

A single-crystal X-ray and Raman spectroscopic study of hydrothermally synthesized arsenates and vanadates with the descloizite and adelite structure types

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ABSTRACT

Studying the reason for the formation of two structural sub-types, seven arsenate and vanadate compounds of descloizite and adelite groups [specifically (1) CdCo(OH)(AsO₄), (2) CdCu(OH)(AsO₄), (3) SrCo(OH)(AsO₄), (4) SrZn(OH)(AsO₄), (5) SrCu(OH)(VO₄), (6) CdCo(OH)(VO₄), and (7) CdCu(OH)(VO₄) (bold numbers throughout paper refer to these compounds)] were synthesized under low-temperature hydrothermal conditions. 1–2 and 6–7 are isostructural with descloizite, and 3–5 are with adelite-group minerals and several synthetic compounds. Together with a sample of conichalcite, (8) CaCu(OH)(AsO₄), they were investigated using single-crystal X-ray diffraction [$R(F)$ = 0.0153–0.0283 for 1–5 and 8; for 6 and 7, $R(F)$ = 0.0603 and 0.0444, respectively] and Raman spectroscopy. Although crystallizing in different orthorhombic space groups, the atomic arrangements of descloizite- $(Pnam)$ and adelite- $(P2_12_12_1)$ type compounds adopt the same topology: the atomic arrangement is characterized by $M2O_6$ octahedrons ($M2 = Mg^{2+}, Al^{3+}, Mn^{2+,3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}$) edge-linked into chains. These chains are interconnected by XO_4 tetrahedrons ($X = Si^{4+}, P^{5+}, V^{5+}, As^{5+}, Mo^{6+}$) into a three-dimensional framework. Cavities host $M1$ atoms ($M1 = Na^+, Ca^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}$); their coordination varies from 7 for descloizite-type representatives to 8 for adelite-type structures. The OH stretching frequencies in the Raman spectra are in good agreement with the observed O–H···O donor-acceptor distances. A detailed discussion of the crystal chemistry of these compounds and their influence on the space-group symmetry indicate a distinct dependence of the structural changes on the average ionic radii $(r_{M1} + r_X)/2$.

Keywords: Crystal structure, XRD data, crystal growth, Raman spectroscopy