MS15-P18 **Lattice thermal expansion of mullite-type PbMBO$_4$ for M = Al, Ga, Fe and Mn.** <u>M. M. Murshed</u>, Th. M. Gesing *Solid State Chemical Crystallography, Inorganic Chemistry, University of Bremen, Germany,*
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Polycrystalline mullite-type PbMBO$_4$ (M = Al, Ga, Fe and Mn) samples were produced using the glycerin method [1]. The lattice thermal expansion of the materials was studied by temperature-dependent X-ray powder diffraction data Rietveld refinements. The crystal structure was refined in the space group *Pnam* following mullite-type standardized setting [2]; therefore, the edge-sharing MO$_6$ octahedral chains run parallel to the crystallographic **c**-axis. The lattice parameters in the cooling cycles exhibit corresponding smaller values than those in the heating cycles. The onset temperature of the deviation differs due to chemical composition of the sample. The consecutive second heating did not show this effect. This irreversible alternation causes to happen due to healing of the intrinsic defects at higher temperatures. The thermal expansion of the lattice parameters is non-linear and highly anisotropic. In PbAlBO$_4$, PbGaBO$_4$, and PbFeBO$_4$ the **a**-parameter first shows a slow decline followed by a steep contraction at higher temperatures. A converse trend was observed in PbMnBO$_4$, that is, rapid contraction follows a slower one. The coefficients of thermal expansion (CTE) $á(a)$, $á(b)$, $á(c)$ and $á(v)$ were calculated for, a, b, c and cell volume, respectively, using higher order polynomial fit. Beside the investigated temperature range, the CTE was studied between 0 K and 1200 K. The proposed CTE's at low temperatures must exclude any possibility of magneto-volume effect, in particular for PbMnBO$_4$ and PbFeBO$_4$. Because, the former one shows ferromagnetism at $T_c = 125$ K, and the latter one antiferromagnetism at $T_N = 31$ K [3]. The **b-** and **c**-parameters and cell volume show positive, and **a** negative CTE at any given temperature. The anisotropy factor (A) depends on the M-cations in the MO$_6$ octahedra of the sample. PbMnBO$_4$ shows the maximum A at 400 K, while the other phases a non-linear increase over the temperature range. The thermal anisotropy between **a** and **b** can be explained in terms of the mechanical model of the 'Nuremberg scissors' [4] within the **ab** plane. This structural property sheds light to the expansion/contraction behavior of the mullite-type PbMBO$_4$ materials with respect to applied pressure. The onset of α→ β phase transition for PbAlBO$_4$ [5] was observed at about 1035 K in a separate temperature dependent X-ray diffraction experiment. The reconstructive phase transition follows a slow transformation and Avrami-type kinetics [6].

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Keywords: mullite-type; metal borate; thermal expansion, phase transition

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MS15-P19 **Novel Hg-rich mercurides BaHg$_6$ and Ba$_{20}$Hg$_{103}$ and their ternary Zn, Cd, Ga and In derivatives**.
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The phase diagram Ba-Hg still shows some inconsistencies in the mercury-rich region [1]. Our synthetic and crystallographic work on ternary Hg-rich compounds of the systems Ba-Zn-Hg [2,3] and Ba-(Ga/In)-Hg also pointed to the existence of new binary barium mercurides.

The structures of the first title compound, BaHg$_6$ (*Pnma*, $a = 1338.9(3)$, $b = 519.39(13)$, $c = 1042.6(4)$ pm, $Z = 4$, $R1 = 0.0885$), and the isotypic indide BaHg$_{4.8}$In$_{1.2}$ as well as the structurally related gallide BaHg$_{5.2}$Ga$_{0.8}$ (*Cmcm*, $a = 729.77(7)$, $b = 1910.1(2)$, $c = 507.48(5)$, $R1 = 0.0606$) consist of planar nets (running perpendicular to the shortest axes) of five- and eight-member Hg rings. Most of the strong short Hg-Hg bonds ($d_{Hg-Hg} = 285$ to 303 pm) are found inside these nets. The Ba cations are situated in the center of the eight-membered ring exhibiting a 5:8:5 coordination.

BaHg$_6$ Ba$_{20}$Hg$_{103}$
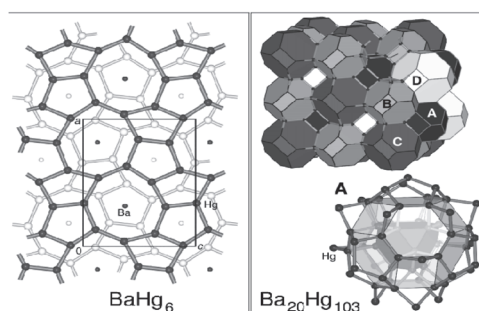
The second new binary Ba-mercuride, Ba$_{20}$Hg$_{103}$, forms a new complex cubic structure (*F-43m*, $a = 2333.30(10)$ pm, $Z = 4$, $R1 = 0.0651$) with four Ba und 13 Hg positions. The structure can be best described by decomposing it into four types of space-filling truncated octahedra (β cages). The polyhedra **C** and **D** are centered by Hg tetrahedra stars (TS), **B** contains a section of the Laves phase MgCu$_2$ (5 Hg$_4$ tetrahedra sharing corners). The smallest polyhedron **A** contains a truncated tetrahedron HgHg$_{12}$ surrounded by a strongly covalently bonded mercury shell. The ternary cadmium derivative Ba$_{20}$Cd$_4$Hg$_{99}$ ($a = 2331.57(14)$ pm, $R1 = 0.0465$) is isotypic, whereas in the related zinc mercuride Ba$_{20}$Zn$_5$Hg$_{99}$ ($a = 2332.33(7)$ pm, $R1 = 0.0436$) one of the TS is filled by Zn and thus distorted towards a ZnHg$_8$ cube.

The Hg-Hg distances as well as the chemical bonding (calculated using FP-LAPW bandstructure methods) of both binary and ternary mercurides are discussed and compared to that of other polar Hg-rich intermetallics.

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