

## SINGLE-CRYSTAL STRUCTURE AND RAMAN SPECTROSCOPY OF SYNTHETIC $\text{CaAlSiO}_4\text{F}$

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Titanite is an orthosilicate and its structure consists of chains of  $\text{TiO}_6$  octahedra which are linked by isolated Si-tetrahedra. The main coupled substitutions that occur are  $(\text{Al}, \text{Fe}^{3+} + \text{F}) = (\text{Ti} + \text{O})$  and  $(\text{Al}, \text{Fe}^{3+} + \text{OH}) = (\text{Ti} + \text{O})$ . The extent of the Al + F substitution in natural titanites is high but complete solid solution in the system  $\text{CaTiSiO}_4\text{O}-\text{CaAlSiO}_4\text{F}$  has only been observed in experimental investigations. TROITZSCH et al. (1999) and TROITZSCH & ELLIS (1999) not only determined the crystal structure of synthetic  $\text{CaAlSiO}_4\text{F}$  but also investigated the structural changes in titanite solid solutions along the join  $\text{TiO} = \text{AlF}$  based on Rietveld analysis.  $\text{CaAlSiO}_4\text{F}$  is monoclinic, belongs to the space group  $A2/a$  ( $a = 6.91$ ,  $b = 8.51$ ,  $c = 6.44 \text{ \AA}$  and  $\beta = 114.7^\circ$ ). In this investigation synthetic  $\text{CaAlSiO}_4\text{F}$ , the AlF analog of titanite, has been investigated using single-crystal synchrotron diffraction experiments at Beamline X06DA (Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland) and for the first time Raman spectroscopy. A single-crystal of  $20 \times 15 \times 7 \mu\text{m}^3$  was selected using a polarising transillumination stereo microscope. The symmetry and reflection conditions are consistent with the model reported by TROITZSCH & ELLIS (1999). Therefore, the known model ( $A2/a$  setting) was used as a starting point for the structure refinement using Jana2006. Forty parameters were refined including anisotropic displacement parameters, resulting in a final fit of  $R_{\text{obs}} = 2.6 \%$ . The Raman spectrum is characterised by two spectral ranges with a distinct gap in between. The first range ( $167\text{-}593 \text{ cm}^{-1}$ ) can be subdivided as follows: peaks in the range of  $150\text{-}361 \text{ cm}^{-1}$  are bending and stretching vibrations involving Ca as well as motions of the tetrahedral and octahedral sites. A second subdivision can be distinguished between  $431$  and  $507 \text{ cm}^{-1}$ . The modes at  $431$  and  $470 \text{ cm}^{-1}$  are dominantly caused by tetrahedral torsion and F-displacement perpendicular to  $a$  with octahedral contribution. Vibrational spectra were calculated in harmonic approximation at G-point from fully relaxed energy optimisations of the crystal structures presented herein, using 3D-periodic density functional theory with Gaussian basis sets and the software CRYSTAL06. The lattice parameters of the fully relaxed structure were in good agreement with the experimental values, with the calculated values  $0.8 \pm 0.4 \%$  too large; the monoclinic angle was calculated  $0.4^\circ$  too large. The agreement of the calculated Raman frequencies with the observed ones was very good, with standard deviation  $\pm 7 \text{ cm}^{-1}$  and maximum deviations of  $\pm 7 \text{ cm}^{-1}$ .

TROITZSCH, U., ELLIS, D.J., THOMPSON, J., FITZ-GERALD, J. (1999): Eur. J. Mineralogy, 11, 955-965.  
TROITZSCH, U., ELLIS, D.J. (1999): American Mineralogist, 84, 1162-1169.