Synthesis of AI-predicted Cuprate and Intermetallic Superconductors

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Abstract— **This work demonstrates the attempted synthesis of AI-predicted compounds to aid in a closed-loop materials design process. One of the predicted compounds resulted in the formation of an unknown phase. This phase was isolated, resulting in a phase-pure powder used for laser diode floating zone (LDFZ) growth. Crystals were made of a compound with the same stoichiometry as predicted, minus the Mg, which allowed for single-crystal X-ray diffraction (SCXRD) to be performed and a preliminary structure to be obtained. An LDFZ growth was conducted with the phase-pure powder, resulting in a polycrystalline sample that was unable to be used for SCXRD. Intermetallic compounds were also synthesized from AI-predicted lists. One compound formed the predicted phase, and the synthesis parameters of others were explored. These results will be fed back into the AI software, closing the loop and aiding in future material prediction.**

I. Introduction

Superconductors are materials that have no resistance below a critical temperature and expel an applied magnetic field via their perfect diamagnetism. These materials are commonly used in MRI technology and power transmission cables. The search is ongoing for room-temperature (or at least higher temperature) superconductors so that they can operate without the use of liquid helium. A family of superconductors that has been widely explored and has relatively high critical temperatures is the Cuprate family. This family of superconductors contains layers of Cu-O planes separated by atoms of other elements. Designing new Cuprates involves consideration of the chemical formula and structure. Feasible chemical formulas will have non-toxic elements and appropriate/stable oxidation states for all elements (often a non-integer Cu oxidation state). Feasible structures will have appropriate sizes and shapes of coordination polyhedral, anions and cations dispersed throughout the structure, and – most importantly for superconductivity in this family – a square net configuration of Cu and O. We lack predictive power of these materials, as this process takes time and intuition. AI software uses a closed-loop process to predict materials to be feasible, offering a new way to approach materials design.

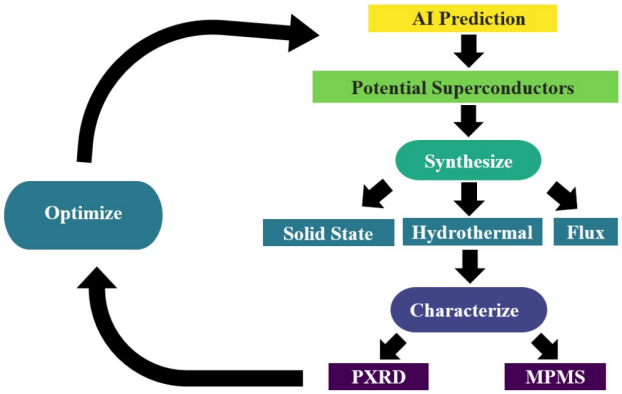

Fig. 1 Diagram of the closed-loop AI prediction process used in this work

This paper focuses on the synthesis and characterization aspects of the closed-loop process, leading to the isolation of an unknown phase.

II. Methods

Lists of millions of AI-predicted superconducting compounds were provided by collaborators with Microsoft and the Johns Hopkins Applied Physics Laboratory (APL). From that list, compounds were chosen with the most feasible crystal structures and the highest predicted critical temperatures. In this work, 30 of the predicted compounds were synthesized at two temperature profiles each. These compounds were synthesized through solid-state synthesis, where the oxide and carbonate reagents necessary to form the compounds were weighed and ground in a mortar and pestle. Each reagent was measured such that it would result in 400 mg of the predicted compound. After combining the reagents, the compounds were placed in alumina crucibles and heated in a box furnace to 800°C for 12 hours. The compounds were ground again after heating, and a portion was

put back into the furnace to heat to 900°C for 12 hours. Powder X-ray diffraction (PXRD) was conducted using a Bruker D8 Focus powder diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å) with 2.5° Soller slits and a LynxEye detector. PXRD was done on each compound, with both 800 and 900°C dwell temperatures, to determine if the predicted phase formed during heating. X-ray diffraction patterns were analysed, and peaks were matched to known phases found in the Bruker Eva database and the Inorganic Crystallographic Structure Database (ICSD) until all known peaks were identified. Peaks not matched to a known compound were classified as unknown and were the focus of isolation, which is discussed later in the results section. After compounds were analysed through PXRD, magnetic testing was done to characterize the properties of each compound. DC magnetic susceptibility tests were conducted on a Quantum Design Magnetic Property Measurement System (MPMS3). These tests were run from 2 to 300 K with an applied field of 10 Oe. Through these measurements, the compounds could be classified as either superconducting or non-superconducting.

Floating Zone Procedure

A phase-pure powder was created, which was made into rods and used to perform a laser diode floating zone (LDFZ) growth. To make the rods, powder was funnelled into a long balloon and compacted with a glass stirring rod. After the powder had been compacted, the balloon was connected to a vacuum pump and evacuated for 30 minutes. Knots were tied to seal the powder under vacuum before removal from the pump. The balloons were then placed in a cold isostatic press to compact the powder further. The final step in preparing the rods involved removal from the balloons and then a heat treatment at 800°C for 44 hours in a box furnace. The floating zone growth was conducted under flowing oxygen, with 10 rpm counterrotation of the rods and a growth rate of 10 mm/hr.

Intermetallic Synthesis

Intermetallic compounds were also synthesized in this work. To synthesize these compounds, metal chunks of each element were measured and arc melted. The buttons obtained from the arc melting process were crushed, and PXRD was done to determine the composition.

III. Results/Discussion

During PXRD analysis, one compound, Ba_3Sr_2LiLaMg_2Cu_5O_14, contained a majority phase that could not be identified as a known phase.

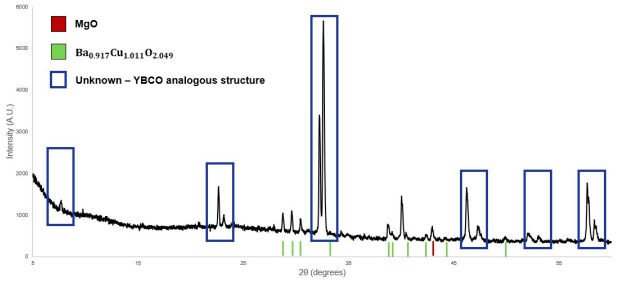

Fig. 1 PXRD pattern of **Ba_3 Sr_2 LiLaMg_2 Cu_5 O_14** matched with known phases and unknown majority phase.

Following initial analysis of the phases present in the powdered compound, the unknown phase was searched to find analogous structure types to guide further isolation attempts. Through this process, it was found that a YBCO analogous structure matched the pattern of the unknown, which was used as a basis for a theoretical crystal structure for the phase. Figure 2 shows the PXRD pattern of the compound with both known and unknown phases identified. From this pattern, it can be observed that the majority phase present is the unknown, furthering the motivation to isolate and identify it.

Isolation of unknown peaks

The isolation process began with determining which of the elements present in the initial compound were present in the unknown phase formed. New compounds were synthesized that had the same stoichiometry as the initial compound with one element removed (i.e., no Ba, no Li, etc). Through analysis of the PXRD patterns for each new compound, it was observed that the phases formed did not match the peaks in the original, suggesting that the unknown phase contained every element in the predicted formula.

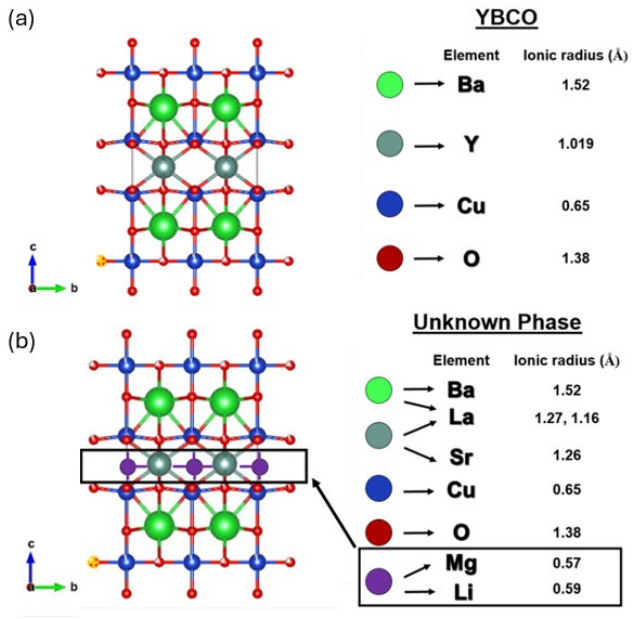

Fig. 3 (a) Labelled YBCO structure; (b) Theoretical structure of the unknown phase

Once it was determined that the unknown phase contained every element, the structure was analysed to predict formulas for the compound. Figure 3 shows the crystal structure and elements contained in YBCO (a) compared to the theoretical crystal structure of the unknown synthesized (b). To construct the theoretical structure, YBCO was used as a template since it was the analogous structure to the unknown formed. In the theoretical structure, the Ba site stayed the same as in YBCO, but it was theorized that it could be sharing a site with the La since they are similar in ionic radius in that coordination environment. The La was also predicted to share a site with Sr for the same reason. The Li and Mg were then suggested to fill the vacancy in the crystal lattice.

To determine whether the proposed structure was consistent with the phase formed, new compounds were synthesized to determine which sites were being shared. Compounds with excess Ba compared to La, Li compared to Mg, and with Mg removed completely were synthesized and analysed. In the compounds synthesized, it was observed that the unknown peaks only formed with excess Ba compared to La, as in the predicted formula, and with excess Li compared to Mg.

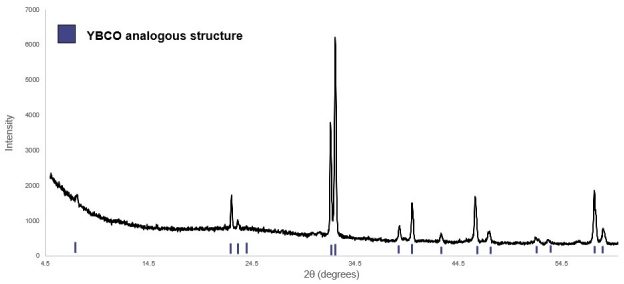

Fig. 4 PXRD pattern of phase-pure unknown with YBCO analogue peaks indicated

Using the results obtained from the PXRD scans, a new formula was targeted to form a phase-pure powder of the unknown. $Ba_2Sr_2LiLaMg_2Cu_4O_{14}$ was synthesized using various temperature profiles to determine the optimum heating conditions for formation. The phase-pure powder consisted of a powder of the unknown with very minor impurities, as shown in Figure 4. The heating profile that accomplished this goal had a peak temperature of 900°C, which was held for 4 hours before cooling to room temperature. This powder was used later in this work for crystal growth.

Crystal growth

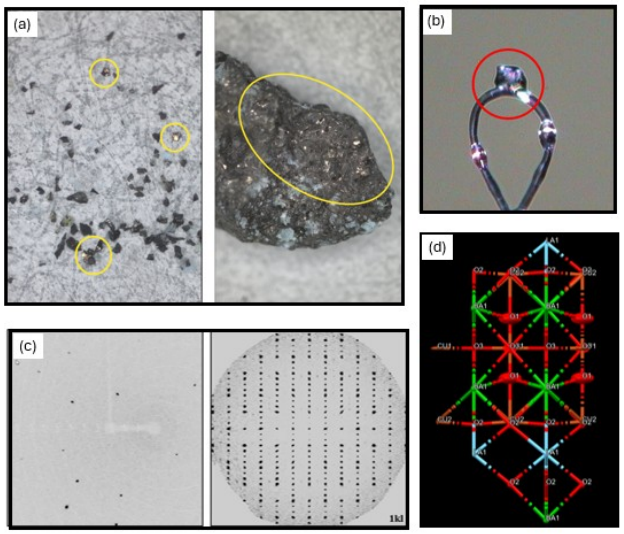

Fig. 5 (a) Crystals grown in a furnace of compound without Mg; (b) Single crystal used for SCXRD; (c) Single crystal diffraction patterns; (d) Preliminary crystal structure

During the process of testing formulas to obtain a phase-pure powder, one batch of compounds was heated to 1050°C instead of 900°C due to a furnace program mishap. A compound that contained

excess Li and no Mg melted and formed single crystals (Fig. 5(a)). These crystals were ground into a powder, and PXRD was used to determine that the phase formed matched the peaks of the unknown phase, except that they were shifted to lower 2theta, indicating larger lattice parameters than the unknown phase. Since the phase present had the same structure, minus the Mg, the single crystals remaining were used in single-crystal X-ray diffraction (SCXRD) (Fig. 5(b), (c)) using a SuperNova diffractometer (equipped with Atlas detector) with Mo Kα radiation (λ = 0.71073˚A) under the program CrysAlisPro (version 1.171.42.49, Rigaku OD, 2020- 2022) to determine if the structure matched that of the predicted YBCO analogue. These measurements allowed for the preliminary structure to be obtained (Fig. 5(d)), which was consistent with the proposed YBCO analogue. The structure was also consistent with site sharing in both the Ba and La sites, as predicted.

The crystals from the compound without Mg were useful for determining structure, so crystals of the unknown compound with Mg were targeted. Phase-pure powder of the unknown compound was pressed into rods to perform a laser diode floating zone (LDFZ) growth.

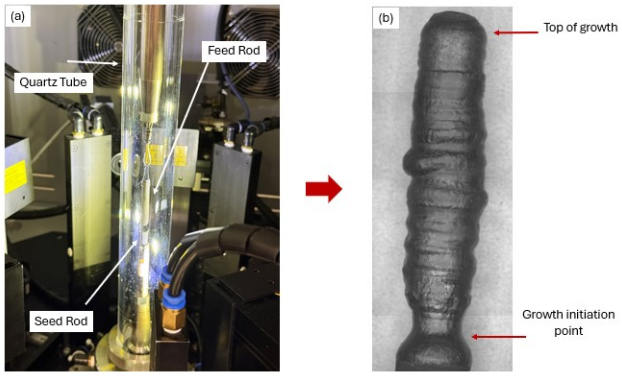

Fig. 6 (a) LDFZ set up with rods of unknown composition; (b) Growth from the LDFZ process.

The rods were cut into two pieces to make a feed and seed rod and placed inside a quartz tube in the LDFZ setup (Fig. 6(a)). The rods were used to make a growth that was roughly three centimetres in length (Fig. 6(b)). This growth was cut into pieces to examine its crystallinity. Upon cutting the growth, it was evident that it was polycrystalline, with few crystals able to be seen and separated. Unfortunately, SCXRD could not be performed on the grown crystal due to its polycrystallinity. This leads to future work in determining the best parameters for growth such that a single crystal is obtained.

Work is currently underway to explore the heating profile of the compound to obtain single crystals of the unknown phase for analysis. These crystals will be used to determine the structure of the unknown compound, as well as to compare it to the structure found without Mg and the expected YBCO analogue.

Intermetallic Compounds

Alongside the cuprate superconductor list, an intermetallic superconductor list was generated by the AI software. From this generated list, the predicted compounds were down-selected based on the feasibility of the structure. From analysis of PXRD patterns, it was determined that only one of the compounds, LaGaPd_2, was synthesized during the first attempt at arc melting. Another target compound was SiHfNi_2, which formed Si_6Hf_7Ni_16. Since the phase that formed was very similar to the predicted formula but with excess Ni, the amount of Ni was changed to observe the effects on the phases formed. Future work would continue to explore the synthesis of these compounds by changing reagent amounts, as well as arc melting parameters, to determine if the predicted compounds could form and what conditions lead to their formation.

IV. Conclusions

This work demonstrates the isolation of an unknown phase through the synthesis of AI-predicted compounds. Through several iterations of solid-state synthesis and direct melting, we determined that the unknown phase contains all the elements (Ba, Sr, Li, La, Mg, Cu) in a YBCO-type structure. Additional testing is required to optimize growth parameters.

One of the predicted intermetallic compounds, LaGaPd_2, formed upon synthesis, while others did not. Additional optimization is needed to determine synthesis parameters for the remaining compounds.

Through the process of synthesis and characterization of the predicted compounds, data

were acquired to feed back into the AI software. This will allow for further development of the software, leading to its eventual use as a tool for materials discovery. This work demonstrates its use in providing a path to discover a new phase with an interesting structure in relation to the potential for superconductivity. This shows progress in the software's predictions, as well as hope for its development moving forward.

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