Influence of Various Impurities on the Optical Properties of YbF₃-Doped CaF₂ Crystals

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Calcium fluoride crystals doped with YbF_3 and co-doped with LiF and
NaF were grown using the vertical Bridgman method. Several of rare-earth
ions (such as Eu, Sm, Ho, Tm, and Yb) can be stabilized in the divalent
state in the CaF_2. The change of valence was attained by various methods.
The optical absorption spectra reveal the characteristic absorption bands of
the Yb^{3+} and Yb^{2+} ions. This means that the developed crystal growth
process achieves a good Yb^{3+} to Yb^{2+} conversion in the as-grown crystals.
The influence of other impurities, such as Na^+ or Li^+, on the absorption
and emission spectrum of YbF_3-doped CaF_2 was studied. The Li^+ and Na^+
ions drastically decrease the absorption coefficient of the Yb^{2+} ions in the
UV band and the emission intensity by excitation in 230 nm.

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1. Introduction

Interest in rare-earth (RE)-doped CaF_2 crystals used as laser material is
still growing due to the well known good optical characteristics of the CaF_2 host.
Several of RE ions (such as Eu, Sm, Ho, Tm, and Yb) can be stabilized in the
divalent state in the CaF_2. The change of valence has been attained by various
methods [1–5]. There are a few reported results [6–8] about the properties of
the Yb^{2+}-ions, with high concentration in the as-grown crystals. The Yb^{3+} ion
properties have been intensively studied due to its strong IR luminescence that
can be easily pumped with laser diodes. The properties of Yb^{2+} ions have been
less investigated, mainly only for its intense and broad yellow-green (535–560 nm)
luminescence [6–8]. The influence of monovalent ions (such as Li^+ and Na^+) on

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the absorption and emission spectra of the YbF_3 doped CaF_2 crystals has been less investigated, mainly on the properties of the Yb^{3+} ions [9].

The goal of this work is to investigate the influence of Li^+ and Na^+ ions on absorption and emission spectra of the divalent ytterbium ions in the as-grown YbF_3-doped CaF_2 crystals. Besides the reported yellow-green luminescence, new emission bands have been observed, not reported before, in the near UV spectral region.

2. Experiment

Pure, YbF_3-doped and LiF-, NaF-codoped CaF_2 crystals have been grown in our crystal research laboratory using vertical Bridgman method [10]. Suprapure grade (Merck) calcium fluoride, YbF_3, LiF and NaF were used as the starting materials. Various two concentrations YbF_3:CaF_2 crystals have been obtained with YbF_3 added to the melts in molar 0.7 and 1.2 concentrations and other NaF and LiF-codoped Yb:CaF_2 crystals. The crystal growth process begins by lowering the crucible in the temperature distribution in the furnace. The pulling rate was 4 mm/h. To prevent the evaporation of the NaF and LiF, a thin graphite lid was put on the charge in the crucible. Transparent colorless crystals of about 10 mm diameter over 6–7 m long were obtained in spectral pure graphite crucible in vacuum ($\approx 10^{-1}$ Pa) using a shaped graphite furnace [10]. The crystals have been cooled to room temperature using an established procedure. The optical absorption spectra reveal the characteristic UV absorption bands of the Yb^{2+} ions with more than ten times higher absorption coefficient than of the Yb^{3+} ions (see Fig. 1). This means that the developed crystal growth process achieves a good Yb^{3+} to Yb^{2+} conversion in the as-grown crystals. Room temperature optical absorption spectra were recorded by a Shimadzu 1650PC. The luminescence
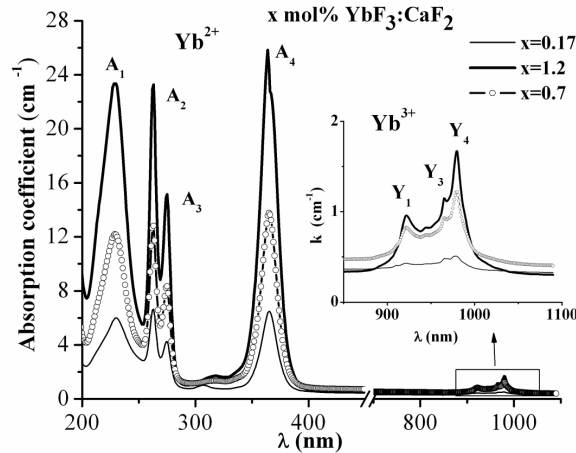

Fig. 1. Absorption spectra of YbF^3-doped CaF_2 crystals. The inset shows the absorption spectra of the trivalent ytterbium. Samples thickness varies between 2–2.6 mm.

measurements were carried out using a Perkin Elmer LS 55 Spectrofluorimeter in the National Institute for Materials Physics, Bucharest, Romania. All the measurements were recorded at room temperature. The studied samples have been cleaved from the obtained crystals and optically polished.

The mean objective of this work is to study the influence of the Li^+ and Na^+ ions on the optical absorption and emission spectra of the YbF_3 doped CaF_2.

3. Results and discussions

When trivalent RE ions are incorporated in CaF_2, lattice charge compensation is required to maintain the electrical neutrality of the system. The extra positive charge is usually compensated by interstitial fluorine ions (F_i^-) which can occupy various positions in the CaF_2 lattice giving rise to various crystal field symmetries: the tetragonal (C_{4v}) symmetry in which F_i^- occupies a nearest-neighbor (NN) interstitial site, the trigonal (C_{3v}) symmetry, the rhombohedral (C_{2v}) or cluster configurations. Such a complicated structure leads in turn to optical transitions having the form of broad bands which can be used advantageously for production of broadly tunable solid-state lasers. In contrast with Yb^{3+}-ions, divalent ytterbium ions do not need charge compensation and usually enter fluorite crystals in a cation substitutional position with cubic (O_h) symmetry.

3.1. Absorption spectra

The absorption spectra of YbF_3-doped crystals in the UV-VIS and near-IR region are shown in Fig. 1. The absorption spectra reveal the existence of both Yb^{2+} (in the near-UV) and Yb^{3+} ions in near-IR domain. The Yb^{3+} ions broad absorption spectrum is due to the spin-allowed $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition. The structure of the Yb^{3+} band is due to the crystal-field split, field with various symmetries, generated by several types of charge compensation. For Yb^{3+} ions the strongest absorption band peak appears around $Y_4 = 979$ nm and corresponds to C_{2v} or C_{3v} symmetries. The other peaks, called Y_1, Y_2, and Y_3 bands, are also observed by several investigators, but there are some discrepancies between their spectra [1–4]. The sharp $Y_1 = 922$ nm band has not been reported by [4] but has been observed by [3, 9, 11]. The intensity of the $Y_2 = 946$ nm increases as the concentration increases. The $Y_3 = 964$ nm band corresponds to transition of tetragonal C_{4v} site. All the absorption peaks increase as the YbF_3 concentration increases.

The absorption spectrum of the Yb^{2+} ions is characterized by four strong absorption bands in UV domain peaked at $A_1 = 230$ nm, $A_2 = 263$ nm, $A_3 = 275$ nm, $A_4 = 365$ nm. These bands are consistent with other reported experiments and calculations [1, 3, 4, 6–9, 12]. The UV region absorptions can be related to the $4f^{14} - 4f^{13}\, 5d$ transitions of the Yb^{2+} ions [1, 3, 6, 12]. Absorption bands at A_1, A_2, and A_4 are assigned as transitions of isolated Yb^{2+} ions and the A_3 band as transition of Yb^{2+} ions surrounded by Yb^{3+} ions. As we can observe in Fig. 1,

the increase in the concentration results in two distinct features: a broadening of the peaks and an increase in the absorption intensities.

Influence of the Li^+ and Na^+ ions. Figure 2 shows the absorption spectra of two YbF_3 doped CaF_2 crystals and Li- and Na-codoped $Yb:CaF_2$ crystals.

The influence of the Li^+ and Na^+ ions on the absorption spectra is clear: both ions diminish drastically the $Yb^{3+} \rightarrow Yb^{2+}$ conversion in the as-grown crystals. The absorption intensity decreases more for the $Yb,Na:CaF_2$ crystals than for the $Yb,Li:CaF_2$ samples (Fig. 2b). The alkaline metal ions work as charge compensator and the sites of Yb^{3+} ions are probably predominantly C_{2v}, in which Na^+ or Li^+ substitutes one of the eight nearest neighbor Ca^{2+} ions along any [110] direction. These structures are probably unfavorable for charge conversion during the growth process. The Li^+ and Na^+ ions do not affect the shape of the IR Yb^{3+} absorption spectra. The Li^+ ion decreases the absorption intensity in contrast with Na^+ ion which increases the intensity of the absorption peaks.
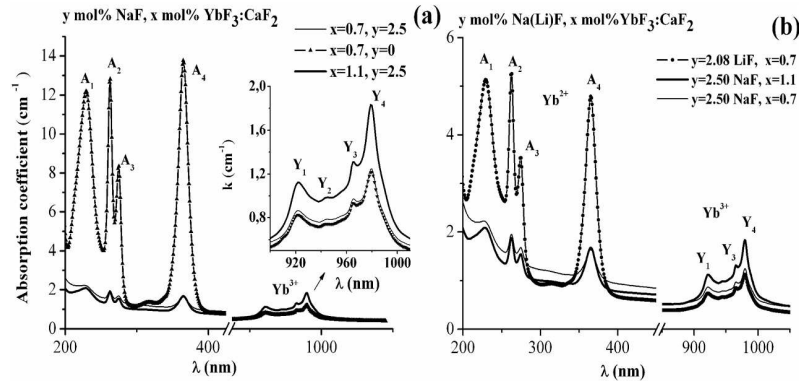

Fig. 2. Influence of Li^+ and Na^+ ions on the absorption spectra of the $YbF_3:CaF_2$ crystals.

3.2. Emission spectra

The room temperature emission spectra of 0.7 mol%$YbF_3:CaF_2$, 1.1 mol%$YbF_3:CaF_2$ samples and codoped with NaF and LiF excited with the 230 nm wavelength are shown in Fig. 3. The emission spectra of these crystals consist of two bands, one in the visible spectral domain, denoted I band, corresponding to the well known yellow-green emission [6–8], red-shifted for our samples, and one other broad band in the near UV-domain (300–400 nm), II band, consisting in some subbands. The emission bands of the $Yb,Li(Na):CaF_2$ samples are weaker than of the YbF_3-doped samples. The strongest peak for both YbF_3 doped CaF_2 crystals is at 338 nm; as the YbF_3 concentration increases the intensity of the emission band decreases. The Na^+ and Li^+ ions do not affect the shape of II band. As the YbF_3 concentration increases the Na^+ change the emission peaks.

This shows a strong dependence of the emission on the concentration. This broad emission band has not been reported before.
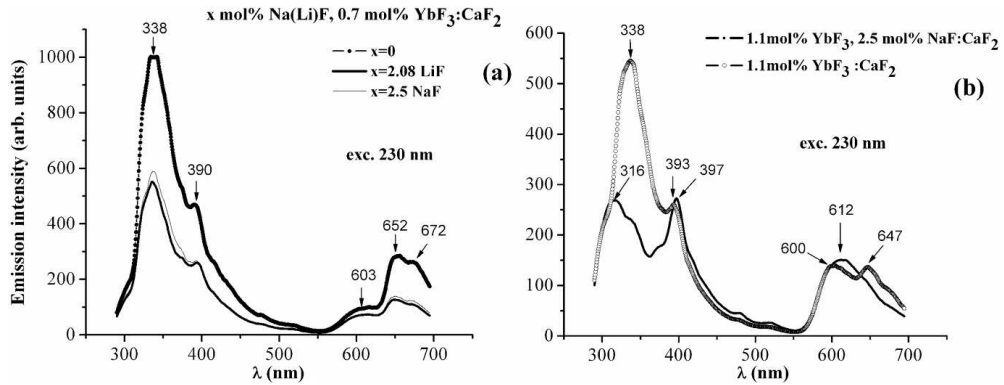

Fig. 3. Room temperature emission spectra of Li, Na-codoped Yb:CaF_2 crystals excited by 230 nm.

Small shifts in the positions of the emission lines in I band occur for the two different YbF_3 concentration samples. These emission lines of this band are red-shifted in comparison with the reported yellow-green luminescence [6–8]. The overlapping between emission and absorption spectra is weak, indicating that the crystals may have high quantum efficiency during the laser operation.

4. Conclusions

Various YbF_3 concentration and NaF-, LiF-codoped CaF_2 crystals have been grown using the conventional Bridgman technique. Room temperature optical absorption and emission spectra have been recorded in order to study the properties of the crystals. The Li^+ and Na^+ ions drastically decrease the absorption intensity of the characteristic UV peaks of Yb^{2+} ions. The luminescence studies reveal a strong concentration and codopant dependence of the emission bands by excitation in 230 nm. Besides the reported yellow-green luminescence, red-shifted for our samples, one broad emission band has been observed in the near UV spectral region with a peak at 338 nm, not reported before. Stabilized and high concentration divalent Yb ions in CaF_2 host should be a good near UV laser material.

Acknowledgments

References

[1] D.S. McClure, Z. Kiss, *J. Chem. Phys.* **39**, 3251 (1963).

[2] J.R. O'Connor, H.A. Bostick, *J. Appl. Phys.* **33**, 1868 (1962).

[3] S.M. Kaczmarek, T. Tsuboi, M. Ito, G. Boulon, G. Leniec, *J. Phys., Condens. Matter* **17**, 3771 (2005).

[4] J. Kirton, S.D. McLaughlan, *Phys. Rev.* **155**, 279 (1967).

[5] F.K. Fong, *J. Chem. Phys.* **41**, 2291 (1964).

[6] P.P. Feofilov, *Opt. Spectrosc.* **1**, 992 (1956).

[7] A.A. Kaplyanskii, P.P. Feofilov, *Opt. Spectrosc.* **13**, 235 (1962).

[8] A.A. Kaplyanskii, V.N. Medvedev, P.L. Smolyanskii, *Opt. Spectrosc.* **41**, 1043 (1976).

[9] L. Su, J. Xu, H. Li, L. Wei, W. Yang, Z. Zhao, J. Si, Y. Dong, G. Zhou, *J. Cryst. Growth* **277**, 264 (2005).

[10] D. Nicoara, I. Nicoara, *Mater. Sci. Eng. A* **102**, L1 (1988).

[11] W. Low, *J. Chem. Phys.* **37**, 30 (1962).

[12] M.V. Eremin, *Opt. Spectrosc.* **29**, 100 (1970).