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High-pressure synthesis and crystal structures of β - MNX ($M = \text{Zr, Hf}$; $X = \text{Cl, Br, I}$)

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Abstract

The single crystals of six kinds of metal nitride halide, β - MNX ($M = \text{Zr, Hf}$; $X = \text{Cl, Br, I}$), were grown in sealed Au (or Pt) tubes by the reaction of MN or MNX powders with NH_4X as fluxes under high-temperature and high-pressure conditions such as 3–5 GPa at 900–1200 °C. The x-ray structure analysis revealed that all six kinds of compound crystallize in a rhombohedral space group $R\bar{3}m$, $Z = 6$. β -ZrNCl, β -ZrNBr, and β -HfNCl are isotypic with SmSI, and the others isostructural with YOF.

1. Introduction

Recently, the layer structured nitride halides MNX ($M = \text{Zr, Hf}$; $X = \text{Cl, Br, I}$) have gained considerable interest because their alkali metal intercalates exhibited superconductivity at rather high transition temperatures (T_c s): $\text{Li}_{0.16}\text{ZrNCl}$ and $\text{Li}_{0.48}(\text{THF})_y\text{HfNCl}$ (THF, tetrahydrofuran) at $T_c = 13$ and 25.5 K, respectively [1]. The crystal structures of the β -ZrNCl, β -ZrNBr, and β -HfNCl host lattices have been determined by several groups using powder x-ray or neutron diffraction [2–5]. However, the powder samples show a very strong preferred orientation due to the layer structured nature of the crystals, and thus the structural data reported by different authors vary substantially. During our investigation of the ternary M -N- X system using a high-pressure technique, we first obtained single crystals of β - MNX ($M = \text{Zr, Hf}$; $X = \text{Cl, Br, I}$). In this work we report on their crystal growth in a special high-pressure condition and accurate structure determinations.

2. Experimental details

The β -ZrNCl, β -HfNCl, β -HfNBr, and β -HfNI crystals were grown by a two-step process. First, the respective MNX powder samples (α - or β -phase) were prepared by the reaction of ZrH_2 and Hf with NH_4X at 650 °C, and then purified by chemical transport reaction in a temperature gradient of 750–850 °C. The chemically transported MNX powders and the

corresponding ammonium halides in a molar ratio of about 1:2.1–1:3.5 were filled in Au ($T < 1050^\circ\text{C}$) or Pt ($T \geq 1050^\circ\text{C}$) capsules (0.1 mm in thickness, 6 mm in inner diameter, and 4 mm in depth), which were in turn placed in h-BN cells, and in carbon tube heaters. The sample assembly was set in a pyrophyllite cube ($2.0 \times 2.0 \times 2.0 \text{ cm}^3$) and subjected to high pressure using a cubic multianvil type apparatus (Riken, model CP-10). The reaction temperature was monitored by a thermocouple placed under the BN cell in the pyrophyllite cube. Under the applied pressure of 3–5 GPa, the samples were rapidly heated to 900–1200 °C, where they were kept for 1 h, then cooled down to 800 °C at a rate of 100°C h^{-1} ; this was followed by quenching to room temperature prior to releasing the pressure. Transparent β - MNX crystals were obtained in about 30–40% yield. The remaining product was found to be a mixture of NH_4X and an unknown amorphous phase based on powder x-ray diffraction measurements. The crystals showed a hexagonal plate-like habit with various sizes ranging from 0.1 to 1.5 mm in diameter and several tenths of a millimetre in thickness. They were isolated by washing the reaction product with distilled water and drying with anhydrous acetone and further characterized by single-crystal x-ray diffraction measurement.

The β -ZrNBr and β -ZrNI crystals were prepared in a similar way except that ZrN powder was used instead of ZrNX ($X = \text{Br}, \text{I}$) as starting materials. These two kinds of crystal can also be obtained by a similar high-pressure and high-temperature (HPHT) treatment of the β -ZrNBr and α -ZrNI powders.

The selected crystals were mounted on glass fibres and the intensity data were collected on a Rigaku AFC7R automatic diffractometer with graphite monochromated Mo $K\alpha$ radiation. The crystal structures were solved and refined by the program SHELX97 and further crystallographic details are given in table 1.

3. Results and discussion

There are two types of layer structured polymorph, α - and β -forms, for MNX . The α -form adopts the FeOCl-type layered structure and all of the compounds MNX ($M = \text{Zr}, \text{Hf}; X = \text{Cl}, \text{Br}, \text{I}$) crystallize in the α -form. The β -forms with the SmSI structure have been prepared only for ZrNCl, ZrNBr, and HfNCl. α -ZrNCl, α -ZrNBr, and α -HfNCl were reported to transform into the corresponding β -forms when heated above 600, 750, and 600 °C, respectively. It had been believed that the β -form is a high-temperature polymorph of the α -form. However, the remaining crystals, α -ZrNI, α -HfNBr, and α -HfNI, were never converted into the β -forms by a similar thermal treatment. A comparison of the calculated densities of the α -forms (3.79, 4.77, 5.31, 6.49, 7.15, and 7.45 g cm^{-3} for ZrNCl, ZrNBr, ZrNI, HfNCl, HfNBr, and HfNI, respectively) with those of the corresponding β -forms (in table 1) reveals that the β -forms have higher densities than the α -forms. Therefore, the β -forms should be characterized as high-density phases and theoretically could be obtained by the transformation of the α -forms under HPHT conditions. The successful HPHT transformation of β -ZrNI, β -HfNBr, and β -HfNI from the α -forms confirmed the above point in a previous study [6].

In this study, single crystals of the six kinds of compound have been prepared under HPHT conditions. The x-ray single-crystal analysis revealed that all β -forms crystallized in a rhombohedral space group $R\bar{3}m$, $Z = 6$ [7]. β -ZrNCl, β -ZrNBr, and β -HfNCl are isotopic with SmSI, and the others isostructural with YOF. Both structure variants are composed of structural slabs [$X-M-N-N-M-X$] ($M = \text{Zr}, \text{Hf}; X = \text{Cl}, \text{Br}, \text{I}$) joined together by $X \cdots X$ van der Waals forces, but the overall layer sequences are different: $X_A M_c N_B N_C M_b X_A | X_C M_b N_A N_B M_a X_C | X_B M_a N_C N_A M_c X_B$ in the SmSI-type modifications, and $X_A M_b N_C N_B M_c X_A | X_C M_a N_B N_A M_b X_C | X_B M_c N_A N_C M_a X_B$ in the YOF-type polymorphs as shown in figure 1.

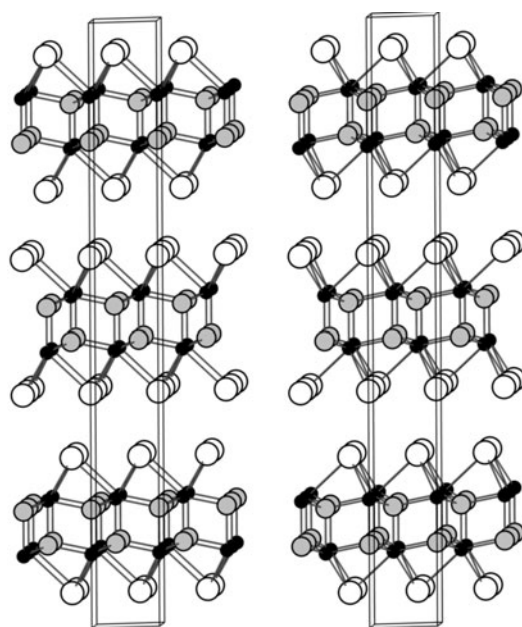


Figure 1. The crystal structures of β -ZrNBr (SmSI-type, left) and β -HfNBr (YOF-type, right). Large open circles: Br; medium grey circles: N; small black circles: Zr and Hf atoms.

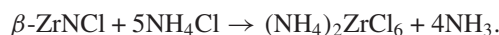
Table 1. Crystallographic data for β -MNX ($M = \text{Zr, Hf}$; $X = \text{Cl, Br, I}$).

	ZrNCl	ZrNBr	ZrNI	HfNCl	HfNBr	HfNI
Space group	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$	$R\bar{3}m$
Structure type	SmSI	SmSI	YOF	SmSI	YOF	YOF
a	3.6046(4)	3.6403(6)	3.718(2)	3.5767(8)	3.610(1)	3.689(1)
c	27.672(4)	29.270(5)	31.381(9)	27.711(7)	29.294(6)	31.329(6)
d_{calc} (g cm^{-3})	4.501	5.491	6.156	7.398	8.209	8.619
M	0.119 24(1)	0.122 17(3)	0.207 40(4)	0.119 50(1)	0.210 96(3)	0.207 14(6)
X	0.387 80(3)	0.388 36(3)	0.389 52(2)	0.387 95(8)	0.388 50(7)	0.389 60(9)
N	0.197 71(8)	0.196 3(2)	0.139 3(3)	0.197 6(2)	0.137 1(5)	0.139 2(11)
Reflections	447	337	418	454	412	113
No of variables	11	10	11	11	11	11
$R1$ ($I \geq 2\sigma(I)$)	0.0270	0.0540	0.0603	0.0372	0.0653	0.0544
$wR2$	0.075	0.1552	0.1885	0.0979	0.1464	0.1583

It is noted that the lattice parameter c , for the axis perpendicular to the basal plane, significantly increases with the increase of halogen radius, while the parameter a , for the in-plane axis, is insensitive to the halogen sizes. It is reasonable to assume that the lattice parameter a is determined by the rigid M -N networks, and will not be influenced by the size of halogen ions. Halogen ions are placed in the centres of the hexagonal rings of the double M -N layers. If the a -value is larger than or close to twice the ionic radius of the halogen ion, the M -N networks can accommodate the halogen ions. In the case of the iodides, however, the ionic radius of iodine (2.06 Å) is too large to fit in M -N networks ($a/2 \approx 1.85$ Å); a higher pressure of 5 GPa is required to compress the iodine ions into the M -N networks of

β -forms. In β -HfNBr, the ionic radius of bromine (1.82 Å) is slightly larger than the network size ($a/2 = 1.805$ Å); it can be easily synthesized at a lower pressure of 3 GPa. In β -MnCl, the ionic radius of Cl⁻ (1.67 Å) is significantly less than the parameter $a/2$ (~1.8 Å); heating at an elevated temperature can result in the formation of the β -phases.

As reported elsewhere [8, 9], β -ZrNCl can be prepared by a direct reaction of Zr metal or ZrH₂ powders with ammonium chloride at elevated temperatures. The as-prepared samples can be purified and changed into highly crystalline samples by chemical transport with the aid of NH₄Cl, although the transported crystals are very thin. We also reported that β -ZrNCl reacted with NH₄Cl to form (NH₄)₂ZrCl₆ and ammonia:



The hexachloride is vaporized into 5 mol of gaseous mixtures at elevated temperatures as follows:



In the high-pressure treatment of MNX (MN) with NH₄X in this study, all of MNX crystals (α - or β -phase) and MN were supposedly decomposed into the gaseous mixtures of metal halides and ammonium halides, from which single crystals were recrystallized on the surface contacting with the wall of the Au (or Pt) cell. The high pressure of 3–5 GPa was required to confine the gaseous mixtures in the Au (or Pt) container at high temperatures, which therefore led to the formation of larger and thicker β -MNX crystals compared with those obtained from the chemical vapour transport method. When the cell was cooled down to room temperature rapidly, the uncrystallized part was supposed to be quenched into an amorphous phase containing NH₄Cl.

4. Conclusions

The successful syntheses of single crystals of the title compounds indicated that high-pressure conditions suppress the crystal growth in the a - b plane, and allow the large and thick β -MNX crystals to become available. The present single-crystal data on β -ZrNCl, β -ZrNBr, and β -HfNCl are more accurate than the powder results in the literature and the crystal structures of the three high-pressure phases of YOF structure, β -ZrNI, β -HfNBr, and β -HfNI are presented here for the first time.

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