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# Spectroscopy of $\text{Sm}^{3+}, \text{Y}^{3+}$ -codoped $\text{CaF}_2$ crystals for visible lasers

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## RÉSUMÉ

A series of  $\text{Sm}^{3+}, \text{Y}^{3+}$ -codoped  $\text{CaF}_2$  crystals was grown by the Bridgman method and their spectroscopic properties were studied. The addition of “buffer”  $\text{Y}^{3+}$  ions breaks the  $\text{Sm}^{3+}$  clusters and enhances the emission intensity in the visible by an order of magnitude.  $\text{Sm}^{3+}, \text{Y}^{3+}:\text{CaF}_2$  is a promising candidate for the development of orange lasers.

**MOTS-CLEFS:** *calcium fluoride; samarium ions; optical spectroscopy; luminescence.*

## 1. INTRODUCTION

$\text{CaF}_2$  is an attractive host matrix for doping with rare-earth ions as it combines good thermal properties, low phonon energy and strong ion clustering at low to moderate doping levels leading to inhomogeneous spectral broadening. The ion clustering, however, may lead to a strong luminescence quenching due to the greatly enhanced energy-transfer processes such as cross-relaxation. This can be prevented by codoping of  $\text{CaF}_2$  crystals with optically passive (“buffer”) ions such as  $\text{Y}^{3+}$ ,  $\text{Gd}^{3+}$  or  $\text{Lu}^{3+}$ , which efficiently enter rare-earth clusters, modify their composition, and prevent excessive luminescence quenching of active centers [1], Fig. 1(a). Trivalent samarium ions ( $\text{Sm}^{3+}$ ) feature multi-color emissions in the visible and they are of interest for orange and red lasers [2]. In the present work, we report on the growth and spectroscopy of  $\text{Sm}^{3+}, \text{Y}^{3+}$ -codoped  $\text{CaF}_2$  crystals.

## 2. CRYSTAL GROWTH

Single-crystals of  $\text{CaF}_2$  codoped with  $\text{Sm}^{3+}$  (0.5 - 2 at.%) and  $\text{Y}^{3+}$  (up to 10 at.%) were grown using the Bridgman-Stockbarger method under  $\text{Ar} + \text{CF}_4$  atmosphere. The starting reagents were  $\text{CaF}_2$ ,  $\text{YF}_3$  and  $\text{SmF}_3$  (purity: 4N). They were mixed, heated above the melting point (1418 °C) and homogenized for 4 h. The crystal growth was achieved by vertical translation of the crucible in a temperature gradient of 30-40 °C/cm. After completing the growth, the crystals were cooled to room temperature during 48 h. The as-grown crystals ( $\Phi 8$  mm, length: 30 mm) were transparent, free of cracks and inclusions and colorless, Fig. 1(b). Under UV lamp illumination, they exhibited orange luminescence whose intensity was enhanced for crystals codoped with  $\text{Y}^{3+}$ . The Raman spectra of  $\text{Sm}:\text{CaF}_2$  contain one band at  $314 \text{ cm}^{-1}$  ( $T_{2g}$  symmetry) which is notably broadened upon  $\text{Y}^{3+}$  addition.

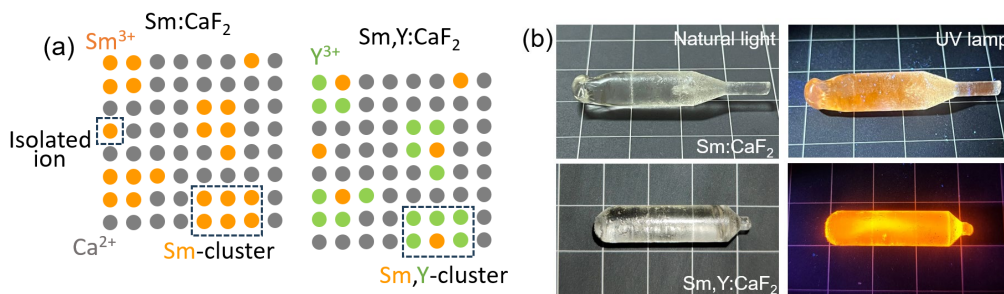


Figure 1:  $\text{Sm}^{3+}, \text{Y}^{3+}$ -codoped  $\text{CaF}_2$  crystals: (a) a scheme indicating the role of “buffer”  $\text{Y}^{3+}$  ions in breaking  $\text{Sm}^{3+}$  ion clusters; (b) photographs of as-grown 1 at.% Sm: and 1 at.% Sm, 3 at.% Y:  $\text{CaF}_2$  crystals taken in natural light and under UV illumination.

### 3. OPTICAL SPECTROSCOPY

The absorption spectra of  $\text{Sm}^{3+}$  ions in  $\text{CaF}_2$  crystals with and without  $\text{Y}^{3+}$  in the UV-visible spectral ranges are shown in Fig. 2(a). The spectra reveal a strong inhomogeneous spectral line broadening (a “glassy-like” behavior) and for the  ${}^6\text{H}_{5/2} \rightarrow {}^4\text{I}_{13/2}$  transition in the blue, the maximum absorption cross-section  $\sigma_{\text{abs}}$  is  $0.15 \times 10^{-20} \text{ cm}^2$  at 464 nm and the corresponding absorption bandwidth is  $\sim 8 \text{ nm}$ . This band is suitable for pumping Sm-lasers with blue GaN-based laser diodes.

The luminescence spectra of  $\text{Sm}:\text{CaF}_2$  and  $\text{Sm},\text{Y}:\text{CaF}_2$  crystals are shown on Fig. 2(b). The observed emissions are related to transitions from the metastable state  ${}^4\text{G}_{5/2}$  to the lower-lying  ${}^6\text{H}_J$  ( $J = 5/2 - 11/2$ ) manifolds. The emission in the orange, around 600 nm (the  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$  transition) dominates in the spectra. The luminescence from  $\text{Sm}:\text{CaF}_2$  is relatively weak and the spectra are structured. On the contrary, for crystals codoped with  $\text{Sm}^{3+}$  and  $\text{Y}^{3+}$ , the luminescence intensity increases by a factor of 40 (for 10 at.%  $\text{Y}^{3+}$ ) and the spectral bands become less structured. The study of luminescence dynamics from the  ${}^4\text{G}_{5/2}$   $\text{Sm}^{3+}$  state also reveals a great difference between crystals singly doped with  $\text{Sm}^{3+}$  and codoped with  $\text{Sm}^{3+}, \text{Y}^{3+}$ , Fig. 2(c). For  $\text{Sm}:\text{CaF}_2$ , the luminescence decay curve presents a very fast component followed by a slow decay with a lifetime of  $\sim 8.4 \text{ ms}$ . For  $\text{Sm},\text{Y}:\text{CaF}_2$  crystals, the luminescence quenching is much less pronounced and the average decay times are shorter, about 4.6 to 5.2 ms.

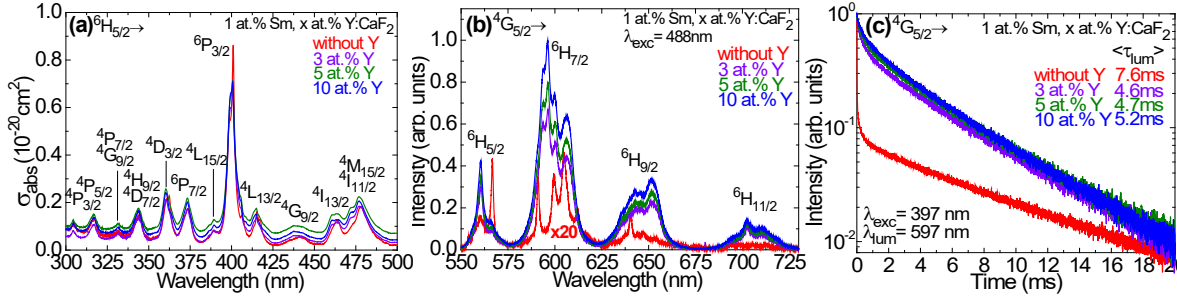


Figure 2: Effect of  $\text{Y}^{3+}$  codoping on the absorption and emission properties of  $\text{Sm}^{3+}$ -doped  $\text{CaF}_2$  crystals: (a) absorption spectra in the UV-visible; (b) luminescence spectra in the visible; (c) luminescence decay curves from the  ${}^4\text{G}_{5/2}$   $\text{Sm}^{3+}$  metastable state,  $\langle \tau_{\text{lum}} \rangle$  - mean luminescence lifetime.

The observed spectral behavior can be explained as following. In  $\text{Sm}:\text{CaF}_2$  crystals, the majority of active ions form Sm-clusters and the  ${}^4\text{G}_{5/2}$   $\text{Sm}^{3+}$  state is almost completely quenched by multiple cross-relaxation processes with adjacent ions. The observed weak luminescence with a long lifetime is due to the residual isolated  $\text{Sm}^{3+}$  ions. In  $\text{Sm}^{3+}, \text{Y}^{3+}$ -codoped crystals, the “buffer”  $\text{Y}^{3+}$  cations enter the rare-earth clusters (Sm-Y) and prevent self-quenching of  $\text{Sm}^{3+}$  luminescence, contributing to enhanced emission intensity, broadened emission profiles and a different decay time.

### 4. CONCLUSION

$\text{CaF}_2$  crystals co-doped with  $\text{Sm}^{3+}$  and  $\text{Y}^{3+}$  ions are attractive for visible (orange and red) lasers as they offer broad absorption bands in the blue accessible by commercial GaN-based laser diodes, broad and intense emissions in the visible and a relatively long luminescence lifetime. The codoping with “buffer”  $\text{Y}^{3+}$  ions enables the reduction of  $\text{Sm}^{3+}$  luminescence quenching by modifying the composition of rare-earth clusters.

### RÉFÉRENCES

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