%Tb³⁺/1 mol.%Eu³⁺ co-doped CaF₂ by monitoring the emission of Tb³⁺ at 541 nm

$$I = A_{1} \exp(-\frac{t}{\tau_{1}}) + A_{2} \exp(-\frac{t}{\tau_{2}})$$
(2)

where *I* is the luminescence intensity; A_1 and A_2 are fitting parameters; *t* is the time, τ_1 and τ_2 are rapid and slow lifetimes for exponential components, respectively. Based on these parameters, the average decay times of Tb³⁺ can be calculated by the following equation^[31]:

$$\tau = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$
(3)

The average lifetimes (τ) were determined to be 2.86, 2.61, 2.78, and 2.39 ms for PG and GC700 with 5%Tb³⁺ and 5 mol.%Tb³⁺/1 mol.%Eu³⁺, respectively. The luminesce lifetime of sensitizer Tb³⁺ is shortened after the Eu³⁺ co-doping, which is an evidence of the ET from Tb³⁺ to Eu³⁺ in PG and GC700.

Besides, the ET efficiency η_{ET} of Tb³⁺ to Eu³⁺ can be calculated based on the following equation^[32]:

$$\eta_{ET} = 1 - \frac{\tau}{\tau_0} \tag{4}$$

where τ_0 and τ are the lifetimes of Tb³⁺ ions in the absence and presence of Eu³⁺, respectively. The calculated ET efficiency η_{ET} is 8.7% and 14% in PG and GC700, respectively. It is further demonstrated that the ET process from Tb³⁺ to Eu³⁺ is more efficient in GC700 than PG. To examine the thermal effect on the photoluminescence, the photoluminescence intensity was investigated in a temperature range from 21 to 300 K under excitation of 485 nm. All the emission spectra were normalized to the 541 nm emission band of Tb^{3+} : ${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{5}$, as shown in Fig. 6(a). It is interesting that the intensity of Tb^{3+} (~541 nm) exhibits a significantly different temperature-dependent luminescence behavior as compared with that of Eu³⁺ (~620 nm). As a consequence, energy transfer from Tb³⁺ to Eu³⁺ in glass ceramics enhances greatly with the increase of temperature, which can be used as a self-calibrated reference for the sample temperature. As shown in Fig. 6(b), the temperature-dependent FIR from 21 to 320 K can be linearly fitted by the following equation:

$$\frac{I_{541}}{I_{620}} = 3.08 - 0.004T \tag{5}$$

The fitting of experimental data gives a sensitivity of 0.4%/K for temperature sensing. This result suggests that 5 mol.%Tb³⁺/1 mol.%Eu³⁺ co-doped CaF₂ GC700 is a promising candidate for thermometer in this temperature range under the 485 nm excitation.



Fig. 6 (a) Normalized emission spectra of GC700 under the excitation of 485 nm in the temperature range of 21–320 K;
(b) Dependence of FIR (*I*₅₄₁/*I*₆₂₀) on temperature for GC700 and the fitted line for experimental data

3 Conclusions

In summary, the transparent glass ceramics containing 5 mol.% $Tb^{3+}/1$ mol.% Eu^{3+} co-doped CaF₂ nanocrystals

were successfully fabricated by conventional meltquenching method and subsequent heat treatment. The formation of CaF₂ nanocrystals were confirmed by XRD, TEM, HRTEM, SAED and photoluminescence spectra. Moreover, the fluorescence intensity ratio between Tb³⁺ at 545 nm (${}^{5}D_{4}\rightarrow{}^{7}F_{5}$) and Eu³⁺ at 615 nm (${}^{5}D_{0}\rightarrow{}^{7}F_{2}$) was investigated and found to be highly temperature-dependent in a wide range from 21 to 320 K under the excitation of 485 nm. The temperature sensitivity of fluorescence intensity ratio was about 0.4%/K, which suggested that the investigated glass ceramics might be a promising candidate as optical temperature sensor.

References:

- Brites C D, Lima P P, Silva N J, Millan A, Amaral V S, Palacio F, Carlos L D. Lanthanide-based luminescent molecular thermometers. *New J. Chem.*, 2011, 35: 1177.
- [2] Zhou S S, Jiang G C, Li X Y, Jiang S, Wei X T, Chen Y H, Yin M, Duan C K. Strategy for thermometry via Tm³⁺doped NaYF₄ core-shell nanoparticles. *Opt. Lett.*, 2014, **39**: 6687.
- [3] Cao Z M, Chen Y H, Zhou S S, Duan C K, Yin M. Optical properties of Er³⁺ doped KYb_xF_{3x+1} (x=2, 3) upconverting nanoparticles. *J. Rare Earths*, 2015, **33**: 911.
- [4] Jiang S, Zeng P, Liao L Q, Tian S, Guo H, Chen Y H, Duan C K, Yin M. Optical thermometry based on upconverted luminescence in transparent glass ceramics containing NaYF₄:Yb³⁺/Er³⁺ nanocrystals. *J. Alloys Compd.*, 2014, **617**: 538.
- [5] Cao J K, Li X M, Wang Z X, Wei Y L, Chen L P, Guo H. Optical thermometry based on up-conversion luminescence behavior of self-crystallized K₃YF₆:Er³⁺ glass ceramics. *Sensor. Actuat. B-Chem.*, 2016, **224**: 507.
- [6] Chen D Q, Liu S, Wan Z Y, Ji Z Y. EuF₃/Ga₂O₃ Dualphase nanostructural glass ceramics with Eu²⁺/Cr³⁺ dualactivator luminescence for self-calibrated optical thermometry. *J. Phys. Chem. C*, 2016, **120**(38): 21858.
- [7] Chen D Q, Wan Z Y, Liu S. Highly sensitive dual-phase nanoglass-ceramics self-calibrated optical thermometer. *Anal. Chem.*, 2016, 88(7): 4099.
- [8] Chen D Q, Wan Z Y, Zhou Y, Zhou X Z, Yu Y L, Zhong J S, Ding M Y, Ji Z G. Dual-phase glass ceramic: structure, dual-modal luminescence, and temperature sensing behaviors. ACS Appl. Mater. Interfaces, 2015, 7(34): 19484.
- [9] Wan Z Y, Chen D Q, Zhou Y, Huang P, Zhong J S, Ding M Y, Yu H, Ji Z G. Eu³⁺ and Er³⁺ doped NaLu_{1-x}Yb_xF₄ (x=0~1) solid-solution self-crystallization nano-glass-ceramics: Microstructure and optical spectroscopy. *J. Eur. Ceram. Soc.*, 2015, **35**(13): 3673.
- [10] Chen D Q, Wan Z Y, Zhou Y, Xiang W D, Zhong J S, Ding M Y, Yu H, Ji Z G. Tuning into blue and red: europium single-doped nano-glass-ceramics for potential application in photosynthesis. J. Mater. Chem. C, 2015, 3(13): 3141.
- [11] Chen D Q, Wan Z Y, Zhou Y, Huang P, Zhong J S, Ding M Y, Xiang W D, Liang X J, Ji Z G. Bulk glass ceramics containing Yb³⁺/Er³⁺: β-NaGdF₄ nanocrystals: phase-

separation-controlled crystallization, optical spectroscopy and upconverted temperature sensing behavior. J. Alloys Compd., 2015, **638**: 21.

- [12] Zhou S S, Li X Y, Cao Z M, Duan C K, Chen Y H, Yin M. An abnormal fluorescence intensity ratio between two green emissions of Er³⁺ caused by heating effect of 980 nm excitation. *J. Rare Earths*, 2015, **33**: 1031.
- [13] Li X Y, Jiang G C, Zhou S S, Wei X T, Chen Y P, Duan C K, Yin M. Luminescent properties of chromium (III)-doped lithium aluminate for temperature sensing. *Sens. Actuat. B-Chem.*, 2014, **202**: 1065.
- [14] León-Luis S F, Rodríguez-Mendoza U R, Lalla E, Lavín V. Temperature sensor based on the Er³⁺ green upconverted emission in a fluorotellurite glass. *Sens. Actuat. B-Chem.*, 2011, **158**: 208.
- [15] Allison S, Gillies G. Remote thermometry with thermographic phosphors: instrumentation and applications. *Rev. Sci. Instrum.*, 1997, 68: 2615.
- [16] Bosze E J, Hirata G A, McKittrick J. An analysis of Y₂O₃: Eu³⁺ thin films for thermographic phosphor applications. *J. Lumin.*, 2011, **131**: 41.
- [17] Zheng S H, Chen W B, Tan D Z, Zhou J J, Guo Q B, Jiang W, Xu C, Liu X F, Qiu J R. Lanthanide-doped NaGdF₄ core-shell nanoparticles for non-contact self-referencing temperature sensors. *Nanoscale*, 2014, 6: 5675.
- [18] Rao X T, Song T, Gao J K, Cui Y J, Yang Y, Wu C D, Chen B L, Qian G D, A highly sensitive mixed lanthanide metal-organic framework self-calibrated luminescent thermometer. J. Am. Chem. Soc., 2013, 135: 15559.
- [19] Cui Y J, Xu H, Yue Y F, Guo Z Y, Yue Y F, Guo Z Y, Yu J C, Chen Z X, Gao J K, Yang Y, Qian G D, Chen B L, A luminescent mixed-lanthanide metal-organic framework thermometer. J. Am. Chem. Soc., 2012, 134: 3979.
- [20] Hirai Y, Nakanishi T, Miyata K, Fushimi K, Hasegawa Y. Thermo-sensitive luminescent materials composed of Tb (III) and Eu (III) complexes. *Mater. Lett.*, 2014, **130**: 91.
- [21] Chen D Q, Wang Z Y, Zhou Y, Huang P, Ji Z G. Tb³⁺/ Eu³⁺:YF₃ nanophase embedded glass ceramics: Structural characterization, tunable luminescence and temperature sensing behavior. *J. Alloys Compd.*, 2015, **646**: 339.
- [22] Li F H, Liu H, Wei S L, Yu L X. Photoluminescent properties of Eu³⁺ and Tb³⁺ codoped Gd₂O₃ nanowires and bulk materials. *J. Rare Earths*, 2013, **31**: 1063.
- [23]Sarakovskis A, Krieke G. Upconversion luminescence in erbium doped transparent oxyfluoride glass ceramics containing hexagonal NaYF₄ nanocrystals. *J. Eur. Ceram. Soc.*, 2015, **35**: 3665.
- [24]Yu D C, Zhang J P, Chen D Q, Zhang W J, Yang Z M, Zhang Q Y. Three-photon near-infrared quantum cutting in Tm³⁺-doped transparent oxyfluoride glass ceramics. *Appl. Phys. Lett.*, 2012, **101**: 171108.
- [25] Imanieh M H, Martín I R, Eftekhari Yekta B, Marghussian V K, Shakhesi S. Improved cooperative emission in ytterbium-doped oxyfluoride glass-ceramics containing CaF₂ nanocrystals. J. Am. Ceram. Soc., 2012, 95: 3827.
- [26] Wu G B, Fan S H, Zhang Y H, Chai G Q, Ma Z J, Peng M Y, Qiu J R, Dong G P. 2.7 μm emission in Er³⁺: CaF₂ nanocrystals embedded oxyfluoride glass ceramics. *Opt. Lett.*, 2013, **38**: 3071.

- [27] Babu P, Jang R H, Rao R S, Shi L, Jayasankar C, Lavín V, Seo H J. White light generation in Dy³⁺-doped oxyfluoride glass and transparent glass-ceramics containing CaF₂ nanocrystals. *Opt. Express*, 2011, **19**: 1836.
- [28] Deng W, Cheng J S. New transparent glass-ceramics containing large grain Eu³⁺:CaF₂ nanocrystals. *Mater. Lett.*, 2012, **73**: 112.
- [29] Hu F F, Wei X T, Qin Y G, Jiang S, Li X Y, Zhou S S, Chen Y H, Duan C K, Yin M. Yb³⁺/Tb³⁺ co-doped GdPO₄ transparent magnetic glass-ceramics for spectral conversion. J. Alloys Compd., 2016, 674: 162.
- [30] Hu F F, Wei X T, Jiang S, Huang S, Qin Y G, Chen Y H,

Duan C K, Yin M. Fabrication and luminescence properties of transparent glass-ceramics containing Eu³⁺-doped TbPO₄ nanocrystals. *J. Am. Ceram. Soc.*, 2015, **98**: 464.

- [31] Wang R F, Zhou D C, Qiu J B, Yang Y, Wang C. Colortunable luminescence in Eu³⁺/Tb³⁺ co-doped oxyfluoride glass and transparent glass-ceramics. *J. Alloys Compd.*, 2015, **629**: 310.
- [32] Xiong J H, Meng Q Y, Sun W J. Luminescent properties and energy transfer mechanism from Tb³⁺ to Eu³⁺ in CaMoO₄:Tb³⁺, Eu³⁺ phosphors. J. Rare Earths, 2016, 34: 251.