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Thermodynamic analysis of the olivenite-libethenite solid solution

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Minerals of the olivenite-libethenite [Cu₂(AsO₄)(OH)-Cu₂(PO₄)(OH)] group appear at many sites with secondary copper oxysalts. Their structural arrangement seems to be particularly stable and is also found in minerals in other classes, such as in andalusite or kieserite. Thermodynamic properties of the end members were investigated before and suggest that olivenite is the most stable Cu arsenate. In this contribution, we inspected in a detail the solid solution series between olivenite and libethenite.

Samples used in this work were synthetic, prepared from aqueous solutions with Cu(NO₃)₂, (NH₄)H₂PO₄, and Na₂HAsO₄. Chemical composition of the members of the olivenite-libethenite solid solution were determined by ICP-OES. The relative proportions of the cations (As/P) differ little from the initial ratios in the parental solutions. For libethenite and a few solid-solution members, the orthorhombic space group *Pnmm* was taken for the refinement of the powder XRD data. For olivenite and the remaining, most solid-solution members, the monoclinic space group *P2₁/n* yielded slightly better results. Acid solution calorimetry in 5 N HCl showed that the solid solution is thermodynamically non-ideal, with positive enthalpies of mixing. The data indicate slight asymmetry and can be fit by a function $H^{\text{ex}} = X_{\text{oli}}X_{\text{lib}} [A + B(X_{\text{oli}} - X_{\text{lib}})]$, where X_{oli} and X_{lib} are the mole fractions of olivenite and libethenite component, respectively, and $A = 6.27 \pm 0.16 \text{ kJ} \cdot \text{mol}^{-1}$, $B = 2.90 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$. The asymmetry and positive excess enthalpies of mixing are confirmed by autocorrelation analysis of Fourier-transform infrared spectra. The results are interpreted as a local heterogeneity that arises from strain relaxation around cations with different sizes (As⁵⁺/P⁵⁺) in the intermediate members. The length scale of the heterogeneity corresponds to the wavelength of the phonons, on the order of one or a few unit cells. A distinct feature in the H^{ex} data is the sudden drop of the mixing enthalpies between $X_{\text{lib}} = 0.7$ and 0.8 . This feature can be explained by a subtle symmetry change in the solid solution from orthorhombic to monoclinic. The energetic difference between these two configurations is $0.9 \text{ kJ} \cdot \text{mol}^{-1}$. Excess entropies are zero within the uncertainties of the measurements, with one exception (at $X_{\text{lib}} = 0.2$). Excess volumes show a complicated, non-linear dependence on X_{lib} . Addition of PO₄ into olivenite causes contraction of the unit cell, as expected for substitution of a smaller for a smaller cation. On the other side of the solid solution, addition of AsO₄ into olivenite causes expansion of the unit cell. The variations of V^{ex} are related to the interplay of cation-size differences and the small driving

force between the two related (orthorhombic/monoclinic) structure. The olivenite-libethenite solid solution is non-ideal but the deviation from ideality is too small for a development of a miscibility gap. In nature, the $As/(As+P)$ ratio in such minerals is controlled by geochemical rather than thermodynamic factors.