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Vergasovaite to cupromolybdite topotactic transformation with crystal shape preservation

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Abstract

Thermal behavior of vergasovaite, ideally $Cu_3O(SO_4)(MoO_4)$, and its synthetic analog has been studied by high-temperature single-crystal X-ray diffraction in the temperature range of 300–1100 K. According to EMPA results, the empirical formulas are $(Cu_{2.36}Zn_{0.61})_{\Sigma 2.97}O[(Mo_{0.91}S_{0.08}V_{0.04})_{\Sigma 1.03}O_4](SO_4)$ for vergasovaite and $Cu_{2.97}O[(Mo_{0.92}S_{0.09})_{\Sigma 1.01}O_4](SO_4)$ for its synthetic analog. The mineral is stable up to 950 ± 15 K; at 975 K, the unit-cell parameters and volume increase abruptly due to topotactic transformation of vergasovaite to cupromolybdite, $Cu_3O(MoO_4)_2$. The transformation is accompanied by loss of sulfur (and excess copper) without destruction of the crystal. The thermal expansion of the vergasovaite structure is strongly anisotropic, being minimal along the $[O_2Cu_6]^{8+}$ chains comprised of vertex-sharing OCu_4 tetrahedra. This peculiar thermal behavior can be explained by the anisotropy of bond-length evolution in the $Cu1O_6$ and $Cu3O_6$ octahedra and the flexibility of the S-O-Cu and Mo-O-Cu bond angles. Synthetic Zn- and V-free analogs demonstrate negative thermal expansion at 425–625 K and melt at as low temperature as 700 K with no indication of transformation or recrystallization at least below 1200 K.

The topotactic transformation observed in vergasovaite may have important implications for the design of novel materials and for understanding the alteration processes of copper minerals.

Keywords: Topotactic transformations, sulfates, molybdates, fumarolic minerals, vergasovaite, single-crystal X-ray diffraction, thermal expansion