

Pressure-induced phase transition of zinc nitride chlorine



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ABSTRACT

The phase stability of Zn₂NCl is systematically studied by using the CALYPSO swarm structure searching method coupled with first principles calculations under pressure up to 100 GPa. The experimental ground state structure *Pna*2₁ (phase) is confirmed. Furthermore, two new high-pressure structures *Pnma* (16 atoms/cell, phase II) and *R-3m* (4 atoms/cell, phase III) are discovered. Phase I transits to phase II at 13.5 GPa and phase II transits to phase III at 35.4 GPa. The phonon-dispersion and elastic constants calculations both show that the two structures are dynamically and mechanically stable in the corresponding pressure ranges. Nevertheless the calculated electronic properties indicate that three phases of Zn₂NCl are semiconductors, pressure drives Zn₂NCl to transform from a wide direct band gap semiconductor to narrow indirect one.

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1. Introduction

Recently, the research of nitride chemistry has attracted huge attentions in the theoretical and experimental community, because of their complex crystal structures and superior electronic properties. In order to improve the superior properties of metal nitrides, a new family of “filled subnitrides” metal nitride halides M_nNX (M = Ca–Ba, Ti–Hf; X = Cl, Br, I) were originally investigated and synthesized several years ago. Recently, the structural and physical properties of these mixed-anion compounds have been deeply revealed [1–3].

The layer-structured polymorphs of metal nitride halides, α - and β -MNX (M = Ti, Zr, Hf; X = Cl, Br, I) are in FeOCl and SmSI structures, respectively [4]. When alkali metals (for example lithium ions) are inserted into MNCl, they exhibit superconducting behavior at low temperatures (around 30 K), which caused the extensive researches in recent years [5,6]. The most famous and only divalent transition-metal nitride halide is Millon's base, Hg₂NX [7]. Many salt-like derivatives of Millon's base Hg₂NX·nH₂O (X = OH⁻, NO₃⁻, ClO₄⁻, Br⁻, I⁻ and n = 0–2) emerge depending on the chemical reaction conditions. Therefore, the ternary M_nNX phase systems are more complex than originally envisaged, and their crystal structure and anion distributions are depend on both the halide and synthesized conditions. Metal nitride halides structures vary from simple rock salt analogues (for example, Sr₂NF) [8] to layered materials (for example,

Ca₂NCl) [9]. In some systems, there are indeed different structural polymorphs which have been reported. For example, Ca₂NF can form various structure type, such as a simple cubic rock salt [18], a doubled cubic rock salt [10], or an ordered rock salt-derived tetragonal cell [11]. Moreover, variation in structure, stoichiometry, and anion distribution are likely to have profound effects on electronic properties (such as Mg–N–F system [12]).

We explore high pressure properties of the divalent transition metal nitride halides more thoroughly. Zinc is an important metal element and becomes our first choice. Zinc nitride chlorine (Zn₂NCl), which was recently synthesized from solid–liquid reactions of zinc nitride with the respective zinc halides under vacuum [13], becomes our research target. However, up to now, there are no relevant reports about new phases and phase transition of Zn₂NCl under pressures. High pressure can alter the bonding patterns of compounds fundamentally and lead to formation of new structures of materials with unusual chemical and physical properties. Therefore, in this work we aimed to search for new stable phases and striking properties of Zn₂NCl under high pressure. An unbiased structural searches based on the CALYPSO (crystal structure analysis by particle swarm optimization) methodology was performed to explore stable structure of zinc nitride chlorine in a large pressure range of 0–100 GPa in combination with density functional total-energy calculation [14,15]. This method has been successfully applied to predictions of high-pressure structures of various systems on elemental, binary, and ternary compounds with metallic, ionic, and covalent bonding (such as Li, BiTeI, and LiFeP) [16–19], which have obtained experimental confirmations. In this work, we unravel two new high-pressure phases of

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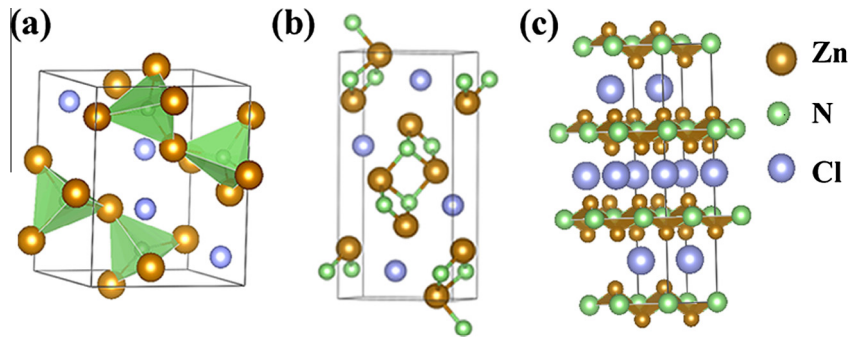


Fig. 1. Crystal Structures of Zn_2NCl phases (a) $Pna2_1$ (b) $Pnma$ (c) $R-3m$.

Table 1
Lattice parameters and atomic coordinates of Zn_2NCl .

Phase	Lattice constants (Å)	Atoms	x	y	z
$Pna2_1$ 10 GPa	$a = 5.996$ $b = 7.065$ $c = 5.771$	Zn1(4a)	0.9674	0.4378	0.8943
		Zn2(4a)	0.6094	0.3295	0.2674
		N(4a)	0.4126	0.1266	0.2032
		Cl(4a)	0.4133	0.6276	0.2006
$Pnma$ 25 GPa	$a = 5.684$ $b = 3.682$ $c = 11.596$	Zn1(4c)	0.037	0.25	0.2012
		Zn2(4c)	0.3102	0.25	0.4833
		N(4c)	0.5516	0.75	0.8859
		Cl(4c)	0.5451	0.25	0.6120
$R-3m$ 50 GPa	$a = b = 3.049$ $c = 15.663$	Zn(6c)	0	0	-0.2726
		N(3a)	0	0	0
		Cl(3b)	0	0	-0.5

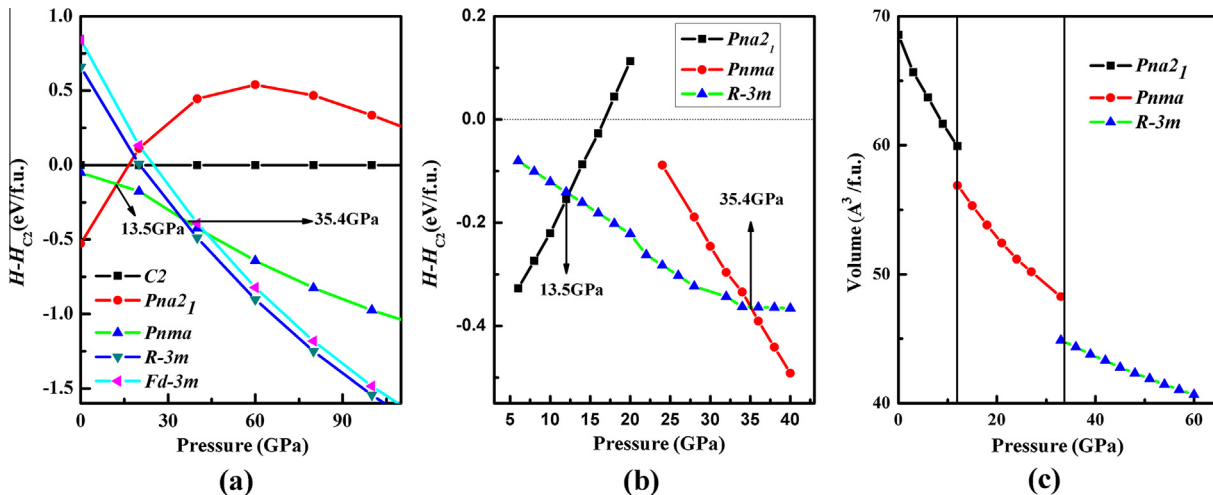


Fig. 2. (a) Enthalpy of the $Pna2_1$ - Zn_2NCl , $Pnma$ - Zn_2NCl , $R-3m$ - Zn_2NCl , and $Fd-3m$ - Zn_2NCl phases relative to $C2$ - Zn_2NCl phase with pressure (b) Enthalpy of $Pna2_1$ - Zn_2NCl , $Pnma$ - Zn_2NCl , $R-3m$ - Zn_2NCl relative to $C2$ phase with pressure in smaller pressure range (c) The P - V curves of $Pna2_1$ - Zn_2NCl , $Pnma$ - Zn_2NCl and $R-3m$ - Zn_2NCl phases.

Zn_2NCl , orthorhombic ($Pnma$) and trigonal structure ($R-3m$), which showed interesting properties for industrial applications.

2. Theoretical methods

The crystal structural predications were performed by PSO methodology as implemented in Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) code [14,15]. The significant feature of this methodology is capable of predicting the stable and metastable structures at given pressure with only the knowledge of the chemical composition. In the calculations, there are

two steps to establish the most stable crystal structure. In the first step, random structures with certain symmetry are constructed in which the atomic coordinates are generated by the crystallographic symmetry operations. Then the structures are optimized to local minima by using DFT (VASP code [20]) calculations. After processing the first generation structures, 60% of them with lower enthalpies are selected to produce the next generation structures by PSO. 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is

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