Theoretical Predication of the Synthesis of ReNCl

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Abstract—Using the idea of Materials Genome Initiative (MGI) for reference, by means of the First-principle calculation method, according to the known MNCl (M = Zr, Hf) structure to build model, we systematically calculated and analysed the binding energy and reaction energy of two phases of lanthanon replaced ReNCl compounds. Finally, we established the mathematical model, predicted the synthesis of ReNCl theoretically.

Keywords—simulation; first-principles calculations; nitride chlorides

I. INTRODUCTION

MXN (M=Zr, Hf; X=Cl, Br, I) were reported by Jusa et al [1] in 1964 for the first time. Further, Yamanaka et al [2] [3] found it as solid lubricant and electrochromic material. Later, Yamanaka [4] also reported that ZrNCl and HfNCl had exhibited superconductivity properties by intercalating lithium in the interlayer. And the layered structure of MNCl is very conducive to the lithium intercalation/ deintercalation, so it also has a potential application for lithium ion batteries. These theoretical and experimental work create new fields for the application research of this kind of materials.

However, MNCl is difficult to synthesize, few MNCl compounds were experimentally confirmed currently. The M mainly includes tetravalent element, such as Ti, Zr, Hf. As we all known that some of lanthanon have +4 valence, such as Ce, Pr, Tb etc. Doping or replacing lanthanon into the crystal lattice structure usually lead to some unique properties, because of its 4f electronic character. In order to explore innovative MNCl compound with special physical and chemical properties, we using the idea of Materials Genome Initiative (MGI) which was proposed by U. S. President Barack Obama in 2011 [5] for reference, and basing on the reported MNCl structure, using the first-principle calculations method to replace lengthy and costly experimental Studys, systematically studied the stability of lanthanon (No.1-15) replaced ReNCl compound. And theoretically predicted the synthesis of ReNCl.

II. RESEARCH METHOD

So far the experimental results showed that MNCl (M=Zr, Hf) crystal has two types, including the α phase type with FeOCl structure and the β phase type with SmSi structure. Figure 1 shows the two different crystal structure models of MNCl, (A) and (B) are α phase and β phase respectively, (C) is the crystal structure of CeNCl which is similar with the α phase.

First-principle energy calculation is firstly performed to obtain total energy of any systems with known lattice parameters and atomic coordinates. In order to study the stability of the β and α phase, it is vital to compare their binding energies $E_B$. The binding energy $E_B$ is defined as the required energy to disassemble the compound into component atoms separated by infinite distance. The binding energy $E_B$ can be given as

$$E_B = \sum E_{\text{Atom}} - E_{\text{Compound}}$$

where $\sum E_{\text{Atom}}$ and $\sum E_{\text{Compound}}$ correspond to the total energy of the isolated atoms and the compound, respectively. In general, the compound maybe stable if $E_B$ is positive. By comparing several different virtual $E_B$, we can confirm the most reasonable structure of the compound theoretically. The different of $E_B$ in the two phases can be given as

$$E_B(\alpha - \beta) = E_B(\alpha \text{ phase}) - E_B(\beta \text{ phase})$$

A positive $E_B(\alpha - \beta)$ indicates that the α phase are more stable than the β phase—the more positive the $E_B(\alpha - \beta)$, the greater the α phase's stability. In general, if the binding energy of the α phase is larger than that of the β phase, the reaction preferentially produces the α phase; otherwise, the phase cannot be created.

On the other hand, it's also essential that the compound can be synthesised, whether the reaction process happen or not can be judged by chemical reaction drive energy $E_RD$, which is defined as the difference of the total binding energy between the reactant and the product for the chemical reactions as

$$E_RD = \sum E_B(\text{Product}) - \sum E_B(\text{Reactant})$$

where $\sum E_B(\text{Product})$ and $\sum E_B(\text{Reactant})$ correspond to the total binding energy of the product and reactant, respectively. For the ReNCl synthetic reaction, which given as

$\text{Re} + \text{NH}_4\text{Cl} = \text{ReNCl} + 2\text{H}_2$,
the ERD can be defined as

\[ \text{ERD} = E_\text{R}(\text{ReNCl} + 2\text{H}_2) - E_\text{B}(\text{Re} + \text{NH}_4\text{Cl}). \]

In general, if \( \text{ERD} > 0 \), the ReNCl can be synthesised; otherwise, the ReNCl cannot be created.

The results were obtained by means of first-principle calculation procedure as implemented in the computer code CASTEP[6] of Material Studio produced by Accelrys company. Through the establishment of model, geometry optimization, task set, calculated the total energy of structures, we calculate \( E_\alpha \) according to the formula given former. The CASTEP module is based on density functional theory (DFT), with Projector Augmented Wave (PAW) pseudo-potentials and plane wave basis set. The exchange-correlation Perdew-Burke-Ernzerhof (PBE) [7] functional was of the GGA-type. We chose the calculation with Ultrasoft-pseudopotential, kinetic energy cutoff for the plane wave basis set was 320 \( eV \), and in order to discuss the stability, indicates that CeNCl exists in the \( \alpha \) phase theoretically; if the data point is located on the zone of \( \beta \) stability, indicates that ReNCl exists in the \( \beta \) phase.

### III. RESULTS AND DISCUSSION

According to the crystal model and method introduced above, we systematically calculated the binding energy of \( \alpha \) and \( \beta \) phase of lanthanon replaced ReNCl, and in order to discuss the synthesis problem, we also calculated the corresponding ERD (Calculated NH4Cl and H2 with the same crystal conditions, 27.340 \( eV \) and -6.778 \( eV \) respectively). K point mesh set as medium option, which are 2×4×4 and 4×4×4 corresponds to CeNCl with \( \alpha \) phase and \( \beta \) phase respectively.

### IV. CONCLUSION

This paper used simulation calculation method, using First-principle calculation method, established the relationship between \( E_\alpha \) and \( E_\text{RD} \) of \( \alpha \) and \( \beta \) phase of ReNCl compound. The experimental results confirms the validity of the theoretical prediction results in some way. The method of computational simulation combined with experimental research greatly shorten the cycle of new materials research and save materials, not only to guide the synthesis of ReNCl compound, but also to provide a reference for other new materials research.

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### REFERENCES


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**FIGURE II. THEORETICAL SYNTHESIS PREDICTION CHART OF RENCL. NO. 1~15 REFERS TO THE ELEMENT LA~LU OF LANTHANON**

Figure 2 shows that the data points of CeNCl, DyNCl and TbNCl are on the \( \alpha \) stable region, and they have large ERD which between 1.0 \( eV \)~2.0 \( eV \), so CeNCl, and DyNCl TbNCl have possibilities for synthesis, and CeNCl compound has the maximum value, indicating that CeNCl is most likely to synthesis theoretically. \( \text{ERD} = -0.7eV \) for GdNCl compound, so GdNCl may be able to synthesis. The PrNCl, LaNCl and ErNCl compounds are on the stable region, but their \( E_\alpha \) value are under 0.5\( eV \), so theoretically they are less likely to synthesis. Based on the calculation results above, we synthesized TbNCl [9] and GdNCl [10] with \( \alpha \) phase successfully, which is consistent with the theoretical prediction results.