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Fast ion conduction character and ionic phase-transition in silver sulfosalts: The case of fettelite $[Ag_6As_2S_7][Ag_{10}HgAs_2S_8]$

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Abstract

The mineral fettelite, $[Ag_6As_2S_7][Ag_{10}HgAs_2S_8]$, has been recently structurally characterized. On the whole, the structure can be described as a regular succession of two module layers stacked along the **c**-axis: a first module layer (labeled *A*) with composition $[Ag_6As_2S_7]^{2-}$ and a second module layer (labeled *B*) with composition $[Ag_{10}HgAs_2S_8]^{2+}$. Here we report an integrated high-temperature single-crystal X-ray diffraction (HT-SCXRD), differential scanning calorimetry (DSC), and complex impedance spectroscopy (CIS) study on a sample of fettelite from Chañarcillo, Copiapó Province, Chile. DSC and conductivity measurements pointed out that fettelite shows a ionic-transition at about 380 K. HT-SCXRD experiments confirmed the phase transition toward a disordered phase having a trigonal symmetry with the *a* and *b* unit-cell parameters halved. In the HT-structure, the disorder is located in the *B* layer where the Ag-Hg cations are found in various sites corresponding to the most pronounced probability density function locations of diffusion-like paths. This indicates that at least two polytypes could exist for fettelite, the ordered, monoclinic RT-structure (space group *C*2), and a fast ion conducting, trigonal, disordered HT-form (space group $P\bar{3}m1$) with *a* and *b* parameters halved. The two unit-cell types (corresponding to two different polytypes) could be also found in nature. 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.

Keywords: Fettelite, HT-data collection, conductivity spectrum, ionic phase transition, fast ionic conductor