

Does the bazhenovite structure really contain a thiosulfate group? A structural and spectroscopic study of a sample from the type locality

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ABSTRACT

Bazhenovite was originally reported as a rare, thiosulfate-containing mineral, with the chemical formula $\text{CaS}_5 \cdot \text{CaS}_2\text{O}_3 \cdot 6\text{Ca}(\text{OH})_2 \cdot 20\text{H}_2\text{O}$. The structure was predicted to be layered, but no structural details were given. A crystal of “bazhenovite” from the pyritized siderite fragments occurring in the melt products of burning dumps at the type locality in the Chelyabinsk coal basin, South Urals, Russia has been examined by single-crystal X-ray diffraction and vibrational spectroscopy (FTIR and Raman). The structure was solved in space group $P2_1/c$ and refined assuming twinning on $\{100\}$ to a final $R_{\text{obs}} = 5.03\%$ (731 reflections) and $R_{\text{all}} = 6.98\%$ (966). Although the unit-cell dimensions of the examined crystal [$a = 8.391(2)$, $b = 17.346(6)$, and $c = 8.221(4)$ Å, $\beta = 119.33(5)^\circ$, $V = 1043.2(8)$ Å³] match those of the original bazhenovite description [$a = 8.45(1)$, $b = 17.47(1)$, and $c = 8.24(1)$ Å, $\beta = 119.5^\circ$, $V = 1059$ Å³], the thiosulfate group was not detected by either structural analysis or spectroscopic investigations. The structure is an alternating sequence of two kinds of layers, labeled A and B respectively, stacked along $[010]$. The A layer is the ordered part of the structure and consists of a linkage of $\text{Ca}(\text{OH})_2(\text{H}_2\text{O})_6$ antiprisms and $\text{Ca}(\text{OH})_4(\text{H}_2\text{O})_2$ octahedra. Taking into account both structural and spectroscopic results, the B layer is inferred to consist of a disordered assemblage of S_4^{2-} , and to a lesser extent, S_4^{1-} groups, with the possible presence of additional H_2O and H_2S . The possibility that bazhenovite and the mineral here examined could represent two distinct phases differing slightly from each other with respect to the thiosulfate content is discussed.