

Short Communication

TEM SAED ANALYSIS OF (Yb, Na)-CO-DOPED LASING FLUORIDE CRYSTALS

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ABSTRACT

Yb-doped optical crystal fluorides are promising as novel lasing cores. Here, the co-doping with Na⁺ ions leads to lattice charge and structural compensation. For achievement of high-intensity laser emissions such materials structurally high-ordered should possess monocrystalline properties. TEM SAED analysis indicates that the entire range of conditions for Bridgman-Stockbarger crystal growth approach in our case, for attaining of the desired single crystal growth, is properly selected.

***Keywords:** co-doped lasing fluorides, Bridgman-Stockbarger method, single crystal growth, TEM SAED.*

INTRODUCTION

In the last decade, highest quality optical crystals appropriately doped by lanthanides (Ln) are subject of interest as ultra-short laser pulse lasing media. The Yb³⁺ ions state consisting of only two electron transition multiplets is most suitable for substantial increasing of the quantum efficiency between the pumped and subsequently emitted laser photons in suchlike solid state quantum systems. Yb³⁺ possesses strong IR luminescence, as well as reduction to Yb²⁺ state exhibits yellow-green luminescence and Stokes/anti-Stokes emissions.

Various Yb-doped crystals are nominated as leading for novel femtosecond solid state laser cores. But only CaGdAlO₄ (CALGO), CaF₂ and SrF₂, as high-ordered crystal structures, exhibit the desired combination of unique properties - high thermal conductivity accompanying reasonable but not quite narrow laser emissions [1 - 3]. In Yb:CaF₂

and Yb:SrF₂ crystal systems, the broad absorptions are due to the heterogeneous substitution of Ca²⁺ or Sr²⁺ for Yb³⁺ ions, which is related to local charge compensations leading to structural changes and modifications of the host crystal matrix field. The Yb:SrF₂ crystal system possesses higher cross-sectional amplification coefficient, lower saturation pumping threshold compared to the crystal system of Yb:CaF₂ (14 kW cm⁻²) and its emission spectra are also blue-shifted which is promising for tunable solid state lasers. Combining the low-phonon lattice frequency of CaF₂ (328 cm⁻¹) with the opposite birefringence signs of SrF₂ vs. CaF₂, allows obtaining of Yb-doped lasing mixed crystal matrices, i.e. isotypes of Ca_{1-x}Sr_xF₂, with broader fluorescent spectrum which allows manipulation shift of oscillator's wavelength (~ 30 nm) [4]. Upon such scenario, it is of a great importance to obtain high-intensity and coherent emission of such enhanced Yb-doped laser grade fluoride crystal

matrices, as obvious is that they should be with single crystal structure configuration.

Desirable mechanism for valence charge and structural compensation and thus electro-neutral accomplishment in dominantly Yb^{3+} -doped cubic fluoride crystal matrices is the introducing of co-dopant as Na^+ (NaF) or Li^+ (LiF).

Essential is that the increasing quality insistences about the optical crystals grown from low grain-sized, relatively poor of rare earths (REEs) and transition metals (TMs), mineral fluorspar leads to its exhausting. Simultaneously, worldwide with uncertain success are developed complicated and cost incapacitated technologies for producing of synthetic CaF_2 as chemical reagent for fluoride crystals growth. The synthetic fluoride crystals usually acquire matt or to varying degree white, pale-pink, yellow or other hues. The reason is the quite developed hygroscopic surface of the synthetic powder fluorides. The last results in their capricious storage/treatment thus substantial adsorption of H_2O and O_2 or other contaminants are depending of the ambient atmosphere. Although that precursor synthetic fluorides preparation in vacuum boxes is possible, it is complicated and cost consuming procedure. Otherwise, during the initial artificial crystal growth stage, when the furnace/crucible compartment(s) of any crystal growing installation evacuates of residual oxygen and water impurities, and the temperature(s) monotonically increases, then the fluorides melting starts and the highly-developed grain-sizing is in direct reactive contact with varied contaminants. The easy pulverization and melt swirls during the heating processes (typically reaching ~ 1700 K, i.e. the m.p. of CaF_2 , or over), together with intensive pumping out of the residual chamber's atmosphere, lead to significant losses of the amount of inserted fluoride precursors [5]. Besides, an accompanying supercooling phenomenon is initiated from easily vaporizing volatile oxides or halides of contaminants, gathering quite high particles pressure which turns out the melts quench depositing in fast polycrystallizing substance [6].

EXPERIMENTAL

Crystal growth of two types of (Yb, Na)-co-doped lasing fluorides systems ($\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$) is performed simultaneously and upon sub-atmospheric slow argon gas

flow in a double-temperature (T) zoned great combined Bridgman-Stockbarger (BS) growing system, tailor-made by CRYSTALOX Co., Cambridge UK. In the BS apparatus, between the upper "hotter" and the down "colder" T-zone, there is a broad (24.7 mm thick) adiabatic zone with distributed thermodynamic parameters where the quenching interface of the fluoride melt is consecutively crystallizing to attain normal (monocrystalline) growth conditions.

For the crystal growth we used a highly-purified ($> 99.6\%$) mineral fluorspar (from Slavyanka deposit, SW Bulgaria), grain-sizing 0.8 - 0.25 mm, repeatedly two-stage purified with 20 mass % HCl and concentrated HF acid, consecutively dried and annealed in advance for optimized laser crystals growth. The rest of the precursor fluorides are Merck Suprapur, Optipur - SrF_2 , YbF_3 , NaF.

By TEM (Transmission Electron Microscopy) the experimental technique of SAED (Selected Area Electron Diffraction) was conducted for the grown (Yb, Na)-co-doped lasing fluoride crystals. For the purpose, from the grown boules of both crystal system types were cut several partitions. Corresponding powder probes were prepared from them by finely grinding with mortar and pestle and consecutive top-down fragmentation to $< 10\ \mu\text{m}$ crystal sizing. The probes were put in solution (or suspension) and micro quantity, from each of both types, is taken by pipette. The separated quantities were dropped over standard cuprum mesh covered beforehand with amorphous carbon. Furthermore, the mesh with the loaded probe quantity are dried at r.t. and mounted on a specimen holder.

Morphological and phase compositional studies are performed by high resolution TEM device HR STEM JEOL JEM 2100. The accelerating voltage was 200 kV. The maximal resolution between couple points is 0.23 nm and 0.14 nm in grating. The actual magnifications are denoted in Fig. 2. The focal length between the studied specimens and the CCD camera GATAN Orius 832 SC1000 for digital imaging is 60 cm. The isolated SAED patterns (in Fig. 2) were crystallographically indexed.

RESULTS AND DISCUSSION

In Fig. 1 there are shown the grown by the combined Bridgman-Stockbarger method couple types of macro-size lasing crystal boules. The strictly set stoichiometry,



Fig. 1. Crystals and finished lasing windows ($1'' \times 2.9 \text{ mm} \pm 0.1$): the brighter boule upper and the windows on left - 1.8 % (YbF_3), 2.5 % (NaF): CaF_2 ; the darker boule down and the windows on right - 1.8 % (YbF_3), 2.5 % (NaF): $\text{Ca}_{0.67}\text{Sr}_{0.33}\text{F}_2$.

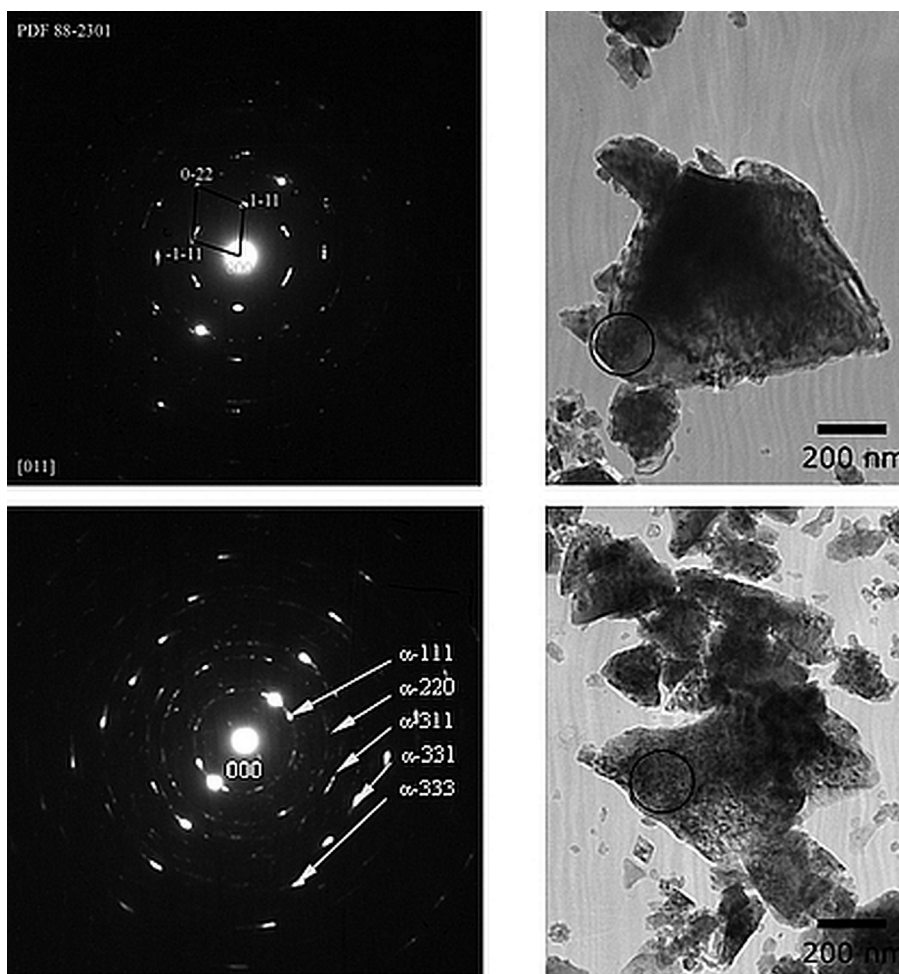


Fig. 2. On left - SAED patterns, on right - respective light-field TEM images (enclosed with black circumferences are the isolated SAEDs); Crystal systems: upper - 1.8 % (YbF_3), 2.5 % (NaF): CaF_2 , down - 1.8 % (YbF_3), 2.5 % (NaF): $\text{Ca}_{0.67}\text{Sr}_{0.33}\text{F}_2$.

1.8 % (YbF_3), 2.5 % (NaF): CaF_2 and 1.8 % (YbF_3), 2.5 % (NaF): $\text{Ca}_{0.67}\text{Sr}_{0.33}\text{F}_2$ (in mass %), is a prerequisite concerning their further intended use in femtosecond laser applications.

The SAED pattern of the system 1.8 % (YbF_3), 2.5 % (NaF): CaF_2 (in Fig. 2, upper on left) reveals monocrystalline behaviour along [011] crystallographic direction. Similar behaviour express the diffraction

peaks of subsequent order observable along [111] and [022] directions.

For the specimen of the system 1.8 % (YbF₃), 2.5 % (NaF):Ca_{0.67}Sr_{0.33}F₂ (in Fig. 2, down on left) the corresponding SAED pattern is of a mixed type. Simultaneous overlapping of mono- and polycrystalline diffraction is observed. There are distinguishable electron diffraction peaks of subsequent order matching [111], [220], [311], [331], [333] crystallographic directions. For the diffraction maxima along [111], [220], [311] directions a polycrystalline diffraction is indicative.

The observed electron diffraction reflexes for both crystal systems, 1.8 % (YbF₃), 2.5 % (NaF):CaF₂ and 1.8 % (YbF₃), 2.5 % (NaF):Ca_{0.67}Sr_{0.33}F₂, respectively, are referred and compared with PDF # 88-2301 and PDF # 35-0816*, for crystal CaF₂, of the powder XRD database ICDD, 2001 [7].

CONCLUSIONS

TEM SAED studies indicate that the entire conditions, by the used Bridgman-Stockbarger method for attaining of desired single crystal growth, can be properly selected. Such novel lasing (Yb, Na)-co-doped high-ordered fluoride crystal structures should be of interest for development of enhanced quantum-amplifying cores, as well as for other photonics issues.

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