

Insights into the structure of disordered layered lead oxychlorides: Twinning and short-range order in janchevite, $\text{Pb}_9\text{VO}_{10.25}\square_{0.75}\text{Cl}_{2.5}$

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ABSTRACT

The crystal structure of the rare mineral janchevite was solved using intensity data collected from a twinned crystal from the Kombat mine in Namibia. This study revealed that, despite the strong tetragonal subcell, the structure is triclinic (space group $P\bar{1}$) with $a = 8.8382(7)$, $b = 8.8567(7)$, $c = 11.7103(17)$ Å, $\alpha = 103.385(10)$, $\beta = 94.192(10)$, $\gamma = 90.294(6)^\circ$, $V = 889.13(16)$ Å³, and $Z = 2$. Chemical data indicate the presence of Mo, As, and Si, besides Pb, Cl, O, and V. The refinement of an anisotropic model, which takes into account a two-domain non-merohedral twinning (twinning matrix $|\bar{1}00/0\bar{1}0/1/2 \ 1/2 \ 1|$), led to an $R = 0.0522$ for 6037 independent observed reflections [$2\sigma(I)$ level] and 165 parameters and an $R = 0.0964$ for all 11 701 independent reflections. The structure consists of PbO litharge sheets alternating with a layer of Cl[−] anions in a 2:1 ratio. The incorporation of high-charge cations (V⁵⁺, Mo⁶⁺, As⁵⁺, Si⁴⁺) into the litharge sheet involves the formation of square cavities where MoO₅ square pyramids and (Si,As,V)O₄ tetrahedra are hosted. On the basis of information gained from the chemical, structural, and spectroscopic characterization, the crystal chemical formula was revised to $\text{Pb}_9\text{VO}_{10.25}\square_{0.75}\text{Cl}_{2.5}$ ($Z = 2$). The presence of additional apical O atoms between Pb layers influences the interlayer thickness, as evidenced by the linear correlation between the interlayer oxygen content and the type of structural defects. A correct comprehension of short- and long-range order is crucial to understanding and predicting the functional properties of this family of materials.

Keywords: Janchevite, crystal structure, short-range order, layered lead oxychloride, Kombat mine, Namibia