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Structure of Na₄OI₂

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Abstract. Na₄OI₂, $M_r = 361.77$, tetragonal, $I4/mmm$, $a = 4.655(2)$, $c = 15.940(4)$ Å, $V = 345.4$ Å³, $Z = 2$, $D_x = 3.479$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 86.4$ cm⁻¹, $F(000) = 316$, $T = 294$ K, $R = 0.0448$ for 172 unique reflections with $F > 3\sigma(F)$. The compound crystallizes in the anti-K₂MgF₄ structure type and is of different stoichiometry to the ternary phases of sodium oxide halides with chlorine or bromine as halogen; the phases observed for these systems, Na₃OCl and Na₃OBr respectively, crystallize in the anti-perovskite structure type.

Introduction. Recently we described the preparation of Na₄OI₂ as part of our investigations into the existence of ternary alkali-metal chalcogenide halides (Sabrowsky, Hippler & Vogt, 1989). The structures of Na₃OCl and Na₃OBr (Sabrowsky, Paszkowski, Reddig & Vogt, 1988) which crystallize in the anti-perovskite structure type led us to question whether related structures (for example those of K₂NiF₄ type) also exist. In agreement with the relations between the radii of metal ions given by Goldschmidt (1926), a considerable number of such compounds can be expected.

In the meantime we succeeded in preparing single crystals of Na₄OI₂. The results of the single-crystal structure determination are presented here.

Experimental. Na₄OI₂ can be obtained by sintering a stoichiometric mixture of Na₂O and NaI in closed silver crucibles at 830 K in an argon atmosphere ($p = 0.3$ MPa) leading to polycrystalline samples. However, well shaped colourless single crystals can only be grown from a mixture with 100% excess of Na₂O in corundum crucibles. We assume that the excess of Na₂O reacts with the crucible material, since the product obtained is a pure phase, as determined by X-ray powder measurements. The compound decomposes in moist air.

A plate-like crystal of approximate dimensions 0.3 × 0.3 × 0.1 mm was used for the data collection. Space group and cell parameters determined by powder and Weissenberg methods; cell dimensions refined by least-squares analysis of 25 diffraction maxima with θ range 12.43–19.95°. The four-circle diffractometer used was a Philips PW1100/15. A total of 1773 reflections was measured with the ω - 2θ scan technique ($hkl, \bar{h}kl$; $1.5 \leq 2\theta \leq 60^\circ$). Three standard reflections monitored every 2 h showed constant intensities. The data were corrected for Lorentz and polarization effects; empirical absorption correction by final $F_o - F_c$ comparison using the

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program *DIFABS* (Walker & Stuart, 1983). Max., min. transmission factors 0.792, 0.241. Refinement on *F* with anisotropic parameters led to the atomic parameters given in Table 1.* Starting values for the refinement cycles were the corresponding ones of the K_2NiF_4 structure. The program used was *SHELX76* (Sheldrick, 1976). $R = 0.0448$; $wR = 0.0389$; $w = 1/\sigma^2(F)$. $|\Delta/\sigma|_{\max} = 0.002$. Max. and min. heights in final difference Fourier synthesis $+2.6/-1.5 e \text{ \AA}^{-3}$. Atomic scattering factors from *SHELX*. Selected interatomic distances are listed in Table 2. A schematic representation of the structure is given in Fig. 1(a).

Discussion. Na_4OI_2 crystallizes in the anti- K_2NiF_4 structure type which is related to the anti-perovskite structure. In Fig. 1(b) a formal development of the Na_4OI_2 structure from the hypothetical anti-perovskite Na_3OI structure is shown. It can be derived from one unit cell of the anti-perovskite structure with the O atoms at the center combined with two unit cells with the I atoms at the center and with two ONa_2 layers removed. The O atoms are coordinated octahedrally by Na atoms. The two crystallographically different Na atoms are also octahedrally coordinated. One octahedron is of type NaO_2I_4 , the second of type $NaOI_5$. The coordination of the I atoms is ninefold. It occupies approximately the basal plane of a quadratic Na_5 pyramid covered by a Na_4 quadrangle, which is twisted about 45° to the base of the pyramid.

It is interesting to note that such a structure can be built up with low-charged ions because up to now it has only been verified in the cases of Ba_4OAs_2 (Taylor, Calvert, Utsunomiya, Wang & Despault, 1978) and Ca_4OSb_2 (Eisenmann, Limartha & Schäfer, 1980) with higher-charged ions. These structures as well as those of the alkali-metal oxide halides Na_4OI_2 , Na_3OCl and Na_3OBr are in agreement with the rules given by Goldschmidt (1926) since the ratio of the radii of the atoms involved are quite comparable. Recently (Sabrowsky, Paszkowski, Reddig & Vogt, 1988), we gave a listing of the tolerance factors for all M_3OX compounds ($M =$ alkali metal, $X =$ halide) assuming anti-perovskite structures calculated on the basis of the radii given by Shannon & Prewitt (1970). Taking these considerations as a basis one would expect that Na_3OI is also possible. For instance, different structure types exist in the system (K, Mg, F), (Sr, Ti, O), and (Sr, Mo, O) (Balz & Plieth, 1955).

The structure of Na_4OI_2 shows that the ratio of the atomic radii plays an important role in answering

* Lists of structure factors and anisotropic atomic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52385 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic parameters for Na_4OI_2

	x	y	z	$U_{eq} (\text{\AA}^2)$
Na(1)	0	0.5	0	0.0250 (24)
Na(2)	0	0	0.1429 (6)	0.0272 (20)
O(1)	0	0	0	0.0187 (42)
I(1)	0	0	0.3467 (1)	0.0203 (4)

Table 2. Interatomic distances (\AA) for Na_4OI_2

Na(1)—O(1)	2.327	2 ×	Na(2)—O(1)	2.278 (9)
Na(1)—I(1)	3.374 (1)	4 ×	Na(2)—I(1)	3.249 (9)
Na(1)—Na(1)	3.292	4 ×	Na(2)—I(1)	3.296 (9)
Na(1)—Na(2)	3.257 (7)	4 ×		

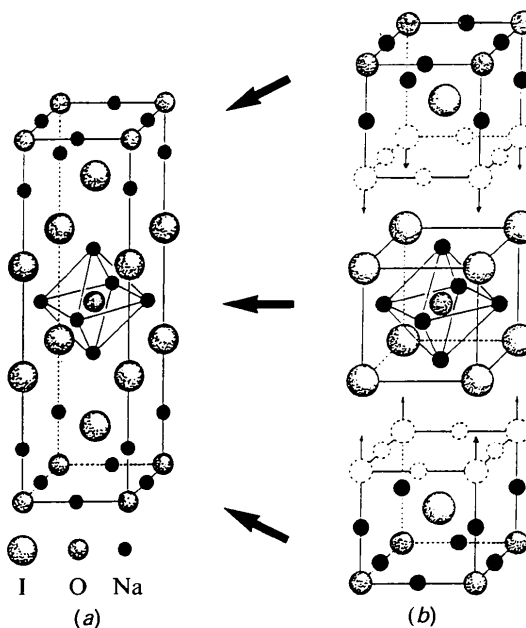


Fig. 1. (a) Structure of Na_4OI_2 . (b) Formal development from Na_3OI units removing two ONa_2 layers.

the question of what type of structure is favored. Other parameters (for example the polarizability) are obviously of minor influence as one would expect, especially in the case of the anion or the highly charged As or Sb anions.

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