Crystal structure of dibarium dimanganese disilicium nonaoxide $Ba_2Mn_2Si_2O_9$

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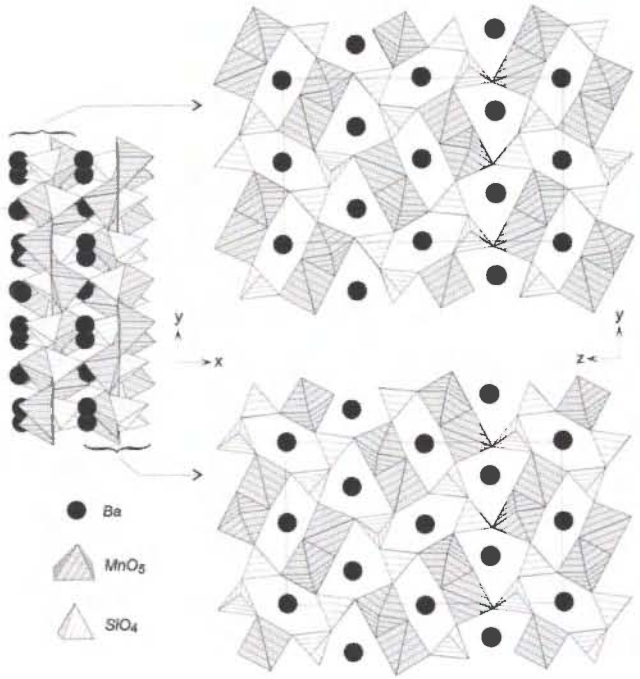

Abstract

$Ba_2Mn_2O_9Si_2$, orthorhombic, *Pbca* (No. 61), $a = 8.568(2)$ Å, $b = 10.741(2)$ Å, $c = 18.287(4)$ Å, $V = 1682.9$ Å^3, $Z = 8$, $R_{gt}(F) = 0.028$, $wR_{ref}(F^2) = 0.075$, $T = 293$ K.

Source of material

$Ba_2Mn_2Si_2O_9$ was prepared in the presence of a salt flux (NaCl/KCl = 1:1) by heating 0.5 g of a mixture of BaO, MnO_2, and SiO_2 with the molar ratio 1:1:1 with 2 g of the flux in an open silica tube for 3 days at 1073 K. The salt-matrix was dissolved in water. An energy dispersive X-ray fluorescence analysis for elements heavier than sodium revealed only barium, manganese, and silicon.

Discussion

The Ba(1) atoms have ten oxygen neighbors with Ba—O distances between 262.8(4) pm and 328.6(4) pm and an average distance of 293.7 pm, the nine oxygen neighbors of the Ba(2) atoms are at between 267.4(4) and 308.0(4) pm with an average of 284.8 pm, thus reflecting the smaller coordination number. The manganese atoms have distorted square-pyramidal coordinaton with Mn—O distances varying between 185.6(4) pm and 210.8(5) pm and average distances of 194.9 pm and 195.0 pm for the Mn(1) and Mn(2) atoms respectively. The Si—O distances within the SiO_4 tetrahedra vary between 160.0(4) pm and 167.8(4) pm with averages of 162.1 pm and 162.8 pm. Topologically, the structure can be described as consisting of layers extending perpendicular to the x direction (figure), although the condensed network of the MnO_5 pyramids and the SiO_4 tetrahedra is three-dimensionally infinite.

The crystal structure of $Ba_2Mn_2Si_2O_9$ has some similarity with the structure of the compounds $BaMSiO_4$ (M = Co, Zn, Mg), which has been described as a filled derivative structure of tridymite, a modification of SiO_2 [1]. The tetrahedral framework of the tridymite structure consists of six-membered rings of corner-sharing SiO_4 tetrahedra pointing alternately up and down. In the structure of the compounds $BaMSiO_4$ every second Si^{+4} ion is substituted by a M^{+2} ion. To maintain charge balance Ba^{+2} ions are stuffed into the cavaties formed by the six-membered rings. In the structure of $Ba_2Mn_2Si_2O_9$ the M^{+2} ions are replaced by Mn^{+3} ions. In order to compensate the additional positive formal charge, more oxygen is required, thus substituting the MO_4 tetrahedra by MnO_5 square pyramids. Thereby the hexagonal symmetry is lost. It seems possible that the compound $Ba_2Mn_2Si_2O_9$ described here is the same as a compound with the tentative composition $BaMnSiO_4$, which has been characterized only by powder data [2].

Table 1. Data collection and handling.

Crystal:	red, rhombohedric, size 0.04 × 0.06 × 0.08 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	124.79 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω/2θ
$2\theta_{max}$:	59.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4697, 2450
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1797
$N(param)_{refined}$:	92
Programs:	SHELXL-97 [3], DIAMOND [4], STRUCTURE TIDY [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
O(1)	8c	0.0077(4)	0.0974(4)	0.4402(2)	0.0094(7)
O(2)	8c	0.0137(5)	0.1859(4)	0.0200(2)	0.0139(8)
O(3)	8c	0.0171(4)	0.2037(3)	0.3218(2)	0.0079(7)
O(4)	8c	0.0742(4)	0.3711(4)	0.1157(2)	0.0084(7)
O(5)	8c	0.2278(5)	0.0690(4)	0.1674(2)	0.0133(8)
O(6)	8c	0.2785(5)	0.3118(4)	0.4158(3)	0.0206(9)
O(7)	8c	0.4455(4)	0.1606(4)	0.3400(2)	0.0096(7)
O(8)	8c	0.4935(4)	0.4362(4)	0.1061(2)	0.0107(8)
O(9)	8c	0.4967(4)	0.4695(4)	0.2495(2)	0.0095(7)

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	8*c*	0.24432(4)	0.29371(3)	0.24104(2)	0.0067(2)	0.0080(2)	0.0103(2)	–0.0002(1)	0.0004(1)	0.0006(1)
Ba(2)	8*c*	0.26381(4)	0.49233(3)	0.00511(2)	0.0067(1)	0.0095(2)	0.0098(2)	0.0002(1)	–0.0006(1)	0.0019(1)
Mn(1)	8*c*	0.03988(9)	0.26388(7)	0.41762(4)	0.0079(4)	0.0031(3)	0.0048(4)	0.0001(3)	0.0000(3)	0.0001(3)
Mn(2)	8*c*	0.46832(9)	0.03920(7)	0.15432(4)	0.0068(3)	0.0037(3)	0.0044(4)	–0.0004(3)	–0.0001(3)	–0.0008(3)
Si(1)	8*c*	0.0471(2)	0.0318(1)	0.17123(8)	0.0046(6)	0.0042(6)	0.0060(7)	0.0010(5)	0.0003(5)	0.0002(5)
Si(2)	8*c*	0.4542(2)	0.2627(1)	0.40931(8)	0.0041(6)	0.0056(6)	0.0047(7)	0.0002(5)	0.0011(5)	–0.0005(5)

References

1. Liu, B.; Barbier, J.: Structures of the Stuffed Tridymite Derivatives, Ba*M*SiO$_4$ (*M* = Co, Zn, Mg). J. Solid State Chem. **102** (1993) 115-125.
2. Nihtianova, D. D.; Ivanov, I. T.; Macicek, J. J.; Georgieva, I. K.: Crystallographic Data for BaMnSiO$_4$: A New Phase in the System BaO-MnO-SiO$_2$. Powder Diffr. **12** (1997) 167-170.
3. Sheldrick, G. M.: SHELXL-97: Program for Refining Crystal Structures. University of Göttingen, Germany 1997.
4. Brandenburg, K.: DIAMOND. Visual Information System for Crystal Structures. University of Bonn, Germany 1996.
5. Gelato, L. M.; Parthé, E.: STRUCTURE TIDY - a Computer Program to Standardize Crystal Structure Data. J. Appl. Crystallogr. **20** (1987) 139-143.