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Report #6053

39280-AC5M Oxide Chemistry of Gallium(I) and Indium(I): ns2 Lone Pairs, Structural Distortions, Metal-Metal Interactions, and Ferroelectric Properties

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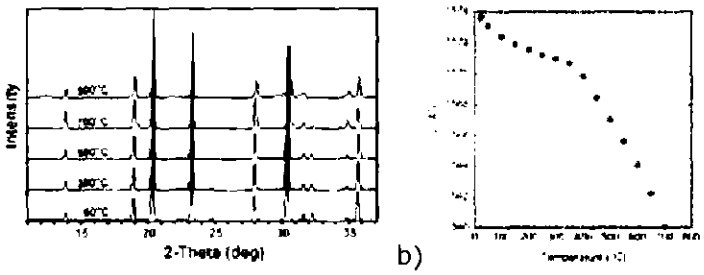
There is very little literature on the oxide chemistry of Ga(I) and In(I), primarily because of the instability of these ions with respect to either oxidation or disproportionation However, there are good reasons to believe that a wide and varied array of oxides containing these ions can be prepared, and that the structural chemistry and physical properties of these materials will be interesting. Under previous support we synthesized and structurally characterized $GaZr_2(PO_4)_3$ and Ga(I)-b" alumina.

Our program makes use of ion exchange in halide melts to prepare Ga(I) and In(I) oxides so that the structural chemistry and properties of the products can be examined and compared with those of corresponding alkali metal containing compounds. Ions with ns^2 valence electron pairs, such as Ga(I) and In(I), are more polarizable than similar size and charge ions with closed shells, and they are particularly susceptible to displacements away from the center of their coordination polyhedra. This susceptibility towards displacement is a consequence of covalent bonding involving both the ns^2 valence pair and np orbitals on the metal ion and it manifests itself as "stereochemically active lone pairs" in many compounds *and in enhanced ferroelectric properties* in materials such as $PbTiO_3$ and $SrBi_2Ta_2O_9$.

In the current reporting period we started to explore the thermophysical properties of $GaZr_2(PO_4)_3$ and $InZr_2(PO_4)_3$. This investigation was undertaken with a view to comparing the thermal expansion characteristics of these materials with the corresponding alkali metal compounds and $AgZr_2(PO_4)_3$. Some members of the $NaZr_2(PO_4)_3$ (NZP) structural family are very well known for their low thermal expansion coefficients and we were interested in uncovering how the presence of an ns^2 valence pair on the univalent cation modified the observed thermal expansion. This has turned out to be a very much more complicated and interesting series of experiments than was initially anticipated! $GaZr_2(PO_4)_3$ and $InZr_2(PO_4)_3$ are very effective oxygen getters at high temperature, presumably, due to the mobility of the Ga(I) and In(I) ions. Heating $GaZr_2(PO_4)_3$ in low vacuum while monitoring using in-situ diffraction methods revealed a small initial thermal contraction, followed by a significant volume reduction and ultimately the formation of a second phase that is a close structural relative of the starting NZP structure (see Figure 1). Ex-situ diffraction and weight gain measurements indicate that this phase is probably $Ga^{III}_{0.33}Zr_2(PO_4)_3$. So far we have been unable to make this phase by direct reaction using Ga(III) starting materials suggesting that it is metastable. Subsequently, we have made high temperature in-situ diffraction measurements in a H_2/N_2 mix in an effort to avoid oxidation. These studies uncovered a complex time dependent behavior that was quite different from that seen under low vacuum conditions. We are still working to understand the origin of the time dependence. The high temperature behavior of $InZr_2(PO_4)_3$ is related to that of the gallium compound.



a) b)

Figure 1. a) Variable temperature diffraction data for $GaZr_2P_3O_{12}$ in low vacuum. A reaction is seen at >700 °C. Below this temperature, b) negative thermal expansion is observed.

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