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Efficient blue up-conversion luminescence of Tm^{3+} ions in transparent oxyfluoride glass ceramics containing $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$ nanocrystals

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Abstract

Oxyfluoride glasses were developed in the $30\text{SiO}_2 \cdot 15\text{AlO}_{1.5} \cdot 28\text{PbF}_2 \cdot 22\text{CdF}_2 \cdot (4.8-y)\text{GdF}_3 \cdot 0.1\text{NdF}_3 \cdot y\text{YbF}_3 \cdot 0.1\text{TmF}_3$ ($y = 0, 0.1, 0.2, 0.5, 1, 2, 3, 4$ and 4.8) composition, in mol%. X-ray diffraction analysis revealed that heat treatments of the oxyfluoride glasses cause the precipitation of (Nd^{3+} , Yb^{3+} , Tm^{3+})-doped fluorite-type $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$ nanocrystals of about 17.8 nm diameter in a glass matrix. Very strong blue up-conversion luminescence which can be assigned to the Tm^{3+} : $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transition under 800 nm excitation was observed in these transparent glass ceramics. The intensity of the blue up-conversion luminescence is strongly dependent on the precipitation of $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$ crystals and the YbF_3 concentration. The reasons for the highly efficient Tm^{3+} up-conversion luminescence are discussed. An energy transfer process and an up-conversion mechanism in the glass and glass ceramics are also proposed.

1. Introduction

The frequency conversion of infrared light to visible light has been extensively investigated in rare-earth-containing crystals and glasses. Most of the oxide glasses have large phonon energies ($>1000 \text{ cm}^{-1}$) due to the lattice vibration of network-forming oxides. Fluoride glasses have the advantage of higher quantum efficiencies of various active transitions of rare-earth ions due to their low phonon energies ($300\text{--}500 \text{ cm}^{-1}$). However, the problem of their chemical and thermal stability remains. Recently, rare-earth-containing oxyfluoride glass ceramics have aroused interest from the viewpoint of applications in up-conversion and light amplification [1–4]. In such glass ceramics, rare-earth elements are preferentially incorporated into crystalline phases with small phonon energies below 500 cm^{-1} . Thus, their active optical properties may be allowed to bring about optimum conditions [1].

In 1993, Wang and Ohwaki [3] reported efficient infrared-to-green up-conversion in a novel and transparent oxyfluoride glass ceramic containing YbF₃ and ErF₃. The green up-conversion luminescence of this glass ceramic was found to be about ten times stronger than that of an equally YbF₃- and ErF₃-doped fluoride glass. This high efficiency of the up-conversion was attributed to Er³⁺-enriched Pb_xCd_{1-x}F₂ crystallites. In the present paper the relationship between the characteristics of the precipitated crystals and the blue up-conversion luminescence intensity of Tm³⁺ ions in Nd³⁺-Yb³⁺-Tm³⁺ co-doped oxyfluoride glass ceramics is reported.

2. Experiment

Glasses were prepared according to a conventional melt-quenching method. High-purity SiO₂, Al₂O₃, PbF₂, CdF₂, NdF₃, TmF₃ and YbF₃ were used as the starting materials. The compositions chosen in the present study are 30SiO₂·15AlO_{1.5}·28PbF₂·22CdF₂·(4.8 - y)GdF₃·0.1NdF₃·yYbF₃·0.1TmF₃ (y = 0, 0.1, 0.2, 0.5, 1, 2, 3, 4 and 4.8), in mol%. Accurately weighted 5 g batches were thoroughly mixed and moved into Pt crucibles. The batches were melted at 820 °C for 10 min under an air atmosphere. The melts were cast into preheated brass moulds. The glasses obtained were annealed at the respective glass transition temperatures determined by differential thermal analysis (DTA).

All the prepared glasses were heat treated at their first crystallization temperature. X-ray diffraction measurements were carried out by using a Rigaku RINT 2100 x-ray diffractometer using Cu K α radiation.

Up-conversion luminescence spectra of Tm³⁺ under 800 nm excitation were measured in the wavelength range of 400–700 nm with a Hitachi F-3010 fluorescence spectrophotometer. A Sony SLD303-XT AlGaAs laser (maximum output power: 150 mW) was used as an excitation source. Specimens of 5.0 × 5.0 × 1.2 mm³ size with optically flat surfaces were used in the measurements.

Optical absorption spectra in the wavenumber range of 3500–30 000 cm⁻¹ were measured with a Shimadzu UV-2200 spectrophotometer.

Fluorescence lifetimes of the Tm³⁺: ¹G₄ levels were measured with a PTI-210SK spectrophotometer.

All the spectral measurements were performed at ambient temperature.

3. Results

In our previous work [5, 6], transparent glass ceramics were obtained by heat treating precursor glasses at the first crystallization temperatures, T_x . The glass samples in this study, therefore, were heat treated at T_x , and x-ray diffraction measurements of the samples before and after heat treatments were carried out.

All the glass ceramics obtained after the heat treatments were transparent. As an example, the x-ray diffraction patterns obtained for the glasses with the composition of 30SiO₂·15AlO_{1.5}·28PbF₂·22CdF₂·3.8GdF₃·0.1NdF₃·1YbF₃·0.1TmF₃ before and after heat treatments are shown in figure 1. Broad halo patterns characteristic of glass structure were observed in the samples before heat treatments, whereas several sharp diffraction peaks were clearly observed in the samples after heat treatments, indicating that very small crystals are precipitated during heat treatments. A comparison of the XRD patterns of crystals precipitated in the glass ceramics with those of β -PbF₂ and CdF₂ crystals with fluorite-type structures is also shown in figure 1. As can be seen from the figure, compared with those for β -PbF₂ crystal, the

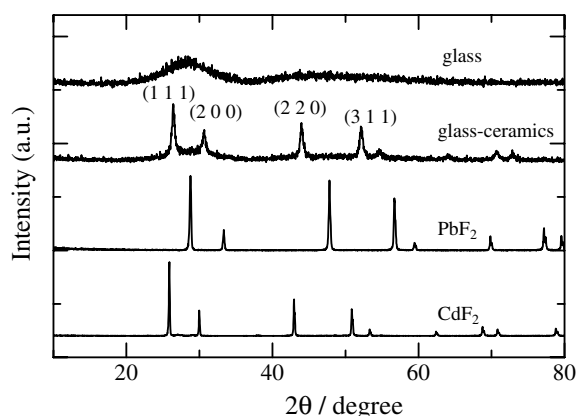


Figure 1. XRD patterns of $\text{Nd}^{3+}\text{-Yb}^{3+}\text{-Tm}^{3+}$ co-doped glass and glass ceramics, together with those of $\beta\text{-PbF}_2$ and CdF_2 crystals.

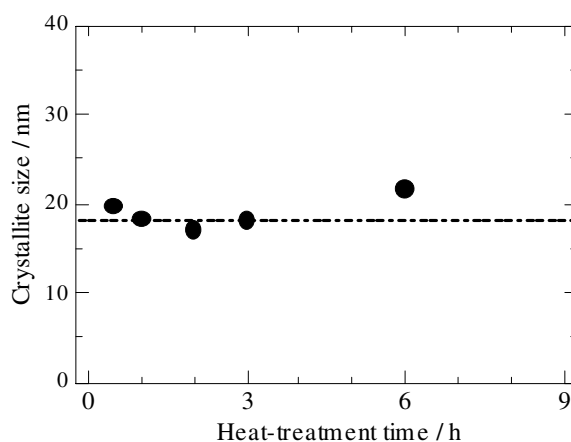


Figure 2. The dependence of the precipitated crystal size on heat treatment time.

positions of the diffraction peaks of the glass ceramics shift to high angles slightly, and shift to low angles slightly compared with those for CdF_2 crystal. Therefore, it is reasonable to consider that the crystalline phases in the present glass ceramics are mixed PbF_2 and CdF_2 crystals with fluorite-type structures, i.e. $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$. By using the Debye–Scherrer equation [7], the diameters of the crystalline precipitates were evaluated to be approximately 17.8 nm. As can be seen from figure 2, the sizes of the precipitated crystals were independent of the heat treatment time.

In figure 3, as an example, the Tm^{3+} up-conversion luminescence spectra obtained for the $30\text{SiO}_2\cdot 15\text{AlO}_{1.5}\cdot 28\text{PbF}_2\cdot 22\text{CdF}_2\cdot 3.8\text{GdF}_3\cdot 0.1\text{NdF}_3\cdot 2\text{YbF}_3\cdot 0.1\text{TmF}_3$ glasses before and after heat treatment under 800 nm excitation are presented. An emission band centred around 490 nm (blue), which corresponds to the $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ transition was observed. In the case of glasses before heat treatments, blue emission bands were hardly detected, whereas the samples after heat treatments gave very strong blue luminescence, and the blue up-conversion luminescence increased with increasing heat treatment time. Figure 4 shows the YbF_3 concentration dependence of Tm^{3+} blue up-conversion luminescence intensities

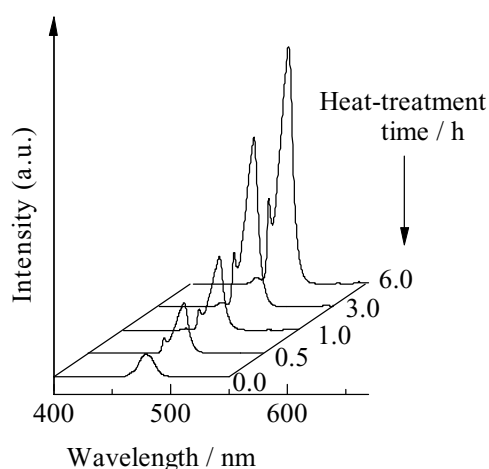


Figure 3. Tm^{3+} up-conversion luminescence spectra of the $30\text{SiO}_2 \cdot 15\text{AlO}_{1.5} \cdot 28\text{PbF}_2 \cdot 22\text{CdF}_2 \cdot 2.8\text{GdF}_2 \cdot 0.1\text{NdF}_3 \cdot 2\text{YbF}_3 \cdot 0.1\text{TmF}_3$ glass after heat treatment.

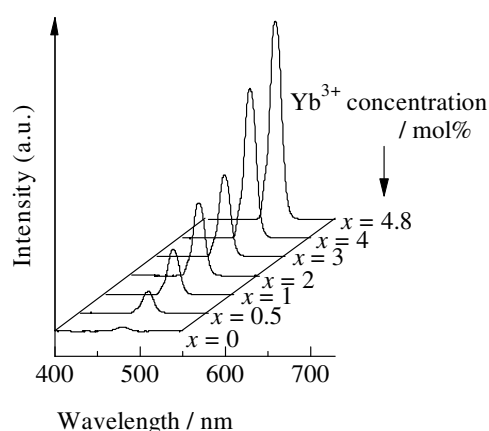


Figure 4. The YbF_3 concentration dependence of the Tm^{3+} up-conversion luminescence intensity in $30\text{SiO}_2 \cdot 15\text{AlO}_{1.5} \cdot 28\text{PbF}_2 \cdot 22\text{CdF}_2 \cdot (4.8 - x)\text{GdF}_3 \cdot 0.1\text{NdF}_3 \cdot x\text{YbF}_3 \cdot 0.1\text{TmF}_3$ glasses.

in the $30\text{SiO}_2 \cdot 15\text{AlO}_{1.5} \cdot 28\text{PbF}_2 \cdot 22\text{CdF}_2 \cdot (4.8 - y)\text{GdF}_3 \cdot 0.1\text{NdF}_3 \cdot y\text{YbF}_3 \cdot 0.1\text{TmF}_3$ glasses ($y = 0, 0.1, 0.2, 0.5, 1, 2, 3, 4$ and 4.8). The intensity of the 490 nm blue up-conversion luminescence in the glasses before heat treatment increased slightly with increasing YbF_3 concentration, whereas the intensity in the glass ceramics increased steeply with increasing YbF_3 concentration. As can be seen from figure 5, we found that the Tm^{3+} blue up-conversion luminescence in the samples with high Yb^{3+} concentration increased at a fast rate with heat treatment, while in the samples with low Yb^{3+} concentration, the blue up-conversion intensity increased slightly with heat treatment.

4. Discussion

According to the results above, therefore, it is reasonable to consider that the reasons for the increase of the Tm^{3+} blue up-conversion intensity after heat treatment are twofold: one reason is the changes in the ligand field around the rare-earth ions upon heat treatment, and the other

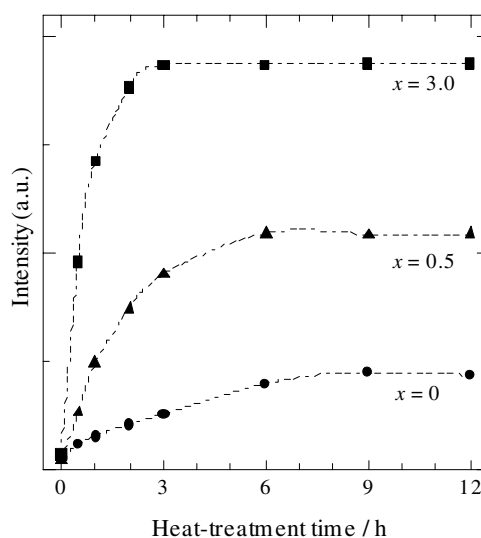


Figure 5. The heat treatment time dependence of the blue up-conversion intensity in $30\text{SiO}_2\cdot 15\text{AlO}_{1.5}\cdot 28\text{PbF}_2\cdot 22\text{CdF}_2\cdot (4.8-x)\text{GdF}_2\cdot 0.1\text{NdF}_3\cdot x\text{YbF}_3\cdot 0.1\text{TmF}_3$ glasses ($x = 0.1, 0.5$ and 3).

is the Yb^{3+} concentration contribution in the energy transfer process. They will be discussed in the following in detail.

According to the Miyakawa–Dexter theory [8], a non-radiative decay rate due to a multiphonon relaxation process is governed by both the phonon energy and electron–phonon coupling strength; this is expressed by

$$W_p = W_0 \exp(-\alpha \Delta E / h\omega) \quad (1)$$

where W_p is the multiphonon decay rate, ΔE is the energy gap to the next lower level and $h\omega$ is the phonon energy. The larger the phonon energy and/or the electron–phonon coupling strength, the larger the non-radiative decay rate. That is to say, a decrease in phonon energy and/or electron–phonon coupling strength results in an increase of the lifetimes and quantum efficiencies of excited levels, and consequently the up-conversion luminescence intensity increases. Therefore, a matrix of low phonon energy, e.g. the fluoride matrix, is of benefit to frequency up-conversion. Qiu *et al* [5, 6]. have found that rare-earth ions in the $50\text{SiO}_2\cdot 50\text{PbF}_2\cdot z\text{ErF}_3$ glasses ($z = 4$ and 5) are strongly coupled to a phonon mode of 930 cm^{-1} , but those in the glass ceramics (crystalline phase: a $\beta\text{-PbF}_2$ solid solution) are strongly coupled to a phonon mode of 230 cm^{-1} .

In the present oxyfluoride glasses, rare-earth ions, e.g. Tm^{3+} , are readily coupled to the non-bridging oxygen on the strong O–Si and/or O–Al bonds [3]. Such a coupling causes an increase in the non-radiative decay rate due to multiphonon relaxation and substantially reduces the lifetimes of excited levels in up-conversion processes. Like most oxide glasses, therefore, oxyfluoride glasses are also not effective for up-conversion. On the other hand, since the rare-earth ions are incorporated into a fluorite-type solid solution after heat treatment, the coordination environments around rare-earth ions lead to low phonon energy. The SiO_2 and $\text{AlO}_{1.5}$ (Al_2O_3) components behave as glass matrices with embedded fluorite-type nanocrystals including Nd^{3+} , Yb^{3+} and Tm^{3+} . This is why the Tm^{3+} up-conversion luminescence is hardly observed in the glasses before heat treatments (precursor glasses), but is strongly observed in the glasses after heat treatments (glass ceramics).

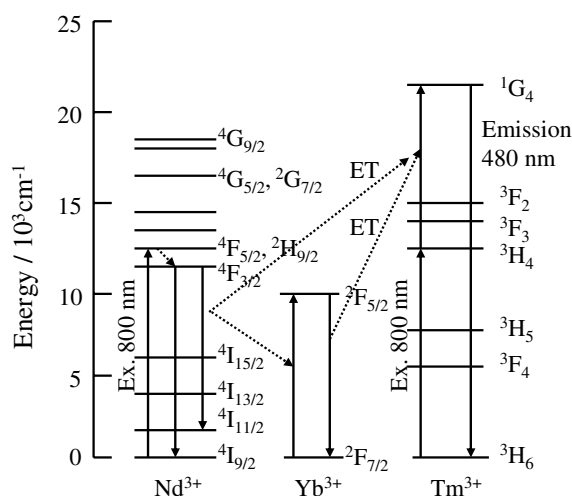


Figure 6. A schematic diagram of the up-conversion mechanism in Nd^{3+} – Yb^{3+} – Tm^{3+} co-doped oxyfluoride glasses under 800 nm excitation.

Blue up-conversion luminescence has also been observed in Tm^{3+} – Yb^{3+} doubly doped materials upon 980 nm excitation [8, 9]. Miyakawa and Dexter [8] have considered a stepwise energy transfer to be dominant on the basis of their calculation: the energy of an excited Yb^{3+} ion is first non-resonantly transferred to the ${}^3\text{H}_5$ level of Tm^{3+} . This transition requires the lattice phonon to absorb at about 1942 cm^{-1} . The 4f electron on this level relaxes non-radiatively to the ${}^3\text{F}_4$ level, from which the second transition to the ${}^3\text{F}_2$ level is caused by the second excited Yb^{3+} ion. This energy transfer loses an energy of about 998 cm^{-1} as the lattice phonon. The ${}^3\text{F}_2$ level relaxes again to the ${}^3\text{H}_4$ level through the ${}^3\text{F}_3$ level by multiphonon relaxation and the third non-resonant energy transfer excites it to the ${}^1\text{G}_4$ level with an energy release of 1467 cm^{-1} . Then the luminescence can be observed at 478 nm from a transition from the ${}^1\text{G}_4$ level to the ${}^3\text{H}_6$ ground state. Since the stepwise energy transfer occurs through three non-resonant energy transfers, a large quantity of energy is lost in the energy transfer processes. Consequently the efficiency of the energy transfer is very low. Thus the up-conversion luminescences in Yb^{3+} – Tm^{3+} doubly doped glasses under 980 nm light are very weak compared with those in Nd^{3+} – Yb^{3+} – Tm^{3+} triply doped glasses under 800 nm light at the same laser power. Therefore the up-conversion excitation mechanism in the Nd^{3+} – Yb^{3+} – Tm^{3+} co-doped glasses under 800 nm excitation is evidently different from that in Yb^{3+} – Tm^{3+} co-doped glasses under 980 nm excitation.

An up-conversion mechanism proposed for the Nd^{3+} – Yb^{3+} – Tm^{3+} co-doped oxyfluoride glasses under 800 nm excitation is schematically depicted in figure 6. First, both Nd^{3+} ions and Tm^{3+} ions are excited by 800 nm radiation which corresponds to the Nd^{3+} : (${}^2\text{H}_{9/2}$, ${}^4\text{F}_{5/2}$) \leftarrow ${}^4\text{I}_{9/2}$ and Tm^{3+} : ${}^3\text{H}_4 \leftarrow {}^3\text{H}_6$ transitions. The Nd^{3+} : (${}^2\text{H}_{9/2}$, ${}^4\text{F}_{5/2}$) excited states relax quickly to the next-lower ${}^4\text{F}_{3/2}$ state through multiphonon relaxation process and then an energy transfer from Nd^{3+} to Yb^{3+} occurs through a pair of transitions: Nd^{3+} : ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{11/2}$ and/or ${}^4\text{I}_{9/2}$; Yb^{3+} : ${}^2\text{F}_{5/2} \leftarrow {}^2\text{F}_{7/2}$. Subsequently the energies are transferred to the 4f electron which is on the ${}^3\text{H}_4$ excited state of Tm^{3+} , resulting in the Tm^{3+} : ${}^1\text{G}_4 \leftarrow {}^3\text{H}_4$ transition. Finally the Tm^{3+} : ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ radiative transition takes place, giving very strong blue up-conversion luminescence around 478 nm. Under 800 nm excitation, therefore, the Yb^{3+} ion is an essential dopant as a ‘bridging ion’ between Nd^{3+} ions and Tm^{3+} ions.

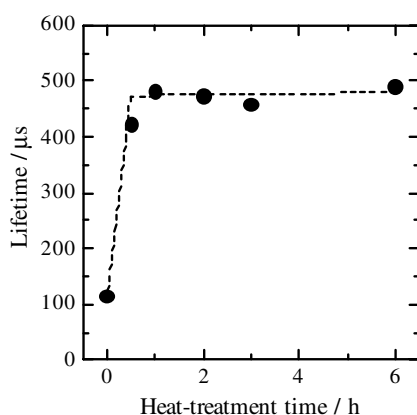


Figure 7. The heat treatment dependence of the lifetime of the $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ fluorescence in $30\text{SiO}_2\cdot 15\text{AlO}_{1.5}\cdot 28\text{PbF}_2\cdot 22\text{CdF}_2\cdot 2.2\text{GdF}_2\cdot 0.1\text{NdF}_3\cdot 2\text{YbF}_3\cdot 0.1\text{TmF}_3$ glass and glass ceramics.

It is well known that the probability of energy transfer due to multipolar interactions increases when the distance R between the sensitizer and the acceptor decreases. According to the theory produced by Dexter [10], the energy transfer probability is proportional to R^{-6} (dipole–dipole interaction), R^{-8} (dipole–quadrupole interaction) or R^{-10} (quadrupole–quadrupole interaction). Although the interaction type which is responsible for the energy transfer from Nd^{3+} to Tm^{3+} is not clarified at the present stage, there is a possibility that the Tm^{3+} up-conversion luminescences in $\text{Nd}^{3+}\text{--}\text{Tm}^{3+}$ co-doped glasses are enhanced with increase in the concentrations of Nd^{3+} ions and/or Tm^{3+} ions in the glasses. Since the rate of energy transfer between two ions depends on their distance, the efficiency of up-conversion due to energy transfer depends on the concentration of rare-earth ions. In other words, the distance between the two ions is less, the probability of energy transfer becomes higher and, consequently, up-conversion luminescence intensity becomes stronger. However, blue up-conversion emission was hardly observed even in $\text{Nd}^{3+}\text{--}\text{Tm}^{3+}$ co-doped glass ceramics of high Nd^{3+} and Tm^{3+} concentrations, because the self-quenching and/or cross-relaxation take place with high probability in their high-concentration regions. On the other hand, Yb^{3+} ions have only one excited state above the ground state. An Yb^{3+} donor ion in the excited state transfers all of its energy to an Yb^{3+} acceptor ion which is in the ground state. In the $\text{Nd}^{3+}\text{--}\text{Yb}^{3+}\text{--}\text{Tm}^{3+}$ co-doped glasses, Yb^{3+} plays the role of an energy transfer bridging ion. In this case, the distance between the Nd^{3+} ion and Tm^{3+} ion becomes ‘contracted’ with Yb^{3+} -ion addition and consequently the efficiency of the energy transfer from the Nd^{3+} ion to the Tm^{3+} ion becomes high. It has been clarified in our previous work that rare-earth ions can be concentrated into precipitated fluorite-type nanocrystals [5, 6]. In this study, the distances among Nd^{3+} , Tm^{3+} and Yb^{3+} become closer upon heat treatment. This may be the another reason that the intensity of Tm^{3+} up-conversion luminescence becomes stronger with heat treatment of glass. In order to clarify the type of electric multipolar interaction between rare-earth ions in the present system, luminescence decay analysis based on the appropriate energy transfer theories, (e.g., the Inokuti–Hirayama theory [11]) is indispensable [12]. Therefore, luminescence decay measurements are planned.

Figure 7 shows the heat treatment time dependence of the lifetime of the 478 nm $\text{Tm}^{3+}: {}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ fluorescence in the $30\text{SiO}_2\cdot 15\text{AlO}_{1.5}\cdot 28\text{PbF}_2\cdot 22\text{CdF}_2\cdot 3.8\text{GdF}_3\cdot 0.1\text{NdF}_3\cdot 1\text{YbF}_3\cdot 0.1\text{TmF}_3$ glasses and glass ceramics under 465 nm excitation. The lifetimes after heat treatments are much larger than those before heat treatments. This result also proves that

rare-earth ions, i.e. Nd^{3+} , Yb^{3+} and Tm^{3+} , are incorporated into a fluorite-type solid-solution phase. It is worth noting that the lifetime does not change with increasing heat treatment time. As can be seen from figure 2, the size of the precipitated crystal is independent of the heat treatment time. These results indicate that the growth of the precipitated $\text{Cd}_x\text{Pb}_{1-x}\text{F}_2$ crystals is very fast and the chief determining factor for the concentration of rare-earth ions dispersed into the crystals is considered to be the size of the precipitated crystal.

5. Conclusions

Oxyfluoride glasses were developed in the $30\text{SiO}_2 \cdot 15\text{AlO}_{1.5} \cdot 28\text{PbF}_2 \cdot 22\text{CdF}_2 \cdot (4.8 - y)\text{GdF}_3 \cdot 0.1\text{NdF}_3 \cdot y\text{YbF}_3 \cdot 0.1\text{TmF}_3$ ($y = 0, 0.1, 0.2, 0.5, 1, 2, 3, 4$ and 4.8) compositions, in mol%. X-ray diffraction analysis revealed that heat treatments of the oxyfluoride glasses cause the precipitation of (Nd^{3+} , Yb^{3+} , Tm^{3+})-doped fluorite-type $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$ nanocrystals of about 17.8 nm diameter in a glass matrix. Very strong blue up-conversion luminescence which can be assigned to the Tm^{3+} : $^1\text{G}_4 \rightarrow ^3\text{H}_6$ transition under 800 nm excitation was observed in these transparent glass ceramics. The intensity of the blue up-conversion luminescence was strongly dependent on the precipitation of $\text{Pb}_x\text{Cd}_{1-x}\text{F}_2$ crystals and the YbF_3 concentration. This indicates that the energies can be transferred from Nd^{3+} ions to Tm^{3+} ions through Yb^{3+} ions, causing the Yb^{3+} ions to shorten the energy transfer distance between Nd^{3+} ions and Tm^{3+} ions, and consequently the probability of energy transfer from Nd^{3+} ions to Tm^{3+} ions is increased.

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