

Abstract No. Khal0231

## Structural Solution of Novel Lanthanum Ruthenate and Lanthanum Iridate Phases from Powder Diffraction Data

P. Khalifah (Princeton U. and ORNL), M. Haas and R. Cava (Princeton U.), C. Rawn, J. Bai, and D. Mandrus (ORNL)

Beamline(s): X14A

**Introduction:** Interest in ruthenium oxides has grown exponentially since the discovery of unconventional superconductivity in  $\text{Sr}_2\text{RuO}_4$ . Most work since then has focused on chemically and structurally similar perovskite and Ruddlesden-Popper phases in the Sr-Ru-O and Ca-Ru-O systems, such as  $\text{SrRuO}_3$ ,  $\text{CaRuO}_3$ ,  $\text{Ca}_2\text{RuO}_4$ ,  $\text{Sr}_3\text{Ru}_2\text{O}_7$ , and  $\text{Ca}_3\text{Ru}_2\text{O}_7$ . However, our parallel work in the La-Ru-O system has shown that extremely interesting physics can be found a little further off the beaten path. The synthesis and characterization of such compounds is important to understanding the fundamental physics of ruthenates.

Three new lanthanum ruthenates with isolated  $\text{RuO}_6$  octahedra have been discovered in the last few years [1,2]. Two of these compounds, rhombohedral  $\text{La}_7\text{Ru}_3\text{O}_{18}$  (or equivalently,  $\text{La}_{4.67}\text{Ru}_2\text{O}_{12}$ ) and monoclinic  $\text{La}_{4.85}\text{Ru}_2\text{O}_{12}$  are non-stoichiometric relatives of the rhombohedral  $\text{Sr}_5\text{Re}_2\text{O}_{12}$  structure type. Due to the nearly perfect triangular arrangement of octahedra in these compounds and the antiferromagnetic coupling between Ru spins, geometric frustration plays an important role in determining the magnetic behavior of these compounds. Both  $\text{La}_7\text{Ru}_3\text{O}_{18}$  and  $\text{Sr}_5\text{Re}_2\text{O}_{12}$  crystallize in the same space group ( $R\bar{3}c$ , #167) with approximate lattice parameters of  $9.8 \times 9.8 \times 56.3 \text{ \AA}^3$ . The monoclinic cell of  $\text{La}_{4.85}\text{Ru}_2\text{O}_{12}$  ( $a = 5.6, b = 10.1, c = 19.0$ ) is derived from a distortion of the parent rhombohedral structure, obeying the expected approximate relations  $a_{\text{mono}} = 1/2 a_{\text{rhom}}$ ,  $b_{\text{mono}} = b_{\text{rhom}}$ ,  $c_{\text{mono}} = 1/3 c_{\text{rhom}}$ .

During the course of powder explorations of the La-Ru-O phase stability regimes, evidence was found for a new structure type with a rhombohedral unit cell of close relation to the structures described above. This cell parameters of this new cell are approximately  $11.5 \times 11.5 \times 19 \text{ \AA}^3$ , as determined from electron diffraction, and refined from XRD powder diffraction data. This cell can be rationalized as a new choice of axes within the  $ab$  plane of the parent rhombohedral structure, with local distortions that disrupt the three-fold screw axis of the  $R\bar{3}c$  space group, leading to a factor of three reduction in the  $c$ -axis lattice parameter. There is a simple transformation (shown in Fig. 1) of the parent  $9.8 \times 9.8$  angstrom unit cell (thin lines) that would give rise to the new  $11.5 \times 11.5 \text{ \AA}$  cell (thick lines). A new compound with a very similar unit cell was also discovered in explorations of the La-Ir-O system.

**Methods and Materials:** Data were collected on the X14A beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Approximately 1g of sample was placed in the depression in a flat plate. The incident beam energy was  $\sim 8\text{eV}$ .

**Results:** We believe that the full crystal structure of these new rhombohedral compounds should be very amenable to solution via powder diffraction techniques. The basic building blocks of this structure almost certainly are just  $\text{RuO}_6$  octahedra and isolated La atoms. This should greatly simplify the use of Monte Carlo techniques for pinpointing atomic positions. In the event that oxygen positions prove difficult to refine, we will collect powder neutron diffraction data.

### References:

[1] P. Khalifah, Q. Huang, D.M. Ho, H.W. Zandbergen and R.J. Cava, "La<sub>7</sub>Ru<sub>3</sub>O<sub>18</sub> and La<sub>4.87</sub>Ru<sub>2</sub>O<sub>12</sub>: Geometric Frustration in Two Closely Related Structures with Isolated RuO<sub>6</sub> Octahedra." J. Solid State Chem., **155**, 189-197, 2000.

[2] P. Khalifah, D.M. Ho, Q. Huang and R.J. Cava, "The Structure and Properties of  $\beta$ -La<sub>3</sub>RuO<sub>7</sub>: A New Structure Type with Isolated RuO<sub>6</sub> Octahedra." J. Solid State Chem., **165**, 359-62, 2002.

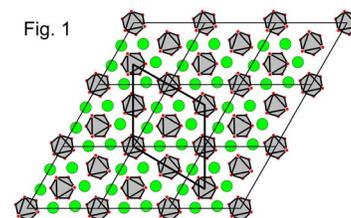


Figure 1: Relation between  $a=9.8 \text{ \AA}$  and  $a=11.5 \text{ \AA}$  unit cells.