

**SYNTHESIS, CRYSTAL STRUCTURE, INFRARED AND RAMAN SPECTRA OF
 $\text{Sr}_5(\text{As}_2\text{O}_7)_2(\text{AsO}_3\text{OH})$**

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The new compound $\text{Sr}_5(\text{As}_2\text{O}_7)_2(\text{AsO}_3\text{OH})$ was synthesized under hydrothermal conditions. It represents a previously unknown structure type and it is the first substance known to contain both $(\text{As}_2\text{O}_7)^{4-}$ and $(\text{AsO}_3\text{OH})^{2-}$ groups.

The crystal structure of $\text{Sr}_5(\text{As}_2\text{O}_7)_2(\text{AsO}_3\text{OH})$ was determined by single-crystal X-ray diffraction (293 K, $\text{MoK}\alpha$, $2\theta_{\text{max}} = 60^\circ$): space group $P2_1/n$ ($a = 7.146(1)$, $b = 7.142(1)$, $c = 32.750(1)$ Å, $\beta = 93.67(3)^\circ$, $V = 1668.0(5)$ Å³, $Z = 4$). It is built from five crystallographically unique SrO_{6-8} polyhedra and two $(\text{As}_2\text{O}_7)^{4-}$ groups besides a protonated $(\text{AsO}_3\text{OH})^{2-}$ group. $(\text{As}_2\text{O}_7)^{4-}$ groups involve four crystallographically non-equivalent $(\text{AsO}_4)^{3-}$ tetrahedra. The position of the hydrogen atom was located experimentally. To obtain further information on the anion groups and especially on the very short hydrogen bond length of 2.494(4) Å, where the donor and acceptor atoms are not equal due to (average) space-group symmetry, infrared and Raman spectra were acquired.

The IR spectral region between 3500 and 1000 cm^{-1} shows a peculiar increase in "background absorption", which is a typical feature of compounds with very short hydrogen bonds. It represents an extremely broad (FWHM ~ 1000 cm^{-1}) and low-energetic band that is assigned to the OH stretching mode of the $(\text{AsO}_3\text{OH})^{2-}$ group. It is quite characteristic that this band can be observed only in one of the polarized spectra, whereas it is absent in the other polarization directions and almost invisible in powder spectra. The former is caused by the preferred orientation of the OH vectors in the structure. Because of the broad band shape, As—O tetrahedral stretching vibrations and lattice modes are superimposed in the low-energy region of the spectrum (stretching modes < 1100 cm^{-1} ; bending + lattice modes < 450 cm^{-1}). The large FWHM aggravates a precise determination of the band center, which is estimated to be roughly at $\sim 1600 \pm 200$ cm^{-1} . According to the d — ν correlation for hydrogen bonds (NOVAK, 1974; LIBOWITZKY, 1999) this wavenumber is in excellent agreement with the refined O_h — $\text{H}\cdots\text{O}$ bond length. The sharp and truncated band at ~ 1250 – 1300 cm^{-1} in the IR powder spectrum is assigned to the bending mode of the OH group and it corresponds with typical bending frequencies of strongly H bonded hydroxyl groups (NOVAK, 1974; BERAN & LIBOWITZKY, 1999).

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References

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