High Dynamic Gas Pressure Single Crystal Growth

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Abstract:

The study of frustrated magnetic systems is of interest due to their potential to elucidate unique low temperature thermodynamics and to advance technological capabilities through quantum computing. One system of particular interest is the $RE_3Sb_3Mg_2O_{14}$ system, where RE represents a rare earth element. This system is a derivative of the classic spin-ice pyrochlore structure, but interestingly, has a 2-D layered kagomé sublattice composed of rare earth atoms (see Figure 1). Additionally, this system shows antiferromagnetic interaction between nearest neighboring atoms, which combined with its kagomé structure, makes it an excellent quantum spin liquid candidate. The difficulty with this material is growing single crystals, which are required to further explore the system's low temperature thermodynamics through inelastic neutron scattering. The crystal growing method of choice is the high pressure floating zone technique. The challenge of growing single crystals with these materials is finding the correct set of thermodynamic conditions where the material melts congruently, and a floating zone can be established. This project will mainly focus on growing single crystals of the neodymium analog of this material for several reasons. Firstly, neodymium has three unpaired electrons in its valence shell, thus it has a magnetic moment. Secondly, the powdered form of this material has been extensively studied [2] and is confirmed to have interesting antiferromagnetic interactions.

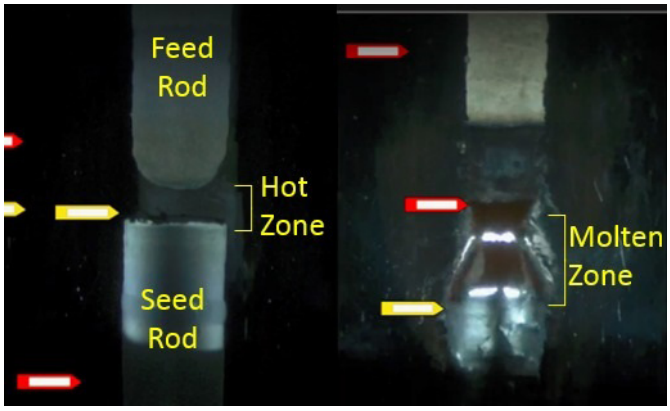

Figure 1: [1] A simplified representation of the structure of the $Nd_3Sb_3Mg_2O_{14}$ system. The image on the left visualizes the corner sharing triangles that compose the neodymium kagomé sublattices. The image on the right displays one ($MgNd_3$) of the two characteristic tetrahedra that compose its pyrochlore structure.

Summary of Research:

The floating zone technique (see Figure 2) utilizes a beam of focused light to create a small "hot zone" where the energy is absorbed by the sample. Two rods, normally composed of polycrystalline powder of the desired composition, are placed on either side of the hot zone. The rod underneath the hot zone is known as the seed rod and it is where the single crystal will be grown. The top rod is known as the feed rod, and it ensures that the molten zone is filled with enough material to maintain its stability. The first step of a floating zone growth is to melt the tip of the seed rod. Then, the feed rod is lowered onto the molten tip of the seed rod and a liquid floating zone is established between the two rods. Once the zone is deemed stable, the feed and seed rods are slowly lowered causing the liquid to crystallize on the

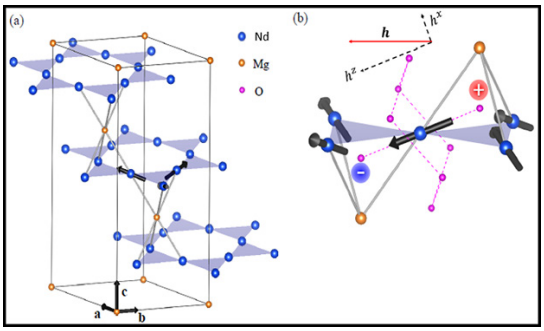

Figure 2: The arrangement of the classical floating zone growth before and after the floating zone is established.

seed rod. Initially, the solidifying liquid will form many domains, but eventually, due to the thermodynamics of the system, a single domain will be selected and a single crystal will have been grown.

This procedure will be known as the "classical floating growth technique", but there are several variations of this technique. The first variation is known as the "pedestal growth technique". This method utilizes a very thin upper rod to attempt to pull a crystal up and out of a melt. Using a thin rod allows for easier access to melts that would be difficult to connect with two full sized rods. Additionally, various materials may be used for this top rod, which may improve the adhesion and stability of the melt. The second variation is known as the "traveling solvent technique". This method is functionally the same as the classical growth technique, but a small pellet of solvent is placed on top of the bottom rod during set up. This pellet of solvent serves to aid the melting of the desired material while, ideally, resulting in as little impurities as possible. All three of these methods were used in this study.

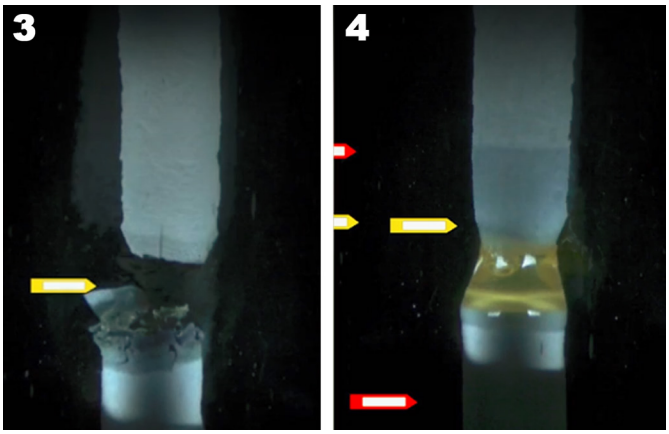

Figure 3, left: Result of the classical floating zone growth attempt at 165 bar. Figure 4, right: Result of the traveling solvent floating zone growth with pure Li_2MoO_4 at 150 bar.

Results and Conclusions:

Classical floating zone growth was attempted at 150 bar, 185 bar and 200 bar. No stable floating zones were established (Figure 3). Powder x-ray diffraction indicates that this material melts congruently (does not change composition when melting) under these thermodynamic conditions, but the molten material does not adhere to the solid rod, forms a solid outer shell, and frequently cracks under the conditions required to melt it.

Pedestal floating zone growth was attempted at 200 bar using an alumina top rod. The molten material also did not adhere to the alumina rod. Additionally, the temperature required to melt the kagomé is too high and causes the alumina to melt prematurely.

Traveling solvent floating zone growth was attempted with $MgSb_2O_6$ at 165 bar and Li_2MoO_4 at 150 bar. After signs of success with pure Li_2MoO_4, pellets of 1:1 and 3:1 molar ratios of Li_2MoO_4 to $Nd_3Sb_3Mg_2O_{14}$ were attempted. The $MgSb_2O_6$ flux is not viable as it has a melting point above that of $Nd_3Sb_3Mg_2O_{14}$. Pure Li_2MoO_4 showed potential as a stable floating zone was established (see Figure 4), but further exploration is needed to find the correct thermodynamic conditions to form a crystal. Powder x-ray diffraction indicates that the Li_2MoO_4 did not form a new compound with $Nd_3Sb_3Mg_2O_{14}$. This is another good indicator that it could be used as a potential flux. No stable floating zones were established using the pellets composed of both Li_2MoO_4 and $Nd_3Sb_3Mg_2O_{14}$.

Future Work:

Future work should target a way to better sinter the rods of $Nd_3Sb_3Mg_2O_{14}$. Increased density of these rods will only serve to increase the consistency of repeated experiments as well as prevent melts from being sucked into the rods. Finally, further research into the traveling solvent, with both Li_2MoO_4 and other solvents, shows the greatest promise toward growing single crystals of $Nd_3Sb_3Mg_2O_{14}$.

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References:

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[2] A. Scheie, et al. arXiv:1604.03950 (2016).

[3] W.A. Phelan, J. Zahn, Z. Kennedy, and T.M. McQueen, "Pushing Boundaries: High Pressure, Supercritical Optical Floating Zone Materials Discovery," Submitted J. Sol. St. Chem. (2018).