Advancing Rare Earth Nickelates Synthesis Through Computational Models

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Abstract

The search for room temperature superconductors has long been a pursuit of condensed matter physicists and materials scientists. In this study, we investigate Lanthanide Nickelates as valuable proxies to gain insights into the behavior and mechanisms of superconductors. We employ Gibbs Free Energy calculations, providing valuable insights into the thermodynamic behaviors of these Nickelates. Leveraging Python programming, we have developed a versatile computational tool capable of performing these calculations for a wide range of compositions. This approach enables us to predict the stability of Lanthanide Nickelates under different conditions aiding in the synthesis. To validate our predictions and refine our computational model, we conducted hydroxide flux and other solid state synthesis techniques on Lanthanide Nickelate structures at different temperatures and pressures. By carefully characterizing the resulting materials using X-ray diffraction (XRD), we were able to assess the accuracy of our computational predictions and refine our understanding of the relationship between structure and composition. Our research contributes to the broader quest for room temperature superconductivity, offering valuable insights into the properties and behavior of Lanthanide Nickelates. The combination of theoretical calculations and experimental validations allows us to bridge the gap between computational predictions and real-world materials, bringing us closer to higher temperature superconductors.

Introduction

To unravel the mysteries of superconductivity, it is imperative to synthesize additional chemical compositions, thereby assessing the potential for achieving superconductivity. Given nickel's structural and compositional similarities to copper, a extensively researched superconductive material, nickel has garnered attention as a candidate for advancing our understanding of superconductivity. Nevertheless, the synthesis of nickelate structures presents a formidable challenge. To facilitate the production of nickelate structures, the application of thermodynamics emerges as a valuable tool, enabling the prediction of their stability and aiding in their synthesis. Moreover, alongside harnessing thermodynamics, experimental techniques are employed to validate the accuracy of the computational model.

Methodologies

Computational Model

In the pursuit of synthesizing novel materials, a range of strategies can be harnessed to effectively manipulate the synthesis process. This encompasses the manipulation of environmental factors such as pressure and temperature. Accordingly, the presented model offers predictions regarding the optimal pressure and temperature conditions essential for material synthesis. These predictions necessitate the acquisition of pertinent data pertaining to the particular material under consideration. The foundational properties of each material were extracted from the federally funded database known as the Materials Project. To forecast stability within lanthanide nickelates, the predictive power of the Gibbs Free Energy equation was harnessed.

$$\Delta G = \Delta H - T\Delta S + nRT \ln P \tag{1}$$

The Gibbs Energy consists of three components: enthalpy, entropy, and pressure. Assumptions were made concerning entropy, wherein oxygen is the sole contributor, primarily due to its gaseous nature. This assumption facilitates a slope dependency on oxygen's stoichiometry. The final component of the equation, nRTlnP, represents changes in delta G attributed to pressure.

Data for each material is extracted from the federally funded Materials Project database. The extraction of each material's formation energy is then converted from electron volts per atom to kilojoules per mole. Enthalpy change is subsequently calculated based on the reactants. Both enthalpy and entropy are normalized to the coefficients of reactants and products. Finally, the equation is adjusted by the nRTlnP component. In scenarios where multiple compositions are graphed together, it's crucial to normalize each equation to the limiting reactant of the

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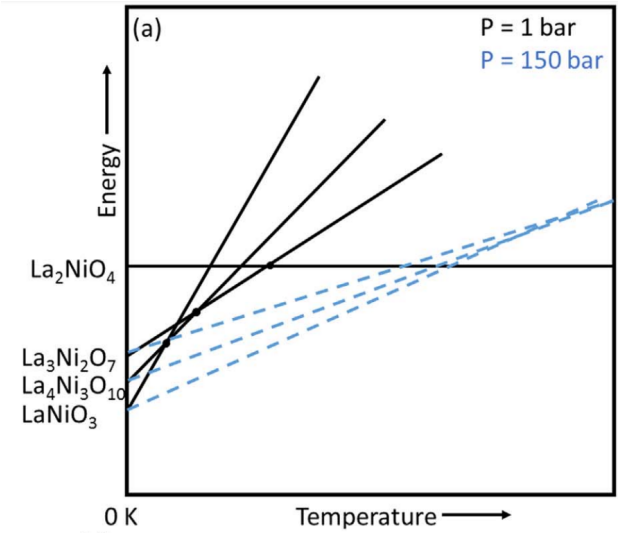

Figure 1: *The accessible pressure frontier for materials discovery, including typical sample sizes and energy equivalents, and technical approaches for achieving different pressure ranges. Source: Heiti Paves,[1]*

anticipated product.

Experimental

To validate computational data, it's imperative to supplement it with experimental data. Experiments involving lanthanide nickelates—lanthanum, praseodymium, and neodymium—were employed for direct comparisons with the predictive model. The baseline involved subjecting a mixture of lanthanide and nickel oxides to elevated temperatures. Multiple trials were conducted ranging from 350°C to 1400°C at 100-degree intervals.

Two synthesis methods were employed: solid state synthesis techniques and hydroxide flux techniques aimed at enhancing kinetics. Two types of hydroxides, potassium hydroxide and sodium hydroxide, were used, selected due to their critical melting points for fluxes. Following the cooling of hydroxide flux, a vacuum filter was employed to dissolve and separate hydroxide from the sample. Subsequently, the X-ray Diffractometer (XRD) was utilized for sample analysis.

Results

Solid-state synthesis experiments under 700 degrees Celsius without oxygen flow faced kinetic challenges, delaying oxide mixing. Conversely, potassium hydroxide fluxes exhibited success in inducing chemical reactions that combined the oxides. For lanthanum and neodymium nickelates, the predictive model effectively anticipated the stability of the 1-1-3 and

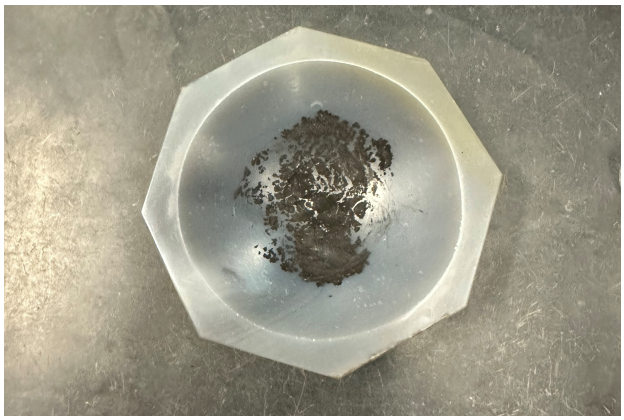

Figure 2: *Motar and pestal of lanthanum and nickel oxide*

2-1-4 structures. Successful synthesis of samples occurred at 450-500°C and 1400°C for both materials.

Conclusions

The predictive model aptly assesses stability ranges for lanthanum and neodymium nickelates, provided kinetic challenges are circumvented. Furthermore, hydroxide fluxes increase the likelihood of desired phase mixtures while introducing impurities.

Next Steps

Due to the success of the predictive model, the model was extrapolated to all ternary oxides. Soon in the future, it will be able to predict the formation energy of any oxide synthesis and eventually any nitrides or carbides. The model is now avalible on the McQueen Lab website. The model is called Synthesis Predictor with Integrated Reactant Exploration (SPIRE). This is a clickable URL link: TOSPIRE

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