# Poster Presentations

**[MS20-P07] Raman studies on mullite-type $PbMBO_4$ (M = Al, Ga, Mn, Fe)**

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Mullite-type $PbMBO_4$ (M = Al, Ga, Mn, Fe) and their solid solutions showed a broad anisotropy in their thermal expansions [1]. The chemical composition, the stereochemically active lone electron pairs of $Pb^{2+}$ cations and the unique B–O bonding strength in the planar $BO_3$ group play diverse roles for the thermal anisotropy, in particular for the negative thermal expansion in the crystallographic a-axis of the orthorhombic (Pnam) phase. The neutron powder diffraction study [1] partly shed light to resolve the crux identifying the physical origin of the axis-directional negative thermal expansion. In this report, we study the thermal behavior of the phonons of $PbMBO_4$ using temperature dependent Raman spectroscopy between 78 K and 973 K. Deconvolution of some spectral parts into single Pseudo-Voigt components were performed. The Lorentzian intrinsic phonon line-widths were obtained from the Voigt profile approximation. The bulk modulus, shifts of the phonon modes and mode Grüneisen parameters were calculated using density functional theory, which helped to assign each mode as well as extract the intrinsic anharmonic contribution to the frequency shift with respect to temperature. Most of the observed phonons concerned either with M−O stretching or M−O−M/O−M−O bending showed straightforward softening with increasing temperature. The temperature-dependent mode shifts and linewidths of these normal modes were modeled using simplified Klemens channels [2-4]. The model offers damping constants, representing the strength of the 3-phonon (cubic decay) and 4-phonon (quartic decay) processes contributing to the frequency shift, respectively. In each case, some low frequency Pb−O stretching and high frequency O−B−O bending modes harden with temperature, identifying the physical origins of the negative thermal expansion. Of particular notes, at least one of the O−M−O bending modes also showed hardening at low temperatures. A sharp magnon at 146 cm-1 was observed below 120 K, which was attributed to the one-dimensional long range antiferromagnetic order in $PbFeBO_4$ [5]; the mode diffused to disappear at higher temperatures. The anomalous scattering of the shifts and broadening of some modes a ~120 K and ~ 280 K relate the antiferromagnetic ordering of $Fe^{3+}$ cations. A combined effect of the negative mode Grüneisen parameters of some phonons and the magneto-volume effect influence the anisotropic thermal expansion of the cell volume of $PbFeBO_4$ at low temperatures. Both the harmonic and the anharmonic phonon behavior would help to understand the thermal transport and phase stabilities of the mullite-type materials.

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**Keywords:** mullite-type; metal borate; phonon, raman spectroscopy; density functional theory