Experimental Report

13/10/2013

Proposal:	**5-24-505**	**Council:**	4/2012
Title:	Temperature dependent investigations on PbMBO4 (M = Al, Mn)		

This proposal is resubmission of: 5-24-475

Researh Area: Materials

Main proposer: **GESING Thorsten M.**

Experimental Team: GESING Thorsten M.
MURSHED Mohammad Mangir

Local Contact: NENERT Gwilherm

Samples: PbAlBO4, PbMnBO4

Instrument	Req. Days	All. Days	From	To
D2B	4	3	02/11/2012	05/11/2012

Abstract:

Metal borates with 6s2 lone electron pair (LEP) elements are tunable for non-centrosymmetric phases, which is a pre-requisite for a variety of technologically important properties. A series of PbAl1-xMnxBO4 (x = 0.0 – 1.0) compounds have been synthesized and investigated by in-house x-ray diffraction, IR and Raman spectroscopes and powder neutron diffraction on D2B for x = 0.5. Whereas the in-house x-ray high absorption due to Pb and the presence of light atoms for x-ray (namely boron) hardly allow the determination of an accurate crystal structure, neutron data have shown to be very successful. Here we ask for beamtime on D2B which would help to a) accurately determine the crystal structure, b) corroborate the spectroscopic evidence of BO3 geometry with the crystal data, c) investigate possible phase transition at high temperatures, d) explore how these compounds with high global instability index (GII > 0.2 v.u.) adopt /change lattice-induced strain from RT to elevated temperatures, and e) check how far the LEP of Pb2+ influences the stereochemistry of the compoundswith respect to the eccentricity parameter. In order to avoid neutron absorption 11B was used for al samples.

Structural properties of mullite-type $Pb(Al_{1-x}Mn_x)BO_4$

Abstract

Structural characterization of mullite-type $PbAl_{1-x}Mn_xBO_4$ series has been reported using neutron powder diffraction. Complementary tools such as high pressure synchrotron powder diffraction, in-house X-ray powder diffraction, Raman spectroscopy and DFT calculations helped to make a full-fledged report [1]. The planar geometry of the BO_3 group changes only slightly over the whole composition range. The rigid BO_3 group plays the dominant roles for the thermal contraction in the *a*-direction followed by expansion in the *b*- and *c*-direction, leading to a correlation $a·b/c$ ~ unity. Thermal expansion of the metric parameters was modeled using first-order Grüneisen approximation for the zero-pressure equation of state. We used double-Debye-double-Einstein-Anharmonicity model to calculate the temperature-dependent internal energy of the crystalline end members. The simulation helped to understand the anisotropic thermal expansion and validate the necessity to take an anharmonicity term in the model.

Experimental report

Due to presence of boron in $PbAl_{1-x}Mn_xBO_4$ relevant structural difficulties could not be resolved from in-house X-ray diffraction, in particular the accurate position of boron when the system was successively tuned with increasing manganese. The local distortion (planarity) of the BO_3 group and its possible influence to the nearby PbO_4 or MO_6 polyhedra through common oxygen vertices bear fundamental question whether the integrated local distortion overcomes the centrosymmetric (*Pnam*) constraint for useful non-linear optical susceptibility. The temperature-dependent neutron powder diffraction was also sought to check how the rigidity of the BO_3 group play roles for the thermal expansion of these compounds, resulting in axis-directional negative thermal expansion [1].

The neutron intensity data were extracted in two ways. First, only a narrow range in the middle of the 2D detector was used to obtain high-resolution data minimizing the curve of the Debye–Scherrer rings. Second, the whole detector range was evaluated resulting in a lower resolution data with higher intensity. Notably, the high-resolution data increases the accuracy of the lattice parameters and the high-intensity data enhances the accuracy of the positional parameters. The lattice parameters obtained from the X-ray data were used to refine the neutron wavelength, which was calculated to be 159.435(5)·pm.

The systematic change of the metric parameters is shown in Figure for the successive replacement of aluminum by manganese. The anisotropy parameter increases with increasing manganese content in the $PbMBO_4$ phase, demonstrating that incorporation of manganese anisotropically influences the expansion of the lattice parameters. The $a \cdot b/c$ vs. composition x plot (Fig.) shows that the manganese substitution has only a small effect on the directions perpendicular (*a*, *b*) and parallel (*c*) to the octahedral chains. This finding supports the common structural features characteristic to mullite-type compounds.

The average M-O distance increases linearly up to 50% substitution, and with a slightly stepper slope with higher manganese content. The Pb-O distances increase as well with increasing manganese content. For the end member aluminum compound two different Pb-O11 distances do not differ much (232.4(4) pm and 234.0(3) pm), whereas in the counterpart manganese compound the respective distances significantly scatter (235.2(5) pm and 241.9(6) pm). With increasing manganese content the average B-O distances increase as well as the difference between B-O2 and B-O12 bonds (Fig.). Whereas this difference is almost zero for $PbAlBO_4$, representing nearly D_{3h} symmetry, a deviation of 3.0(5) pm in $PbMnBO_4$ refers to lowering the symmetry. Careful Rietveld refinement of the neutron data confirmed that the boron atom locates as much as 0.8(1) pm above the BO_3-plane, thus represents C_S symmetry for BO_3. Raman spectra also confirmed that local symmetry of the BO_3 decreased with increasing manganese.

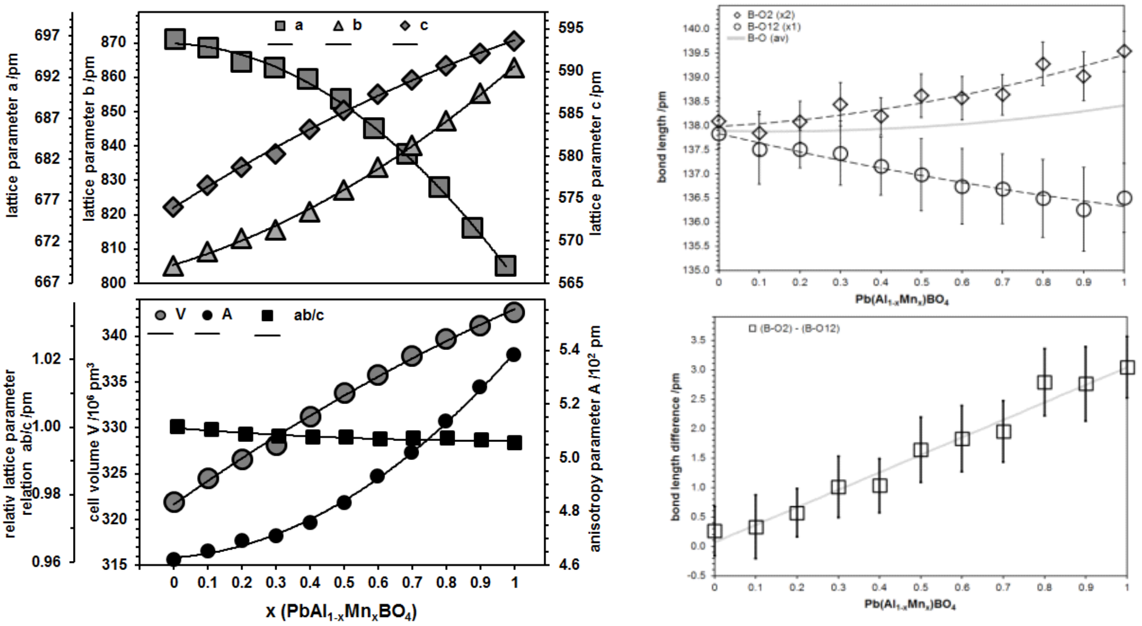

Figure: *Left panel*: Development of the metric parameters, the relative lattice parameter relations and the metric anisotropy parameter in Pb(Al$_{1-x}$Mn$_x$)BO$_4$ with respect to the chemical composition. *Right panel*: The change of the B-O bond lengths and their deviations.

Both the two end members show negative thermal expansion in the *a* cell parameter and positive for the *b* and *c* with an overall positive thermal expansion for the unit cell volume. With increasing temperature the rigid BO$_3$ becomes more symmetric, leading to transfer distortion to the PbO$_4$ geometry and tilting to the AlO$_6$ octahedra. This combined effect eventually elongates the **b**-axis at the expense of the **a**-axis. Since the tilt of the AlO$_6$ octahedra is very small, it is not clear if the effect considered here is the only driving force for the negative thermal expansion of the *a* lattice parameter. Upon manganese substitution in PbAlBO$_4$ the rigidity of BO$_3$ changes only slightly (including its planarity) leading to insignificant degree of freedom for structural changes. Probably due to the highest distortion of the BO$_3$ group in PbMnBO$_4$ the thermal expansion coefficient of the *a* lattice parameter changes from negative to positive at around 950 K.

The mullite-type PbMBO$_4$ seems to be intrinsically anharmonic at a very fundamental level associated with soft modes of PbO$_4$E, rigid modes of BO$_3$ and intermediate rigidity of MO$_6$. It is therefore reasonable to assume that neither the Einstein harmonic nor the Debye quasi-harmonic model adequately explain the thermal expansion of the materials, and adopting an anharmonic term is reasonable. Along with the low temperature neutron powder data collected at POWGEN, SNS Oakridge we modeled the thermal expansion of the metric parameters of two end members using first order Grüneisen approximation for the zero-pressure equation of state; that is, the internal energy for the thermal expansion was calculated using double-Debye-double-Einstein-Anharmonicity (DDEEA) model [1].

Reference

[1] Th. M. Gesing, C. B. Mendive, M. Curti, D. Hansmann, G. Nénert, P. E. Kalita, K. E. Lipinska, A. Huq, A. L. Cornelius, M. M. Murshed, *Structural properties of mullite-type Pb(Al$_{1-x}$Mn$_x$)BO$_4$*. Z. Kristallogr. 228 (2013) online. DOI 10.1524/zkri.2013.1640