

Phosphate substitution in synthetic schultenite PbHAsO_4 : vibrational spectroscopic study

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Synthetic schultenite PbHAsO_4 and its phosphate analogue PbHPO_4 have been extensively studied due to their ferroelectric properties. They have also been found to occur in Earth's surface environments. Although the natural occurrence of PbHPO_4 has not been well documented yet, the experimental works showed that both phases can form a continuous solid solution series. Raman and infrared (IR) spectroscopy are complementary analytical techniques that enable the identification and semi-quantitative analysis of the molecular compositions; therefore, they should prove useful for investigation of such solid solutions. In this study, a total of six compounds of the PbHAsO_4 – PbHPO_4 solid solution series were synthesized from aqueous solutions at ambient conditions and characterized using Raman and IR spectroscopy. The results showed that the positions and band shape in both Raman and IR spectra depend on the extent of phosphate substitution making it possible to estimate the overall P/(P+As) ratio in synthetic or natural samples based on their detailed vibrational spectroscopic study. In Raman spectra, the band originating from the stretching vibrations (ν_3) of As–O bonds shifts linearly with increasing P content towards higher wavenumbers (823–838 cm^{-1}), while the peak ν_1 shifts inversely (798–790 cm^{-1}) resulting in broadening of the entire band. The bands originating from the stretching vibrations of P–O bonds shift linearly from 1011 to 1034 cm^{-1} (ν_3) and from 902 to 938 cm^{-1} (ν_1) with increasing P content. The systematic changes in band positions result partly from increasing average X–O bond strength and partly from decreasing average molecular weight of XO_4 (where X=As, P). The IR data support the interpretation of the Raman spectra, but phosphate substitution has a stronger effect on the shape of the IR bands, and therefore, the peak position shifts are less consistent. Moreover, the vibrational modes ν_1 are weakly active and the corresponding bands occur as shoulders to ν_3 peaks. Additionally, the IR bands in the range from ~2750 to ~1330 cm^{-1} suggest medium strong O–H–O bonds as well as an off-center location of the hydrogen in the crystal structure.

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