

## **Co<sup>2+</sup>-Cu<sup>2+</sup> substitution in bieberite solid-solution series, (Co<sub>1-x</sub>Cu<sub>x</sub>)SO<sub>4</sub>·7H<sub>2</sub>O, 0.00 ≤ x ≤ 0.46: Synthesis, single-crystal structure analysis, and optical spectroscopy**

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### **ABSTRACT**

Single crystals of Cu-substituted bieberite (Co<sub>1-x</sub>Cu<sub>x</sub>)SO<sub>4</sub>·7H<sub>2</sub>O have been synthesized from aqueous solution by the evaporation method. It is shown that the solubility of Cu<sup>2+</sup> in bieberite is limited to 0.46 atoms per formula unit (apfu). Chalcantite CuSO<sub>4</sub>·5H<sub>2</sub>O only accommodates a very small amount of ~0.03 Co<sup>2+</sup> atoms. Structure analysis by X-ray diffraction of single crystals along the join CoSO<sub>4</sub>·7H<sub>2</sub>O–CuSO<sub>4</sub>·5H<sub>2</sub>O showed that the hepta-hydrate phases are monoclinic with *P*2<sub>1</sub>/*c* symmetry at room temperature, whereas the penta-hydrate phases are triclinic, *P*1̄. Within the Co<sub>1-x</sub>Cu<sub>x</sub>SO<sub>4</sub>·7H<sub>2</sub>O series (0 ≤ x ≤ 0.46), lattice parameters are distinctly altered by the Cu<sup>2+</sup> substitution, however, the observed changes cannot be ascribed to different ionic radii of Co<sup>2+</sup> and Cu<sup>2+</sup> but are due to an increasing distortion of the lattice by increasing Cu<sup>2+</sup> content. Cu<sup>2+</sup> is not distributed randomly over the two possible crystallographic metal sites but exclusively enters the M2 site. While all the oxygen atoms coordinating the M1 site act as donors of hydrogen bonding to the sulfate tetrahedron, one oxygen atom at the M2 site is a hydrogen bond acceptor. This may cause the slight tetragonal elongation of the M2 coordination polyhedron, which favors the preferential occupation of this site by Cu<sup>2+</sup>. Optical spectra show typical features of both the Co<sup>2+</sup> and the Cu<sup>2+</sup> absorption signatures. While in Co<sup>2+</sup>-rich hepta-hydrate phases Co<sup>2+</sup> absorption bands arising from both M1 and M2 sites are detected, there are only bands arising from the M1 site in Co<sub>0.54</sub>Cu<sub>0.46</sub>SO<sub>4</sub>·7H<sub>2</sub>O. This supports the observation of selective substitution of Cu<sup>2+</sup> at the elongated M2 octahedral site. Cu<sup>2+</sup> absorption bands can be assigned on the basis of *D*<sub>4h</sub> symmetry with increasing splitting of the Cu<sup>2+</sup>, <sup>2</sup>T<sub>2g</sub>, and <sup>2</sup>E<sub>g</sub> energy levels with increasing Cu<sup>2+</sup> content.

**Keywords:** Bieberite, crystal structure, optical spectroscopy, metal sulfate, synthesis