A Preliminary Synthesis of Ruthenium-doped Oxyfluoride Perovskites

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Layered perovskites are structures composed of anionic perovskite blocks interleaved with metal cations and their rich chemistry makes them amenable to ion-exchange and exfoliation reactions. Layered oxide materials are used in diverse applications such as superconductors, semiconductors, ferroelectrics and photovoltaics. Late transition metal perovskites are particularly interesting due to their correlated electronic properties but cannot be exfoliated into nanosheets. This study sought to create ruthenium-doped layered oxyfluoride perovskites due to ruthenium's d^n electrons which may give rise to metallic phases and can also be exfoliated into thin sheets and restacked for designer materials.

TWO-STEP SYNTHESIS

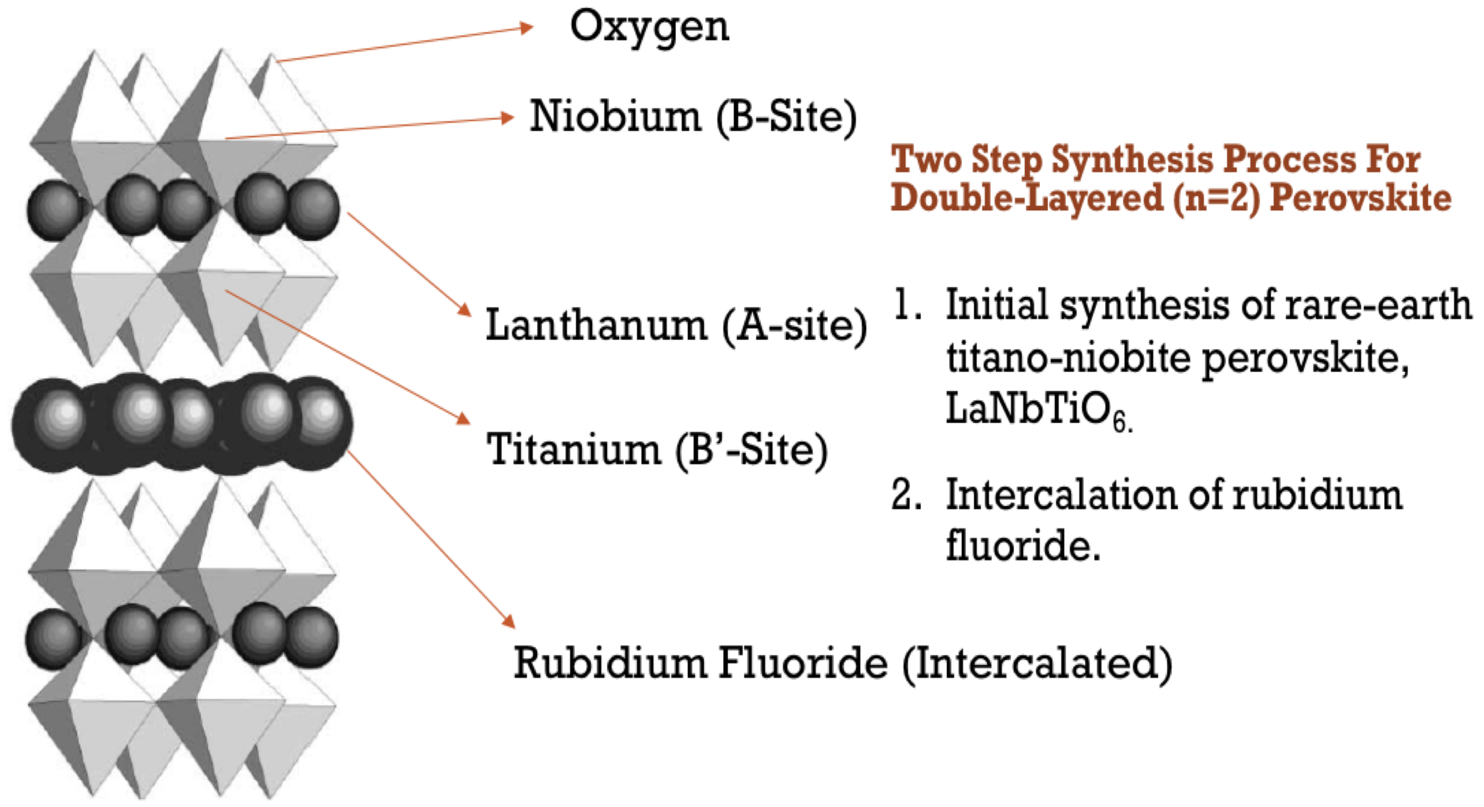

Figure 1. RbLaNbTiO6F layered perovskite structure with fluoride salt intercalated (Observed by the John B. Wiley Group, University of New Orleans[1]).

Why Ruthenium?

1. Mid to late transition metal.
2. Available d^n electrons which can give rise to interesting conductive and magnetic properties.
3. Synthesis of these ruthenium-doped perovskites can give insight into later transition metals. This can allow us to "pond jump" to later transition metals.

SYNTHESIS PROCESS

1. Precursor powders were ground together and heated at around 1200 degrees Celsius for 24 to 36 hours.
2. Heated powders were structurally and chemically analyzed using x-ray powder diffraction and EDX techniques.
3. Rubidium fluoride was then ground into the sample in a glove box and pelleted.
4. Samples were then placed in cylindrical crucibles and sealed in an evacuated test tube and heated at 800°for 24 additional hours.
5. Final structural analysis was conducted using x-ray powder diffraction, SEM, and EDX.

PREDICTED RESULTS

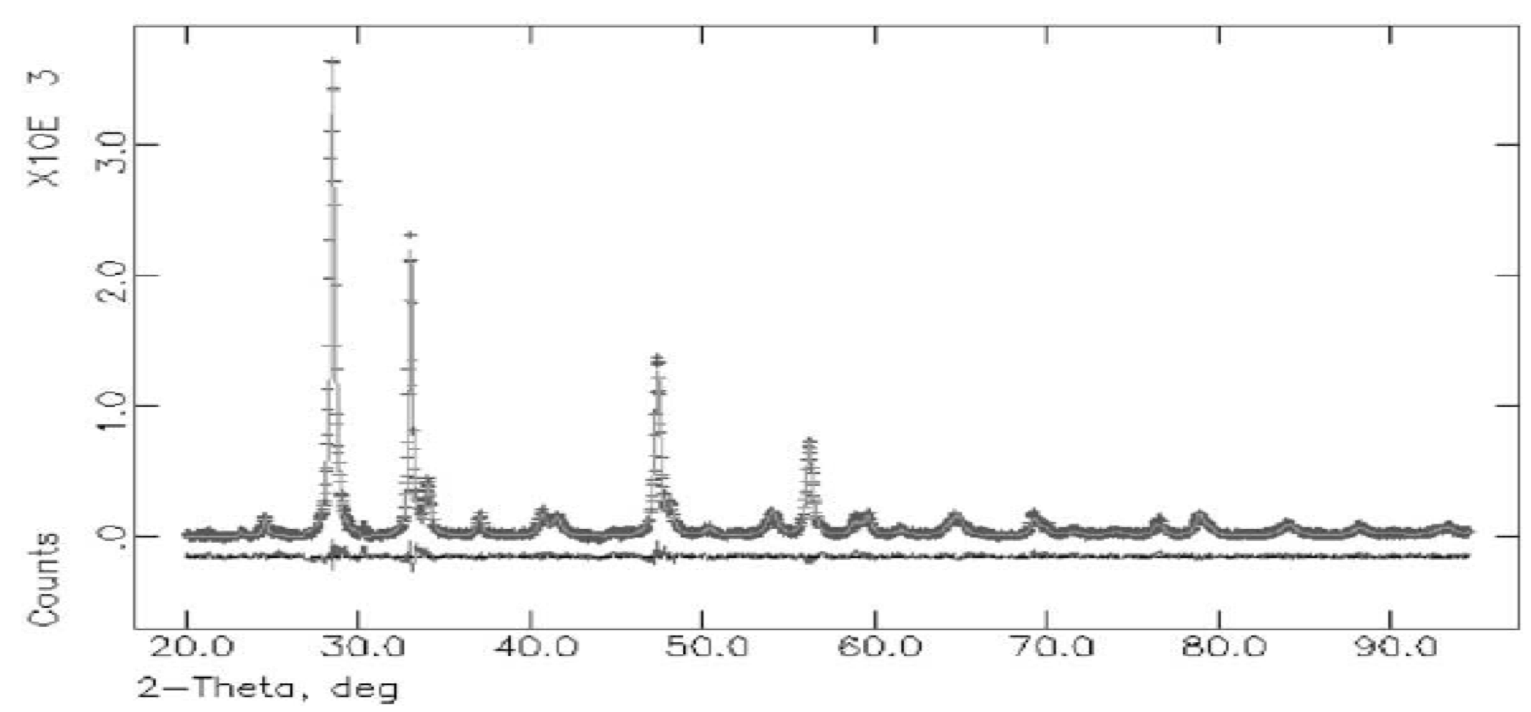

Figure 2. [1] X-Ray powder pattern of the rubidium oxyfluoride perovskite identified by Gabriel Caruntu from the University of New Orleans (John B. Wiley Group) [1]. After doping rubidium into the B-sites within the perovskite we expect to see this x-ray pattern.

RESULTS

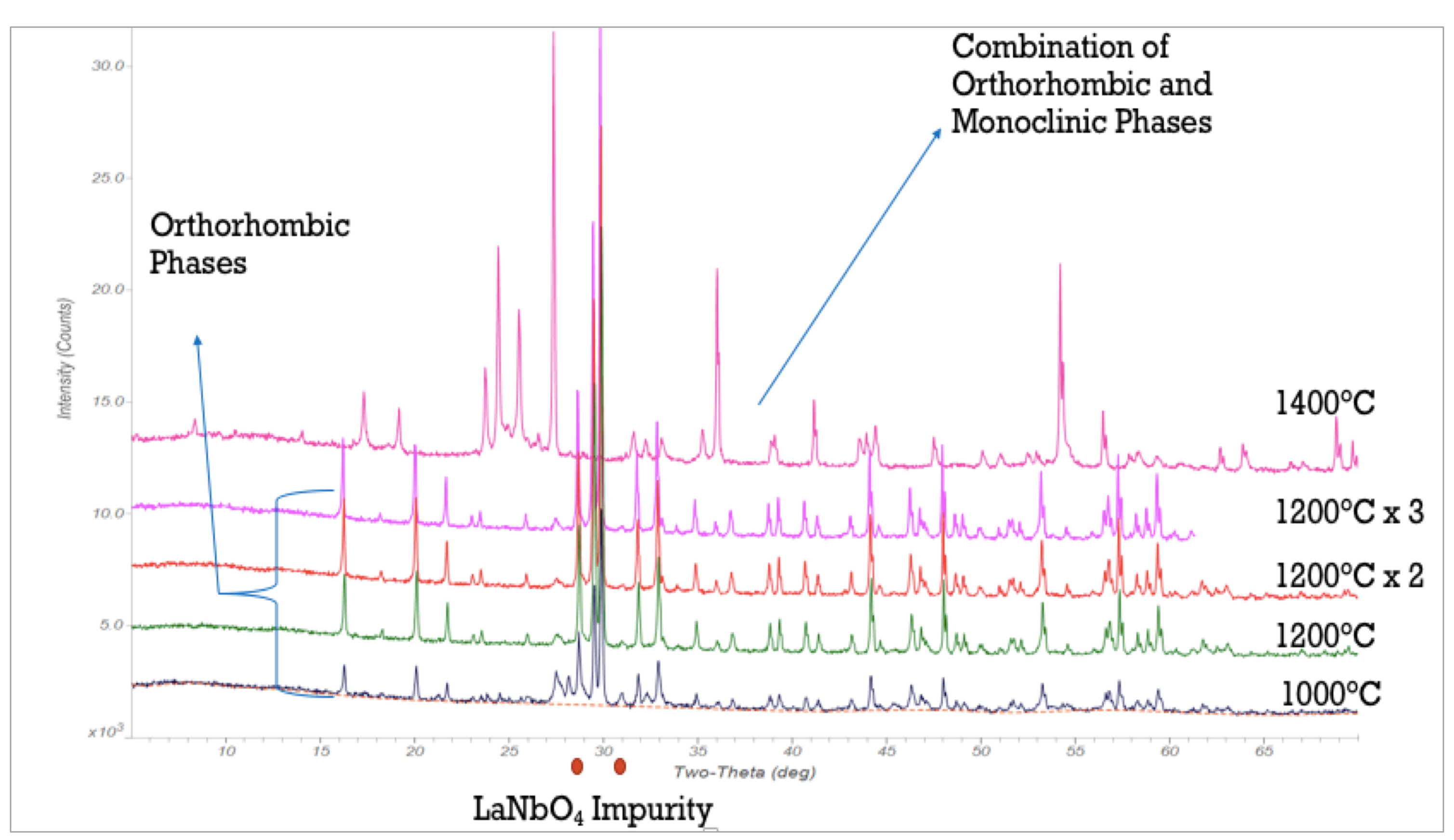

Figure 3. Results obtained from x-ray powder diffraction after five cycles of heating at temperatures ranging from 1000°C to 1400°C. Each cycle was run for 12 hours with intermittent grinding. Results showed a transition from orthorhombic phases to monoclinic phases as temperature increases. Likewise small unreacted niobate impurities were formed, $LaNbO_4$.

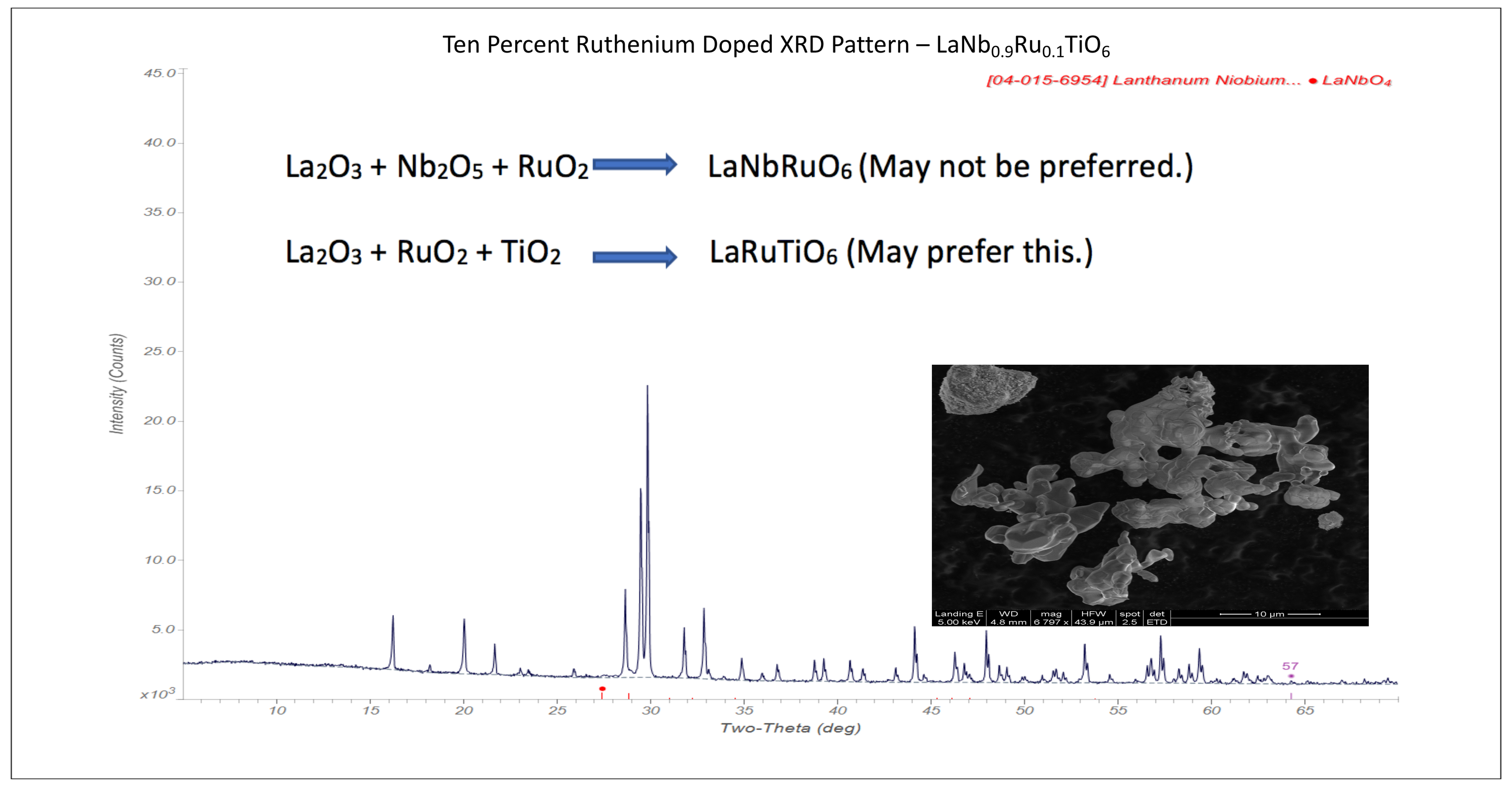

Figure 4. Pattern obtained via x-ray diffraction of synthesized sample after extensive grinding and heating at 1100°C for 14 hours. Pattern matched the predicted structure and relative phase purity was achieved. The structure had the orthorhombic structure and doped ruthenium preferred the B-site cation (Niobium) site as opposed to the B'-site cation (Titanium).

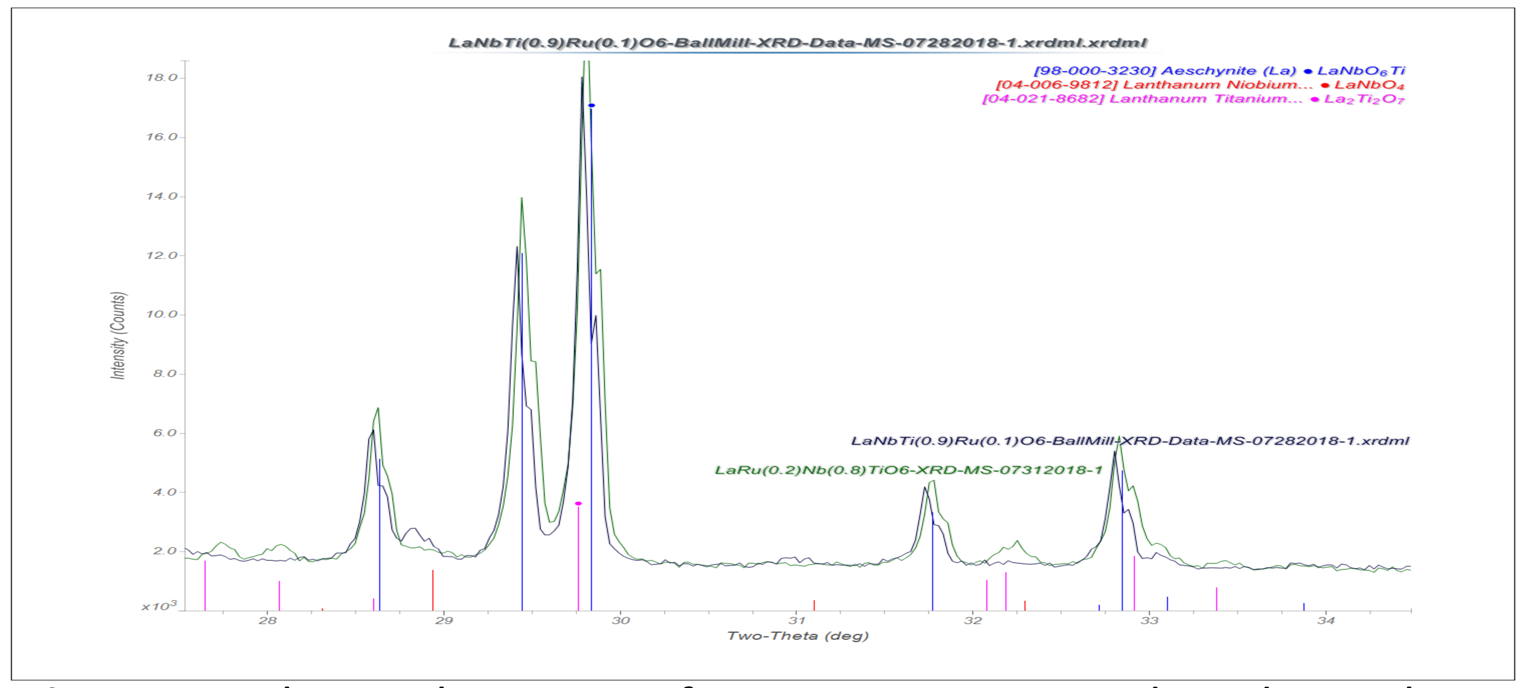

Figure 5. Below is the pattern for a twenty percent doped sample. Here the sample retains it's orthorhombic phase but a pyrochlore phase begins to form. Ruthenium doping is limited to around 10%.

CONCLUSION

1. Ruthenium dopants preferred to push out the B-site cation.
2. Phases formed transitioned from Orthorhombic to monoclinic above 1100 degrees Celsius.
3. Doping with 10 percent ruthenium successfully reproduced the expected XRD pattern.
4. A maximum of twenty percent ruthenium could be doped with relative purity (small amount of $La_2Ti_2O_7$ formation.
5. Second phase of synthesis may yield similar results.
6. Attempts at intercalation of RbF into the structure were met with mixed results. Further investigation is needed.

[1] Caruntu, Gabriel. Leonard Spinu, John B. Wiley, University of New Orleans, New Orleans, *New Rare-Earth Double-Layered-Perovskite Oxyfluorides, RbLnTiNbO6F (Ln = La, Pr, Nd)*. 28 Dec. 2001,

DMR1460920 and DMR 1420620 and DMR1523588).