Mechanical defects and impurities in laser crystals grown from natural fluorspar

Механични дефекти и примеси в лазерни кристали, израствани от флуорит

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Introduction

The optical crystal CaF_2 reveals broad light-transparent region from mid-IR to DUV, low refractive index and minor intrinsic birefringence. At wavelengths as short as 157 nm, commonly used for lithography stepper optics, the refractive index of CaF_2 undergoes nonlinear effects at high power densities. The opposite intrinsic birefringence signs of crystal CaF_2 vs. crystal SrF_2 (BaF_2) allows elimination of the effect of materials inherited optical anisotropy even at lattice level in synthetically grown mixed solid solution systems as $Ca_{1-x}Sr(Ba)_xF_2$.

The cubic fluoride crystals possess many cleavability planes (e.g., totally 7 about CaF_2) and low degree of hardness (e.g., 4 on the Mohs scale about CaF_2). Such inherent features result in capricious optical fluoride crystals processing and the use of specific cutting, grinding and polishing techniques. Even applying full operational precision, the latest inevitably lead to arising of variety of mechanical defects. Residual impurity traces additionally influence the fluoride crystals processing and supports the existence of inclusions (mechanical defects, cracks, phase segregations).

Materials and methods

By combined (triple zoned) Bridgman-Stockbarger (BS) growing method, there were produced co-doped single and mixed fluoride crystals intended for toward laser issues. For the purpose, it was used repeatedly purified natural powdered CaF_2 and SrF_2 (Merck – Suprapur). The lasant “species” hosting co-doping was performed by adding several wt% of YbF_3 and NaF (Merck – Optipur).

Slices were cut, in (111) growing crystallographic plane, of each of both novel types co-doped crystal matrixes (single CaF_2 and mixed $Ca_{0.67}Sr_{0.33}F_2$). The cut slices are turned into thin polished sections, cemented by Canada balsam over supporting quartz glasses. For investigation it was used optical microscope Jenapol of Carl Zeiss working in transmitted light regime. The studies were conducted using non-polarized and cross-polarized light.

Results and discussion

Microscopic observable in both types crystal matrixes (Fig. 1) are many dug scratch lines (oriented in one preferred direction, probably along to cleavability). The crystal of $Ca_{0.67}Sr_{0.33}F_2$ possesses higher value of hardness than that of CaF_2. The last is a reason for more found out scratch lines in the single-crystal CaF_2 and thus different mechanical defects content in both types of fluoride crystals. In both specimens are also visible ticker streaks, caused during the mechanical specimen processing. The scratches lie geometrically perpendicular to the thicker streaks.

Applying cross-polarized light, the two thin polished sections reveal the thick streaks in red colored interference tints. The same is not observable for the dug scratches. The scratch lines divide the thin polished

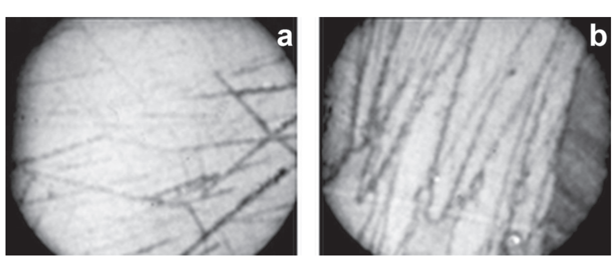

Fig. 1. Optical microscopy images of thin polished sections (non-polarized transmitted light, magnification ×32, visible field 6 mm): *a*, $Ca_{0.67}Sr_{0.33}F_2$; *b*, CaF_2

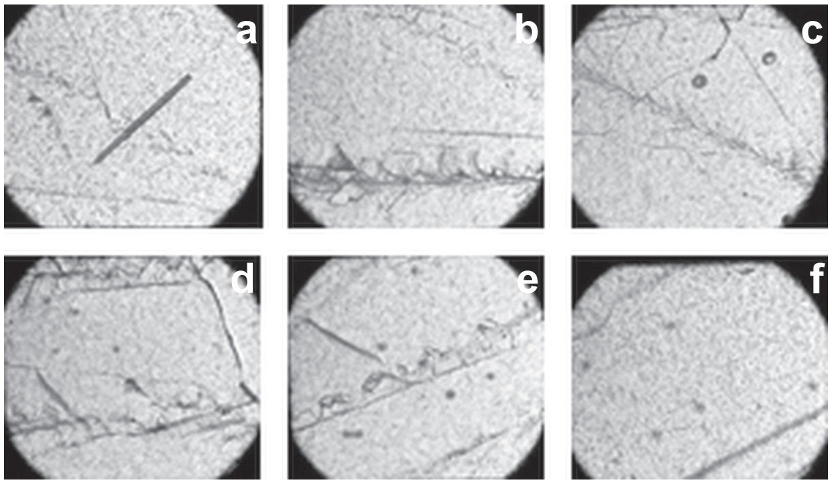

Fig. 2. Mechanical defects and impurities of $Ca_{0.67}Sr_{0.33}F_2$ thin polished section (non-polarized transmitted light, magnification ×500, visible field 0.125 mm)

sections into several homogeneous areas (Fig. 2) which could be related with the twinning along (111) crystallographic plane typical for the natural fluorspar.

Among the inclusions of $Ca_{0.67}Sr_{0.33}F_2$ (Fig. 2a), it is shown a "needle" in red-orange color (~0.3 mm long). Applying crossed Nicols it reveals pleochroism and high-colors. In Figs. 2b, d, e there are visible surface triangles induced from mechanical efforts over cleavability planes of $Ca_{0.67}Sr_{0.33}F_2$. Same dug triangle structures exist also in CaF_2 (Fig. 3a). There are shown in Figs. 2c, f and Fig. 3 (in all photos) black spherical phases, in some of which there is distinguishable second anisotropic phase. Long "dendritic" cracking lines, commonly exhibiting anisotropic effects, are observed in the photos in Fig. 2 and Fig. 3.

In Fig. 3a for CaF_2 are also visible two single long cracks in two priority directions supported by much shorter perpendicular cracks and featured by a dusty grey-lighting upon cross-polarized light.

Cleavability in different directions responses to different for overpowering assigned binding energy levels and diverse fragment forming (Hartman, 1974). The cubic CaF_2 possesses least threshold cleavability in (111) plane which dominantly induces small triangle prismatic fragments. The non-regular or "needle"-cleaved fragments in crystal fluorides indicate existence of disoriented local tensions (Vitov, Konstantinov, 2001).

Impurities and cracks and as well as lucid point defects (O^{2-}, OH^-) might be explained by local presence of secondary phases (CaO and SrO) sited along hardly distinguishable mosaic borders. According to Mouchovski (2012) suggestion, the so-observed black spherical phases are sulfur trace agglomerations due to the decomposition of pyrite, accompanying the fluorite ores and as a rule existing in even repeatedly purified fluorspars.

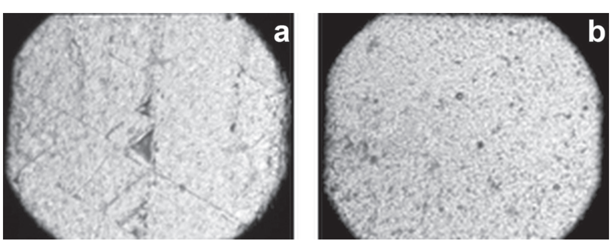

Fig. 3. Mechanical defects and impurities of CaF_2 thin polished section (non-polarized transmitted light, magnification ×500, visible field 0.125 mm)

Conclusions

Even minor impurity amounts in natural fluorspar disrupt the initial normal BS crystal growth causing various inclusions, i.e. the crystals' properties lead to light wavefronts distortions. The subsequent optical fluoride crystals processing is delicate and oftentimes results in caused mechanical defects. Here, the role of SrF_2 in the mixed laser host crystal matrix of $Ca_{0.67}Sr_{0.33}F_2$ is to improve the hardness lowering the mechanical defects and thus improving the overall optical quality. All the mechanical defects to a great extend are possible for effective removal upon additional the crystal fluoride boules fine annealing.

References

Hartman, P. 1974. On the crystal habit of fluorite. – In: Aleksiev, I., T. G. Radonova (Eds.). *Mineral Genesis.* Sofia, Publishing House of the Bulg. Acad. of Sci., 111–116.

Mouchovski, J. T. 2012. Supercooling. – In: Wilson, P. (Ed.). *Supercooling at Melt Growth of Single and Mixed Fluoride Compounds: Criteria of Interface Stability.* Rijeka, Croatia, InTech – Open Access Publisher, Ch. 5, 71–104.

Vitov, O., L. Konstantinov. 2001. Method for determining the cleavability of fluorite. – *Compt. rend. Acad. bulg. Sci.*, *54*, 3, 55–58.