



IR investigation of repeatedly purified optical fluor spar from Slavyanka deposit (SW Bulgaria)

ИЧ спектроскопия на многократно пречистван оптичен флуорит от находище Славянка (Югозападна България)

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Introduction

The constantly growing demands on the fluorite optical elements quality, lead to exhaustion of the finer, relatively poor of rare earth elements (REEs) and transition metals (TMs), fluor spar. Simultaneously worldwide, there are developing technologies for synthetic CaF_2 producing but the variety of steps and difficult purification lead to economical unreasonableness. Synthetic crystals of CaF_2 usually possess matt or/and white, pale pink, yellow or another tinge. The reason is the too hygroscopic developed surface of the powder synthetic fluorides, which, no matter of the taken prerequisite safety procedures, absorbs high amounts of water, oxygen or other impurities depending on the surrounding atmosphere.

Materials and methods

There were selected two sorts of raw fluor spar pieces (size ~10–20 cm) with purity of 98–99%, taken from different mining sections of Slavyanka deposit (SW Bulgaria). The pieces are fragmented, thermally and electro-mechanically, to sub-mm fractions. Separated batch fractions are repeatedly two-stage purified by consecutive treatment with 20% HCl and concentrated HF acid. Both developed batches (denoted as sort I and II) are with purity >99.4 wt%. They are thermally annealed to 500 °C – Batch I, for 20 min; Batch II, for 30 min. Their grains size varies in the range 0.25–0.5 and 0.25–0.8 mm, respectively

MIR and NIR measurements are provided, by FTIR Tensor 37 Bruker equipped with ATR accessory, of two pellet probes of Batch I and II prepared in KBr of same stoichiometric ratio. Spectra are measured in regime of light transmittance at NTP, after 32 scans each, beam hitting aperture 4 mm.

Results and discussion

The IR spectra of the two batch fluor spars (Fig. 1.), initially show light transmittance decreasing level with rising the wavelength (about MIR sheer beyond 2.5 μm and about NIR abruptly beyond 0.7 μm). Thus, engendered are global intervals with lower values of light transmittance, which ends smoothly returning to the typical transmittance – about MIR beyond 11.5 μm and about NIR with coming to the measuring range end. Such global behaviour in MIR and NIR is mostly due to strong hydrogen (H) bonds in structurally trapped OH^- groups leading to absorptions, as their vibration frequency lowers with rising the H-bonds strength. With the temperature increase, the absorptions transform in low hooked-up OH^- groups because of the H-bonds lowering strength. Small asymmetric minima, sited in the global ones are due to existence of structurally trapped waters (with respective O–H elastic vibration bonds) of hydrated ions in the fluorite lattice (Aines, Rossman, 1984; Tahvildari et al., 2012).

In MIR region is observable absorption band of Batch I at 2.80–2.91 μm marked as A_1 , while for Batch II the corresponding absorption band is remarkably wider, i.e. at ≈ 2.79 –3.4 μm marked as B_1 . Such absorption bands are ascribed to structurally bonded H_2O in hydrothermal fluorite ores (Singh, 2013) as these of Slavyanka deposit. Batch I shows also transmittance minima (A_2) at 3.325 and 3.558 μm , as Batch II possesses (B_2) wider one at 3.422 μm as well a weaker at 3.506 μm minima. The latest should be caused due to H-bonds in hydroxyl groups of structurally hooked-up waters in the fluorites. The minima at 4.184 μm of Batch I and 4.198 μm of Batch II are of KBr but slightly shifted to its characteristic peak at 4.205 μm . About both fluor spar batches, it is also observable a characteristic absorption peak of CO_2 at 4.351 μm (Pandurangappa, Lakshminarasappa, 2011; Kim et al., 2012). The absorption peaks commonly de-

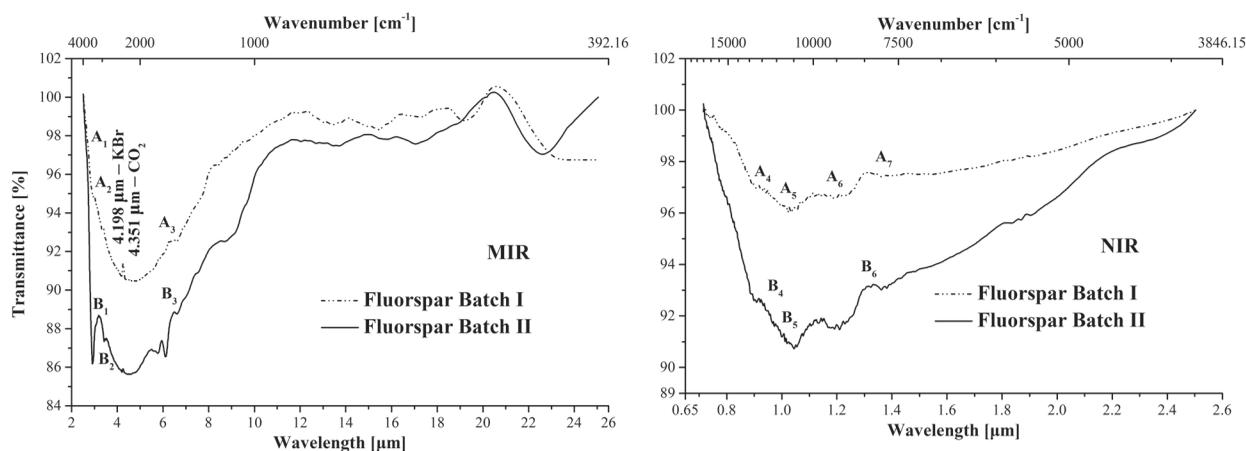


Fig. 1. IR spectra of light transmittance of fluorspars Batch I and II: on left, MIR; on right, NIR region

noted as A_3 at 6.254 and 6.630 μm of Batch I and those corresponding denoted as B_3 at 5.780, 6.121, 6.672 μm of Batch II are as a result of vibration modes arisen from rotational hydroxyl ions states, H–O–H bonds or O–H elastic vibration bands (Aubry et al., 2009; Kim et al., 2012). Isomorphous ions, of trace elements of REEs or/and TMs in the fluorite lattice, result in specific absorptions beyond 8 μm .

In NIR region observable are mainly specific absorption peaks and bands caused by electron transitions between REEs and TMs centers in the cubic fluorite lattice. Such are A_4 at 896 and 905 nm (Batch I) as well B_4 at 898 and 1000 nm (Batch II). These weak outer electron transitions are caused by partial clustering of near sited impurities ions in the fluorite lattice, acting as inhomogeneous charge compensators (Nelson, 2003). The absorption bands around 1057 and 1078 (A_5 and B_5) are vibration analogs of the electron transitions at 1024 and 1045 nm in fluorspars Batch I and II respectively (Elcombe, 1972). Otherwise, many small absorption peaks in the ranges 1147–1263 nm (A_6) and 1333–1463 nm (A_7) of Batch I, as well as between 1333 and 1453 nm (B_6) of Batch II are ascribed to phonon interactions associated with the fluorite lattice (Nelson, 2003).

Conclusions

The absorption peaks and bands observed in MIR and NIR regions are broader, deeper and more asymmet-

ric about fluorspars Batch II in comparison with fluorspars Batch I. Possible reason for such phenomena is the more heterogeneous sub-mm grain-sizing of Batch II vs. Batch I, i.e. its bigger active surface and hygroscopy.

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