

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 [$R(F) = 0.0153\text{--}0.0283$ 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-(*P2₁2₁2₁*) type compounds adopt the same topology: the atomic arrangement is characterized by M_2O_6 octahedrons ($M_2 = Mg^{2+}$, 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 M_1 atoms ($M_1 = Na^+$, 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 ($r_{M_1} + r_X$)/2.

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