

## REFINEMENT OF THE SYNGENITE STRUCTURE AND INVESTIGATION OF ITS HEATING AND MOISTURING PRODUCTS BY MEANS OF IR-SPECTROSCOPY

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We studied the sulphate mineral syngenite,  $K_2Ca(H_2O)[SO_4]_2$ , from Kalush, Ukraine, by IR-spectroscopy. On the IR-spectrum (obtained on KBr pellet) the following absorption bands related to the S-O bonds of the  $SO_4$ -tetrahedra were observed:  $\nu_3$  (asymmetric stretchings) 1190, 1138, 1126 and  $1110\text{ cm}^{-1}$ ;  $\nu_1$  (symmetric stretchings) 1005 and  $985\text{ cm}^{-1}$ ;  $\nu_2$  (bendings) 470 and  $442\text{ cm}^{-1}$ ; and  $\nu_4$  (bendings) 675, 645,  $605\text{ cm}^{-1}$  and a shoulder near  $620\text{ cm}^{-1}$ . The broad band with the main maximum at  $3315\text{ cm}^{-1}$  and the shoulders at  $3520$  and  $3385\text{ cm}^{-1}$  are usually attributed to the stretching vibration  $\nu_{OH}$  of the water molecule, while the band at  $1675\text{ cm}^{-1}$  to the bending vibration  $\delta_{OH}$  of the water molecule. The interpretation of the band at  $750\text{ cm}^{-1}$  is not as obvious as those of the previous bands, since it could be caused both by one of the vibrations of the  $SO_4$ -tetrahedra or the librations of the water molecule.

The presence of four bands in each of the  $\nu_3$ - and  $\nu_4$ -regions and two bands in the  $\nu_1$ -region is possible if the two  $SO_4$ -tetrahedra in the syngenite structure are not equivalent (CORRAZA & SABELLI, 1967). The factor-group calculation for  $P2_1/m$  ( $C_{2h}^2$ ) group,  $Z=2$  yields two independent sets of vibrations:  $2 \cdot [\nu_1(B_u) + \nu_2(A_u+B_u) + \nu_3(A_u+2B_u) + \nu_4(A_u+2B_u)]$  that would be active in IR-spectra. However, the number of bands observed in the powder spectra is less than that of the calculated bands. To refine the structural position of the  $SO_4$ -tetrahedra, IR-reflection spectra of the (100), (110) and (101) faces of a single crystal were obtained (Fig. 1). Five out of six possible bands in the  $\nu_3$ -region were registered.

The IR-spectra of deuterated syngenite display not only the isotopic shift to the low frequencies of all bands related to the water molecule, mentioned above, but also the shift of a rather intense band from  $750\text{ cm}^{-1}$  to  $550\text{ cm}^{-1}$  ( $\nu_{OH}/\nu_{OD}=750/550=1.36$ ). This allows assigning the latter band undoubtedly to the librating vibrations of the water molecule involved in hydrogen bonds with sulphate oxygen atoms belonging to one of the two different  $SO_4$ -groups. The

other type of  $SO_4$ -groups has no water molecules in its nearest surrounding.

Six maxima in the region of  $\nu_3$  vibrations and four in the region of  $\nu_4$  vibrations of the IR-spectrum of the deuterated sample represent a further argument in favour of the structural non-equivalency of two  $SO_4$ -groups.

The fractional loss of water on heating at  $200\text{ }^\circ\text{C}$  causes some structural changes and at  $250\text{ }^\circ\text{C}$  anhydrous sulphate phases (?) forms.

The mineral, moistened by water on air, slowly transforms into gypsum.

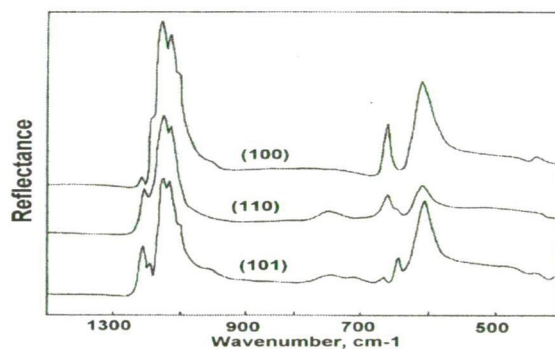


Fig.1: IR-reflection spectra of the different faces of syngenite single crystal.

### Reference

CORRAZA, E. & SABELLI, C. (1967). Zeit. Kristal., 124/6: 398-408.