

## Raman spectra of adelite-descloizite group compounds and crystal structure of SrZn(OH)(AsO<sub>4</sub>)

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In order to understand the role of arsenic in the environment, one has to investigate structural features and stabilities of naturally occurring arsenic compounds. In addition, a study of mineral-related synthetic phases should be very helpful because they can appear as a result of human activities. SrCo(OH)(AsO<sub>4</sub>) (SrCoAs), SrZn(OH)(AsO<sub>4</sub>) (SrZnAs), CdCo(OH)(AsO<sub>4</sub>) (CdCoAs), CdCu(OH)(AsO<sub>4</sub>) (CdCuAs) were hydrothermally synthesised (Teflon-lined steel autoclaves, 493 K, 3–4 days) during an on-going research on natural and synthetic arsenates, with a focus on their structural and spectroscopic classification. Additionally, a sample of conichalcite, Ca(Cu<sub>0.97</sub>Zn<sub>0.02</sub>Mg<sub>0.01</sub>)(OH)[(As<sub>0.97</sub>P<sub>0.3</sub>)O<sub>4</sub>] (CaCuAs) from the Maria Catalina mine, Copiapó Province, Chile and hydrothermally synthesised SrCu(OH)(VO<sub>4</sub>) (SrCuV) were investigated in the course of this study.

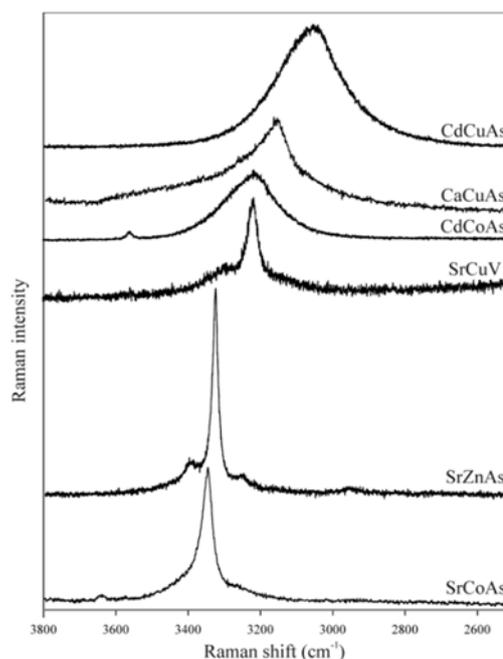
Adelite-descloizite group of orthorhombic compounds adopt general formula  $M1^{1+,2+}M2^{2+,3+}(\text{OH},\text{O})[X^{4+,5+,6+}(\text{O}_4,\text{O}_3\text{OH})]$  ( $M1 = \text{Na}^+, \text{Ca}^{2+}, \text{Cd}^{2+}, \text{Pb}^{2+}$ ;  $M2 = \text{Mg}^{2+}, \text{Al}^{3+}, \text{Mn}^{2+,3+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$ ;  $X = \text{Si}^{4+}, \text{P}^{5+}, \text{V}^{5+}, \text{As}^{5+}, \text{Mo}^{6+}$ ). More than 16 minerals belong to this group, but synthetic compounds are relatively rare. The parental structure is centrosymmetric (s.g. *Pnma*) - *descloizite type* (named after the mineral descloizite, PbZn(OH)(VO<sub>4</sub>)); it shows [7]-coordination of the *M1* cation. A slight deviation from the parental structure yields an acentric structure variant (s.g. *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>*) - *adelite type* (named after the mineral adelite, CaMg(OH)(AsO<sub>4</sub>)); it shows [8]-coordination of the *M1* cation.

The crystal structure of SrZnAs was determined using single-crystal X-ray diffraction data (MoK $\alpha$  radiation, 293 K,  $2\theta_{\text{max}} = 60^\circ$ ). It crystallise as adelite-type compound in space group *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* ( $a = 7.6454(12)$ ,  $b = 9.2632(19)$ ,  $c = 6.0298(12)$  Å,  $V = 427.04(14)$  Å<sup>3</sup>,  $Z = 4$ ). Its structure was refined starting from the atomic coordinates of CaZn(OH)(AsO<sub>4</sub>) (Clark et al. 1997). The refinement yielded  $R1(F) = 0.019$ ,  $wR2(F^2) = 0.035$  for 1242 unique reflections; for 1194 ‘observed reflections’ with  $F_o^2 \geq 4\sigma(F_o^2)$   $R1(F)$  is 0.022. The structure was refined from a merohedral twin (twin ratio 0.446(14):0.554(14)). The H atoms were found from a difference Fourier map and refined isotropically. The octahedrally coordinated Zn atoms, are linked by O–O edges to chains parallel [100]:  $\langle \text{Zn–O} \rangle = 2.132$  Å. Each of the AsO<sub>4</sub> tetrahedra links such chains to a 3D framework:  $\langle \text{As–O} \rangle = 1.690$  Å. SrO<sub>7</sub>(OH) square antiprisms are located in these cavities. The hydrogen bond O–H $\cdots$ O is 2.680(5) Å. The structural studies of the other five samples have already been undertaken (Đorđević 2007; Đorđević and Kolitsch 2008; Effenberger 2002). CdCoAs and CdCuAs crystallise in descloizite type, while the other four compounds crystallise in adelite type.

To obtain further information on the anion groups and especially on hydrogen bonds Raman spectra were acquired. Un-polarised Raman spectra of CaCuAs and SrCoAs were obtained with a Renishaw RM1000 system using He-Ne 632.8 nm emission, and a Horiba LabRAM-HR800 spectrometer using the 473 nm emission of a diode laser or the He-Ne 632.8 nm line.

The Raman spectra reflect the complexity of the crystal structures under discussion. The distinct frequency ranges may be assigned as described below.

Band in the O–H stretching region (4000–2500  $\text{cm}^{-1}$ ): According to the  $d-\nu$  correlation for hydrogen bonds (Libowitzky 1999) the stretching frequencies are in very good agreement with the refined Oh–H $\cdots$ O bond lengths of 2.622 (4) Å for CdCuAs (3051  $\text{cm}^{-1}$ ), 2.688(2) Å for CaCuAs (3162  $\text{cm}^{-1}$ ), 2.670(6) Å for CdCoAs (3217  $\text{cm}^{-1}$ ), 2.757(4) Å for SrCuV (3217  $\text{cm}^{-1}$ ), 2.680(5) Å for SrZnAs (3300  $\text{cm}^{-1}$ ) and 2.766(3) Å for SrCoAs (3345  $\text{cm}^{-1}$ ). Figure 1 shows the Raman spectra of the hydroxyl stretching region of the six investigated compounds. The major band for CaCuAs is observed at 3162  $\text{cm}^{-1}$ , which is in a very good agreement with the position of the 3158  $\text{cm}^{-1}$  conichalcite band from Lorena mine, Queensland, Australia (Martens et al. 2003). The major band for SrCoAs is observed at 3345  $\text{cm}^{-1}$  and one very weak band at 3640  $\text{cm}^{-1}$ . For SrZnAs strong and sharp band was observed at 3330  $\text{cm}^{-1}$  and further two weak bands are observed at 3398 and 3254  $\text{cm}^{-1}$ . For the SrCuV major band was observed at 3217  $\text{cm}^{-1}$  and the second very weak and broad band was observed at 3297  $\text{cm}^{-1}$ . The bands for CdCoAs are observed at 3217 and 3560  $\text{cm}^{-1}$ , and for CdCuAs, one broad and intensive band at 3051  $\text{cm}^{-1}$  was observed. It may be concluded that the type of  $M2$  cation plays an important role in the position of the hydroxyl stretching bands. The smaller cation on  $M2$  position shifts the hydroxyl stretching bands to higher wavenumbers. If we compare the position of the OH stretching bands of SrCuV, with that of mottramite, PbCu(OH)(VO $_4$ ) at 3548 and 3515  $\text{cm}^{-1}$  (Frost et al. 2001), the same applies to the  $M1$  cation.



The 1500–700  $\text{cm}^{-1}$  range shows the As–O stretching modes of the (AsO $_4$ ) $^{3-}$  groups. The most intense Raman bands are around 820 and 800  $\text{cm}^{-1}$  for SrCoAs, 818, 804 and 790  $\text{cm}^{-1}$  for SrZnAs, 823 and 797  $\text{cm}^{-1}$  for CdCoAs, 833 and 824  $\text{cm}^{-1}$  for CaCuAs and for CdCuAs at 834 and 809  $\text{cm}^{-1}$ . They are in excellent agreement with each other and with the adelite-group minerals (Martens et al. 2003). For SrCuV, V–O stretching modes are around 840, 821 and 805  $\text{cm}^{-1}$  and correlate very good with vanadate representatives of the descloizite group minerals (Frost et al. 2001). In the region below 550  $\text{cm}^{-1}$  appear the bending modes of the (AsO $_4$ ) $^{3-}$  groups, and various external lattice modes of the compounds.

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