Transition-metal substitution in PbAlBO$_4$: Synthesis, structural and spectroscopic studies of manganese containing phases

M. Mangir Murshed [a,*], Aydin Rusen [b,1], Reinhard X. Fischer [b], Thorsten M. Gesing [a]

[a] Chemische Kristallographie fester Stoffe, Universität Bremen, Leobener Straße, D-28359 Bremen, Germany
[b] Kristallographie, FB Geowissenschaften, Universität Bremen, Klagenfurter Straße, D-28359 Bremen, Germany

A B S T R A C T

Mullite-type metal borates PbAlBO$_4$ with planar BO$_3$ groups are potential candidates for nonlinear optical properties. We successively substituted aluminum with manganese in the composition PbAl$_{1-x}$Mn$_x$BO$_4$, which would help tuning the crystal chemistry and related physical properties. The end member PbAlBO$_4$ was synthesized by conventional solid state reaction; the other members of the PbAl$_{1-x}$Mn$_x$BO$_4$ series were prepared by glycerin method. The fundamental parameter approach was applied in the Rietveld refinements to describe the X-ray powder diffraction profiles. The cell parameters and interatomic bond distances were studied with respect to the chemical composition x. The MO$_6$ octahedral distortion linearly increased with the averaged M–O bond distance, which is correlated with the increasing amount of manganese atoms in the structure. The change of the average crystal size and microstrain were explained in terms of Al/Mn ratio in the solid solution. While the empirical bond-valence sums (BVS) of one oxygen atom, bridging the edge-sharing MO$_6$ octahedron, were found to be under-bonded, the other one was over-bonded. The stereoactivity of the 6s^2 lone electron pair of the Pb^{2+} cation was characterized in terms of the absolute value of eccentricity parameter ($|\Phi_i|$). Both bond valence parameter (r_{0i}) and BVS of Pb showed a linear correlation with $|\Phi_i|$. Deconvolution of the absorption feature of the infrared powder spectra between 1000 cm^{-1} and 1400 cm^{-1} required four fitted bands, which were assigned to B–O stretching vibrations of the trigonal planar BO$_3$ groups. With increasing Al^{3+} dilution in PbAl$_{1-x}$Mn$_x$BO$_4$ almost all observed modes shifted toward lower wavenumbers confirming the solid solution. The absorptions caused by the vibrations of the heavy atom Pb were observed in the far-IR region.

1. Introduction

In search of nonlinear optical (NLO) properties metal borates have been a subject of considerable research interests due to the presence of structural B$_x$O$_y$ subunits [1]. The metal borate PbGaBO$_4$ was first reported by Park and Barbier [2] followed by isostructural PbMBO$_4$ phases for M = Al, Cr, Mn, Fe [3,4]. Magnetic properties of the Cr, Mn, and Fe forms were investigated by density functional calculations [5]. In the Pnma space group setting chosen by Park et al. [2–4] the edge-sharing MO$_6$ octahedral chain runs parallel to the crystallographic b-axis. Such a choice is unfavorable for the description of many physical properties if they are to be compared with other mullite-type compounds described in the conventional setting. Therefore, we

present the crystal structure in the mullite-type standardized setting in space group Pnam to better understand its physical properties compared with other members of the mullite-type family [6–8]. Fig. 1 shows the crystal structure of PbMBO$_4$ in the Pnam setting where the infinite chains of edge-sharing MO$_6$ octahedra run parallel to the c-axis. The MO$_6$ octahedra are bridged by trigonal planar BO$_3$. The large Pb^{2+} cation occupies the interstitial position in the structural channels, located at the apex of a PbO$_4$ square pyramid. Therefore, the stereoactivity of the 6s^2 lone electron pair (LEP) of each Pb^{2+} cations is assumed to point toward the channel. Incorporation of transition metals (e.g., Fe, Mn, Cr) into the octahedral chains of the PbMBO$_4$ system was reported to induce one-dimensional magnetic behavior [3,5]. The chromium and iron containing phases showed intra-chain anti-ferromagnetism and the manganese compound a ferromagnetic coupling. PbAlBO$_4$ showed a reconstructive $\alpha \rightarrow \beta$ phase transition above 1000 K. The low- and high-temperature modifications were investigated by neutron powder diffraction methods [4]. However, similar phase transitions were not observed in PbMBO$_4$ (M = Cr, Mn, Fe) phases. Here, we describe the syntheses and

* Corresponding author. Tel.: +49 0421 218 63144; fax: +49 0421 218 9863141.
E-mail address: murshed@uni-bremen.de (M.M. Murshed).
[1] Present address: Department of Metallurgical and Materials Engineering, Middle East Technical University, 06531 Ankara, Turkey.
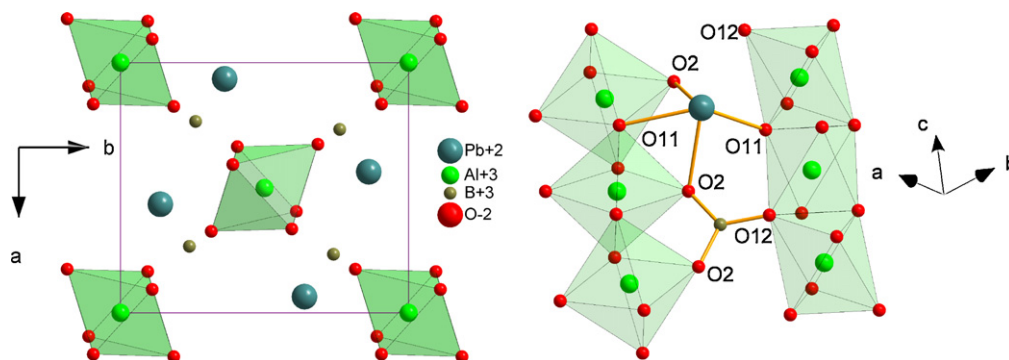
Fig. 1. The structure of PbAlBO$_4$, showing the edge-sharing AlO$_6$ octahedra parallel to the *c*-axis (left) and the AlO$_6$ octahedra linked by planar BO$_3$ and square pyramidal PbO$_4$ groups (right).

crystal structures of a series of PbAl$_{1-x}$Mn$_x$BO$_4$ compounds. The successive replacement of Al^{3+} by Mn^{3+} would help to understand the (a) crystal chemistry and related physical properties, (b) thermal stability, (c) $\alpha \rightarrow \beta$ phase transition and (d) stereoactivity of LEP of Pb^{2+} cations in the PbAl$_{1-x}$Mn$_x$BO$_4$ system. We also present for the first time infrared spectroscopic (FTIR) results on PbMBO$_4$, which will help to gain deeper insights into the observed phases.

2. Experimental methods

2.1. Synthesis of PbAlBO$_4$

According to Park et al. [4] the pure α-PbAlBO$_4$ phase can be readily produced in two stages. Firstly, in order to avoid the formation of the low melting Pb$_2$B$_2$O$_5$ compound (melting point 768 K), stoichiometric mixtures of PbO and Al$_2$O$_3$ powders were transferred to a platinum crucible and heated at 1123 K to form Pb$_9$Al$_8$O$_{21}$. Secondly, this Pb$_9$Al$_8$O$_{21}$ powder was reacted with B(OH)$_3$ up to 1023 K for 5 days with intermediate re-mixing. However, we could not produce Pb$_9$Al$_8$O$_{21}$ in the first stage even after several trials at different conditions (duration, crucible, temperature, cooling/heating rate). A pure Pb$_9$Al$_8$O$_{21}$ phase was obtained only when a stoichiometric mixture of Pb$_3$O$_4$ and Al$_2$O$_3$ powder was pressed into pellets and heated to 1223 K at 10 K/min in an alumina crucible. The sample was immediately cooled to 1123 K, held at this temperature for 72 h, and finally cooled to room temperature. X-ray diffraction analyses confirmed the purity of the Pb$_9$Al$_8$O$_{21}$ sample. Finally, an appropriate amount of Pb$_9$Al$_8$O$_{21}$ was reacted with B(OH)$_3$ at 1023 K for 5 days to produce α-PbAlBO$_4$; intermediate remixing was not followed as applied by Park et al. [4]. The as-synthesized α-PbAlBO$_4$ compound was washed with 0.1 M HNO$_3$ to remove unreacted metal oxides.

2.2. Synthesis of PbMnBO$_4$

A two stage conventional solid state reaction procedure was also suggested [3] to prepare PbMnBO$_4$, that is, formation of MnBO$_3$ followed by stoichiometric reaction with PbO to produce PbMnBO$_4$. In this regard, Norrestam et al. [9] suggested an alternative solid state route. However, none of the author's experiments following these procedures were successful in producing pure PbMnBO$_4$ due to the lack of experimental details in the respective literature. We followed Gesing et al. [10] who recently reported a glycerin method for the synthesis of Bi$_2$M$_4$O$_9$ phases: Pb(NO$_3$)$_2$, Mn(NO$_3$)$_2$·4H$_2$O and B(OH)$_3$ were dissolved in 50 ml deionized water 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 h and then pressed into a pellet. Finally, the PbMnBO$_4$ compound was produced by heating the pellet at 973 K in a platinum crucible for 5 days. The sample contained a small amount of Pb$_2$MnO$_4$ which was washed out using diluted HNO$_3$ (0.1 M).

2.3. Syntheses of Pb(Al$_{1-x}$Mn$_x$)BO$_4$

Each member of the PbAl$_{1-x}$Mn$_x$BO$_4$ series (x = 0.1–0.9) was produced by the glycerin method [10] from the corresponding stoichiometric amount of Al(NO$_3$)$_3$·9H$_2$O, Mn(NO$_3$)$_2$·4H$_2$O, Pb(NO$_3$)$_2$ and B(OH)$_3$. The synthesis conditions were used as in the synthesis of PbMnBO$_4$ (see above). The X-ray powder patterns of some as-synthesized samples showed little impurities. Whereas the impurity phases of the end members were removed using 0.1 M HNO$_3$, the other members of the PbAl$_{1-x}$Mn$_x$BO$_4$ series (x = 0.1–0.9) were found to be completely dissolved in HNO$_3$, thus were not washed with diluted nitric acid. The impurity phases amounting to less than 1 wt.% were not considered in the Rietveld refinement.

2.4. X-ray diffraction and infrared spectroscopy

The X-ray powder diffraction data for all synthesized products were collected on a Panalytical MPD powder diffractometer using Bragg-Brentano geometry equipped with a secondary Ni filter, Cu K$\alpha_{1,2}$ radiation and an X'Celerator detector. 4905 data points were collected between a 2θ range of 5° and 87° with a step width of 0.0167°/step and a collection time of 20 s/step. Rietveld refinements were carried out using the "DiffracPlus Topas 4.2" (Bruker AXS GmbH, Karlsruhe) software. To describe the X-ray diffraction profile, the fundamental parameter approach was applied in the Rietveld refinements. For each diffractometer configuration, the corresponding fundamental parameters were fitted to standard powder data of LaB$_6$. During refinements, general parameters such as sample displacement, the scale factor and six background parameters (Chebychev polynomial function) were optimized. Additionally, the cell parameters, atomic coordinates, atomic displacement parameters, average crystal size L_{Vol}(IB) and microstrain (ε_0) were refined.

The Fourier transform infrared (FTIR) spectra were measured on a Bruker IFS 66v/S spectrometer using the standard KBr method (2 mg sample in 200 mg KBr) for the mid-infrared (MIR), and polyethylene method (1 mg sample in 100 mg polyethylene) for far-infrared (FIR) regions, which were normalized and added together providing a range of 50–5000 cm^{-1}. The deconvolution of the powder spectra into single Gaussian-shaped absorption bands was carried out using the peak-fitting facilities provided by "DiffracPlus Topas 4.2" (Bruker AXS GmbH, Karlsruhe).