

HT-study on fettelite, $[\text{Ag}_6\text{As}_2\text{S}_7][\text{Ag}_{10}\text{HgAs}_2\text{S}_8]$: ionic phase transition indicating the possible existence of different polytypes

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The crystal structure of fettelite, $[\text{Ag}_6\text{As}_2\text{S}_7][\text{Ag}_{10}\text{HgAs}_2\text{S}_8]$, a rare silver sulfosalt, was recently solved and described by Bindi et al. [1] from a twinned crystal from Chañarcillo, Copiapó Province, Chile. The structure consists of the stacking of two module layers along [001]: an *A* module layer with composition $[\text{Ag}_6\text{As}_2\text{S}_7]^{2-}$ and a *B* module layer with composition $[\text{Ag}_{10}\text{HgAs}_2\text{S}_8]^{2+}$. The As atoms form isolated AsS_3 pyramids typical of sulfosalts, Hg links two sulfur atoms in a linear coordination, and Ag occupies sites with coordination ranging from quasi linear to almost tetrahedral. The *A* module layer found for fettelite is identical to that described for the minerals belonging to the pearceite-polybasite group [2]. Differential Scanning Calorimetry experiments were carried out on the sample from Chañarcillo on 25 mg of powders sealed in aluminium pans using a Mettler DSC 30 instrument from 218K to 423K. The experiments did indicate a phase transition occurring at about 380K. To analyze the HT-structural behaviour by means of X-ray diffraction, a crystal was mounted on a CCD-single-crystal diffractometer equipped with a N_2 -heating device. Unfortunately, the highest temperature allowed by the nitrogen device we used (i.e., 350K) was not sufficient to explore the eventual phase transition in fettelite, but the structural results we obtained clearly point toward a structural phase transition likely due to the increase of ionic conductivity with the increase of temperature. The structural data we collected seem indicate a halving of cell along the *a* and *b*-directions and an increase of structural disorder in the *B* module layer. This does mean that at least two polytypes could exist for fettelite. The ordered, monoclinic structure (with unit-cell parameters: $a = 26.0388(10)$, $b = 15.0651(8)$, $c = 15.5361(8)$ Å, $\beta = 90.48(1)^\circ$ and space group $C2 - [1]$), and a fast ion conducting, disordered HT-form with *a* and *b* parameters halved. The two unit-cell types (corresponding to two different polytypes) could be also found in nature. This would account for the different unit-cell types observed for different fettelite samples coming from different localities (e.g., Odenwald, Chañarcillo, Imiter). In addition, slightly different chemical compositions for different fettelite samples (e.g., different Ag/Hg ratios) could play a crucial role as driving forces for different unit-cell stabilizations.

[1] Bindi, L. et al. (2009) *Am. Mineral.*, **94**, 609-615. [2] Bindi, L. et al. (2007) *Am. Mineral.*, **92**, 918-925.

Structural study of members of the polysomatic series epidote-törnebohmite from Stetind pegmatite, northern Norway

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Modules (*E*) of epidote-type structure were found to match easily with those (*T*) of törnebohmite, $(\text{REE})_2\text{Al}[\text{SiO}_4]_2(\text{OH})$, to form a polysomatic series (*E*, *ET*, *T*). In particular, the presence of REE being essential to form *T* modules, *E* modules of epidote members belonging to the allanite or dollaseite subgroups are expected to form *ET* polysomes. Up to now, two minerals – gatelite-Ce [1] and västmanlandite-(Ce) [2] – were found which can be regarded as a regular alternation of (001) slabs of epidote-type structure and (-102) slabs of törnebohmite-type structure. They differ in unit-cell, space-group symmetry and in composition of the epidote-type module, which is of dissakisite-(Ce) composition in gatelite-(Ce) and of dollaseite-(Ce) composition in västmanlandite-(Ce).

This work reports the results of a structural study on crystals resembling gatelite-(Ce) found by one of the author (T.A.H) in the yttrian fluorite masses within the Stetind pegmatite of the Tysfjord granite, northern Norway. The Stetind pegmatite is a granitic REE-pegmatite enriched in niobium, yttrium and fluorine (NYF family) and hosts a large number of different REE- and Y-bearing silicates, REE-bearing carbonates and niobian oxides [3].

The unit-cell dimensions of the examined crystals are in the range $a = 8.907\text{-}8.933.0$, $b = 5.639\text{-}5.699$, $c = 17.525\text{-}17.600$ Å, $\beta = 116.3\text{-}116.6^\circ$, without any evidence of doubling of the translation unit along the *a*-axis observed in gatelite-(Ce). Although all the crystals were examined with long exposure times on a CCD-equipped diffractometer (Oxford Xcalibur™ 2), neither superstructure reflections such as in gatelite-(Ce) nor the weak, continuous streaking as in västmanlandite-(Ce) were detected. Thus, like in the case of västmanlandite-(Ce), the average structure was refined in the $P2_1/m$ instead of $P2_1/a$ space group, disregarding the slight distortion away from the mirror plane normal to the *b*-axis. However, whereas the continuous streaking in västmanlandite-(Ce) is due to the offset from the (010) mirror plane of two sites (A3 and O15, occupied by REE and oxygen, respectively), in the crystals here studied only O15 exhibits an offset from the mirror plane; therefore, continuous streaking at $a^*/2$ due to short-range order, if any, would be here even weaker than in västmanlandite-(Ce).

Semiquantitative SEM-EDS analyses together with structural data point toward a mineral related to gatelite-(Ce) having the *E* module approaching that of allanite-(Ce).

[1] Bonazzi, P. et al. (2003) *Am. Mineral.*, **88**, 223-228.

[2] Holtstam, D. et al. (2005) *Eur. J. Mineral.*, **17**, 129-141. [3]

Husdal, T.H. (2008) *Kongsberg Mineralsymposium*, 5-28.