Synthesis of Transition Metal halides: Discovering Ferroelectric materials

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Abstract

Ferroelectricity has long been discovered and explained by different research groups. We have decided to look into how to expand ferroelectricity into inorganic, organic hybrids by looking into inorganic substrates that can serve as the template for ferroelectric polymers and aiming to create new innovative technology. These polymers will self-assemble due to the interactions with the inorganic ferroelectrics. Here we have taken the geometrically forced polar bond of Nb3Cl7X(S, Se, Te) and tested it to see if we can create that growth and see if the transition has a magnetic field. We used chemical vapor transport to create these growths. Our transport agent was ammonium chloride, chosen to help the formation of crystals at the hot end of the temperature gradient. Running X-ray diffraction, XRD, and single crystal diffraction provided insight into the material made. As well as taking a closer look and using Energy Dispersive X-Ray Spectrometry, EDS/EDX, map scans for further investigation on the stoichiometry of the different variations. The next steps are electrical measurements which will be tested using the Physical Property Measurement System, PPMS, and checking its polarization-current loops.

Introduction

Ferroelectricity, which has switchable electric dipole moments, can improve the internal potential and output power of energy in devices. They are used in advanced technologies and electronic devices such as phones and computers. Our goal is to create a new type of flexible ferroelectric substrate that can be used to enhance the power efficacy of technology and new kinds of devices. In this study, I am focusing on 2D inorganic ferroelectrics that can be used as a template for the self-assembly of organic substrates—creating new types of ferroelectric materials that use Nb3Cl7X (X=S, Se, Te), materials that will be prepared and tested for ferroelectric behaviors.

Methods

To create and study Nb3Cl7X(X=S, Se, Te), a single crystal structure must be made by Chemical Vapor transport, CVT. CVT is the process of taking a transport agent and a condensed solid phase and creating a crystal on the opposite end of the temperature gradient[1]. The transport agent is a volatile material mixed with your starting material to create a gaseous phase. In my experiments, ammonium chloride was used. The multi-zone furnace produces larger crystals because you can control the temperature gradient and increase the transport rate. Leaving the reaction for roughly three to four days and then running XRD and SEM to check what was created from the CVT. To improve my growth, I purified all of my halides and mixtures to remove oxygen by vapor transport. Everything must be done in the glove box and pukes covered in tape to

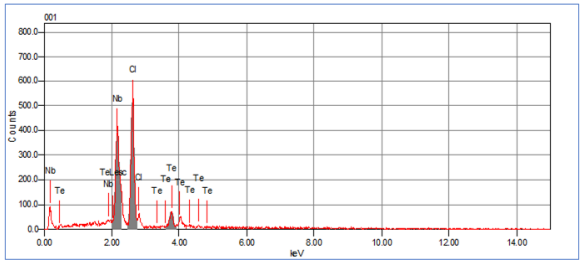
set up the XRD samples because my samples are moisture sensitive. The SEM was set up similarly but sealed inside a larger air-sensitive container.

Results

A subset of transition metal halides was heated in the multi-zone furnace and had a temperature gradient of 820℃, at the hot end, 785℃ where the actual crystal growth takes place at the cold end and 795℃ at the middle growth to ensure that the crystals evenly distribute throughout the quartz. They were left for three days, then ramped back down to room temperature, and were then ready for XRD and SEM tests.

Figure 1. Chemical Vapor Transport Growth Nb_3Cl_7Te

Sealed sample Ag-tube XRD was run on the delicate crystalline structures produced due to a lack of results with normal XRD. Which is due to the decomposition of the growths. SEM results showed that I had created the substrates but that they lacked the purity needed to be given the accurate ratio. The test also showed that a homogeneous structure was produced. I got a pretty accurate percentage that was intended with the Te growth, shown in figure 2, and then ran a PPMS scan on four-wire resistivity, proving my material was insulating. I could infer that the growth of the Te variant was a semiconductor and needed further purifications to be well on the way to creating a ferroelectric material. To understand the electrical behavior I worked with Jason Zhang, a fellow undergraduate, to compute with DFT to form a band structure that indicated a minimal band gap, as shown in figure 3. The spin-orbit coupling was suspected of changing this by at least 30% but had no fundamental shift in my case. This small change is necessary to note, as well as the small band gap indicating that my material is semi-conducting.



Formula	mass%	Atom%	Sigma	Net	K ratio	Line
Cl	36.58	62.26	0.33	15161	0.0022767	K
Nb	43.85	28.48	0.62	15881	0.0029626	L
Te	19.57	9.25	0.50	4049	0.0010524	L
Total	100.00	100.00				

Figure 2. EDS Scan of Nb_3Cl_7Te

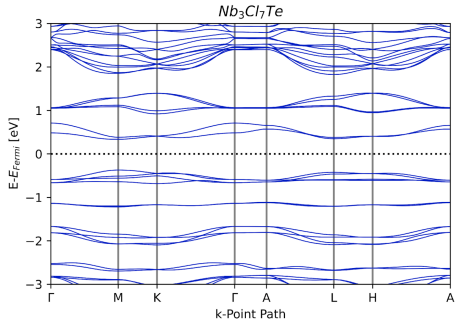


Figure 3. Band Structure with band Gap of 0.7107ev.

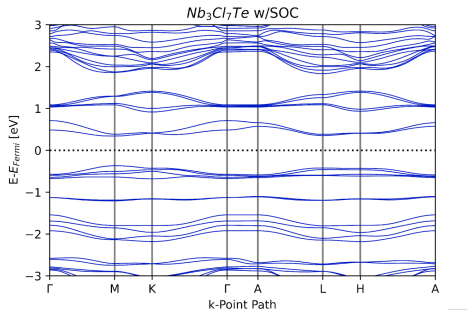


Figure 4. Spin Orbital Coupling band gap of 0.7105eV.

Conclusion

My initial results were contaminated by air, causing oxygen to infiltrate my substrates. Using XRD patterns, I could see a mixture of Nb3O and NbCl5 was included in my creation. I fixed this issue to the best of my ability, but it is tough to eliminate all impurities. Once the ratio of Cl: Te is accurate further PPMS scans could be run on the sample to see if the growth is ferroelectric.

References

[1] *Chemical vapor transport*. Mpg.de. https://www.cpfs.mpg.de/2651362/chemical-vapor-transport. (accessed 2022-07-18).

[2] Globalsino.com. https://www.globalsino.com/EM/page3544.html (accessed 2022-07-18).

[3] Miller, G. J. Solid State Chemistry of Nb3Cl8: Nb3TeCl7, Mixed Crystal Formation, and Intercalation. J. Alloys Compd. 1995, 217 (1), 5–12. https://doi.org/10.1016/0925-8388(94)01298-v.

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