

## On the crystal chemistry of sulfur-rich lazurite, ideally $\text{Na}_7\text{Ca}(\text{Al}_6\text{Si}_6\text{O}_{24})(\text{SO}_4)(\text{S}_3)^{\cdot-} \cdot n\text{H}_2\text{O}$

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### ABSTRACT

Dark blue lazurite from the Malo-Bystrinskoe lazurite deposit, Baikal Lake area, Eastern Siberian region, Russia, was analyzed by electron microprobe and revealed an unusually high content of total sulfur corresponding to 8.3 wt% S. The relative content of sulfur in sulfate and sulfur in sulfide form was determined by wet chemical analysis. The H<sub>2</sub>O content was measured by means of differential thermal analysis in combination with mass spectrometry and infrared (IR) spectroscopy. The charge-balanced empirical formula of lazurite calculated on the basis of 12 (Al+Si) atoms per formula unit was  $(\text{Na}_{6.97}\text{Ca}_{0.88}\text{K}_{0.10})_{\Sigma 7.96}[(\text{Al}_{5.96}\text{Si}_{6.04})_{\Sigma 12}\text{O}_{24}](\text{SO}_4)_{1.09}^{2-}(\text{S}_3)_{0.55}\text{S}_{0.05}^{2-}\text{Cl}_{0.04} \cdot 0.72\text{H}_2\text{O}$ . The presence of H<sub>2</sub>O molecules and (S<sub>3</sub>)<sup>·-</sup> and (SO<sub>4</sub>)<sup>2-</sup> groups was confirmed by the combination of IR, Raman, electron paramagnetic resonance (EPR), and X-ray photoelectron spectroscopy (XPS) methods. The idealized formula of lazurite is  $\text{Na}_7\text{Ca}[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)^{2-}(\text{S}_3)^{\cdot-} \cdot \text{H}_2\text{O}$ , and it is believed that extra-framework cations and anions are grouped into clusters of  $[\text{Na}_3\text{Ca} \cdot \text{SO}_4]^{3+}$  and  $[\text{Na}_4(\text{S}_3)^{\cdot-}]^{3+}$ . The types of isomorphous substitutions in nosean and hauyne are discussed. Lazurite is a clathrate-type mineral, which may be an effective (S<sub>3</sub>)<sup>·-</sup> sensor due to the stability of the trisulfur radical anion in isolated cages of the crystal structure. This specific feature makes it possible to study the behavior of this ubiquitous radical anion over larger *T* and *P* ranges as compared to free species. This kind of lazurite, with oxidized and reduced sulfur species, seems to be appropriate for the estimation of the fugacity of SO<sub>2</sub> and O<sub>2</sub> in metasomatic systems forming lazurite-containing rocks. The systematic presence of incommensurate modulations is a unique structural feature of Baikal lazurite and may be an important marker indicating provenance of the mineral.

**Keywords:** Microporous mineral structure, lazurite, sulfide radical ion, X-ray diffraction, spectroscopy, superstructure