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Spectroscopic study of thulium doped transparent glass ceramics*

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A systematic investigation on fluorescence spectroscopy of trivalent thulium doped in oxyfluoride glass ceramics containing LaF_3 nanocrystals has been carried out in a spectral range from 400 to 900 nm under the direct excitation of $^1D_2$ level at a low temperature. Specific optical transitions related to the fluorescence emissions are studied based on experimental measurements in frequency and time domain. Fluorescence emissions from the ions in crystal phase are distinguished from what in glass phase and their spectroscopic properties are explored. The dynamical process shows that the temporal decay of fluorescence emission consists of two parts: a rapid decay from the ions in glass phase and a slower decay from the ions in crystal phase.

Keywords: trivalent thulium, transparent oxyfluoride glass ceramics, optical transition
PACC: 7855H, 7820, 8120Q

1. Introduction

Transparent glass ceramics has attracted much attention since it was reported by Wang and Ohwaki in 1993 for the first time.[1−4] Compared with conventional glass ceramic materials, it contains nanometre scale crystalline particles in the glass matrix. Optically active ions doped in the sample are generally distributed both in nanoparticles and in glass matrix due to the preparation process, which provides the doped ions with two different local environments: crystal phase and glass phase in one sample. Oxyfluoride glass ceramics containing fluoride nanocrystals combines optical advantages of fluoride crystal host with chemical and mechanical advantages of oxide glass matrix, which improves the chemical and mechanical durability of fluoride material while the optical characteristics of fluoride crystal is maintained. Up to now, many studies have been carried out on thulium doped in fluoride crystals and glasses.[5−12] Some investigations have also been conducted on the Tm^{3+} doped in transparent glass ceramic systems.[13−16] Here we present a systematic investigation on the fluorescence emission spectroscopy for Tm^{3+} doped in oxyfluoride glass ceramics containing LaF_3 nanocrystals under the direct excitation of $^1D_2$ level at a temperature of about 20 K. The specific energy levels related to the corresponding transitions are analysed, and fluorescence emissions from the ions in the crystal phase of the ceramic sample are extracted. Spectral and temporal properties of fluorescence emissions from doped Tm^{3+} ions in glass and glass ceramics are also discussed.

2. Experiments

Transparent glass ceramic sample used in our study are oxyfluoride glass ceramics containing Tm^{3+}:LaF_3nanocrystals, which are obtained from Corning, Inc. New York.[3] The nanocrystal size is about 20 nm, which is controlled with annealing temperature. The average concentration of Tm^{3+} is 1.0 mol%. Tm^{3+} doped glass sample has the same components as the glass ceramic sample. Micro-sized Tm^{3+}:LaF_3 powder sample is prepared by using the hydrothermal method. The third harmonic output from Quanta Ray Lab-170 Nd^{3+}:YAG pulsed laser is used for the excitation of the sample. CCD system equipped with an SP2750 monochrometer is employed for collecting and recording spectroscopic signals. Temporal decay measurements are made by using a TDS 5000B digital oscilloscope. The specified temperature environments are supplied with DE-202NI closed cycling system, which is made from Advanced Research Systems, Inc.

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3. Results and discussion

3.1. Spectroscopic characterization

$^1D_2$ state can be directly excited by using a 355 nm laser based on the energy level diagram of Tm^{3+} in LaF_3 crystal. Figure 1 shows the fluorescence emission spectra of Tm^{3+} doped in glass ceramics and glass, excited by a 355 nm laser at a temperature of 20 K. It can be seen that six broad bands with some fine structures occur in a spectral range from 400 to 900 nm. The corresponding peak positions are 453, 485, 514, 651, 667, 754, and 804 nm, respectively. Energy levels associated with each emission band can be determined based on the energy level diagram and temporal property of fluorescence.

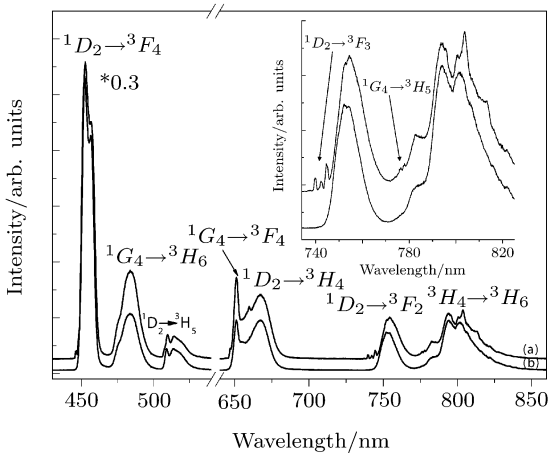


Fig.1. Fluorescence spectra of Tm^{3+} doped in transparent oxyfluoride glass ceramics (a) and glass (b) under 355 nm laser excitation at a temperature of 20 K. The average Tm^{3+} concentration is 1.0 mol %. The inset shows the bands at around 754 and 804 nm.

Figure 2 is the schematic energy level diagram of Tm^{3+} doped in LaF_3 for those levels associated with current study.[9] According to the absorption spectra and energy level diagram, most of emission bands have been assigned,[5,10,17] but some of them have not and their corresponding mechanism also needs further investigating.

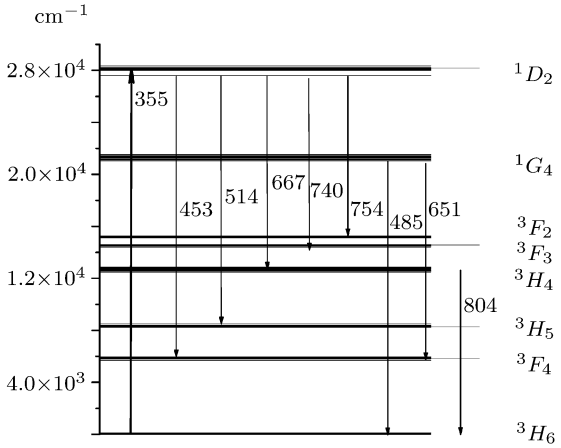


Fig.2. Energy level diagram of Tm^{3+}:LaF_3.

To determine the specific transition for each emission band, we measure the fluorescence lifetime and its temperature dependence. Table 1 presents the measured results on fluorescence emission, lifetime and corresponding transitions of Tm^{3+} doped in glass ceramics and glass at 20 K. The temperature dependence of fluorescence lifetime is plotted in Fig. 3. The proposed specific transitions in each band are listed in the table too. For emissions centred at 453, 514, 667, and 754 nm, they all exhibit very close fluorescence decay time and similar temperature dependence. It is easy to connect them with transitions from $^1D_2$ to $^3F_4$, $^3H_5$, $^3H_4$, and $^3F_2$, respectively, which accord with previous investigations.[5,10,17] The emission at 804 nm is assigned to the transition of $^3H_4 -^3 H_6$. The population on the excited $^3H_4$ state is fed either by a 667nm emission from $^1D_2$ to $^3H_4$, or by a transition from $^1D_2$ to $^3F_2$ accompanied with the 754 nm photon emission, then followed by nonradiative relaxation from $^3F_2$ to $^3H_4$ with the assistance of phonons.

Table 1. Fluorescence emission, lifetime and corresponding transitions for 1.0 mol% Tm^{3+} doped in glass ceramics and glass measured at 20 K.

wavelength/nm	$\tau/\mu s$[a]	$\tau/\mu s$[b]	transition	wavelength/nm	$\tau/\mu s$[c]	transition
453/456	22±2	18±2	$^1D_2 \rightarrow {}^3F_4$	446.6	37±3	$^1D_2 \rightarrow {}^3F_4$
485	102±5	55±5	$^1G_4 \rightarrow {}^3H_6$			
510/514	23±2	17±2	$^1D_2 \rightarrow {}^3H_5$			
651	95±6	46±5	$^1G_4 \rightarrow {}^3F_4$	647.6	78±5	$^1G_4 \rightarrow {}^3F_4$
667	23±3	18±2	$^1D_2 \rightarrow {}^3H_4$	737.4/739.8/742.2/744.5	40±3	$^1D_2 \rightarrow {}^3F_3$
754	17±3	14±3	$^1D_2 \rightarrow {}^3F_2$	776.0/778.0/782	49±5	$^1G_4 \rightarrow {}^3H_5$
794/804	68±3	45±3	$^3H_4 \rightarrow {}^3H_6$	795.6/800.8/813.3	68±3	$^3H_4 \rightarrow {}^3H_6$

[a]from the ions in the glass environment of transparent glass ceramics sample,

[b]from the ions in the glass environment of glass sample,

[c]from the ions in the nanocrystalline environment of transparent glass ceramics.

It has been suggested that the emission at 651 nm located on the higher energy side of 667 nm emission band is a result of $^3F_2 - {}^3H_6$ transition in the cascade emissions $^1D_2 - {}^3F_2 - {}^3H_6$,[8] while in Ref.[18], 651 nm mission was assigned to the transition from $^1G_4$ to $^3F_4$. Since three transitions $^3F_2 - {}^3H_6$, $^1D_2 - {}^3H_4$, and $^1G_4 - {}^3F_4$ are possible to cover the radiative emissions ranging from about 667 to 651 nm for Tm^{3+} doped in LaF_3 crystal, we must examine their lifetimes and temperature dependence before the final assignment is given. Table 1 and Fig.3 show that the lifetime of 651 nm emission drops from 95 to 31 μs, and the lifetime of 667 nm decreases from 23 to 19 μs when the sample temperature changes from 20 to 300 K. Obviously the temperature has a greater influence on the fluorescence decay at 651 nm than that at 667 nm, which suggests that 651 nm emission should arise from an excited state other than $^1D_2$. Because of the very small energy gap between the $^3F_2$ and its nearest lower level $^3F_3$ (about 500 cm^{-1}), a big nonradiative relaxation rate is expected to exist for $^3F_2$ level. Thus, it is not very possible to have a radiative emission from $^3F_2$. Therefore the fluorescence emission at 651 nm should be ascribed to the transition of $^1G_4 \rightarrow {}^3F_4$, while 667 nm originates from the transition $^1D_2 \rightarrow {}^3H_4$.

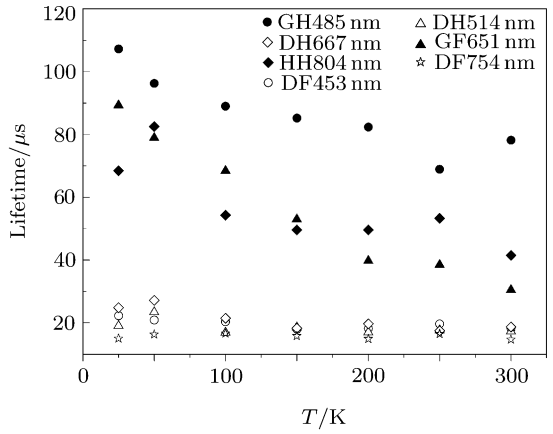


Fig.3. Temperature dependence of fluorescence lifetimes.

Emission at 485 nm is assigned to the transition from $^1G_4$ to $^3H_6$, which is supported by our results (see Figs.1 and 3 and Table1). There are three possible ways to populate $^1G_4$ state: (i) the excited $^1D_2$ state relaxes to $^1G_4$ state nonradiatively, (ii) radiative emission from $^1D_2$ state to $^1G_4$ state, (iii) phonon assisted cross relaxation from $^1D_2 + {}^3H_6$ to $^1G_4 + {}^3F_4$ /or $^3F_4 + {}^1G_4$. Since the maximum phonon energies are around 400 cm^{-1} for LaF_3 crystal and 1100 cm^{-1} for the glass matrix, multi-phonon relaxation has an extremely small probability for an energy gap of about 6700 cm^{-1} between $^1D_2$ and its next lower level $^1G_4$. Thus the process (i) is not likely to happen. Since both processes (ii) and (iii) are dependent on the relaxation of $^1D_2$, it is hard to distinguish them by studying only the dynamical process of related levels. Further investigation is required in order to find out the exact process.

3.2. Fluorescence emissions from the ions in crystal phase of the ceramic sample

Figure1(a) shows that some weak but sharp peaks are detected from glass ceramic samples. The inset in Fig.1 is one part of the spectrum, and it shows these peaks more clearly. A similar phenomenon is not detected indeed for the counterpart glass sample. Based on the peak position and its decay time, we suggest that the shoulder at 647.6 nm is a branch of the transition from $^1G_4$ to $^3F_4$. Peaks on the higher energy side of 754 nm are assigned to the transitions from $^1D_2$ to $^3F_3$ sublevels, while peaks at 776 and 778 nm are determined originate from the transition from $^1G_4$ to $^3H_5$. Those at 795.6, 800.8 and 813.3 nm correspond to the transitions from $^3H_4$ to $^3H_6$, and the peak at 446.6 nm is ascribed to the transition from $^1D_2$ to $^3F_4$.

It is noticeable that the decay time associated with the $^1D_2$ level presented in the right part of the table is much longer than that listed on the left side. Considering that fluorescence from the ions doped in crystal phase has a longer lifetime than those in amorphous phase, we suggest that the longer lifetimes for the transitions from $^1D_2$ to $^3F_4$ and $^3F_3$ arise from the excited ions in crystal phase of the sample. To support this interpretation, spectroscopic study on a micro-sized Tm^{3+}:LaF_3 powder sample is conducted. Figure 4 is for the fluorescence spectra of a micro-sized Tm^{3+}:LaF_3 powder sample and transparent oxyfluoride glass ceramics containing Tm^{3+}:LaF_3 nanocrystals. Peaks that appear in the ceramic sample can be observed more clearly in the micro-sized powder sample. The lifetime of $^1D_2$ increases to about 70 μs for the micro-sized powder sample even though the excitation by a 355 nm laser is not exactly at resonance. Thus, it is proved that those weak but sharp peaks presented in Fig.1(a) are emissions mainly from the ions in the crystal phase of nanoparticles. Fluorescence emission bands that are observed in both

glass and ceramic samples as listed in the left part of Table 1, are mainly due to the excitation of Tm^{3+} ions in the glass phase of the sample. For the ions in the glass sample, there exists only glass phase environment. But in the glass ceramic sample, the glass phase and the crystalline phase can coexist, ions in both phases make contributions to the observed fluorescence lifetimes. Since the ions in the crystalline phase have a longer relaxation time than those in the glass phase, a longer fluorescence lifetime should be observed for the ceramic sample than that in the glass sample, which explains the difference in fluorescence lifetime listed in the left part of Table 1.

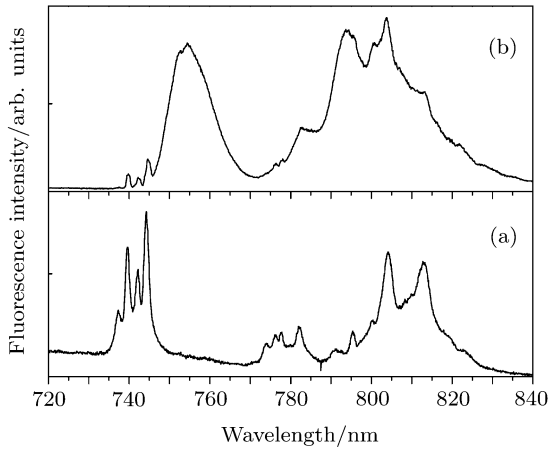


Fig.4. Fluorescence emissions of micro-sized Tm^{3+}:LaF_3 powder sample (a) and transparent oxyfluoride glass ceramics containing Tm^{3+}:LaF_3 nanocrystals (b), where T=20 K.

3.3. Temporal decay of fluorescence emission

The probabilities of radiative relaxation and nonradiative relaxation including multi-phonon relaxation and energy transfer determine the lifetime of fluorescence emission. Site defects, surface effect, and concentration quenching effect are possible sources to cause further reduction in fluorescence lifetime. It is also possible that the concentration quenching is more significant in nanocrystals than in the glass matrix due to a possible increase in Tm^{3+}concentration in crystal phase of the glass ceramic sample.[3] Since our goal is to explore the influence of crystal phase and glass phase environment on the fluorescence of Tm^{3+} ion, the surface and the concentration quenching effects will not be emphasized here as long as the fluorescence lifetime of Tm^{3+} in the crystal phase and in the glass phase can be distinguished.

Table 1 shows that the overall fluorescence lifetimes are shorter for Tm^{3+} doped in glass than in glass ceramics, which is not difficult to understand if the big phonon energy of the glass sample is considered. In glass matrix, the increasing of maximum phonon energy and lattice defects will lead to an increase in nonradiative relaxation, which consequently decreases fluorescence lifetime.[19]

During the study of fluorescence relaxation, most of decay curves measured experimentally cannot be well fitted with the single exponential nature. Data for lifetime presented in the Table 1 are average values, which are calculated with double exponential decay model $I(t) = A_1\exp\left(\frac{-t}{\tau_1}\right) + A_2\exp\left(\frac{-t}{\tau_2}\right)$, where A_1 and A_2 are amplitudes, and τ_1 and τ_2 are decay times. The mean lifetime of excited state is calculated from $\tau = \sum_i f_i * \tau_i$, where $f_i = \frac{A_i\tau_i}{\sum_j A_j\tau_j}$ is the fractional contribution of each component.

If one neglects the surface/interface effects of nanoparticles that are contained in the glass ceramic sample, there exist two different local environments for Tm^{3+} ions: crystal phase with a lower phonon energy and glass phase with a much higher phonon energy. Since the sample is prepared by using the melting method,[3] Tm^{3+} ions are distributed in both crystal phase (inside the nanoparticles) and glass phase (in the glass matrix). When the sample is excited, ions in both crystal and glass phases are excited. Contribution from the ions in crystal phase can make the relaxation time longer, while the emissions from the ions in glass phase makes the lifetime much shorter, which finally results in a non-single exponential decay nature of the fluorescence. When most of the ions in the crystal phase are excited, the fluorescence from the ions in crystal phase dominates, and we say the fluorescence to originate from crystal phase of the ceramic sample.

4. Concluding remarks

Fluorescence spectroscopy of Tm^{3+} doped in oxyfluoride glass ceramics containing LaF_3 nanocrystals has been studied experimentally in a spectral range from 400 nm to 900 nm under the direct excitation of $^1D_2$ level at a low temperature. Specific optical transitions associated with the corresponding emission bands are presented. It is concluded that the emission at 485 nm is ascribed to the transition from

$^1G_4$ to $^3H_6$. Fluorescence observed from the ions in crystal phase of the ceramic sample is discussed. The fluorescent dynamical process also shows that the temporal decay of fluorescence emission is composed of two parts: rapid decay from the ions in glass phase and slower decay from the ions in crystal phase.

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