

## CRYSTAL CHEMISTRY OF KIESERITE-COBALTKIESERITE SOLID SOLUTIONS, $Mg_{1-x}Co_x(SO_4)\cdot H_2O$

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The formation of solid solutions, i.e. the complete or partial replacement of crystal chemical related elements along joins of isotypic endmember structures, is a very common phenomenon in mineralogy. In rock-forming minerals in particular, the mutual substitution of Mg and  $Fe^{2+}$  is one of the most important and best investigated replacement mechanisms, e.g. in the olivine solid solution system. Studies of solid solution systems of Mg with divalent 3 configured transition metal cations other than  $Fe^{2+}$  are comparatively rare, but the synthetic 'olivines'  $(Mg,Co)_2(SiO_4)$  attracted attention (e.g. MÜLLER-SOMMER et al., 1995 and references therein); as to be expected, the slightly larger ionic radius (SHANNON, 1976) of octahedral  $Co^{2+}$  ( $r = 0.745 \text{ \AA}$ ) vs. Mg ( $r = 0.720 \text{ \AA}$ ) results in an increase of octahedral bond lengths and unit cell parameters with  $Co^{2+}$  content.

However, for some groups of isotypic compounds a larger unit cell volume was surprisingly observed for the Mg representative compared to the respective  $Co^{2+}$  endmember, in spite of longer Co–O bond distances, among them the kieserite-type compounds  $Me^{2+}(XO_4)\cdot H_2O$  (WILDNER & GIESTER, 1991, GIESTER & WILDNER, 1992).

Hence, in our present investigation we aim to synthesise representatives along the kieserite-cobaltkieserite solid solution series,  $Mg_{1-x}Co_x(SO_4)\cdot H_2O$ , and to characterise them in detail by single crystal X-ray diffraction methods, in order to (i) check for complete miscibility along the solid solution series, (ii) check for possible cation ordering effects reducing symmetry and especially to (iii) thoroughly characterise the type and extent of the subtle structural changes governing the contradictory behaviour of polyhedral vs. unit cell dimensions.

First results confirm the above mentioned inconsistencies for the endmember phases [ $V_{kies} = 355.53(20)$ ,  $V_{Co-kies} = 354.77(14) \text{ \AA}^3$ ; but  $\langle Mg-O \rangle = 2.077(1)$ ,  $\langle Co-O \rangle = 2.097(1)$ ], and also indicate that complete miscibility along the solid solution series actually exists. Judging from the presently still limited number of X-ray data sets for mixed compositions, Vegard-type or at least approximate Vegard-type behaviour seems to prevail for most of the structural changes along the join. Further syntheses and X-ray diffraction experiments are in progress to fill compositional gaps and corroborate our preliminary results.

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