

$M^{3+}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}$ ($M = \text{In, Ga}$), TWO SYNTHETIC ANALOGUES OF THE IRON HYDROGENARSENATE MINERAL KAATIALAITE

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Kaatialaite, $\text{Fe}^{3+}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}$ (RAADE et al., 1984), is a rare iron hydrogenarsenate mineral that typically occurs as a supergene phase at very low pH. Its crystal structure is known from a synthetic analogue (BOUDJADA & GUITEL, 1981), although it appears that the water content of the natural material is variable, with 3-5 H_2O per formula unit (RAADE et al., 1984).

The Ga- and In-analogues of kaatialaite are, similar to kaatialaite itself, secondary phases grown in a highly acidic environment. They were encountered during a reinvestigation of the primary reaction products, stored in plastic boxes in air, of hydrothermal syntheses conducted about 11 years ago during an extensive study of the system $M^{1+}\text{-}M^{3+}\text{-As-O-H}$ (SCHWENDTNER, 2008).

Previously unknown $\text{In}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}$ grew as tiny subparallel acicular crystals in small droplets of a very acidic solution formed from hygroscopic acid arsenates (syntheses in systems $M^+\text{-In-As-O-H}$). The compound was characterised by a structure refinement ($R \sim 5.8\%$) from single-crystal XRD data (MoK α ; 293 K). Since the crystal was gradually decomposing during the measurement, until it was completely X-ray amorphous (probably due to dehydration), additional low-temperature measurements will be conducted.

$\text{Ga}(\text{H}_2\text{AsO}_4)_3 \cdot \sim 5\text{H}_2\text{O}$ is a fine-grained decomposition product of synthesised $\text{Ti}_3\text{Ga}_2\text{-(HAs}_2\text{O}_7)_3 \cdot n\text{H}_2\text{O}$ and formed after immersion and grinding of the latter compound in acetone for several minutes. Comparison of the powder XRD pattern gave a good fit for “ $\text{Ga}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}$ ” (“blank” ICDD-PDF file; RONIS et al., 1972). Using the model of BOUDJADA & GUITEL (1981) as a starting point, a Rietveld refinement led to $R_{\text{wp}} = 10\%$.

Most hydrogen bonds in both In- and Ga-analogues appear to be split, in view of multiple possible acceptor atoms ($\text{O} \dots \text{O} < 3.0 \text{ \AA}$). Unit-cell parameters of all compounds are compared in the table below [¹RAADE et al (1984) for synthetic material, refined from powder XRD data; ²BOUDJADA & GUITEL (1981), single-crystal structure determination].

Compound	SG	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	β [°]	<i>V</i> [Å ³]
$\text{Fe}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}^1$	<i>P</i> 2 ₁ or <i>P</i> 2 ₁ / <i>m</i>	15.363(5)	19.844(5)	4.736(2)	91.77(3)	1443.2(9)
$\text{Fe}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}^2$	<i>P</i> 2 ₁ / <i>n</i>	15.25(3)	19.60(5)	4.72(5)	91.8(8)	1410.1(1)
$\text{In}(\text{H}_2\text{AsO}_4)_3 \cdot 5\text{H}_2\text{O}$	<i>P</i> 2 ₁ / <i>n</i>	15.514(3)	19.901(4)	4.890(1)	91.51(3)	1509.2(5)
$\text{Ga}(\text{H}_2\text{AsO}_4)_3 \cdot \sim 5\text{H}_2\text{O}$	<i>P</i> 2 ₁ / <i>n</i>	15.3206(8)	19.7843(1)	4.6850(3)	91.956(4)	1419.3(1)

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