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**Abstract:**

**Molten Halide Flux Growth of Hollandite-type and Zeotype Complex Iron Based Oxides**

We have been exploring the crystallization of complex iron based oxides employing carbonate and hydroxide melts that serve as high-temperature solutions in which a broad variety of binary or higher order precursors can be dissolved and from which high quality single crystals of new compositions can be grown. Using this approach complex di-, tri-, and tetravalent iron containing oxides have been synthesized. Hydroxide fluxes have also been shown by other groups to work well for complex iron oxides. We are further interested in expanding the application of flux growth approach for complex iron oxides from hydroxide or carbonate melts to alkali halide melts with the motivation to explore new and more intriguing complex ferrates. Recently, we succeeded in crystallizing a new noncentrosymmetric polar cesium iron germanate, $CsFeGeO_4$, from a eutectic CsCl/CsF flux at 900 °C employing a dwell time of 12 h. Interestingly, doubling the dwell or soaking time of the reaction yielded a centrosymmetric polymorph of $CsFeGeO_4$ crystallizing in space group *Pbcm*. In this paper, we report on the flux growth syntheses and structural characterization of both $CsFeGeO_4$ polymorphs. In addition, the solid-state synthesis, polarization, magnetic, optical and SHG property measurements for the noncentrosymmetric, mononclinic $CsFeGeO_4$ phase are also provided.

Using the flux growth technique, we also report the synthesis of $Rb_{1.66}Fe_{1.66}Ti_{6.34}O_{16}$ (RFTO) herein, representing the first rubidium containing hollandite type ferrotitanate crystallizing in the tetragonal space group I4/m. Most reports on Ti-based hollandites focus on K

or Ba as the A site cation in the hollandite structure, and to the best of our knowledge, no reports yet exist on the single crystal growth of a rubidium containing ferrotitanate belonging to the hollandite family. Some all iron containing framework materials, such as the ferrolite, are also known. Herein, we report the synthesis, solid state synthesis, crystal structure determination via single crystal X-ray diffraction, magnetic susceptibility measurements, and optical properties of RFTO measured via UV-vis diffuse reflectance and FT-IR spectroscopy respectively. Magnetic property measurements of the previously reported $K_{1.55}Fe_{1.5}Ti_{6.5}O_{16}$ are also provided and briefly discussed.