

NOVEL COMPOUNDS IN THE SYSTEM $M^{1+}M^{3+}(\text{HAsO}_4)_2$ ($M^{1+} = \text{Li, Na, K, Rb, Cs, Ag, Tl}$; $M^{3+} = \text{Al, Ga, In, Sc, Cr, Fe}$) – AN OVERVIEW

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Arsenates tend to form stable framework structures, similarly to phosphates and silicates. While the latter have been studied extensively and are used in a variety of technical applications, arsenates have been somewhat neglected so far although microporous arsenates, with promising zeolite-like properties together with superior thermal stabilities of up to 650 °C, have been reported (e.g. HUANG et al., 1999). Therefore, an extensive study in search of new compounds and structure types in the system $M^{1+}M^{3+}(\text{HAsO}_4)_2$ was initiated. $M^{1+}\text{CO}_3$, $M^{3+}_2\text{O}_3$, H_3AsO_4 und H_2O were used as starting materials for hydrothermal syntheses at 220°C (7 d, pH 0.5-2). The crystal structures of the following new, mixed T-O-framework-compounds were solved by single-crystal X-ray diffraction:

$\text{TlFe}(\text{HAsO}_4)_2$ ($a = 7.346$, $b = 9.148$, $c = 9.662$ Å, $\alpha = 64.89$, $\beta = 70.51$, $\gamma = 69.94$, $V = 538.6$ Å³, $Z = 3$) and $\alpha\text{-CsSc}(\text{HAsO}_4)_2$ (SCHWENDTNER & KOLITSCH, 2004a) crystallize in the triclinic space group $P\bar{1}$. Both compounds are the first arsenates adopting the $(\text{NH}_4)\text{Fe}(\text{HPO}_4)_2$ -structure type which was originally described by YAKUBOVICH (1993). A second Cs-Sc-arsenate, $\beta\text{-CsSc}(\text{HAsO}_4)_2$ (SCHWENDTNER & KOLITSCH, 2004a), is the first arsenate having the monoclinic ($P2_1/c$) structure type of $(\text{H}_3\text{O})\text{Fe}(\text{HPO}_4)_2$ (VENCATO et al., 1989). The monoclinic compound $\text{KSc}(\text{HAsO}_4)_2$ (SCHWENDTNER & KOLITSCH, 2004b) represents a novel microporous structure type with space-group symmetry $C2/c$. The recently synthesized compound $\text{AgGa}(\text{HAsO}_4)_2$ ($a = 7.826$, $b = 10.216$, $c = 8.694$ Å, $\beta = 107.77$, $V = 661.9$ Å³, $Z = 4$) crystallizes in the same structure type.

A further framework structure characterized by a very long c -axis is adopted by the following new hydrogenarsenates: $\text{RbFe}(\text{HAsO}_4)_2$, $\text{RbGa}(\text{HAsO}_4)_2$, $\text{RbIn}(\text{HAsO}_4)_2$, $\text{CsIn}(\text{HAsO}_4)_2$ ($R\bar{3}c$, $a = 8.425 / 8.385 / 8.512 / 8.629$, $c = 54.749 / 53.880 / 56.434 / 56.986$ Å, $V = 3365.5 / 3280.7 / 3541.1 / 3674.7$ Å³, $Z = 18$) are isotypic to $\text{RbFe}(\text{HPO}_4)_2$ (LII & WU, 1994) and represent the first arsenates crystallizing in this rhombohedral structure type.

All these arsenates form microporous mixed T-O-framework structures, which are characterized by intersecting tunnels containing the M^{1+} -cations. Therefore, further studies addressing the ion exchange properties of these novel compounds are planned. Investigations of the thermal stabilities as well as IR-spectroscopic studies will be discussed.

References

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