Synthesis and Structural Characterization of Geometrically Frustrated Double Perovskites Ba_2YbMoO_6, Ba_2LuMoO_6, and Sr_2YMoO_6

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Abstract

Geometric magnetic frustration[1] occurs in a material when magnetic order is inhibited by the arrangement of magnetic ions. Commonly associated with triangular or tetrahedral coordination of moments favoring antiparallel (antiferromagnetic) alignment, frustrated materials can exhibit a variety of magnetic ground states because of the cancellation of normally dominant interactions. Geometrically frustrated materials are thus of interest for elucidating how magnetism arises in materials. Double perovskites of composition $A_2BB'O_6$, with 'rock-salt' order of magnetic B' ions[2], potentially exhibit frustration, with chemical versatility enabling the synthesis of many different compounds with divergent magnetic properties, with great potential to yield new insights into frustration physics.

We report several compounds synthesized via solid state methods based on the Mo^{5+} ion, particularly focusing on Sr_2YMoO_6, Ba_2YbMoO_6, and Ba_2LuMoO_6. These compounds, as well as several others, were predicted to have relatively stable lattices according to their calculated Goldschmidt tolerance factors. We report the results of structural characterization by the use of x-ray diffraction (XRD) and Rietveld refinement. We found that Ba_2YbMoO_6 and Ba_2LuMoO_6 crystallize in a simple cubic perovskite structure whereas Sr_2YMoO_6 exhibits a monoclinic structure. Syntheses of Sr_2GaMoO_6, Ca_2AlMoO_6, Sr_2ScMoO_6, Ba_2InMoO_6, Sr_2AlMoO_6, Ba_2ScMoO_6, Ba_2GaMoO_6, and Ba_2AlMoO_6 were attempted by the use of similar solid state methods. However, structural studies revealed that the desired phases were not produced. Possible causes for these discrepancies can include unreacted precursors, loss of volatile precursors, and formation of a non-perovskite structure.

Theory

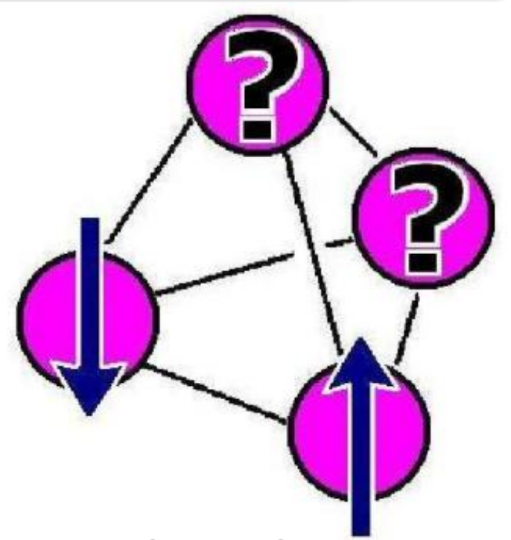

Fig. 1: Frustration of antiferromagnetically correlated moments, whose interaction energy is minimized by antiparallel arrangement, on a tetrahedron. No arrangement of the moments allows all interactions to be satisfied at once. This causes magnetic order to be suppressed to lower temperatures, or altogether, and leads to rich phase diagrams featuring exotic magnetic ground states, as moments attempt to relieve the frustration.

Double perovskites[2] with composition $A_2BB'O_6$ can form from most elements in the periodic table as indicated by the following Figure.

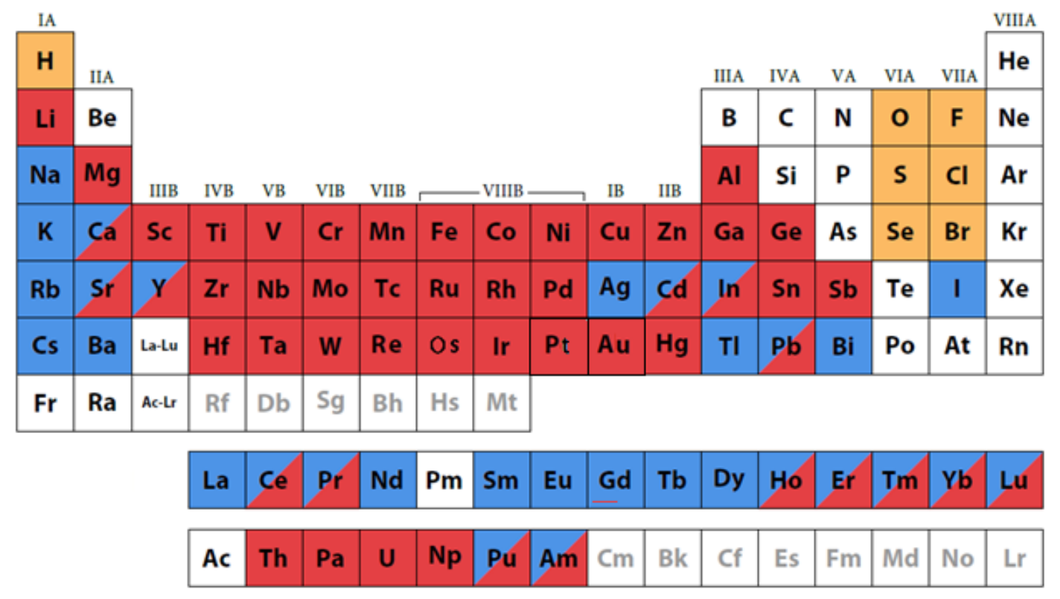

Fig. 2: Periodic table depicting which elements may be incorporated into the perovskite structure ABX_3, in the A (blue), B (red), and X (yellow) sites. The chemical versatility of the perovskite structure enables synthesis of a wide variety of compounds. (Adapted from a graphic by J. Rondinelli.)

The stability of perovskite structures may be characterized by the Goldschmidt tolerance factor[3], t:

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}$$

where r_A is the radius of the A-cation, r_B is the radius of the B-cation, and r_0 is the radius of the anion. For t ≈ 1, an ideal cubic perovskite structure is predicted. When t < 1, the BO_6 octahedra are too large to fit into the cubic structure, thus the octahedra are forced to rotate and tetragonal, orthorhombic, or monoclinic distorted unit cells result. t > 1 generally corresponds to instability of the perovskite structure, and a different structure forms instead.

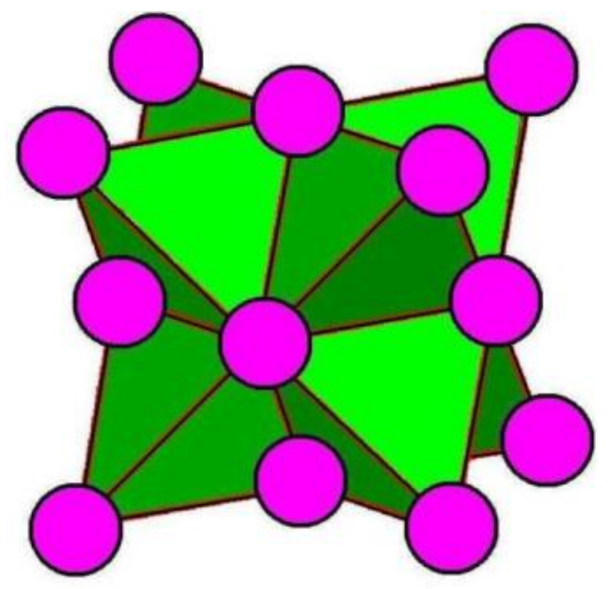

Fig. 3 (right): In rock-salt ordered double perovskites, the magnetic B′ cations comprise a face-centered cubic lattice, or, equivalently, a network of edge-sharing tetrahedra, which exhibit frustration in the presence of antiferromagnetic correlations.

Barium Lutetium Molybdenum Oxide: Ba_2LuMoO_6
Barium Ytterbium Molybdenum Oxide: Ba_2YbMoO_6

Background

Previous studies of Ba_2LuMoO_6[4] revealed that, in analogy to Ba_2YMoO_6[5], the structure crystalizes into face-centered cubic symmetry as shown in Figure 4. Powder neutron diffraction showed that both specimens retained cubic symmetry to 2K. However, no long-range magnetic order was observed in either case to 2K, and a spin-singlet ground state has been observed in Ba_2YMoO_6[6]. Ba_2LuMoO_6 has a Goldschmidt tolerance factor of 0.997, whereas t = 0.988 for Ba_2YMoO_6, so a cubic structure is predicted in both cases.

Similarly, it is expected that Ba_2YbMo0_6 will crystallize in a face-centered cubic structure, as its Goldschmidt tolerance factor is 0.995.

Synthesis

For the synthesis of these specimens, the following reactions were used:

$$2BaCO_3 + MoO_3 + \frac{1}{2}Yb_2O_3 \rightarrow Ba_2YbMoO_6 + 2CO_2 + \frac{1}{4}O_2$$

$$2BaCO_3 + MoO_3 + \frac{1}{2}Lu_2O_3 \rightarrow Ba_2LuMoO_6 + 2CO_2 + \frac{1}{4}O_2$$

The process began by pre-firing the precursors $BaCO_3$, Yb_20_3 (or Lu_20_3), and $Mo0_3$. The precursors were mixed in stoichiometric amounts to produce 1.000 g of final product, and then pressed into a pellet to ensure homogeneity.

Both specimens were prepared using the following cycle. The sample was first heated to 950 ºC for 12 hours, with heating and cooling times of 5 hours. The sample was then reground and pressed again into a pellet. To drive Mo into the relatively unfavorable 5+ state ($4d^1$electronic configuration) the final heating cycle was conducted under a 95% Ar / 5% H_2 reducing atmosphere, firing at 1250 ºC for 48 hours, with 12 hour heat up and cool down times.

X-ray diffraction on Ba_2YbMoO_6 revealed the expected cubic structure, and Rietveld refinement using the software suite *GSAS*[7] and *ExpGUI*[8] revealed three small unindexed peaks at $2\theta = 33.91^o, 2\theta = 49.01^o, 2\theta = 58.28^o$,with the 33.91^o peak coinciding with the odd-odd-even peak {310} forbidden for FCC symmetry. While these peaks are small, they suggest the presence of a small impurity phase, or a small level of cation displacement or oxygen non-stoichiometry.

In the case of Ba_2LuMoO_6, we found two small unindexed peaks corresponding to the Miller indices {312} and {310}, and one additional peak not corresponding to any indices of the indexed cubic cell. Further attempts to eliminate these peaks were made with another annealing cycle under a reducing atmosphere at 1100^oC, resulting in minimal change to the diffraction profile.

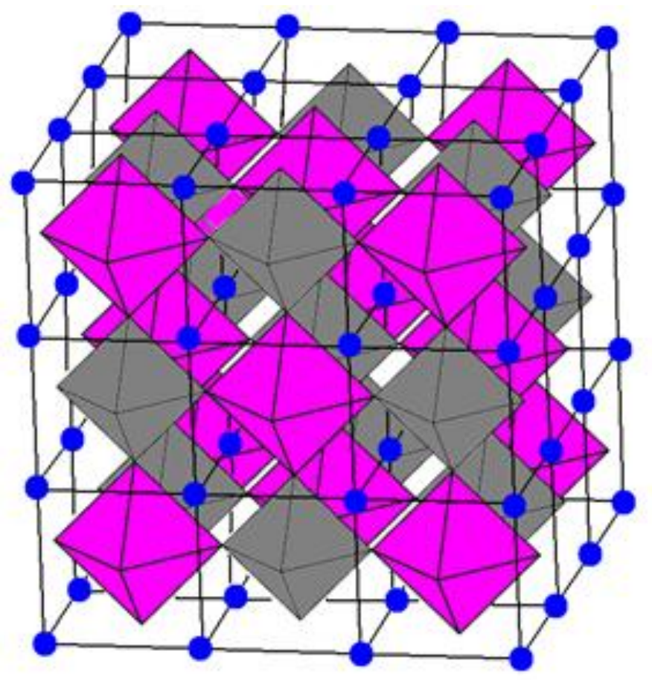

Fig. 4 (right): The ideal face-centered double perovskite structure $A_2BB'O_6$, exhibited by Ba_2YbMoO_6 and Ba_2LuMoO_6. In this structure, the A cation (Ba) is shown in blue, the non-magnetic B cation (Y) is at the center of the gray YO_6 octahedra, and the magnetic B′ cation (Yb or Lu) is at the center of the magenta $B'O_6$ octahedra.

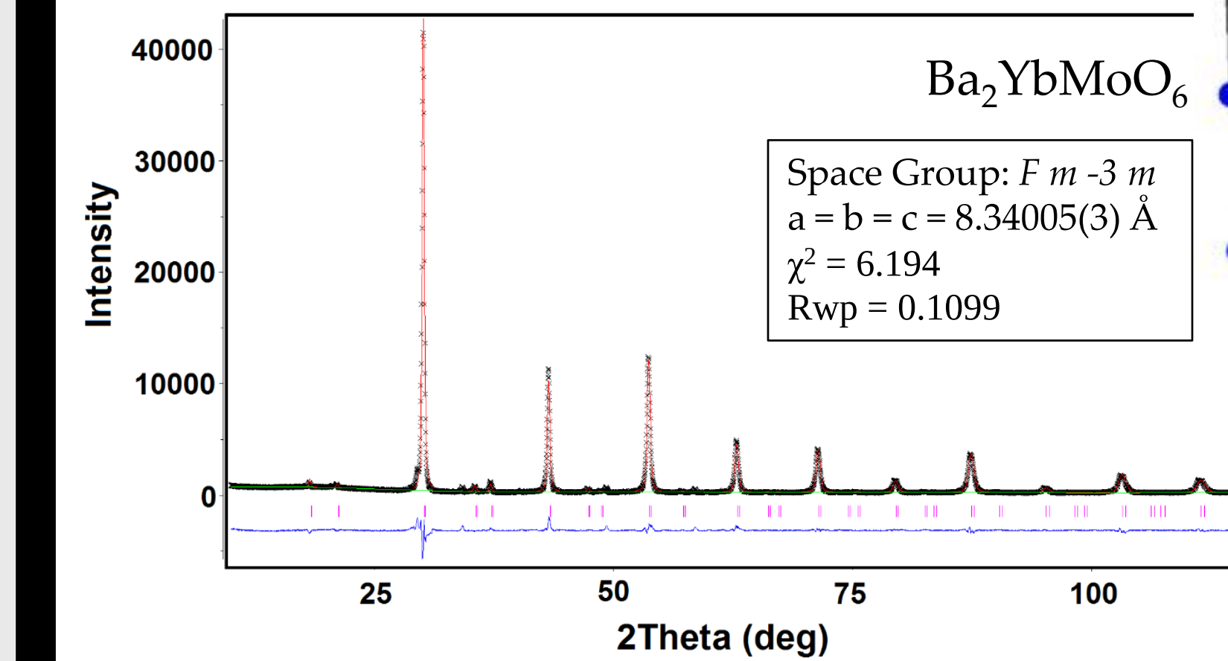

Fig. 5 (above left): Rietveld-refined fits of the XRD data for Ba_2YbMoO_6 synthesized under reducing atmosphere to an ideal face-centered cubic double perovskite structure, space group Fm-3m, consistent with previously published reports[9].

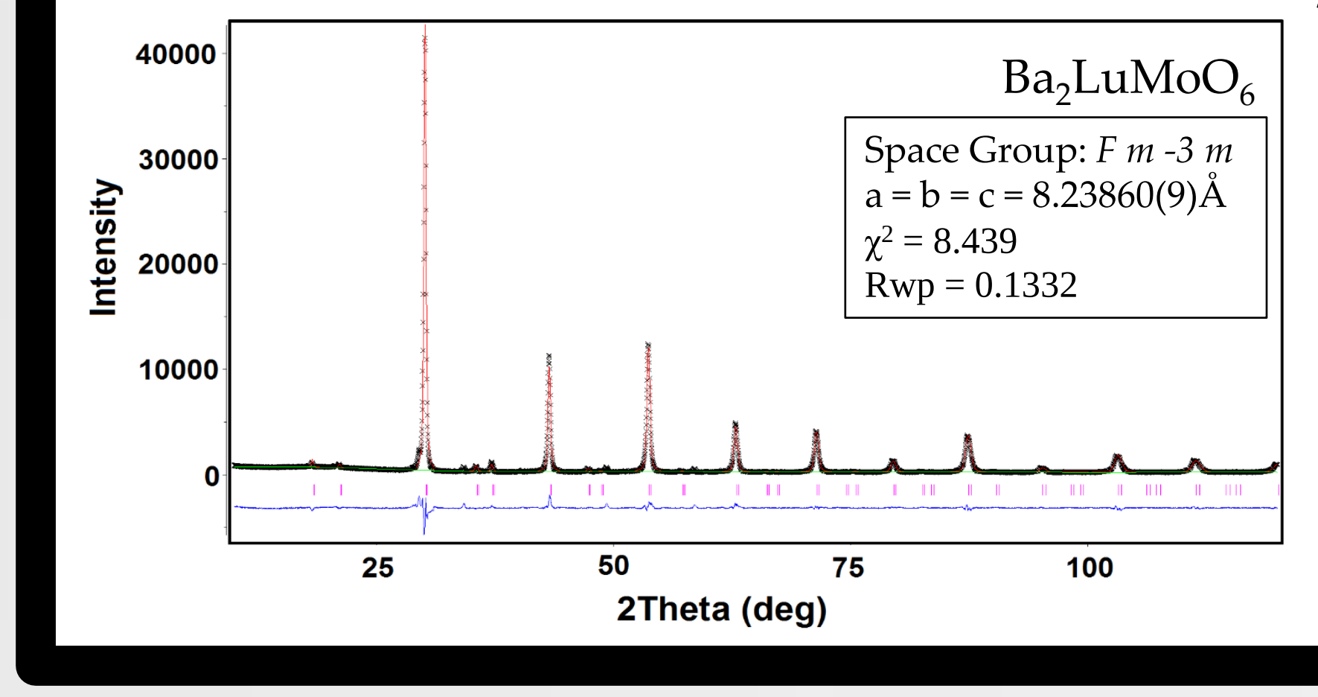

Fig. 6 (bottom left): Rietveld refined fit for Ba_2LuMoO_6. The data was analyzed using GSAS[7] and ExpGUI[8], indicating face-centered cubic structure.

Strontium Yttrium Molybdenum Oxide: Sr_2YMoO_6

Background

In contrast to the previous cases, Sr_2YMoO_6 – also based on the $4d^1$ Mo^{5+} ion – is expected to crystallize into a monoclinically distorted structure, based on its Goldschmidt factor t = 0.932. Previous studies of this compound[10] have shown weakly ferromagnetic interactions below 8K although more detailed magnetic characterization has not yet been performed.

Synthesis

We began the synthesis of Sr_2YMoO_6 by prefiring the necessary components measured out in stoichiometric amounts with the goal of making 1.000 grams of the final compound. We followed the chemical reaction

$$2SrCO_3 + MoO_3 + \frac{1}{2}Y_2O_3 \rightarrow Sr_2YMoO_6 + 2CO_2 + \frac{1}{4}O_2$$

After the precursors were fired and mixed in stoichiometric amounts, the first heating process was done under a 5% H_2/Ar reducing atmosphere in a tube furnace. The sample's mass was recorded to obtain the mass loss due to the annealing process, which was 17.6% compared to the expected mass loss of 21%. The sample was then ground up and re-made into a pellet. The sample was loaded into a tube furnace again and was heated in pellet form at 1250 °C and held for 48 hours. The mass loss after this heating cycle was 1.4% of the initial mass which totals to 19%, compared to the expected 21%.

XRD scans of the sample identified a monoclinic structure $P2_1/n$ with a few very small unindexed peaks appearing at low angle positions. Rietveld refinements using GSAS were made to fit the structural model, which was expected to be monoclinic based on the Goldschmidt tolerance factor.

To ensure a complete reaction, the sample was again heated in pellet form under a reducing atmosphere at 1100 °C and held for 48 hours. XRD measurements showed very minimal change in the diffraction patterns, although it did shrink the unindexed peaks slightly to better fit the theoretical model.

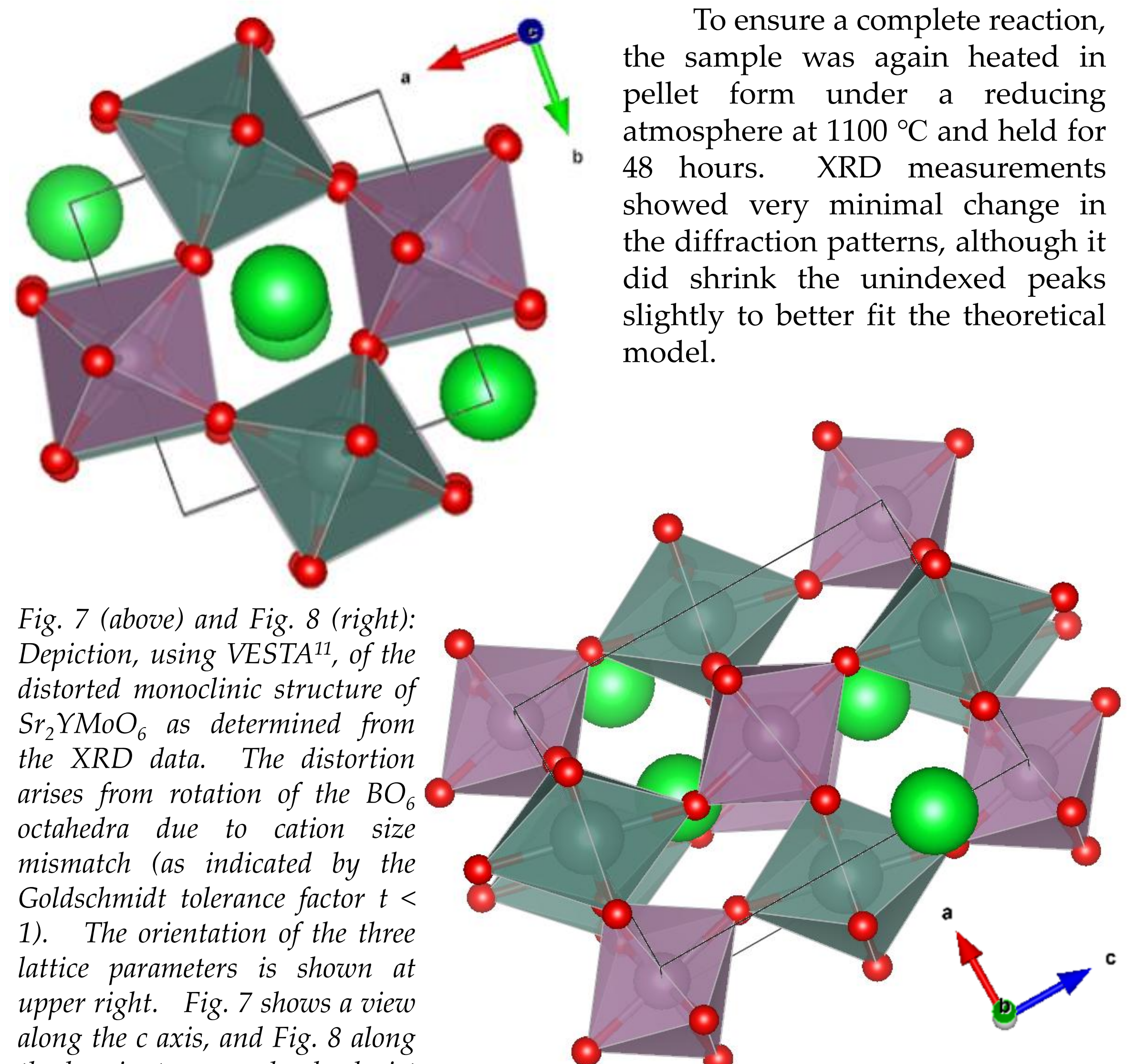

Fig. 7 (above) and Fig. 8 (right): Depiction, using VESTA[11], of the distorted monoclinic structure of Sr_2YMoO_6 as determined from the XRD data. The distortion arises from rotation of the BO_6 octahedra due to cation size mismatch (as indicated by the Goldschmidt tolerance factor t < 1). The orientation of the three lattice parameters is shown at upper right. Fig. 7 shows a view along the c axis, and Fig. 8 along the b axis, to more clearly depict the octahedral rotations.

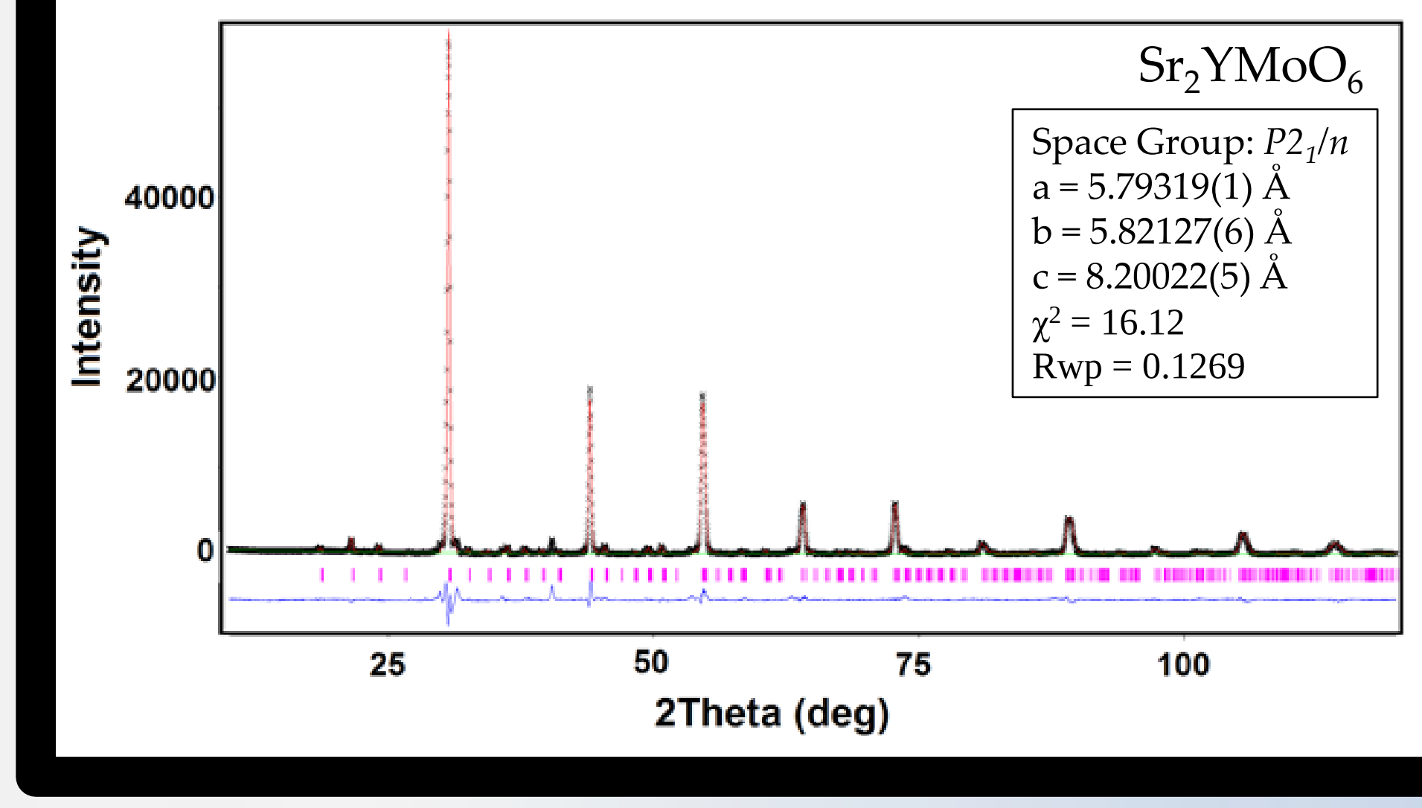

Fig. 9 (left): Rietveld-refined fits of the XRD data for Sr_2YMoO_6. The data were fitted to a distorted monoclinic double perovskite structure, space group $P2_1/n$, although a few small unindexed peaks suggest the existence of a small impurity phase.

Results & Conclusions

Magnetic frustration in double perovskites has garnered significant interest, as there is strong potential for systematic investigation of frustration physics, due to the chemical versatility of the perovskite structure.

We have successfully synthesized Ba_2YbMoO_6, Ba_2LuMoO_6, and Sr_2YMoO_6, using analogous techniques to those previously used for Ba_2YMoO_6[5].

X-ray diffraction analysis shows that the double perovskites Ba_2YbMoO_6 and Ba_2LuMoO_6 exhibit cubic symmetry, while Sr_2YMoO_6 exhibits monoclinic symmetry, as expected from their Goldschmidt tolerance factors.

Each sample was synthesized using a standard heating process under a reducing Ar/H_2 atmosphere, to stabilize the desired Mo^{5+} ($4d^1$) state.

Ba_2YbMoO_6 and Ba_2LuMoO_6 were observed to have a few very small peaks that corresponded to forbidden FCC symmetry, suggesting a small level of cation displacement or oxygen non-stoichiometry.

Attempts to synthesize several other double perovskites were unsuccessful, as determined by XRD measurements. In some cases there was clear loss of volatile precursors, or unreacted precursors remained. In some cases, it may be that no stable perovskite compound may be formed.

However, there are a great variety of synthesis conditions possible, as both the temperature and atmosphere play a large role in determining the synthesis environment, and different combinations of precursors can be attempted. Changing these factors could result in a successful formation. Sol-gel methods could also be another route to synthesizing these perovskites, particularly when volatility at high temperatures is a concern.

Further measurements on our successful samples include magnetic susceptibility, heat capacity, muon spin relaxation, and neutron scattering. These measurements will allow us to observe any potential phase transitions and magnetic behavior, enabling a fuller characterization of these specimens.

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