Crystal structure of disodium dimanganate(II), $\text{Na}_2\text{Mn}_2\text{O}_3$

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Abstract

$\text{Mn}_2\text{Na}_2\text{O}_3$, tetragonal, $P4_32_12$ (no. 96), $a = 6.4205(9)$ Å, $c = 9.477(2)$ Å, $V = 390.6$ Å³, $Z = 4$, $R_{\text{ref}}(F) = 0.025$, $wR_{\text{ref}}(F^2) = 0.058$, $T = 293$ K.

Source of material

The title compound was obtained via the azide/nitrate route [1]. Starting materials for the preparation of $\text{Na}_2\text{Mn}_2\text{O}_3$ were NaN_3 (Sigma-Aldrich, 99.5 %), NaNO_2 (Riedel-de Haën, purest) and Mn_3O_4 (Alfa Aesar, 97 + %). The precursors were mixed in the ratios required according to the equation: $11 \text{ NaN}_3 + \text{NaNO}_2 + 4 \text{ Mn}_3\text{O}_4 = 6 \text{ Na}_2\text{Mn}_2\text{O}_3 + 17 \text{ N}_2$. This mixture was ground down thoroughly in an agate mortar, pressed to a pellet, dried under vacuum at 403 K for 12 h and placed under argon in a tightly closed steel container provided with a silver inlay [2]. In a flow of dried Ar the following temperature profile was applied: 298 K to 533 K (100 K/h), 533 K to 653 K (5 K/h), 653 to 773 K (20 K/h), and subsequent annealing for 30 h at 773 K. The obtained red powder is sensitive to air and moisture. Transparent red single crystals have

been grown by annealing a mixture of NaN_3 (Sigma-Aldrich, 99.5 %), NaNO_3 (Sigma-Aldrich, 99 %) and Mn_2O_3 (Chempur, 99.9 %) in the ratio 4 : 1 : 1 at 773 K for 1000 h in silver crucibles, which were sealed in glass ampoules under dried Ar.

Discussion

$\text{Na}_2\text{Mn}_2\text{O}_3$ is isostructural to $\text{Na}_2\text{Zn}_2\text{O}_3$ [3]. The main feature of the crystal structure are corner- and edge-sharing MnO_4 tetrahedra, which built up a three-dimensional framework. The Mn—O bond distances are in the range from 1.995 to 2.136 Å, the O—Na—O angles lie between 92.8° and 123.2°. The bond lengths are thus in the expected range, and very similar to those found in $\text{Na}_2\text{Mn}_2\text{O}_2$ [4] and $\text{Na}_{10}\text{Mn}_4\text{O}_9$ [5]. Since there is no simple ordering principle underlying the anion packing an approach suggested by O'Keefe and Hyde [6] is used to describe the crystal structure, which is based on the packing of cations with the voids being filled by anions. In $\text{Na}_2\text{Mn}_2\text{O}_3$ the cations form an approximate cubic close packed arrangement. There are two alternating double layers consisting of cations, where in the first one 3/4 of the octahedral voids are filled with oxygen, in the second layer 1/4 of the tetrahedral and 1/4 of the octahedral voids are filled with oxygen atoms. The resulting coordination-polyhedra are all edge- and corner-sharing. The structure of $\text{Na}_2\text{Mn}_2\text{O}_3$ may therefore be regarded an anti-type of the spinel structure.

Table 1. Data collection and handling.

Crystal:	red irregular, size 0.05 × 0.1 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	65.22 cm ⁻¹
Diffractometer, scan mode:	Stoe IPDS II, ω
$2\theta_{\text{max}}$:	70.04°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	865, 865
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 651
$N(\text{param})_{\text{refined}}$:	35
Programs:	SHELXS-97 [7], SHELXL-97 [8], DIAMOND [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	8b	0.7535(1)	0.54232(7)	0.11387(5)	0.0088(2)	0.0088(2)	0.0085(2)	−0.0006(2)	0.0005(2)	0.0009(2)
Na(1)	8b	0.4755(2)	0.2601(3)	0.8618(1)	0.0113(5)	0.0173(5)	0.0129(5)	−0.0019(7)	0.0011(5)	−0.0002(7)
O(1)	8b	0.0000(3)	0.2572(7)	0.6461(2)	0.0100(8)	0.0097(9)	0.0088(8)	−0.0014(6)	0.0014(5)	−0.002(2)
O(2)	4a	0.1844(4)	x	0	0.0151(9)	U_{11}	0.012(1)	0.001(1)	−0.0031(7)	U_{13}

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