Purification of natural fluorspar for optical crystal growth

Очистване на природен флуорит за израстване на оптични кристали

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Introduction

The alkaline-earth elements (AEE) fluoride crystals are attractive for optical and laser applications. Among them, CaF_2 gains advantage because of the lower light dispersion, radiation hardness and favorable luminescence peculiarities and availability from natural sources as mineral fluorite. In the present communication, purification of natural fluorspar and its chemical control are discussed on the base of two representative samples of optical fluorite from Slavyanka deposit (Southwestern Bulgaria) referred as FO-Probe-1 (Sample 1) and 3-1-1 (Sample 2) used for growth of optical crystals. The purification control was performed using Infrared (IR) Spectroscopy (FTIR spectrometer Tensor 37 Bruker, for MIR and NIR, with ATR accessories), LA-ICP-MS (Perkin Elmer Elan 9000 with equipped DRC-e quadrupole detector and NWR/ESI CP-193FX excimer laser ablation) and SEM-EDX analysis (SEM/FIB LYRA I XMU TESCAN equipped with Bruker Quantax 200 EDX).

Results and discussion

The initial fluorspar samples are with pureness about 98-99% and proven impurities of SiO_2, Al and Fe-oxides, traces of Pb, Mg, Mn, Be, Cu, Sr, Y and rare earth elements (REE) (Zidarova, 1992). The samples are fragmented to sub-mm grain size by thermo-hydraulic crashing and separated into fractions +1.0, +0.8, +0.5 and +0.25 mm. It is found that the quantities of impurity chemical elements and their compounds decrease at this stage of fluorite processing due to the mechanical, thermal and infrasonic treatment. The further chemical purification with concentrated HCl and HF acids additionally lowers to a different extent the content of Si-, Al-, Fe-oxides.

Nevertheless, the IR spectra of the two materials, besides the bands typical for CaF_2, contain a lot of absorption bands below 1000 cm^{-1} probably related to the presence of optical active centers of transition metals (TM) and REE. In addition, the IR spectra of sample 2 show pronounced bands around 3400 and 1700 cm^{-1} indicating water presence into starting material. The ionized at high temperature OH^- and O^{2-} ions occur deeply absorbed into fluorspar grains so that an original specific thermal treatment is performed in vacuum Bridgman-Stockbarger furnace, including slow heating the material up to 1100 °C, its hold-up at this temperature and fast cooling to room temperature. Meanwhile, the starting fluorspars are scavenged with add-ons of PbF_2 or/and ZnF_2 which produce easily volatile Pb- and Zn-oxides, helping on O^{2-} and OH^- desorption and preventing a possible formation of CaO and $Ca(OH)_2$. It is supposed only neglected quantities of OH^- and O^{2-} to remain soluted in the CaF_2 melt (Mouchovski at al., 1999). During the growth of the two CaF_2 boules, the so called “self-purification” procedure from REE impurities is accomplished. The process goes with effective restiction of penertation into growing space of ionized, oxygen containing ions, coming from vacuum ambient, due, first of all, to appropriately configured gas-permeability openings of the crucibles’ lids, puting under control the mass-transport phenomena and materials sublimation (Mouchovski, 2007).

Thus grown two boules are cut into several slices, grinded and optically polished; then, representative slices of the boules are chosen for analytical examination (Fig. 1). Application of SEM-EDX analysis allows one to reveal that the samples are characterized by different degree of homogeneity concerning mainly the distribution of Ca. For example, the calculated coefficient of variance for the Ca content is 0.02 – for the Sample 2 and 0.05 – for the Sample 1, while the coefficient of variance for the F content is very close in both samples being 0.04 and 0.03, respectively. Slightly higher value of this coefficient found for F in the Sample 2 well correlates with the initial higher content of OH^- and O^{2-} groups in the initial material.

The application of LA-ICP-MS (Ganev, 2013) confirms inhomogeneous distribution of Ca in the

Fig. 1. From left to right grown boules and their slices from Sample 1 and Sample 2, respectively

Sample 1 and reveals comparatively low contents of impurity elements, – the averaged contents of 35 elements of interest are (in ppm): Be <5; Na 1.88; Mg 2.875; Al <1.25; Si <350; P 17.33; Mn 0.74; Fe 73.19; Cu 0.88; Zn <1.25; Ru 0.34; Sr 249.24; Y 15.89; Ba 4.165; La 0.155; Ce 0.44; Pr 0.08; Nd 0.56; Sm 0.43; Eu 0.165; Gd 0.97; Tb 0.245; Dy 2.135; Ho 0.41; Er 1.25; Tm 0.18; Yb 0.995; Lu 0.155; Hf <0.1; Ta <0.25; Pb <0.06; Th 0.02; U 0.015.

Conclusion

The carried out purification of two representative samples of optical fluorite from Slavyanka deposit (Southwestern Bulgaria) shows comparatively good results in diminishing contents of several impurity elements. At the same time, the established inhomogeneous distribution of Ca in the grown boules is a possible obstacle to growing of high-quality fluorite crystals. This problem requires the further detailed study.

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