

The crystal structures of the low-temperature phases of leonite-type compounds, $\text{K}_2\text{Me}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($\text{Me}^{2+} = \text{Mg}, \text{Mn}, \text{Fe}$)

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ABSTRACT

Recent optical and differential scanning calorimetry measurements indicate phase transitions in leonite-type compounds at low temperatures. The crystal structures of these phases, i.e., leonite, $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, “Mn-leonite”, $\text{K}_2\text{Mn}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, and mereiterite, $\text{K}_2\text{Fe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, have been determined at low temperatures. The leonite structure (space group $C2/m$ at room temperature) is composed of sulfate tetrahedra and MeO_6 octahedra which are interconnected by K cations and hydrogen bonds of the H_2O molecules. Previous structure investigations at room temperature have shown that one of the sulfate groups is disordered. Refinements of single-crystal X-ray data at ambient and low temperatures indicate that the dynamic disorder in leonite and “Mn-leonite” is “frozen” in two steps and thus results in two new, ordered structures at low temperatures. In mereiterite only one transition from the dynamically disordered to the ordered structure is observed.

The two low-temperature crystal structures of leonite have been refined to $R = 0.0236$ at 170 K (space group $I2/a$, $Z = 8$, $a = 11.780(2) \text{ \AA}$, $b = 9.486(2) \text{ \AA}$, $c = 19.730(4) \text{ \AA}$, $\beta = 95.23(3)^\circ$, $V = 2195.6 \text{ \AA}^3$), and to $R = 0.0230$ at 100 K (space group $P2_1/a$, $Z = 4$, $a = 11.778(1) \text{ \AA}$, $b = 9.469(1) \text{ \AA}$, $c = 9.851(2) \text{ \AA}$, $\beta = 95.26(1)^\circ$, $V = 1094.01 \text{ \AA}^3$). The two low-temperature crystal structures of “Mn-leonite” have been refined to $R = 0.0272$ at 185 K (space group $I2/a$, $Z = 8$, $a = 12.035(2) \text{ \AA}$, $b = 9.549(2) \text{ \AA}$, $c = 19.839(4) \text{ \AA}$, $\beta = 94.99(3)^\circ$, $V = 2271.3 \text{ \AA}^3$), and to $R = 0.0237$ at 110 K (space group $P2_1/a$, $Z = 4$, $a = 12.031(1) \text{ \AA}$, $b = 9.531(1) \text{ \AA}$, $c = 9.902(1) \text{ \AA}$, $\beta = 95.02(1)^\circ$, $V = 1131.08 \text{ \AA}^3$). The low-temperature crystal structure of mereiterite has been refined to $R = 0.0219$ at 185 K (space group $P2_1/a$, $Z = 4$, $a = 11.834(2) \text{ \AA}$, $b = 9.502(1) \text{ \AA}$, $c = 9.913(2) \text{ \AA}$, $\beta = 94.87(1)^\circ$, $V = 1110.66 \text{ \AA}^3$).

The different behavior of mereiterite (i.e., stability range, sequence of transitions) in comparison to the Mg and Mn endmembers may be explained by more distorted MeO_6 octahedra and by strongly different hydrogen bond lengths around the disordered sulfate groups.