Crystal structure of mullite-type $PbMn_{0.5}Al_{0.5}BO_4$ determined by combined X-ray and neutron diffraction data

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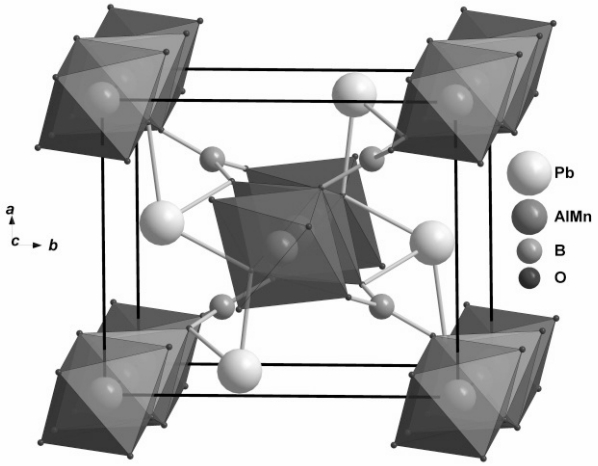

Abstract

$PbMn_{0.5}Al_{0.5}BO_4$, orthorhombic, *Pnam* (no. 62), $a = 6.88207(22)$ Å, $b = 8.26813(31)$ Å, $c = 5.84767(20)$ Å, $V = 332.74$ Å^3, $Z = 1$, $R_p = 0.0381$(i), 0.0458(ii), 0.0505(iii), $R_{wp} = 0.0491$(i), 0.0676(ii), 0.0677(iii), $T = 298$ K.

Source of material

Since none of the reported solid state routes [1-3] were successful to produce pure $PbAl_{0.5}Mn_{0.5}BO_4$, we used the glycerine method [4]. ^{11}B enriched $^{11}B(OH)_3$ was used to avoid neutron absorption. 10 mol% additional boric acid was mixed with the stoichiometric amount of $Al(NO_3)_3{\cdot}9H_2O$, $Mn(NO_3)_2{\cdot}4H_2O$ and $Pb(NO_3)_2$ together with 10 wt.% glycerin. The mixture was stirred at 358 K till it solidified upon release of NO_x. It was dried at 473 K for 2 hours and then pressed into pellets. Finally, the $PbAl_{0.5}Mn_{0.5}BO_4$ compound was produced by heating the pellets at 973 K in a platinum crucible for 24 hours.

Experimental details

The crystal structure of $PbMBO_4$ was refined in *Pnam* using a nonstandard setting of the Pnma space group. Using Pnam the infinite chains of the edge-sharing MO_6 octahedra run parallel to the *c*-axis, which is consistent with other mullite-type compounds [5]. For the structure refinements three sets of powder diffraction data were used for the identical sample:

(i) high intensity neutron data
(ii) high resolution neutron data
(iii) *X*-ray data.

The lattice parameters obtained from the *X*-ray data were used to refine the wavelength of the neutron beam. The combined approach and the neutron quality data led to accurate positional parameters, in particular for the light atoms oxygen and boron, and realistic displacement parameters. The occupancy of *M*-site was shared by aluminium and manganese, that is, occ(Mn) = 1-occ(Al).

Discussion

New metal borates are of considerable research interests for the search of nonlinear optical (NLO) properties [6 and Refs. therein]. The presence of different structural B_xO_y subunits showed versatile crystal chemistry. Distortion in B_xO_y polyhedra leads to inhomogeneous electron density around the boron atom, resulting in the second-order microscopic susceptibility. As potential NLO candidates mullity-type $PbMBO_4$ with M = Al, Cr, Mn, Fe were reported by Park et al. [1,2,7]. Here we present the crystal structure of the compound $PbAl_{0.5}Mn_{0.5}BO_4$ determined from the *X*-ray and neutron powder diffraction data. The site symmetry of BO_3 group with light elements is always challenging to in-house *X*-ray diffraction, whereas an accurate crystal structure of such an intermediate mullite-type phase is of crucial importance to understand the associated optical properties.

The infinite MO_6 octahedral Einerchains (Fig.), typical for mullite-type compounds, which are bridged by trigonal planar BO_3 groups [1,2,7]. The boron atoms are found at the plane (negligible 0.68(19) pm above the plane) formed by the three connecting oxygen atoms. Boron was not found at the center of an equilateral triangle due to two different types of B–O bond lengths. Therefore, the BO_3 groups do not hold a D_{3h} point symmetry; an intriguing issue can be cross-checked by infrared spectroscopy. The large Pb^{2+} cations occupy the interstitial position in the structural channels, located at the apex of a PbO_4 square pyramid. Therefore, the $6s^2$ lone electron pair of Pb^{2+} cations are stereochemically active and directed towards the channel.

Table 1. Data collection and handling.

Wavelength:	(i+ii): neutron (1.59435(5) Å) (iii) : Cu K_α radiation (1.540596 / 1.544493 Å)
Diffractometer, scan mode:	(i+ii): D2B ILL Grenoble, transmission and Debye-Scherrer (iii) : Panalytical PW1800, reflection and Bragg-Brentano
$2\theta_{max}$:	(i+ii): 150.04, (iii): 130,4°
$N(\text{total})_{measured}$:	(i+ii): 342, (iii): 316
$N(points)_{meas}$, $N(\text{points})_{proc}$:	(i+ii): 3197, 3500 (iii): 7000, 7000
Programs:	Diamond 3.2q [8], TOPAS 4.2 [9]

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

Atom	Site	Occ.	*x*	*y*	*z*	B_{iso}
Pb(1)	8*d*		0.0571(2)	0.3580(1)	¼	1.326(48)
Al(1)	4*a*	0.5247(48)	0	0	0	1.27(14)
Mn(1)	4*a*	0.4753(48)	0	0	0	1.27(14)
B(1)	4*c*		0.2790(3)	0.7618(3)	¼	0.657(77)
O(11)	4*c*		0.3982(4)	0.3937(3)	¼	0.649(74)
O(12)	4*c*		0.1809(4)	0.9057(4)	¼	1.503(77)
O(2)	8*d*		0.3312(3)	0.6877(2)	0.0468(4)	1.282(73)

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