



Mid-IR study of impurities and defects in (Yb, Na)-co-doped fluorite crystals

Изследване в средния ИЧ диапазон на примеси и дефекти в (Yb, Na)-кодотирани кристали от флуорит

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Introduction

Crystals grown of CaF_2 and its isotypes (SrF_2 , BaF_2) are attractive as optical and femtosecond laser host materials for multipurpose applications including communication, UV/VUV microlithography, sensorics, etc. Doping with Yb^{3+} ions is promising because of their strong laser emissions in NIR range. The heterogeneous mechanisms of substitution of Yb, into the fluoride lattice during the growth, here are charge/structurally compensated with additional introducing of Na ions.

Materials and methods

In a combined Bridgman-Stockbarger (BS) growth system were produced, simultaneously and upon identical conditions, laser-generational crystals of the types of $(\text{Yb}_{0.007}, \text{Na}_{0.05})\text{Ca}_{0.72}\text{Sr}_{0.223}\text{F}_2$ and $(\text{Yb}_{0.006}, \text{Na}_{0.04})\text{Ca}_{0.917}\text{Sr}_{0.073}\text{F}_2$.

Mainly, it was used a repeatedly purified optical natural CaF_2 (>99.4 wt%) from Slavyanka deposit, SW Bulgaria, which is not too hygroscopic as the synthetic CaF_2 powders. Otherwise, the rest of the used precursor fluorides are synthetics. The strictly set stoichiometry is a prerequisite concerning the further intended fluoride crystals' use in femtosecond laser applications. Main and trace elements chemical composition of the crystals are obtained by ICP-OES and LA-ICP-MS. The trace elements content was determined about a ppm for Ce, Sm, Eu, Er and Pb (used as scavenger in the growing procedure) and ~10 ppm for Y.

From couple of boules, by one of each crystal grown type, are prepared two series of three equal laser-generational windows, finished consecutively bottom-up one over another, with dimensions: 1" in diameter \times 2.9 \pm 0.1 mm in thickness, denoted as 1, 2, 3 (1", 2", 3"), respectively.

MIR spectra in regime of transmittance (2.5–10 μm), at NTP, for the windows of both types co-doped fluoride crystal systems, are recorded (Fig. 1.) by FTIR Tensor 37 Bruker equipped with ATR accessory.

Results and discussion

Fig. 1 reveals the transmittance spectra of both equally prepared laser-generational windows sets of the crystal systems of $(\text{Yb}_{0.007}, \text{Na}_{0.05})\text{Ca}_{0.72}\text{Sr}_{0.223}\text{F}_2$ and $(\text{Yb}_{0.006}, \text{Na}_{0.04})\text{Ca}_{0.917}\text{Sr}_{0.073}\text{F}_2$. From 2.5 μm up to 7 μm , it is $\geq 90\%$ as after that starts to decrease in “exponential” manner, where after 8 μm the transmittance level drops down more tangibly to the end's measured range. The transmittance spectra levels are quite slightly higher of the laser-generational windows of $(\text{Yb}_{0.007}, \text{Na}_{0.05})\text{Ca}_{0.72}\text{Sr}_{0.223}\text{F}_2$. Also in both crystal systems spectra, the 1st and 2nd windows exhibit transmittance level $\geq 90\%$ (2.5–7 μm), as it slightly changes in some lower values ($\approx 87\%$) in the way to the highest parts of the boules, i.e. laser-generational windows 3 and 3". The last suggests that in the highest parts of the crystal grown boules, there is an existence of more considerable structural defects and impurities acting as light absorbing/scattering centers.

Solely the system $(\text{Yb}_{0.007}, \text{Na}_{0.05})\text{Ca}_{0.72}\text{Sr}_{0.223}\text{F}_2$ shows weak absorptions of O^{2-} peaks at 2.473 μm , 2.716 μm and 2.967 μm . It is supposed that such induced specific absorptions are due to precipitated $\text{Sr}(\text{OH})_2$ phase (Bollmann, 1980). The last is assumed, in unison with the fact, that isolated OH^- ions possess sole vibration mode, the position of which is defined by such OH^- ions vicinity in the crystal lattice (Lipson et al., 1975).

In both laser-generational windows sets are distinguishable two asymmetric sited, partially overlapped band minima, i.e. stronger one centered at $\approx 3.422 \mu\text{m}$ and a weaker centered at $\approx 3.506 \mu\text{m}$. They should be

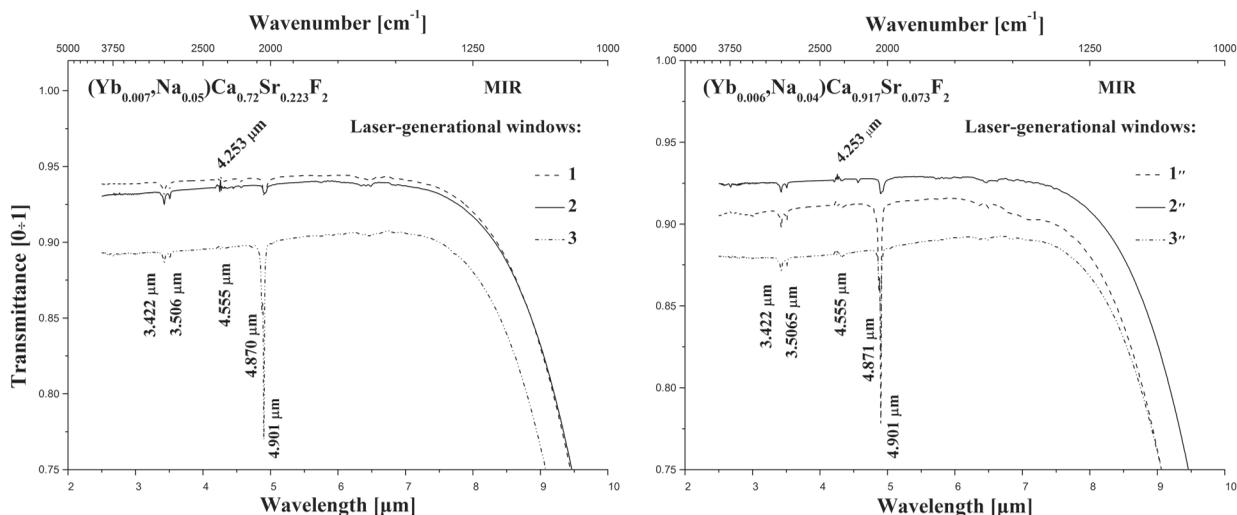


Fig. 1. Mid-IR spectra of laser-generational windows: *left*, $(\text{Yb}_{0.007}, \text{Na}_{0.05})\text{Ca}_{0.72}\text{Sr}_{0.223}\text{F}_2$; *right*, $(\text{Yb}_{0.006}, \text{Na}_{0.04})\text{Ca}_{0.917}\text{Sr}_{0.073}\text{F}_2$

engendered by strong hydrogen bonds in OH^- groups of structurally trapped fluorite waters.

The absorption bands in the range 4.2–4.5 μm are associated with the existence of CO_2 (Pandurangappa, Lakshminarasappa, 2011; Kim et al., 2012), as the strong positive peak at 4.253 μm caused by poor light transmittance increase is characteristic and due to CO_2 in the grown crystals. The existence of bridge-bonded CO to OH^- groups is the possible reason (Huang et al., 1990) engendering the strong absorption band ≈ 4.7 –4.9 μm . With the temperature increase or after a long-term annealing procedure this band shifts to higher wavelengths in the MIR region and gradually weakens (Ryczkowski, 2001). The broadest peak minima in Fig. 1, centered at ≈ 4.9 –4.92 μm for the different laser-generational windows of $(\text{Yb}_{0.007}, \text{Na}_{0.05})\text{Ca}_{0.72}\text{Sr}_{0.223}\text{F}_2$ are slightly shifted to lower wavelengths (at ≈ 4.9 μm) for the windows of $(\text{Yb}_{0.006}, \text{Na}_{0.04})\text{Ca}_{0.917}\text{Sr}_{0.073}\text{F}_2$. Again, the appearance of such peak minima is associated with absorption of CO, as a product of a chemical reaction between the carbon sputtering of the graphite BS crucible furnishing and oxygen consisting ions in the fluoride melts.

Both types co-doped fluoride crystal systems express some minor spectral fluctuations, which could be assigned to the existence of residual structurally trapped waters as well to rare-earths or/and transition metals traces.

Conclusions

The system of $(\text{Yb}_{0.007}, \text{Na}_{0.05})\text{Ca}_{0.72}\text{Sr}_{0.223}\text{F}_2$ reveals slightly higher light transmittance level in comparison with $(\text{Yb}_{0.006}, \text{Na}_{0.04})\text{Ca}_{0.917}\text{Sr}_{0.073}\text{F}_2$, which could be expressed in the context of some lower amount of impurities and defects in this (Yb,Na)-co-doped mixed fluoride crystal matrix.

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