

**CRYSTAL CHEMISTRY OF THE ALUNITE SUPERGROUP: HYDROTHERMAL SYNTHESIS AND CRYSTAL STRUCTURES OF THE CHROMATES  $\text{KSc}_3(\text{CrO}_4)_2(\text{OH})_6$ ,  $\text{KIn}_3(\text{CrO}_4)_2(\text{OH})_6$  AND  $\text{RbIn}_3(\text{CrO}_4)_2(\text{OH})_6$**

**Kolitsch, U.<sup>1</sup>, Schwendtner, K.<sup>1</sup> & Pring, A.<sup>2</sup>**

<sup>1</sup> Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, Althanstr. 14, 1090 Wien, Austria

<sup>2</sup> Department of Mineralogy, South Australian Museum, North Terrace, Adelaide, SA 5000, Australia

e-mail: uwe.kolitsch@univie.ac.at

Three new alunite-type chromates,  $\text{KSc}_3(\text{CrO}_4)_2(\text{OH})_6$ ,  $\text{KIn}_3(\text{CrO}_4)_2(\text{OH})_6$  and  $\text{RbIn}_3(\text{CrO}_4)_2(\text{OH})_6$ , have been grown as well-developed, thick tabular to pseudo-octahedral crystals by hydrothermal synthesis (starting materials:  $\text{K}_2\text{CO}_3/\text{Rb}_2\text{CO}_3$ ,  $\text{Sc}_2\text{O}_3/\text{In}_2\text{O}_3$ ,  $\text{CrO}_3$  and distilled water; Teflon vessels in stainless-steel bombs,  $T = 220^\circ\text{C}$ , 7 d, pH range = 2-4). They represent the first structurally characterised Sc and In members of the large alunite supergroup (e.g., KOLITSCH & PRING, 1996; JAMBOR, 1999). The crystal structures were refined from single-crystal intensity data (Mo- $K\alpha$  X-radiation, CCD area detector,  $2\theta_{\text{max}} = 70^\circ$ ). The new members adopt the alunite parent structure type [rhombohedral, space group  $R\bar{3}m$  (no. 166)], with  $a = 7.763(1) / 7.813(1) / 7.817(1)$ ,  $c = 17.575(3) / 17.682(3) / 18.075(3)$  Å and  $V = 917.2(2) / 934.8(2) / 956.5(2)$  Å<sup>3</sup> ( $Z = 3$ ), and  $R(F) = 1.36 / 1.21 / 1.23$  %, respectively. The H atoms could be clearly detected in each compound and were freely refined. Hydrogen bonds are all within a very close range (2.981 - 3.020 Å). All alkali and Sc/In sites are fully occupied, and the alkali atoms are not positionally disordered. Average bond lengths are as follows:  $^{121}\text{K}-\text{O} = 3.003$ ,  $^{61}\text{Sc}-\text{O} = 2.106$ , and  $\text{Cr}-\text{O} = 1.653$  Å (KSc);  $^{121}\text{K}-\text{O} = 3.000$ ,  $^{61}\text{In}-\text{O} = 2.145$ ,  $\text{Cr}-\text{O} = 1.653$  Å (KIn);  $^{121}\text{Rb}-\text{O} = 3.051$ ,  $^{61}\text{In}-\text{O} = 2.147$  and  $\text{Cr}-\text{O} = 1.653$  Å (RbIn). The average Cr-O bond distances are identical within error limits and longer by 0.01 Å than those in  $\text{KFe}_3(\text{CrO}_4)_2(\text{OH})_6$  (1.643 Å; CUDENNEC et al., 1980).

Alunite-type Cs analogues could not be synthesised, in agreement with the fact that no Cs compound with the alunite topology is known. Instead, orthorhombic  $\text{CsSc}(\text{CrO}_4)_2$  [ $\text{CsCr}^{3+}(\text{Cr}^{6+}\text{O}_4)_2$ -type] and monoclinic  $\text{CsIn}(\text{CrO}_4)_2$  [ $(\text{NH}_4)\text{Fe}(\text{CrO}_4)_2$ -type] were obtained. The two alunite-type In chromates synthesised were accompanied by very small amounts of  $\text{In}(\text{OH})_3$  as an impurity phase.

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**References**

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