Investigation on crystallization and optical properties of rare earth doped oxyfluoride glass ceramics

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Rare earth doped oxyfluoride glass-ceramics containing CaF_2 nano-crystals were prepared by melt quenching. For the crystallized samples, scanning electron microscopy (SEM) and X-Ray diffraction (XRD) experiments indicated the existence of nano-crystals with the incorporation of Rare earth ions in the lattice among the oxide glassy matrix, which is important for obtaining desirable luminescent performance of glass-ceramics. Absorption spectra of the obtained oxyfluoride glass-ceramics were studied. Emission spectra of the obtained samples were also studied under different excitation wavelengths.

1. Introduction

Rare earth doped oxyhalide glass ceramics have received considerable attention in recent years [1-5]. In these kinds of glass ceramics, Rare earth ions are incorporated into the halide nanocrystals immersed in an oxide glassy matrix; so they will have excellent luminescent properties due to low phonon energy environment of halide crystalline for luminescent ions and good mechanical and chemical properties of oxide matrix [6-10]. Therefore, fabrication of Rare earth doped oxyhalide glass ceramics and investigation of their optical properties have attracted a lot of attention nowadays. In this work, oxyfluoride glasses containing different Rare earth ions were fabricated and then heat treated. These heat-treatments cause the precipitation of fluorite type crystals in which doped Rare earth ions are concentrated. The distribution of CaF_2 nanocrystals was shown by (SEM) and XRD. The absorption and emission spectra of the obtained samples were studied.

2. Experiment

The precursor glasses were prepared with the following compositions (in mol %):

$$45P_2O_5\text{-}14.9\ Na_2HPO_4\text{-}25CaF_2\text{-}15LiF\text{-}0.1HO_2O_3$$
(Oxyfluoride; sample 1)
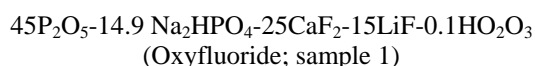
For each batch, about 50g of each starting material was fully mixed and preheated for 10 min; then, it was melted in an alumina crucible in air atmosphere at 900°C for 1 h using an electric furnace. Finally, it was quenched to room temperature in a stainless steel mold. The oxyfluoride glasses were then heat treated at 410°C for 4 h to obtain glass ceramics. The oxyfluoride glass and glass ceramics were named G and GC in the following text. To investigate crystallization, XRD experiment was carried out by (Seifert3003TT) diffractometer. The microstructure of samples was studied using scanning electron microscope (HITACHI-S-4160). The absorption spectra were recorded on a spectrophotometer (lambda 25, Perkin-Elmer) with a spectral range from 0 to 1000nm. The emission spectra under different excitation wavelengths were recorded on fluorescence spectrophotometer (Cary Eclipse). The fluorescence spectrum was also recorded on USB 2000-FLG.

3. Results and discussion

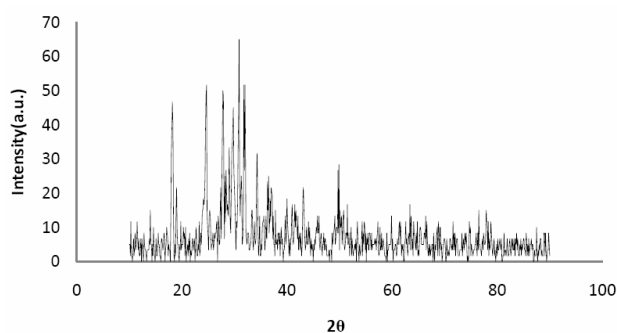The typical XRD pattern for GC sample is shown in Fig. 1.

Fig. 1. XRD patterns of GC sample

These peaks are just observable in XRD pattern of glass ceramic sample so they are appeared as a consequence of glass sample heat treatment. It is believed that the existence of strong peaks in XRD pattern of glass ceramics is the sign of crystallization. Since CaF_2 in the composition that is used for preparing the precursor glass,

has capability of crystallization, the peaks indicate the crystallization of CaF_2 from the glass matrix.

For more precision the SEM micrograph of GC sample with different enlargements from different parts of glass ceramic is shown in Fig. 2. The spherical CaF_2 crystals are observable in the pictures; they are mainly from 60 to 150 nm in size among glassy matrices.
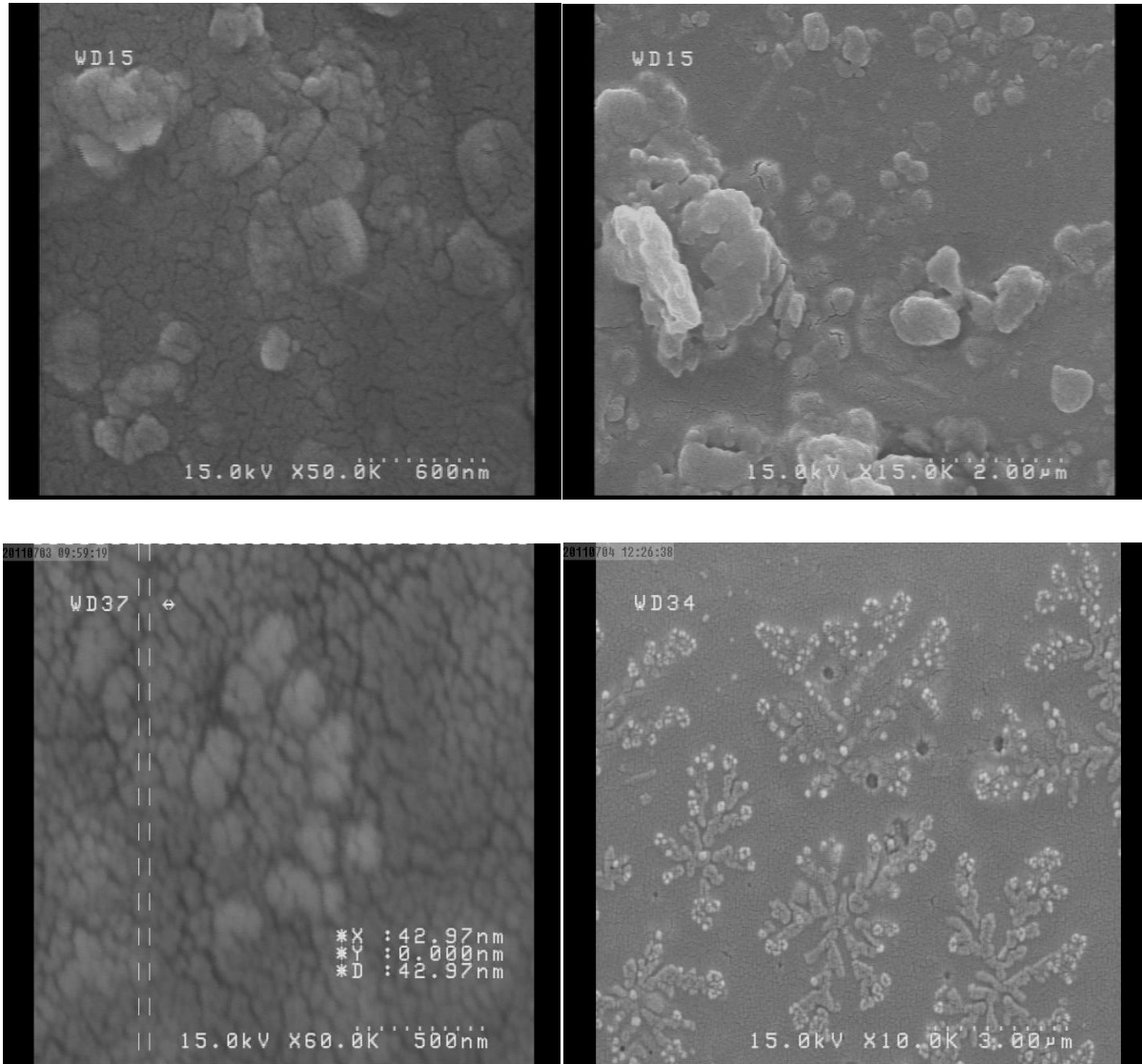

Fig. 2. SEM micrographs of CG sample with different enlargements.

The absorption spectrum of GC sample and the related energy levels are presented in Fig. 3. There are seven peaks in the absorption spectrum at 361, 420, 453, 474, 488, 539 and 648nm which correspond to the transitions from the ground state ($^5I_8$) to the excited states of Ho^{3+} (shown in Fig. 3), there is a maximum in 453nm that is proportional to $E=22075cm^{-1}$, it is related to $^5I_8 \rightarrow {}^5G_6$ transition. The sample had good absorption in blue and violet spectral regions and also it had some weaker absorption in green and red spectral regions. These results were expected since oxyfluoride glass-ceramics, due to their lower phonon energies, should have good optical properties. Energy levels of holmium ion and absorption processes are shown in Fig. 4.
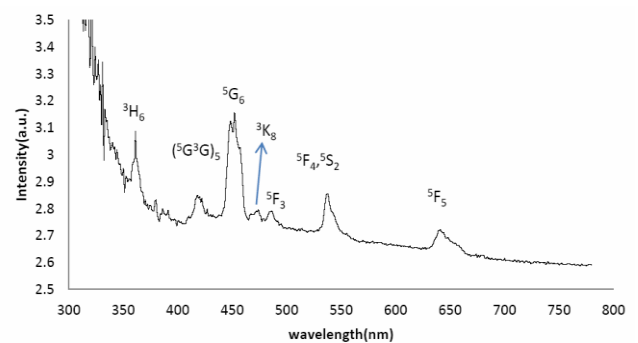

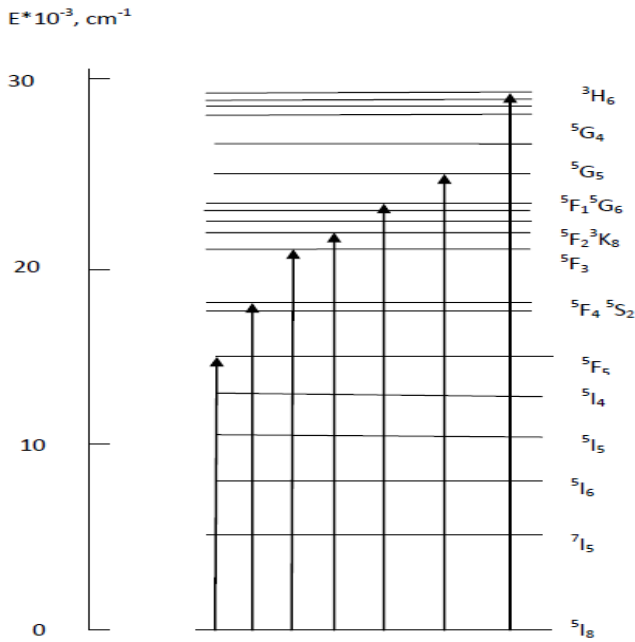*Fig. 3. Absorption spectrum of GC sample.*

E*10^{-3}, cm^{-1}

Fig. 4. Energy level diagram for the holmium ions system.

Fig. 5 shows down conversion emission spectra of GC samples under 220 nm excitation wavelengths. As it can be seen, there were many sharp peaks with considerable intensities in the emission spectrum.
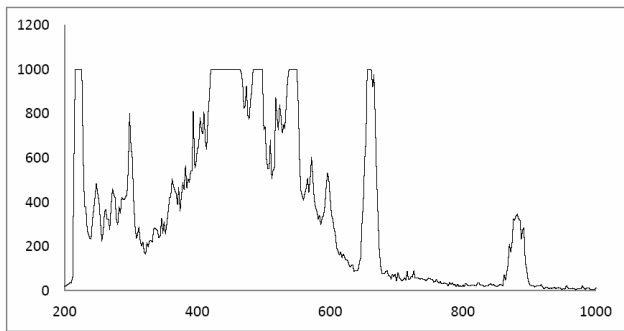

Fig. 5. Down-conversion emission spectrum of obtained GC samples under 220 nm excitation.

Up-conversion took place when the samples were excited at 550nm. As it is demonstrated in Fig. 6, the up-conversion emission spectrum showed good emission in blue spectral region. The considerable peaks of samples were in 484, 465, 433 and 423 nm. The up-conversion mechanism is given in Fig. 7. Two kinds of absorption took place in this mechanism; first one was ground state absorption (GSA) and then excited state absorption (ESA) occurred to populate upper levels and then emissions took place.
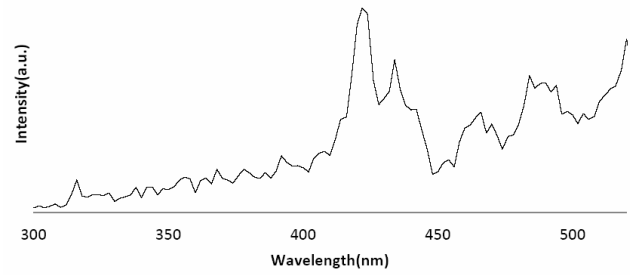

Fig. 6. Up conversion emission spectrum of GC samples under 550 nm excitation.

The transitions that are shown in energy level diagrams (Figs. 4&7) are related to different peaks in absorption and emission spectra. The way of finding the transitions is brought in the following, for more information see [11-16].
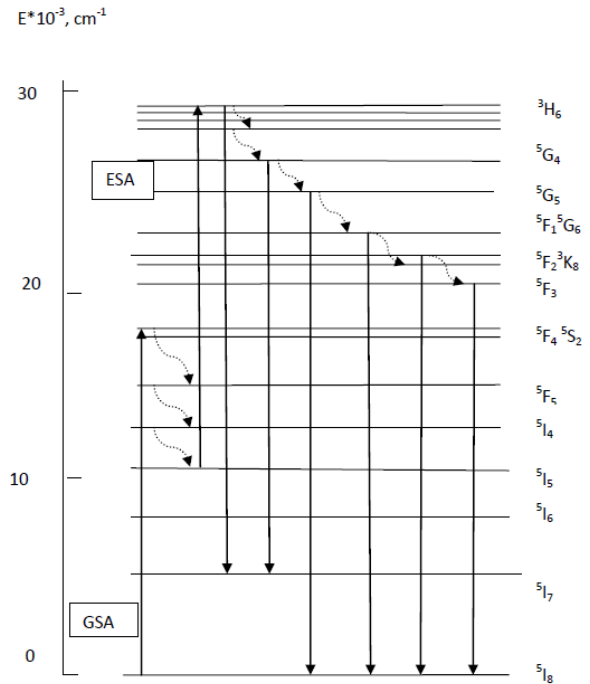
E*10^{-3}, cm^{-1}

Fig. 7. Energy level diagram of Ho^{3+} ion and up conversion mechanism of Ho^{3+} doped glass ceramic.

As it is mentioned the up conversion has taken place in the excitation wavelength of 550 nm. Since the required wavelength for transition from $^{8}I_5$ level (ground state) to $^{5}F_4$, $^{5}S_2$ is about 550 nm (from E=h/λ by taking h=1 the required energy is about 18182 cm^{-1}), ground state absorption has taken place as it is shown in Fig. 7. Then according to the different wavelengths in which the peaks exist in spectrum the transitions that are shown in the diagram have achieved, for example the wavelength required for transition from $^{5}F_3$ to $^{5}I_8$ is about 480-490 nm, since there is a peak at 484nm (E=20661cm^{-1}) in emission spectrum (Fig. 6), the $^{5}F_3 \rightarrow {}^{5}I_8$ transition has occurred, it

can be concluded that the emission transitions has occurred after the excited state absorption.

4. Nd^{3+} and Yb^{3+} doped samples (sample 2)

The composition of sample 2 was:

$$45\%P_2O_5\text{-}14.25\%Na_2HPO_4\text{-}25\%CaF_2\text{-}15\%LiF\text{-}0.25\%Nd_2O_3\text{-}0.5\%Yb_2O_3$$
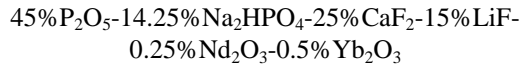
The glass and glass ceramics samples were prepared in the same way as sample 1. The absorption spectra of obtained glass and glass ceramic samples are demonstrated in Fig. 8.
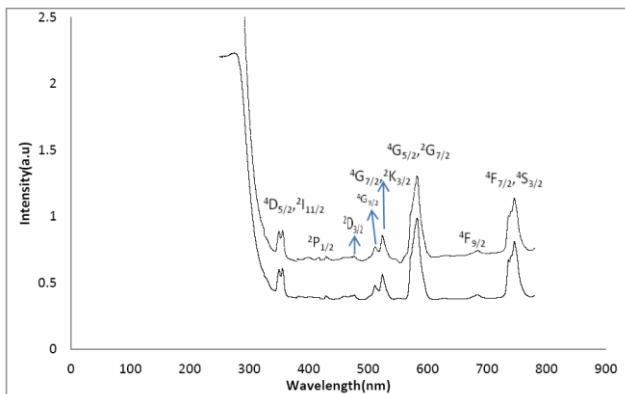

Fig. 8. The absorption spectra of G (dashed) and GC (full).

The transitions shown in Fig. 8 were related to the transitions from Nd^{3+} ground state ($^4I_{9/2}$) to different excited states, for example the sharpest peak is around 584 nm (E=17123cm^{-1}), so this maximum is the sign of $^4I_{9/2}{\rightarrow}^4G_{5/2}$,$^2G_{7/2}$ transition. Stark splitting can be seen in some peaks. The absorption spectra of both samples were similar. The only difference between these two diagrams was related to the area under them. The area order of the diagram in glass ceramic samples was less than that in glass sample. As it is known, the similarity between the two spectra could be because of the existence of the same lanthanide ions in both of them; so, the difference between the two spectra was due to the formation of nanocrystals in glass ceramic samples and lanthanide ions gathering inside them. The fluorescence spectrum of Nd^{3+}/Yb^{3+} doped sample is shown in Fig. 9.

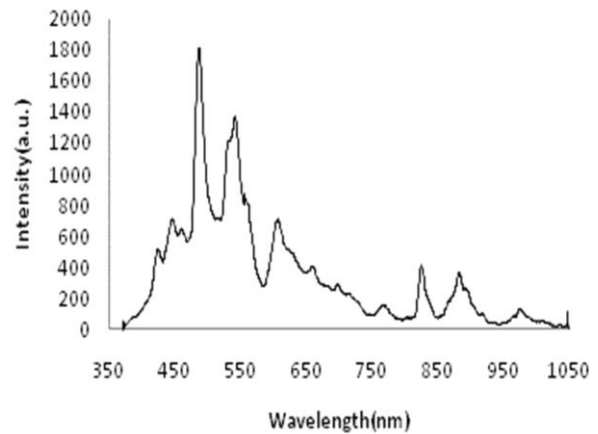*Fig. 9. The fluorescence spectrum of Nd^{3+} / Yb^{3+} doped glass ceramic.*

It can be seen from Fig. 9 that the intensity of peaks was maximum in 450 nm-550 nm. Thus, the glass ceramic samples showed good emission in blue and green spectral regions.

For observing the importance of existing of lanthanide ions in the samples, the absorption spectra of the mentioned samples were compared with the following sample:
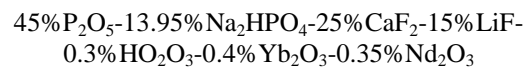
$$45\%P_2O_5\text{-}13.95\%Na_2HPO_4\text{-}25\%CaF_2\text{-}15\%LiF\text{-}0.3\%HO_2O_3\text{-}0.4\%Yb_2O_3\text{-}0.35\%Nd_2O_3$$

Fig. 10 shows the difference between the samples. As it is clear, the existence of Ho^{3+} had a good effect on absorption spectrum. More absorption peaks were observed in red diagram which was because of Ho^{3+}; also, in red diagram, the intensity of absorption peaks was more than that of the blue one which was due to different concentrations of Nd^{3+}.
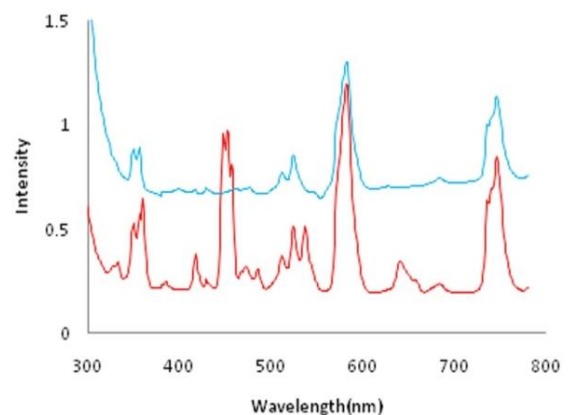

Fig. 10. The absorption spectra of Nd^{3+} / Yb^{3+} doped samples (blue diagram),and Nd^{3+}/Yb^{3+}/Ho^{3+} doped samples.

5. Conclusions

Ho^{3+} doped oxyfluoride glass and glass ceramics were fabricated. XRD and SEM experiments showed crystalline structures of the samples. Up-conversion emission bands centered at 484, 465, 433 and 423 nm of the obtained samples were obtained under 550 nm excitation. The absorption and down-conversion emission spectra showed absorption and emission intensities of oxyfluoride samples. The Nd^{3+}/Yb^{3+} doped oxyfluoride glass and glass ceramics were fabricated in the same way as Ho^{3+} doped oxyfluoride samples. The absorption spectra of glass and glass ceramic samples were studied and compared with each other. The fluorescence spectrum of Nd^{3+}/Yb^{3+} doped samples was also investigated. The desirable emission was shown in blue and green spectral regions. Moreover, the absorption spectrum of Nd^{3+}/Yb^{3+} doped samples and the Nd^{3+}/Yb^{3+}/Ho^{3+} doped ones were compared with each other.

References

[1] M. J. Dejneka, MRS Bull. 23 (1998) 57.
[2] W. Holand, G. Beall,in: Glass-Ceramic Technology, The American Ceramic Society, 2002.
[3] Y. Yu, D. Chen, Y. Cheng, Y. Wang, Z. Hu, F. Bao, J. European Ceramic Society **26**, 2761 (2006).
[4] Y. Wang, J. Ohwaki, Appl. Phys. Lett., **63**(24), 3268 (1993).
[5] F. Goutaland, P. Jander, W. S. Dei.Brockleshy, Opt. Mater, **22**(4), 383 (2003).
[6] J. Yang, S. Dai, N. Dai, L. Wen, L. Hu, Z. Jiang, J. Lumin. **106**, 9 (2004).
[7] N. O. Dantas, F. Qu, J. T. Arantes Jr, J. Alloys Compounds **344**, 316 (2002).
[8] H. Lin, S. Tanabe, L. Lin, Y. Y. Hou, K. Liu, D. L. Yang, T. C. Ma, J. Y. Yu, E. Y. B. Pun, J. Lumin. **124**, 167 (2007).
[9] Y. Wang, J. Ohwaki, Appl. Phys. Lett. **63**, 3268 (1993).
[10] M. Mortier, G. Patriarche, J. Mater. Sci. **35**, 4849 (2000).
[11] J. Qiu, A. Makishima, Science and Technology of Advanced Materials **5**, 313 (2004).
[12] Brian M. Walsh, Gary W. Grew, Norman P. Barnes, J. Physics and Chemistry of Solids **67**, 1567 (2006).
[13] A. S. Gouveia-Neto, L. A. Bueno, A.C.M. Afonso, J. F. Nascimento, E. B. Costa, Y. Messaddeq, S.J.L. Ribeiro, J. Non-Crystalline Solids **354**, 509 (2008).
[14] Ch. Liu, J. Heo, J. Non-Crystalline Solids **352**, 5325 (2006).
[15] Xi. Zhang, J-P Jouart, G´e Mary, J. Phys, Condens. Matter **10**, 493 (1998).
[16] A. V. Kir'yanova, V. Aboites, A. M. Belovolov, M. J. Damzen, A. Minassian, M. I. Timoshechkin, M. I. Belovolov, Journal of Luminescence **102–103**, 715 (2003).

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