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On the labyrinthine crystal-chemistry of boleite, a Pb-Ag-Cu hydroxyhalide

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Abstract

The chemical composition and crystal structure of boleite from the Amelia Mine (Boléo District, Mexico) were investigated by a series of chemical analytical techniques and single-crystal X-ray (data collected at 293 K) and neutron diffraction (at 20 K). The concentrations of more than 60 elements were measured. The empirical formula of boleite, based on the multi-analytical approach, is: $(K_{0.390}Ca_{0.165}Na_{0.095}Rb_{0.075}Cd_{0.040}Cs_{0.035}Tl_{0.002})_{\Sigma 0.80}Pb_{26.05}Ag_{8.93}Cu_{23.91}Cl_{61.64}(OH)_{48.39}$, of which the simplified formula should be given as $(K,Ca,Na,Rb,Cd,Cs)Pb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$. However, as Cd can also be considered as a potential substituent for Ag or Cu, the simplified formula transforms to $(K,Ca,Na,Rb,Cs)Pb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$. This finding indicates a more complex scenario with respect to the previous formula reported in the literature, i.e., $KPb_{26}Ag_9Cu_{24}Cl_{62}(OH)_{48}$. Chemical data obtained in this study show no significant evidence of potential substituents of Pb, Ag, and Cu; the concentrations of REE, PGE, and other industrially relevant elements are insignificant. Despite a lack of crystallographic evidence, chemical data appear to suggest that partial Cl^- vs. OH^- substitution can occur. Other potential substituents of Cl^-, such as F^-, have not been detected at a significant level. X-ray and neutron diffraction data confirm the previously reported general structural model of boleite but consistently show that a substitutional disorder affects the *K* site, manifested by a large and unusual displacement parameter. The magnitude of the displacement parameter reflects static disorder, in the form of substitutional disorder, due to differences in the local bonding topology among K, Ca, Na, Rb, (Cd), and Cs statistically populating the same site. The H-bonding network in the structure of boleite is now unambiguously described on the basis of the neutron structural model, with two energetically favorable bonds, both having an O_{donor}-H···$Cl_{acceptor}$ configuration. The structure of boleite does not contain H_2O molecules but, instead, only two crystallographically independent hydroxyl groups.

Keywords: Boleite, crystal chemistry, X-ray diffraction, neutron diffraction, hydrogen bonding