

THE ISOTYPIC CRYSTAL STRUCTURES OF $K_2Mn(SO_4)_2 \cdot 2H_2O$ AND $K_2Cd(SeO_4)_2 \cdot 2H_2O$:
COMPARISON WITH THE KROEHNKITE-, COLLINSITE-, AND FAIRFIELDITE-GROUP

by

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The crystal structures of the isotypic compounds $K_2Mn(SO_4)_2 \cdot 2H_2O$ and $K_2Cd(SeO_4)_2 \cdot 2H_2O$ (space group $P\bar{1}$, $Z = 2$) have been investigated by single-crystal X-ray diffraction using a CCD area detector. The crystal structure of $K_2Mn(SO_4)_2 \cdot 2H_2O$ was determined by Patterson methods and refined to $R = 0.023$ with cell parameters $a = 6.574(1) \text{ \AA}$, $b = 7.332(1) \text{ \AA}$, $c = 10.700(1) \text{ \AA}$, $\alpha = 72.89(1)^\circ$, $\beta = 73.91(1)^\circ$, $\gamma = 69.77(1)^\circ$, $V = 453.6(1) \text{ \AA}^3$. The crystal structure of $K_2Cd(SeO_4)_2 \cdot 2H_2O$, previously described by Peytavin et al. [1], was refined to $R = 0.025$ with cell parameters $a = 6.625(1) \text{ \AA}$, $b = 7.542(1) \text{ \AA}$, $c = 11.349(1) \text{ \AA}$, $\alpha = 72.17(1)^\circ$, $\beta = 74.55(1)^\circ$.

A large number of sulphate, phosphate, and arsenate minerals with the general formula $A_2M^{II}(XO_4)_2 \cdot 2H_2O$, with $A = Na$ or Ca , and $M^{II} = Cu, Mg, Co, Mn, Fe, Ni, \text{ or } Zn$, and $X = S, P, \text{ or } As$ have been found up to date. These natural compounds have triclinic or monoclinic symmetry. The triclinic minerals (space group $P\bar{1}$) are the Ca-arsenates talmessite ($M = Mg$) [2], β -roselite ($M = Co$) [3], gaitite ($M = Zn$) [4], and the Ca-phosphates collinsite ($M = Mg, Fe, Zn$) [5], fairfieldite ($M = Mn$) [6], messelite ($M = Fe, Mn$) [3] and cassidyite ($M = Ni$) [7]. The monoclinic minerals (space group $P2_1/c$) are the Ca-arsenates brandtite ($M = Mn$) [8], roselite ($M = Co, Mg$) [9], Zn-roselite ($M = Zn$) [10], and wendwilsonite ($M = Mg$) [11], as well as kroehnkite, $Na_2Cu(SO_4)_2 \cdot 2H_2O$ [12, 13].

The crystal structures of the synthetic compounds $K_2Mn(SO_4)_2 \cdot 2H_2O$ and $K_2Cd(SeO_4)_2 \cdot 2H_2O$ are closely related with the minerals of the $A_2M^{II}(XO_4)_2 \cdot 2H_2O$ type. In all these compounds chains built up by MO_6 and XO_4 polyhedra are interconnected via A–O bonds and hydrogen bonds, forming layers parallel to (010). While the topology of the chains is similar in all these structures, there are differences concerning their linkage to layers as well as the stacking of the layers. Based on these features, four structure types can be distinguished.

Compared with the crystal structures of $K_2Mn(SO_4)_2 \cdot 2H_2O$ and $K_2Cd(SeO_4)_2 \cdot 2H_2O$ (type I, $P\bar{1}$), adjacent layers are shifted by $c/2$ in the monoclinic structures of the isotypic minerals kroehnkite, brandtite, roselite, and wendwilsonite (type II, $P2_1/c$). Consequently, the translation period along [010] is doubled referring to $K_2Mn(SO_4)_2 \cdot 2H_2O$ and $K_2Cd(SeO_4)_2 \cdot 2H_2O$.

The crystal structures of collinsite, talmessite and cassidyite are isotypic with the synthetic compounds $\text{Na}_2\text{Cu}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ [14], $\text{K}_2\text{Co}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$, and $\text{Na}_2\text{Ni}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ (both WILDNER, pers. comm.) (type III, $\text{P}\bar{1}$). There, all A- and X-atoms, respectively, are crystallographically equal, resulting in a unit cell halved along [001] in comparison to the $\text{K}_2\text{Mn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{Cd}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$ structures.

Finally, the formation of the chains and layers of the isotypic structures of fairfieldite and messelite (type IV, $\text{P}\bar{1}$) is analogue to that of $\text{K}_2\text{Mn}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{K}_2\text{Cd}(\text{SeO}_4)_2 \cdot 2\text{H}_2\text{O}$. However, the stacking of the layers is modified: two adjacent layers are shifted along [100], which results in γ being nearly 90° in the fairfieldite-type structure.

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