Structural Investigation of Epitaxial Thin Film Pyrochlores

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Abstract:

Epitaxial stannate pyrochlores ($A_2Sn_2O_7$) thin films were synthesized on commercially available substrates by way of Molecular Beam Epitaxy (MBE). The limits of cation non-stoichiometry were probed in order to demonstrate precise stoichiometric control enabling doping of these films.

Summary of Research:

Metal oxides are no stranger to industry as they are regularly used in a wide variety of applications. These applications are heralded by the broad array of properties that metal oxides can possess. One class of metal oxides that demonstrates a variety of physical properties are pyrochlores. Pyrochlores take the form $A_2B_2O_7$, where A is a rare earth metal or inert lone-pair electron element, and B is a transition or post transition metal [1]. The structure of a pyrochlore is very similar to that of a fluorite with the difference being a systematic oxygen deficiency in the pyrochlore's cubic structure [6].

Pyrochlore stannates (of the form $A_2Sn_2O_7$) are particularly interesting as they exhibit a wide variety of properties by themselves. For example, lanthanide stannate pyrochlores ($La_2Sn_2O_7$) have demonstrated photoluminescence, radiation tolerance, and the capability of retaining their pyrochlore structure under extreme conditions [2-3]. Hence, the applicability of stannates is quite promising.

Despite their interesting properties, there is a lack of literature on the synthesis of epitaxial stannate pyrochlore thin films. This project demonstrates how epitaxial pyrochlore stannates ($La_2Sn_2O_7$ and $Y_2Sn_2O_7$, specifically) of high crystalline quality can be grown on the commercially available fluorite substrate yttria-stabilized zirconia (YSZ). The stoichiometries of these films were varied to demonstrate the limits of crystalline growth and the preliminary cation ratios estimates were provided by a Quartz Crystal Microbalance (QCM). X-ray Diffraction (XRD) and Reflection High Energy Electron Diffraction (RHEED) were used to determine crystal quality of the grown films.

Results and Conclusions:

RHEED analysis provides information on the surface crystallinity of the thin films. Figure 1 (a-c) displays diffraction patterns for yttria-based films while Figure 1 (d-f) displays such for the lanthanum-based films. A trend in both sets of these materials is the increasingly diffuse pattern resulting from tin excess with the additional emergence of spots that indicate 3D growth. Another trend is lack of half-order peaks, which are to be expected for well-grown pyrochlores since the lattice constants are roughly double that of the fluorite substrate, in the patterns for samples with an excess of the A-site cation. Hence, the films that demonstrate the best crystallinity are those in the center column with their pronounced patterns and present half-order peaks.

XRD provides information on the bulk crystallinity of the thin films. Similarities between the two different stannates *via* XRD can be seen in Figure 2. The poor thickness fringes in the most tin-rich samples demonstrate that these samples are far from perfect in crystallinity. For the $Y_2Sn_2O_7$ graph, the dampened peak

and slight peak shift in the Sn/Y = 1.01 suggest that the sample is actually more tin-rich than the QCM ratio indicates. The peak shifts depicted here are manifestations of changes in the lattice parameters, or unit cell dimensions, established by the composition of each material.

Further analysis of the films and substrates through phi scans and rocking curves demonstrated that the films with shifts are still epitaxial and of high crystallinity. Hence, the visible peak shifts to lower angles can be explained by an expansion in the lattice caused by the compensation from the A-site excess through the oxygen vacancies [4]. From these peak shifts, it appears that the sample with Sn/Y = 0.89 is closest to the ideal stoichiometry. Similarly, the lanthanum-based film closest to ideal stoichiometry is likely between Sn/La = 0.93 and Sn/La = 1.00.

The stoichiometric control in the growth of high-quality films demonstrated here allowed for the synthesis of each stannate doped with 20% of antimony, which was predicted to result in conductivity due to the heterostructure of both stannates [5]. As depicted in Figure 3, there are no noticeably significant peak shifts or abnormalities in the diffraction patterns for the doped samples, so the doped films are epitaxial and of good crystalline quality.

Future Work:

The immediate next step will be the electrical characterization of the doped thin films to probe the degree of metallicity achieved, if any. Further a good control of this material system potentially allows us an application in heterostructures predicted to result in superconductivity by She et al. Finally, the precise stoichiometry control makes these materials even more interesting for investigating their catalytic properties.
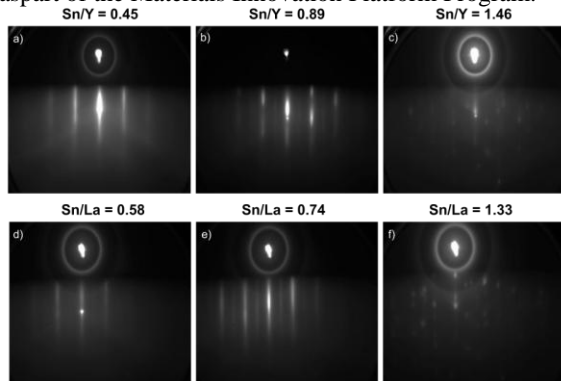
Acknowledgements:

Figure 1: *RHEED diagrams of selected samples of both stannates. Diagrams (a-c) show patterns for Y-based samples whereas (d-f) show patterns for La-based samples.*
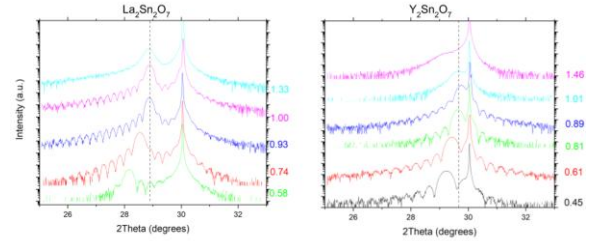

Figure 2: *X-ray diffraction patterns situated around the 222 peaks of each film and shifted for convenience. The ratios Sn/La (Left graph) and Sn/Y (Right graph) are displayed on the right side of each graph to identify the sample. The dotted lines indicate the expected peak value for bulk stoichiometric samples [7-8].*
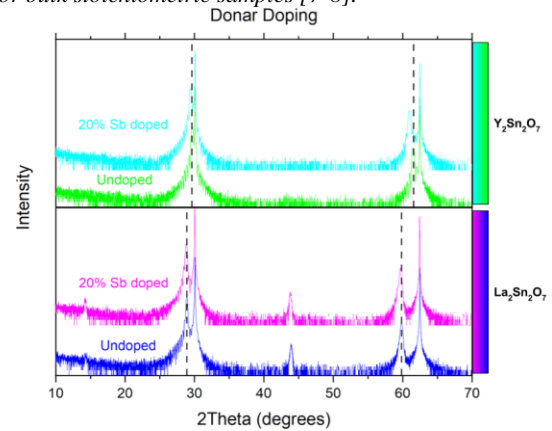

Figure 3: *X-ray diffraction patterns of 20% Sb-doped vs. undoped stannate samples with the Y-based patterns above the La-based. The dotted lines indicate the peaks for the undoped samples.*

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