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Structural behavior and magnetic properties of coquimbite $AlFe^{3+}_3(SO_4)_6(H_2O)_{12}·6H_2O$ over a wide temperature range

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ABSTRACT

Hydrated iron sulfate minerals have received considerable attention from the standpoint of environmental science, as well as due to extensive studies on the mineralogy of Mars. In this paper, we report on the thermal evolution of coquimbite $AlFe^{3+}_3(SO_4)_6(H_2O)_{12}·6H_2O$ by single-crystal X-ray diffraction (SCXRD) from −173 to 77 °C. Powder X-ray diffraction (PXRD) was performed in the temperature range of −180 to 740 °C and low vacuum of 600 Pa. Magnetic properties for coquimbite are reported in the range of −271 to 7 °C. It was observed that coquimbite is stable between −180 and +145 °C and at a low vacuum of 600 Pa. We observed a gradual transition from coquimbite to the amorphous phase at 150 °C, followed by a transition to mikasaite at 225 °C, and a second amorphization at 575 °C, with afterward crystallization to hematite. SCXRD shows that the behavior of coquimbite with increasing temperature can be divided into two stages, with negative and strongly anisotropic thermal expansion at Stage I (−173 to −143 °C) and only positive thermal expansion at Stage II (−133 to 77 °C). All the O-H···O bonds remain virtually intact during Stage I, except for Ow2-H3···O2. The negative thermal expansion observed along the *c*-axis in the LT range is a result of the simultaneous reduction of several bond lengths and angular distortions: (1) decrease of Ow2-H3···O2 hydrogen bonds oriented approximately along the *c*-axis; and (2) shrinkage of $M3O_3(H_2O)_3$ octahedra, evidenced by the decrease in *M*3-O3 and *M*3-Ow3 bonds. The nature of the expansion of the coquimbite structure during Stage II is better understood in terms of the orientation of $[M2M3_2(SO_4)_6(H_2O)_6]^{3-}$ clusters along the *c*-axis. *M*-O and S-O bonds are only slightly affected by the temperature rise at Stage II, whereas O-H···O angular transformations seem to be the main driving force for the expansion of the coquimbite structure along the α_{11} direction upon heating.

Coquimbite exhibits distinct magnetic properties compared to other iron sulfates, driven by antiferromagnetic interactions within its *M*3-*M*2-*M*3 trimeric clusters of Fe^{3+}. The presence of Al^{3+}-Fe^{3+} site mixing in coquimbite introduces structural disorder, partially disrupting its magnetic ordering and contributing to magnetic entropy and magnetization features, such as a 1/3 magnetization plateau.

Keywords: Coquimbite, sulfates, iron, non-ambient single crystal X-ray diffraction, magnetism, non-ambient powder X-ray diffraction, thermal expansion, thermal analysis, Mars