Frequency up-conversion luminescence in Yb\(^{3+}\)–Ho\(^{3+}\) co-doped Pb\(_x\)Cd\(_{1-x}\)F\(_2\) nano-crystals precipitated transparent oxyfluoride glass-ceramics

Jianbei Qiu*, Akio Makishima

Center for Nano Materials and Technology, Japan Advanced Institute of Science and Technology, Asahidai 1-1, Tatsunokuchi, Ishikawa 923-1292, Japan

Received 21 October 2003; revised 20 November 2003; accepted 25 November 2003

Abstract

Oxyfluoride glasses were developed with composition 30SiO\(_2\)·15AlO\(_1.5\)·28PbF\(_2\)·22CdF\(_2\)·(4.9 – x)GdF\(_3\)·0.1HoF\(_3\)·xYbF\(_3\) (x = 0, 0.1, 0.2, 0.5, 1, 2, 3, and 4) in mol%. Powder X-ray diffraction analysis revealed that the heat-treatments of the oxyfluoride glasses at the first crystallization temperature cause the precipitation of Yb\(^{3+}\)–Ho\(^{3+}\) co-doped fluorite-type nano-crystals of about 17.8 nm in diameter in the glass matrix. These transparent glass-ceramics exhibited very strong green up-conversion luminescence due to the Ho\(^{3+}\):(\(^5\)F\(_4\), \(^5\)S\(_2\)) \(\rightarrow\) \(^7\)I\(_{6}\) transition under 980 nm excitation. The intensity of the green up-conversion luminescence in the glass-ceramics was much stronger than that in the precursor oxyfluoride glass. The reasons for the highly efficient Ho\(^{3+}\) up-conversion luminescence in the oxyfluoride glass-ceramics are discussed.

\(\text{q}\) 2004 Elsevier Ltd. All rights reserved.

Keywords: Up-conversion luminescence; Rare-earth; Oxyfluoride; Glass-ceramics

1. Introduction

In recent years, the up-conversion of infrared light to shorter wavelengths by rare-earth ions glasses have been carried out to develop transparent materials capable of efficient frequency up-conversion and to utilize these materials as green and/or blue solid-state lasers. Currently, a number of up-conversion luminescence studies are being advanced on heavy metal fluoride glasses with low vibrational frequencies, e.g. fluoride glasses based on ZrF\(_4\), HfF\(_4\), and so on [1–5]. This is because the small phonon energies of host glasses reduce non-radiative losses due to multi-phonon relaxation, leading to high emission efficiency of up-conversion luminescence.

Rare-earth-doped oxyfluoride glass-ceramics have been reported in the 1970s. These glass-ceramics are produced by melting of oxygen fluoride glasses followed by heat-treatments above the glass-transition temperatures. Such heat-treatments bring about the precipitation of fluorite-type crystals in which doped rare-earth ions are selectively concentrated [6,7]. The crystal sizes can be controlled small enough to cause no light scattering. Thus, the obtained glass-ceramics are transparent to the naked eye. The advantages of this approach are the following two points: (1) Doped rare-earth ions are confined in crystalline environments of low phonon energies. Consequently, excited-state lifetimes and optical absorption cross-sections of the doped rare-earth ions become large compared with those in vitreous environments. (2) The glass host matrices are based on silicates with mechanically and chemically desirable characteristics.

In 1993, Wang and Ohwaki [7] have reported efficient infrared-to-green up-conversion in a transparent oxyfluoride glass-ceramic containing with YbF\(_3\) and ErF\(_3\). The green up-conversion luminescence of this glass-ceramic was found to be about 10 times stronger than that of an equally YbF\(_3\) and ErF\(_3\)-doped fluoride glass. This high efficiency of up-conversion was attributed to Er\(^{3+}\)-enriched Pb\(_x\)Cd\(_{1-x}\)F\(_2\) crystallites. After the Wang and Ohwaki work, Tick et al. [8] have substituted Y\(^{3+}\) for Yb\(^{3+}\) and Pr\(^{3+}\) for Er\(^{3+}\) in an oxyfluoride glass--ceramic and have produced a two-phase system for Pr\(^{3+}\)-doped amplifier applications. The Pr\(^{3+}\) fluorescence lifetime at
1.3 μm in this glass–ceramic has been found to be longer than that in a fluorozirconate glass.

In the present paper, the relationship between crystalization characteristics and mechanism of the Ho$^{3+}$ up-conversion luminescence in Yb$^{3+}$–Ho$^{3+}$ co-doped oxyfluoride glass-ceramics under 980 nm light are reported.

2. Experimental procedure

Glasses were prepared according to a conventional melt-quenching method. High purity SiO$_2$, Al$_2$O$_3$, PbF$_2$, CdF$_2$, HoF$_3$ and YbF$_3$ were used as the starting materials. Compositions chosen in the present study are 30SiO$_2$·15-AlO$_1$·5·28PbF$_2$·22CdF$_2$·(4.9 – x)GdF$_3$·0.1HoF$_3$·x YbF$_3$ (x = 0, 0.1, 0.2, 0.5, 1, 2, 3, and 4) in mol%. Accurately weighted 10 g batches were thoroughly mixed and placed in Pt crucibles. The batches were melted at 860°C for 12 min in an electric furnace, and then the melts were cast into preheated brass molds. The obtained glasses were annealed at the respective glass-transition temperatures which were determined by differential scanning calorimeter (SEIKO EXSTAR 6000) with the 10 K min$^{-1}$ heating rate under an Ar atmosphere.

All the prepared glasses were heat-treated at the first crystallization temperature obtained by DSC measurement for 1.0 h. In order to identify the precipitated crystals, X-ray diffraction measurements were carried out on the precursor glasses and the heat-treated glasses with a Rigaku RINT 2500 X-ray diffractometer using Cu K$_\alpha$ radiation.

Up-conversion luminescence spectra of Ho$^{3+}$ under 980 nm excitation were measured in the wavelength range of 400–700 nm by using a Hitachi F-4500 fluorescence spectrophotometer. A diode laser of 980 nm (Newport LD-980-HHL200) was used as an excitation source. Specimens with the size of 5.0×5.0×1.5 mm$^3$ 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 Ho$^{3+}$; (5F$_4$, 5S$_2$) levels were measured with a PTI-210SK spectrophotometer.

All the spectral measurements were performed at ambient temperature.

3. Results

Fig. 1(a) shows a typical DSC curve of the oxyfluoride glasses, where $T_g$ and $T_x$ indicate the glass-transition temperature and the first crystallization temperature, respectively. The $T_g$ and $T_x$ values slightly increased with increasing YbF$_3$ concentration. All the glass-ceramics obtained after heat-treatments at the first crystallization temperatures for 1 h were transparent. As can be seen in Fig. 1(b), the first crystallization peak disappeared after heat-treatment, this result implies that a kind of component maybe precipitated from glass matrix. The X-ray diffraction patterns of the samples before and after heat-treatment with the composition of oxyfluoride glasses are shown in Fig. 2. Broad halo pattern characteristic of glass-structure was 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 were successfully precipitated during heat-treatments. A comparison of the XRD pattern between the crystals precipitated in the glass-ceramics and reference crystals (β-PbF$_2$ and CdF$_2$) is shown in Fig. 2. As can be seen from the figure, the positions of diffraction-peaks of the glass-ceramics shift to slightly high angles compared with those of β-PbF$_2$ crystal and also shift to slightly low angles compared with those of CdF$_2$ crystal. Therefore, it is reasonable to consider that the crystalline phases in the present glass-ceramics are attributed to the mixed PbF$_2$ and CdF$_2$ crystals with fluorite-type structures, i.e. Pb$_{x}$Cd$_{1-x}$F$_2$.

![Fig. 1. Typical DSC curves of oxyfluoride glasses before and after heat-treatment. (T_g is glass-transition temperature, T_x is the first crystallization temperature).](image1)

![Fig. 2. Powder XRD patterns of oxyfluoride glass (a) and glass ceramics (b), together with those of β-PbF$_2$ (c) and CdF$_2$ (d) crystals as references.](image2)
By using the Debye–Scherrer equation [9], the diameters of crystalline precipitates were evaluated to be approximately 17.8 nm.

Three emission bands centered around 490 (blue), 545 (green) and 650 nm (red), which correspond to the Ho$^{3+}$: $\left(5F_3 \rightarrow 5I_8\right)$, $\left(5F_4, 5S_2 \rightarrow 5I_8\right)$ and $\left(5F_5 \rightarrow 5I_8\right)$ transitions, respectively, were strongly observed in the oxyfluoride glasses after heat-treatment (glass-ceramics) under 980 nm excitation. The glasses before heat-treatments (precursor glasses), however, only very weak green and red emission bands were observed and no blue emission bands were detected. In Fig. 3, typical Ho$^{3+}$ up-conversion luminescence spectra in glass and glass-ceramics are presented. Comparing with the sample before heat-treatment, very strong green up-conversion luminescence at around 545 nm were observed in glass-ceramics. As shown in Fig. 4, the intensity ratios of green luminescence to red luminescence, $I_{545}/I_{650}$, is much lager in glass-ceramics after heat-treatment than that in the sample before heat-treatment in same YbF$_3$ concentration glass. Fig. 5 shows the YbF$_3$ concentration dependence of Ho$^{3+}$ green up-conversion luminescence intensities in the 30SiO$_2$·15AlO$_1.5$·28PbF$_2$·22CdF$_2$·(4.9 – $x$)GdF$_3$·0.1HoF$_3$·$x$YbF$_3$ glasses and glass-ceramics ($x = 0, 0.1, 0.2, 0.5, 1, 2, 3$ and $4$). The intensity of the 545 nm green up-conversion luminescence in the precursor glasses gradually increased with increasing YbF$_3$ concentration in the range of below 3 mol% and then increased slightly with further YbF$_3$ addition. On the other hand, the intensity of the 545 nm up-conversion luminescence in glass-ceramics steeply increased with increasing YbF$_3$ concentration below 1 mol% and then kept almost in a same intensity level with increasing YbF$_3$ concentration.

4. Discussion

According to the Miyakawa–Dexter theory [10], a non-radiative decay rate due to a multi-phonon relaxation process is governed by both phonon energy and electron-phonon coupling strength, which is expressed by

$$W_p = W_0 \exp\left(-\frac{a\Delta E}{\hbar\omega}\right)$$

(1)

where $W_p$ is the multi-phonon decay rate, $\Delta E$ is the energy gap to the next lower level and $\hbar\omega$ 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 increases the emission intensity of up-conversion luminescence. Therefore, a matrix of low phonon energy, e.g. fluoride matrix, is of benefit to frequency up-conversion. Fig. 6 presents the optical absorption spectrum of Ho$^{3+}$ in the 30SiO$_2$·15AlO$_1.5$·28PbF$_2$·22CdF$_2$·4GdF$_3$·1HoF$_3$.
glass. An energy gap between the (5F2, 3K8) levels and the next lower level 5F3 is about 560 cm\(^{-1}\). This energy gap is very narrow and the former level is very sensitive to a change of ligand field. Qiu and co-workers [11] have found that rare-earth ions in the 50SiO\(_2\)-50PbF\(_2\)-xErF\(_3\) glasses (x = 4 and 5) are strongly coupled to a phonon mode of 930 cm\(^{-1}\) but those in the glass-ceramics (crystalline phase: a \(\beta\)-PbF\(_2\) solid-solution) are strongly coupled to a phonon mode of 230 cm\(^{-1}\). Since non-radiative decay is due to multi-phonon relaxation, it is understandable that blue (490 nm) up-conversion luminescence could not be observed in oxyfluoride glasses, but is obviously observed in oxyfluoride glass-ceramics.

In the oxyfluoride glasses, rare-earth ions, e.g. Ho\(^{3+}\), are readily coupled to the non-bridging oxygen on the strong O–Si and/or O–Al bonds [7]. Such a coupling causes an increase in non-radiative decay rate due to multi-phonon relaxation and largely reduces the lifetimes of excited levels in up-conversion processes. As well as most of oxide glasses, therefore, oxyfluoride glasses also are not effective for up-conversion. On the other hand, in the present work, because the rare-earth ions are incorporated into a fluorite-type solid–solution after heat-treatment, so that the coordination environments around rare-earth ions were dispersed to the precipitated nanocrystals. Thus, the coordination environment of rare-earth ions is more sensitive to a change of ligand field. We suggested that the concentration of Yb\(^{3+}\) ions to one Ho\(^{3+}\) ion. In fact, twice of the energy of the Yb\(^{3+}\): \(2F_{5/2} \rightarrow 2F_{7/2}\) transition is almost equal to the energy corresponding to the Ho\(^{3+}\): \((F_2, 3K_8) \rightarrow 5I_8\) transition.

This result also proved that rare-earth ions, i.e. Yb\(^{3+}\) and Ho\(^{3+}\), are incorporated into a fluorite-type solid-solution phase.

In order to examine the number of photons required to excite one Ho\(^{3+}\) ion followed by the radiative transition from the Ho\(^{3+}\): \(F_4, 5S_2\), the excitation power dependence of the emission intensity was examined. It was found that the intensities of emission observable from the Ho\(^{3+}\): \(F_4, 5S_2\) level exhibits the quadratic dependence on excitation power, indicating that all the emissions are obtained through the absorption of two photons. It is mentioned that no absorption bands at 980 nm for Ho\(^{3+}\) ion, and we could not observe green up-conversion luminescence in Ho\(^{3+}\) singly doped glasses, this means a co-operative energy transfer from two Yb\(^{3+}\) ions to one Ho\(^{3+}\) ion. In fact, twice of the energy of the Yb\(^{3+}\): \(2F_{5/2} \rightarrow 2F_{7/2}\) transition is almost equal to the energy corresponding to the Ho\(^{3+}\): \(F_2, 3K_8\) \(\rightarrow 5I_8\) transition.

It has been already known that the nearest neighboring two excited Yb\(^{3+}\) ions in an YbPO\(_4\) crystal can radiate green luminescence of h\(\nu\) by the following mechanism

\[
Yb^{3+} : 2F_{5/2} + Yb^{3+} : 2F_{5/2} \rightarrow Yb^{3+} : 2F_{7/2} + Yb^{3+} : 2F_{7/2} + h\nu.
\]

This luminescence is called ‘co-operative luminescence’ [12]. This co-operative phenomenon occurs between two excited Yb\(^{3+}\) ions when the distance between the two ions becomes close. In the case of glass before heat-treatment, the green up-conversion luminescence intensity gradually increased with increasing YbF\(_3\) concentration, whereas in the case of glass-ceramics, the intensity of the 545 nm green up-conversion luminescence steeply increased with increasing YbF\(_3\) concentration below 1 mol%, and then kept almost in a same intensity level with increasing YbF\(_3\) concentration. This is principally explained from a consideration that the distance among Yb\(^{3+}\) ions becomes closer with increasing YbF\(_3\) concentration and then the co-operative phenomenon between two Yb\(^{3+}\) ions is liable to occur. In our previous work [13], almost all the rare-earth ions were dispersed to the precipitated nanocrystals. Thus, we suggested that the concentration of Yb\(^{3+}\) ion may be condensed in precipitated nanocrystals, the distance between two adjacent Yb\(^{3+}\) ions became shorter, which resulted in higher possibility of co-operative up-conversion. The up-conversion luminescence hence became stronger because the energy will be transferred from two adjacent Yb\(^{3+}\) ions and Ho\(^{3+}\) ions more efficiently in glass-ceramics.

According to the above results, therefore, a possible mechanism proposed for Yb\(^{3+}\) – Ho\(^{3+}\) co-doped oxyfluoride glasses is schematically depicted in Fig. 7. First, 4f electrons on the ground state \(3F_{7/2}\) of Yb\(^{3+}\) ions were excited to \(2F_{5/2}\) state, the energies of adjacent two excited Yb\(^{3+}\) ions transferred to one Ho\(^{3+}\) ion (this is called co-operative energy transfer), resulting in Ho\(^{3+}\): \(F_2, 3K_8\) \(\rightarrow 5I_8\)
transition. Finally, transitions from the excited states $^5F_3$, $^5F_4$, $^5S_2$ and $^5F_5$ to ground state, blue (490 nm), green (545 nm) and red (650 nm) up-conversion luminescence, respectively, were observed.

5. Conclusion

Transparent glass-ceramics in which fluorite-type nanocrystals with a diameter of about 17.8 nm were dispersed in the glass matrix, were obtained after heat-treated at the first crystallization temperature of the Yb$^{3+}$–Ho$^{3+}$ co-doped 30SiO$_2$·15AlO$_1.5$·28PbF$_2$·22CdF$_2$·(4.9–x)GdF$_3$·0.1HoF$_3$·xYbF$_3$ (x = 0, 0.1, 0.2, 0.5, 1, 2, 3, and 4) oxyfluoride glasses. Compared with the glasses before heat-treatment, the glass-ceramics showed the Ho$^{3+}$ green up-conversion luminescence with very high efficiency under 980 nm excitation. The reasons for the changes of Ho$^{3+}$ up-conversion luminescence are considered to be due to a difference in the coordination environments around the Yb$^{3+}$ and Ho$^{3+}$ ions in the oxyfluoride glasses before and after heat-treatment, and distances between two kinds of rare-earth ions contracted in precipitated nano-crystals. The mechanism for Ho$^{3+}$ up-conversion luminescence is proposed to be from co-operative energy transfer between two adjacent Yb$^{3+}$ ions and one Ho$^{3+}$ ion.

Acknowledgements

This work was carried out in Nanotechnology Glass Project as part of Nanotechnology Materials Program supported by New Energy and Industrial Technology Development Organization (NEDO).

References

[1] D.C. Yeh, W.A. Sibley, M. Sascavage, M.G. Drexhage, Multiphonon relaxation and infrared-to-visible conversion of Er$^{3+}$ and Yb$^{3+}$ ions in barium-thorium fluoride glass, J. Appl. Phys. 62 (1987) 266–275.
[2] M. Takahashi, R. Kanno, Y. Kawamoto, S. Tanabe, K. Hirao, Compositional dependence of Er$^{3+}$ upconversion luminescence in MF–LiF–ZrF$_4$ glasses (M: alkali metals), J. Non-Cryst. Solids 168 (1994) 137–143.
[3] J. Qiu, M. Shojiya, M. Takahashi, R. Kanno, Y. Kawamoto, Selectively strong green up-conversion luminescence in Nd$^{3+}$–Ho$^{3+}$ co-doped ZrF$_4$-based fluoride glasses under 800 nm excitation, J. Phys. Condens. Matter. 10 (1998) 11095–11102.
[4] Y. Kawamoto, R. Kanno, Y. Yokota, M. Takahashi, S. Tanabe, K. Hirao, Compositional dependence of upconversion luminescence of Er$^{3+}$ in ZrF$_4$-based glasses: III. Anion substitution effect, J. Solid State Chem. 103 (1993) 334–340.
[5] J. Qiu, M. Shojiya, Y. Kawamoto, K. Kadono, Energy transfer process and Tb$^{3+}$ up-conversion luminescence in Nd$^{3+}$–Yb$^{3+}$–Tb$^{3+}$ co-doped fluorozirconate glasses, J. Lumin. 86 (2000) 23–31.
[6] F. Auzel, K.E. Lipinska-Kalita, P. Santa-Cruz, A new Er$^{3+}$-doped vitreous fluoride amplification medium with crystal-like cross-sections and reduced inhomogeneous line width, Opt. Mater. 5 (1996) 75–78.
[7] Y. Wang, J. Ohwaki, New transparent vitrocermics codoped with Er$^{3+}$ and Yb$^{3+}$ for efficient frequency upconversion, Appl. Phys. Lett. 63 (1993) 3268–3270.
[8] P.A. Tick, N.F. Borrelli, L.K. Cornelius, M.A. Newhouse, Transparent glass ceramics for 1300 nm amplifier applications, J. Appl. Phys. 78 (1995) 6367–6374.
[9] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials, Wiley, New York, 1954, p 512.
[10] T. Miyakawa, D.L. Dexter, Phonon sidebands, multi-phonon relaxation of excited states, and phonon-assisted energy transfer between ions in solids, Phys. Rev. B1 (1970) 2961–2969.
[11] Y. Kawamoto, J. Qiu, R. Kanno, Upconversion luminescence of Er$^{3+}$ in transparent SiO$_2$–PbF$_2$–ErF$_3$ glass ceramics, J. Mater. Sci. 33 (1998) 63–67.
[12] E. Nakazawa, S. Shionoya, Cooperative luminescence in YbP$_{1.5}$, Phys. Rev. Lett. 25 (1970) 1710–1712.
[13] J. Qiu, R. Kanno, Y. Kawamoto, Microstructure of transparent SiO$_2$–PbF$_2$–ErF$_3$ glass ceramics with highly efficient Er$^{3+}$ upconversion luminescence, Mater. Sci. Lett. 17 (1998) 653–655.