Up-conversion process in erbium doped lithium fluoride bulk crystal, lithium borate glass and glass ceramics

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Abstract. In our research the up-conversion processes in Er doped bulk LiF crystal, lithium borate oxyfluoride glass and lithium borate oxyfluoride glass ceramics were studied: up-conversion and traditional photoluminescence spectra, the up-converted signal as a function of the laser power are presented. It was found that sharp luminescence bands in the visible part of the spectrum appear when the bulk crystal is subjected to IR irradiation at 980 nm by a laser diode. After the heat treatment of the glass submicron crystallites were detected by SEM technique. The presence of LiF crystalline phase in the oxyfluoride glass ceramics was proved by XRD method. The questions about the synthesis of the oxyfluoride glass ceramics and the possible mechanisms of the up-conversion process in the mentioned hosts are discussed.

1. Introduction

Low phonon energy glasses are desirable hosts for rare-earth ions because they enable emission from rare-earth energy levels that would otherwise be quenched in high-phonon energy glasses [1]. The phonon energy of the host becomes especially important in the case of up-conversion (UC) process, when low energy photons are converted to higher energy photons. UC process could be used in a wide range of applications like white light simulation [2], improvement of solar battery efficiency [3], high temperature sensor [4] etc. The UC has proved to be very effective in the various types of heavy-metal fluoride glasses (for example ZBLAN [5]). Unfortunately often the fluoride glasses have poor durability, are not fusion-spliceable to conventional telecommunication fibres, are toxic, corrosive and very expensive. These difficulties can be overcome by synthesizing oxyfluoride glass ceramics, which in some cases can provide even higher UC efficiency than in fluoride glasses comparable to that of the bulk crystal.

There are different ways to synthesize the ceramics. The most popular one involves preparation of a rare earth doped glass with a dissolved crystalline phase (in the case of oxyfluoride glass ceramics – the oxide glass with fluoride crystalline component). Subsequent annealing of the glass at certain temperature (crystallization temperature) for certain period of time leads to the formation of nanocrystallites in the glass [6]-[10]. If rare earth ions incorporate into the low-phonon energy environment, e.g. in the fluoride crystallites, the efficiency of the UC increases compared to the glass. Thus, controlling the annealing temperature and the heat treatment time, the size of the crystallites and

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the mean distance between them can be varied to achieve optimum combination of the efficiency of the UC process still keeping the material optically transparent.

In the present research we report our studies on the erbium doped oxyfluoride glass ceramics with LiF crystallites. UC and traditional photoluminescence spectra (PL) are analyzed and compared with the spectra of the bulk crystal and the glass. Structure of the ceramics is analyzed by means of XRD and SEM.

2. Experimental

Erbium doped LiF bulk crystal, erbium doped lithium borate glass and erbium doped glass ceramics were prepared in the Institute of Solid State Physics Crystals Growth laboratory. The bulk crystal was grown by Kyropulous method in Ar He atmosphere from LiF (3N) and ErF$_3$ (3N) powders. An erbium concentration of 2 mol% was used in the starting material. For the glass synthesis 60 mol% B$_2$O$_3$ (2N), 28 mol% Li$_2$CO$_3$ (2N), 10 mol% LiF (3N) and 2 mol% ErF$_3$ (3N) powders were used. The mixture was melted in a corundum crucible at 1200°C, poured into a copper mold and cooled to room temperature. The ceramics sample was prepared by means of annealing of the glass. UC luminescence was excited by a laser diode power up to 1 W of CW radiation at 980 nm. PL spectra were obtained under excitation of a 150 W arc Xe lamp. Luminescence spectra were recorded using a Czerny-Turner type monochromator equipped with a photomultiplier tube. X-ray diffraction measurements were performed using x-ray powder diffractometer with Cu K$_\alpha$ radiation (40 kV and 30 mA). Differential thermal analysis (DTA) of the glass samples were registered by Shimadzu DTG-60. Heating rate of 10°C/min was used. All the spectral measurements were conducted at room temperature.

3. Results and discussion

3.1. Bulk crystal sample

Figure 1 shows UC luminescence spectra of Er doped LiF bulk crystal excited at 980 nm. The main emission bands typical for Er$^{3+}$ ion at about 410 nm, 550 nm, 650 nm and 820 nm are present in the spectrum. The spectrum is constructed of sharp overlapping spectral lines that appear due to Stark splitting of the energy levels of the activator ion in the crystalline field (figure 1 upper right corner).

![Figure 1. Up-conversion spectrum measured for erbium doped LiF crystal excited at 980 nm, in the upper right corner magnified part of the spectrum](image-url)
PL spectrum of the sample excited at 380 nm looks similar to the UC spectrum preserving the main emission bands. A strong increase in the intensity of 650 nm band was observed when the sample was excited at 450 nm, while the intensity of the band was negligible exciting at 480 nm and 540 nm. This allows us to conclude that the transition $^4F_{5/2}, ^4F_{3/2} \rightarrow ^4I_{13/2}$ in Er$^{3+}$ ion is responsible for the red band in the crystal.

Dependence of the UC signal versus the power of the laser is shown in figure 2. Since the UC luminescence involves multiple photon absorption, the dependence of the intensity of the UC signal on the incident light power is not linear and can be expressed as $I \sim P^x$, where $x$ is indicative of an UC process, which involves at least $n$ photons, where $n$ is the smallest integer greater or equal to $x$ [11]. The coefficient $x$ can be read from the slope of an experimental curve placed in the double logarithmic representation.

There are different mechanisms how the population of the emitting state in the UC process is reached (for deeper review [12]). More often two types of the mechanisms are considered: excited state absorption (ESA) and energy transfer (ET). In the first case the emitting level is being populated by multistep excitation while the second one involves radiative and non-radiative energy transfer between the dopant ions. In our case rather simple ESA or ET processes involving two photon absorption might be responsible for the UC at 800 nm and 650 nm. For the bands at 550 nm and 400 nm a combination of ESA, ET and cross-relaxation processes might be the case involving 3 and 4 photon absorption, respectively.

![Figure 2. Up-conversion intensity versus excitation light power for different luminescence bands along with the slope parameter $x$.](image)

3.2. Glass sample

The PL spectrum of Er doped borate glass excited at 450 nm is shown in figure 3. Only a broad green band at 550 nm is present in the spectrum and the overall intensity of the luminescence signal is of 3 orders lower compared to that in the bulk crystal.
The UC luminescence spectrum is also presented in figure 3. It can be seen that the both spectra coincide, though the intensity of the UC luminescence is about one order lower than the PL (in the figure both spectra presented normalized). The much smaller intensity of the signal can be explained by the differences in the maximum phonon energies of these media: the effective phonon energy of LiF is about 660 cm\(^{-1}\) [13] while the effective phonon energy of the glass is \(~1500\) cm\(^{-1}\) [14]. The greater phonon energy of the glass leads to greater non-radiative transitions probabilities thus decreasing the UC efficiency. Moreover the red band defined by the transition \(^{4}F_{5/2},^{4}F_{3/2} \rightarrow ^{4}I_{13/2}\) present in the spectra of the crystal is absent in the PL and UC spectra of the glass sample due to rather high phonon energy of the glass leading to higher non-radiative process probability from the levels \(^{4}F_{5/2},^{4}F_{3/2}\) to lower lying levels.

![Figure 3. Up-conversion and traditional luminescence spectra measured for erbium doped lithium borate glass excited at 980 nm (solid red line) or at 450 nm (dashed line)](image)

3.3. Glass ceramics sample

3.3.1. Sample preparation

DTA technique was used to detect the crystallization temperature of the glass samples (figure 4). The temperature of the positive peak (\(T_c = 450^\circ\)C) corresponds to the beginning of the crystallization in the glass and at this temperature glass samples were annealed for different periods of time.

![Figure 4. DTA signal for the glass sample](image)
The samples remained transparent for the annealing times till 10 minutes but became opaque after heat treatment for 20 minutes and longer. After the annealing of the samples SEM (figure 5) and XRD (figure 6) techniques were used to study the structure of the samples.

SEM images of the oxyfluoride glass ceramics annealed for 20 minutes show presence of submicron grains in the glass matrix. The grains seem to be of regular shape having cubic structure. The mean size of the grains is approximately 150 nm. Figure 6 shows XRD patterns for the glass and the ceramics. Indeed well defined reflexes corresponding to LiF crystalline phase are present in the pattern for the ceramics sample. This fact allows us to conclude that the grains present in the SEM image are small LiF crystallites.

Unfortunately no expected increase of the UC signal for the ceramics was observed compared to the glass sample. This might be explained by an inefficient incorporation of erbium ions in the forming LiF crystallites during ceraming process: in the case of crystalline phase there are rather strict requirements of charge compensation for the trivalent erbium ion, while these requirements might be relaxed in the case of the glass.

4. Conclusions

- Erbium doped bulk LiF crystal was grown, UC luminescence spectrum for the crystal was measured.
• Erbium doped lithium borate glass was synthesized. UC luminescence for the glass was found to be at least 4 orders lower than for the crystal.
• Oxyfluoride glass ceramics was prepared by means of annealing of the lithium borate glass. Submicron LiF crystallites appeared in the ceramics but no increase of the luminescence signal was observed.

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References
[1] Dejneka J M 1998 MRS Bull. 23 57
[2] Expedito J, Silva C, Sa G F de and Santa-Cruz P A 2001 J. of Alloys and Compounds 323-324 336
[3] Shalav A, Richards B S and Green M A 2007 Sol. Energy Mater. Sol. Cells (Preprint doi:10.1016/j.solmat.2007.02.007)
[4] Dong B, Yang T and Lei M K 2006 Optical high temperature sensor based on green up-conversion emission in Er3+ doped Al2O3 Sens. Actuators B Chem. (Preprint doi:10.1016/j.snb.2006.10.002)
[5] Ferber S, Gaebler V and Eichler H-J 2002 Optical Materials 20 211
[6] Dantele G, Mortier M, Patriarche G and Vivien D 2006 J. of Sol. St. Chem. 179 1995
[7] Jin W, Xusheng Q, Xianping F and Minquan W 2006 J. of Rare Earths 24 67
[8] Silva J E C, Sa G F de and Santa-Cruz P A 2001 J. of Alloys and Compounds 323-324 260
[9] Mortier M and Patriarche G 2000 J. of Materials Science 35 4849
[10] Yu Y, Chen D, Wang Y Liu F and Ma E 2007 J. of Non-Crystalline Solids 353 405
[11] Polnau M, Gamelin D R, Luthi S R, Gudel H U and Hehlen M P 2000 Phys. Rev. B 61 5 3337
[12] Auzel F 2004 Chem. Rev. 2004 104 139
[13] Humlicek J 1999 phys. stat. sol. (b) 215 155
[14] Tsvetkov E G, Pylneva N A and Davydov A V 2006 J. of Crystal Growth 292 358