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 *M*NCl (M = Zr, Hf) structure to build model, we systematically calculated and analysised the binding energy and reaction energy of two phases of lanthanon replaced *Re*NCl compounds. Finally, we established the mathematical model, predicted the synthesis of *Re*NCl theoretically.**

Keywords-simulation; first-principles calculations; nitride chlorides

I. INTRODUCTION

*M*N*X* (*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 *M*NCl 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, *M*NCl is difficult to synthesize, few *M*NCl 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 4*f* electronic character. In order to explore innovative *M*NCl 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 *M*NCl structure, using the first-principle calculations method to replace lengthy and costly experimental Studys, systematically studied the stability of lanthanon (No.1-15) replaced *Re*NCl compound. And theoretically predicted the synthetic of *Re*NCl.

II. RESEARCH METHOD

So far the experimental results showed that *M*NCl (*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 *M*NCl, (A) and (B) are α phase and β phase respectively, (C) is the crystal structure of CeNCl which is similar with the α phase.
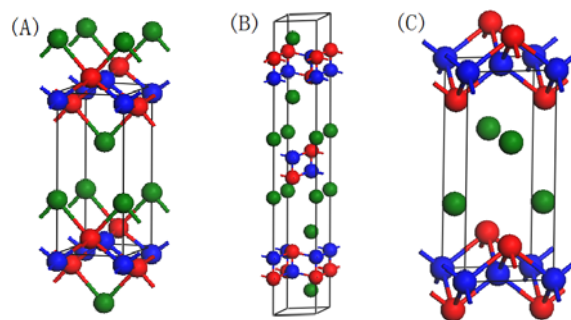

FIGURE I. CRYSTAL STRUCTURE MODELS: (A) *A* PHASE OF *M*NCL, (B) *B* PHASE OF *M*NCL, (C) CENCL STRUCTURE

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

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

where $\sum E_{Atom}$ and $\sum E_{Compound}$ correspond to the total energy of the isolated atoms and the compound, respectively. Ingeneral, 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. Ingeneral, 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 α phase can not be created.

On the other hand, it's also essential that the compound can be synthesised, wether the reacting 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 *Re*NCl synthetic reaction, which given as
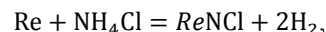
$$Re + NH_4Cl = ReNCl + 2H_2,$$

the E_{RD} can be defined as

$$E_{RD} = E_B(Re\text{NCl} + 2H_2) - E_B(Re + NH_4\text{Cl}).$$

Ingeneral, if $E_{RD} > 0$, the ReNCl can be synthesised; otherwise, the ReNCl can not 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_r 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 cut-off for the plane wave basis set was 320 eV, the convergence precision was 1.0×10^{-4}eV atom^{-1}, and we specify spin direction of all the magnetic elements, ultimate atom displacement and stress of virtual process were less than 0.002 Å and 0.1 GPa, respectively. K point mesh set as medium option, which are $2 \times 4 \times 4$ and $4 \times 4 \times 4$ corresponds to CeNCl with α phase and β phase respectively

III. RESULTS AND DISCUSSION

According to the crystal model and method introduced above, we systematically calculated the binding energy of α and β phase of lanthanon replaced ReNCl, and in order to discuss the synthesis problem, we also calculated the corresponding E_{RD} (Calculated NH$_4$Cl and H$_2$ with the same crystal conditions, 27.340 eV and -6.778 eV respectively). One drawing is made with E_{RD} as abscissas and $E_{B(\alpha-\beta)}$ as ordinate, which shown in figure 2 below. When $E_{RD} > 0$, ReNCl can exist, and if the data point is located on α stable region, indicates that ReNCl exists in the α phase theoretically; if the data point is located on the zone of β stability, indicates that ReNCl exists in the β phase.
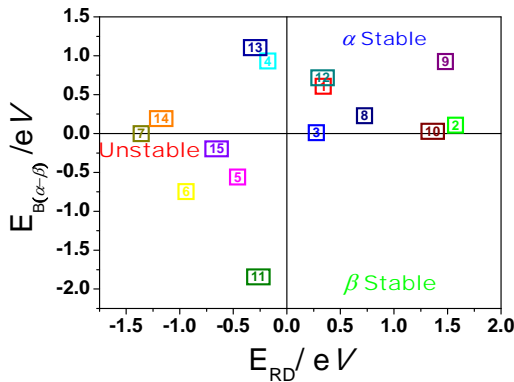

FIGURE II. THEORETICAL SYNTHESIS PREDICTION CHART OF RENCL. NO. 1~15 REFERS TO THE ELEMENT LA~LU OF LANTHANON

Figure 2 shows that the data points of CeNCl, DyNCl and TbNCl are on the α stable region, and they have large E_{RD}, 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. E_{RD}=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_r value are under 0.5eV, so theoretically they are less likely to synthesis. Because the date point is on the unstable region, compound of NdNCl、 PmNCl and SmNCl does not have the necessary conditions for synthesis, theoretically, they are almost impossible to synthesis. The CeNCl compound with α phase in reference [8] was the only lanthanon replaced ReNCl material that has been reported. Based on the calculation results above, we synthesized TbNCl [9] and GdNCl [10] with α phase successfully, which is consistent with the theoretical prediction results.

IV. CONCLUSION

This paper used simulation calculation method, using First-principle calculation method, established the relationship between E_B and E_{RD} of α and β phase of ReNCl compound. theoretically predicted the synthesis of ReNCl, The experimental results confirms the validity of the theoretical prediction results in some way. The method of computational simulation combined with experiment 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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