Synthesis and Characterization of Novel Rare-Earth Oxychloride Single Crystals

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ABSTRACT
The novel Ba$_2$Ln$_3$O$_5$Cl$_2$ (Ln = Gd–Lu) series of single crystals were produced using an alkaline-earth metal flux, then examined to determine the structural and magnetic characteristics.

The series forms in the $I4/mmm$ symmetry (grsrp. #139) with cell parameters ranging from $a = 4.46(6)$ Å and $c = 24.87(6)$ Å for Ba$_2$Gd$_3$O$_5$Cl$_2$ to $a = 4.35(6)$ Å and $c = 24.57(6)$ Å for Ba$_2$Lu$_3$O$_5$Cl$_2$. The series follows an expected trend of lattice contraction due to the decreasing ionic radius of the lanthanide series as atomic number increases. Magnetic susceptibility measurements were performed from 300 – 2 K.

SYNTHESIS

Flux Method

Load flux, metal, oxide powders, and other constituents into stainless steel crucible

Heat to 1000 °C to allow reactants to dissolve in flux

Invert above melt temperature

Dissolve about 1.5 °C/h based on flux melt

Cantellage and allow to cool

Barium cut into sheets

Chemical Ratios / Temperature Profile

A ratio of 20:1:5:0.25 mmol Ba$_2$Ln$_3$O$_5$BaO$_2$:BaCl$_2$ was used. The reactions were heated to 1000°C in 10 hours, solvated for 20 hours, then cooled to 820°C in 150 hours.

ANALYSIS

Morphology / Appearance

Transparent single crystals with color dependent on the incorporated lanthanide were obtained. Transparency differed depending on sample thickness, with thinner (<0.1mm) crystals being more transparent than thicker ones.

The phases are highly air sensitive, and stored in an inert environment.

SEM / EDS

Scanning electron microscopy was used in conjunction with energy dispersive spectroscopy (EDS) to determine elemental composition.

PROPERTIES

The Ba$_2$Ln$_3$O$_5$Cl$_2$ series of compounds form in the tetragonal crystal system with a body-centered crystal structure type. The family has a layered structure with respect to the Ln, which consists of perovskite (Ba$_2$Ln$_3$O$_5$) double-layers that are separated by distorted BaCl$_2$ rocksalt layers.

SC XRD

Unit cell parameters and molecular structure were determined via single crystal x-ray diffraction using an Oxford 4-circle diffractometer.

Magnetism

The magnetic susceptibility was measured using a Quantum Design MPMS SQUID magnetometer over a wide temperature range. The majority of the series displays typical Curie-Weiss behavior. The Gd compound shows Curie-Weiss behavior and onset of magnetic order at 2K. The Ba$_2$Dy$_2$O$_5$Cl$_2$ magnetization shows strong crystal field effects, with large deviations from Curie-Weiss behavior.

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CONCLUSIONS / FUTURE WORK

The stability of the Ba$_2$Ln$_3$O$_5$Cl$_2$ layer is investigated for different sized Ln. Gd is the largest lanthanide that is stable for this unit. The bonding of Ba in the layer becomes increasingly unstable for Ln larger than Gd. Future work may consist of overcoming the instability of the structure for Ln = Ce – Eu, where the lanthanide ionic radius is larger than Gd. This may be accomplished by synthesis utilizing halides other than chlorine, such as bromine or iodine.