High-Pressure Synthesis of the Polymorph of Layer Structured Compounds MNX (M = Zr, Hf; X = Cl, Br, I)

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Received September 1, 1999

Transition metal nitride halides MNX (M = Zr, Hf; X = Cl, Br, I) have two types of layer structured polymorphs, the α-form with the FeOCl type and the *β*-form with the SmSI type. Both polymorphs consist of corrugated double M−N layers sandwiched between halogen layers, but with different atomic arrangements within the layers. The *β*-form had been considered to be a high-temperature polymorph, because some *β*-forms were obtained by thermal treatment of the corresponding α-forms. Here, the α-form was successfully transformed into the *β*-form under high-pressure and high-temperature conditions; the new members of the *β*-form were prepared for the first time from α-HfNBr, α-ZrNI, and α-HfNI using a high pressure of 3−5 GPa at 900 °C. The *β*-form should be characterized as the high-pressure form rather than the corresponding high-temperature polymorph. This is the first high-pressure study on the polymorphs of metal nitride systems.

1. Introduction

There are two types of layer structured polymorphs in metal nitride halides MNX (M = Ti, Zr, Hf; X = Cl, Br, I): the α-form with the FeOCl layer structure and *β*-form with the SmSI layer structure.[1] Both polymorphs consist of metal nitride double layers sandwiched by two halogen layers, but the atomic arrangements within the layers are different. The α-form is not stable against humidity of air and is easily hydrolyzed, while the *β*-form can stand even in hot acid solutions. *β*-MNX is isoelectronic with the corresponding transition metal dichalcogenides such as ZrS_2 or HfS_2 with empty d-bands, and a semiconductor with a band gap larger than 3 eV.[2] Recently, we have intercalated alkali metals between the halogen layers of *β*-ZrNCl and *β*-HfNCl.[3,4] On intercalation of alkali metals, electrons are doped into the d-bands and the compounds changed into superconductors with the transition temperatures (T_c) at 13 and 25.5 K for *β*-ZrNCl and *β*-HfNCl, respectively. It is well-known that most of transition metal nitrides with the rock salt structure show superconductivity, for example, MN (M = Ti, Zr, Hf, Nb) with T_c = 5.5, 10.7, 8.8, and 18.0 K, respectively.[5] By the electron doping the MN layers of *β*-MNCl may have band structures similar to those of the rock salt type nitrides, which are favorable for superconductivity. Note that the T_c of the electron-doped *β*-HfNCl (25.5 K) is surprisingly higher than that of the three-dimensional HfN (8.8 K) with the rock salt structure. This T_c is even higher than the 23.2 K of Nb_3Ge, the highest T_c ever reported for metals and intermetallic compounds.[6] The metal nitride layers are considered to be a promising matrix for superconductivity like the CuO_2 layers for high-T_c superconductivity.

β-ZrNCl was first prepared by Juza and Heners[7] by the reaction of $ZrCl_4$ and NH_3. Juza and Friedrichsen[8] proposed a crystal structure consisting of [Cl−Zr−N−N−Zr−Cl] layers stacked on each other by van der Waals interactions in a disordered manner of mixed $CdCl_2$ and CdI_2 types of stacking. We developed a new preparation method for MNX by the reaction of metal or metal hydrides with ammonium halide at elevated temperatures,[9,10]

$$\text{M (or MH}_2) + \text{NH}_4\text{X} \rightarrow \text{MNX} + 2 \text{ (or 3) H}_2$$

The obtained compounds were transported from a low-temperature zone to a high-temperature zone as highly crystalline crystals. This finding enabled us to prepare all of the combinations of MNX (M = Zr, Hf; X = Cl, Br, I) by simply changing the combinations of metals and ammonium halides as the starting materials.[2,4] The highly crystalline *β*-ZrNCl was obtained in the form of a rhombohedral symmetry (3*R*) with three [Cl−Zr−N−N−Zr−Cl] layers in a unit cell. We proposed an ordered stacking sequence of the $CdCl_2$ type for *β*-ZrNCl, but the unit layer of [Cl−Zr−N−N−Zr−Cl] proposed by Juza and Friedrichsen was used.[3] Recently, Shamoto et al.[11] determined the crystal structure of *β*-ZrNCl using neutron diffraction; they revealed that the *β*-ZrNCl was isostructural with SmSI as shown in Figure 1, where the double metal nitride layers are shifted with each other to form interlayer bonds between nitrogen and zirconium. This structure has been supported by recent studies

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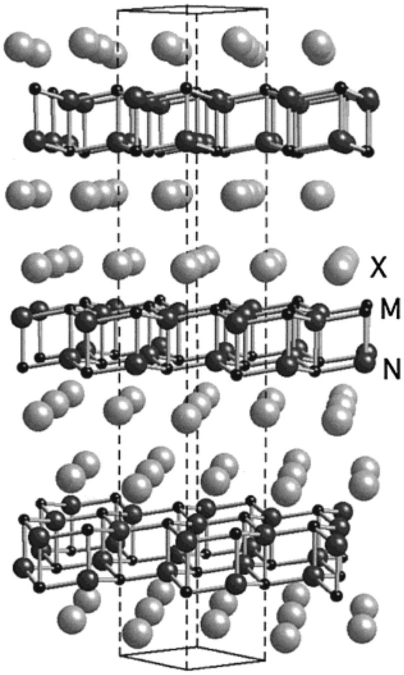

Figure 1. Schematic illustration of the crystal structure of β-MNX (SmSI type).

Table 1. Polymorphs Found in MNX (M = Ti, Zr, Hf; X = Cl, Br, I)[a]

M	X		
	Cl	Br	I
Ti	α	α	α
Zr	α, β	α, β	α
Hf	α, β	α	α

[a] α: FeOCl layered structure. β: SmSI layered structure.

by Fogg et al.,[12] Fuertes et al.,[13] and Istomin et al.[14] on the basis of X-ray diffraction analysis. The electronic band structures have also been proposed on the basis of these structures.[13-17] Woodward and Vogt[18] calculated the electronic band structure of β-ZrNCl on the basis of the crystal structural model of Juza and Friedrichsen.[8] Hase and Nishihara[16] calculated the band structures for four different structural models of β-ZrNCl and β-HfNCl, including the models of Shamoto et al.[11] and Juza and Friedrichsen.

All kinds of the combinations of metal nitride halides, MNX (M = Ti, Zr, Hf; Cl, Br, I), are known. The polymorphs reported for these compounds are listed in Table 1. β-Forms with the SmSI structure have been prepared only for ZrNCl, ZrNBr, and HfNCl. All of the iodides MNI, and the titanium compounds TiNX, are crystallized in the form of the FeOCl structure (α-form). Juza and Heners[7] prepared β-ZrNCl and β-ZrNBr by thermal treatment of the corresponding α-forms. We obtained ZrNBr by the reaction described above at 650 °C as the α-polymorph.[2] It was chemically transported to the higher temperature zone in a glass tube sealed with NH_4Br. In a temperature gradient of 450−550 °C, ZrNBr was transported as the α-form, whereas in a temperature gradient of 750− 850 °C, it was transported as the β-form. From these findings, although the mechanism of the transformation is not clear, there is a belief that the β-form should be the high-temperature polymorph of the α-form.

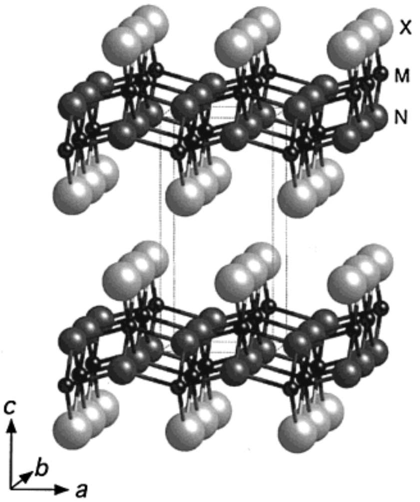

Figure 2. Schematic illustration of the crystal structure of α-MNX (FeOCl type).

The schematic structural model of the α-form is given in Figure 2. If we compare this structure with that of the β-form in Figure 1, the metal atoms in the β-form are coordinated by four nitrogen atoms and three halogen atoms, whereas the metal atoms in the α-form are coordinated by four nitrogen atoms and two halogen atoms. In addition, if the densities of α-ZrNCl and α-ZrNBr are calculated on the basis of the unit cell dimensions determined by X-ray diffraction analysis, the β-forms always have higher densities than the corresponding α-forms. It appears that β-forms are high-density forms. In this study, the transformation of the α-forms under high pressure is attempted for MNX (M = Zr, Hf; X = Cl, Br, I), and we have managed to obtain the β-forms for all of the combinations.

2. Experimental Section

Materials. MNX (M = Zr, Hf; X = Cl, Br) were prepared according to the methods reported elsewhere.[9,10] In the case of iodides, ammonium iodide was vacuum-sealed with metal powder with a molar ratio of 1.05:1 in silica glass tubes, which were first heated at 450 °C for 1 day, and then kept in a furnace with a temperature gradient of 750− 850 °C for 5 days. The crystals were chemically transported to the higher temperature zone. Since hydrogen is evolved in this reaction, the vacuum-sealed method should be limited for a small scale synthesis of about 200 mg in a silica glass tube of about 15 mm in bore diameter and 250 mm in length.

High-pressure synthesis was performed by using a cubic multianvil type press (Riken, model CP-10). The powder samples of the α-forms were filled in h-BN cells (6 mm in inner diameter, and 5 mm in depth) which were placed in a carbon tube heater in a pyrophyllite cube as pressure media. The reaction temperature was monitored by a thermocouple placed under the BN cell in the cube. The pressure applied was in the range 1−5 GPa.

Analysis. The X-ray diffraction (XRD) patterns of the samples were measured using a MAC Science diffractometer (model M18XHF) with graphite-monochromated Cu $K\alpha$ radiation. The X-ray diffraction patterns of the α-forms were measured on the goniometer covered with a polyethylene cylindrical cover to protect the sample from the humidity of air. The XRD profile data were collected at every 0.02° over the range 5−70° in 2θ by a continuous scan mode with a scanning speed of 1°/min. The diffraction peaks due to Cu $K\alpha_1$ radiation were separated by the program in the diffractometer and used for indexing.

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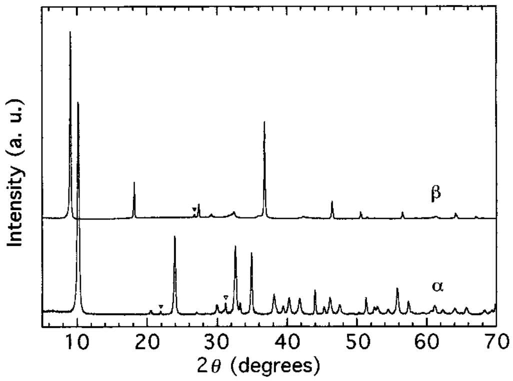

Figure 3. XRD patterns of α- and β-HfNBr. The reflection peaks due to the contamination of NH_4Br in the α-form sample and BN from the reaction cell in the β-form sample are marked by ▽ and ▼, respectively.

Table 2. X-ray Diffraction Data of α-HfNBr

h k l	I_{obs}	$1/d_{obs}^2$, 10^2 nm^{-2}	$1/d_{cal}^2$,[a] 10^2 nm^{-2}
0 0 1	1000	0.01332	0.01340
0 0 2	14	0.05368	0.05360
1 0 1	377	0.07250	0.07252
1 0 2	39	0.11276	0.11272
0 1 2	322	0.13277	0.13256
1 1 0	49	0.13821	0.13807
1 1 1	306	0.15156	0.15147
1 0 3	90	0.17991	0.17972
1 1 2	33	0.19171	0.19168
0 1 3	76	0.19962	0.19956
0 0 4	70	0.21449	0.21441
2 0 0	128	0.23652	0.23647
2 0 1	33	0.24974	0.24987
1 1 3	76	0.25880	0.25868
1 0 4	42	0.27360	0.27352
0 2 0	87	0.31604	0.31583
2 1 1	32	0.32923	0.32882
0 0 5	32	0.33485	0.33501
1 1 4	19	0.35239	0.35248
2 1 2	134	0.36904	0.36903
1 2 1	73	0.38844	0.38834
1 2 2	13	0.42877	0.42855
2 1 3	42	0.43570	0.43603
2 0 4	19	0.45098	0.45087
1 1 5	25	0.47302	0.47308
1 2 3	31	0.49512	0.49555
2 1 4	17	0.53003	0.52983
3 0 1	17	0.54539	0.54545
2 2 0	52	0.55200	0.55229

[a] d_{cal} was calculated on the basis of the orthorhombic unit cell, $a = 0.41129(5)$ nm, $b = 0.35586(5)$ nm, $c = 0.8638(1)$ nm.

Table 3. X-ray Diffraction Data of β-HfNBr

h k l	I_{obs}	$1/d_{obs}^2$, 10^2 nm^{-2}	$1/d_{cal}^2$,[a] 10^2 nm^{-2}
0 0 3	1000	0.01056	0.01049
0 0 6	175	0.04198	0.04196
0 0 9	69	0.09440	0.09441
1 0 −2	28	0.10695	0.10701
1 0 −5	10	0.13134	0.13149
0 0 12	548	0.16775	0.16783
1 0 10	11	0.21922	0.21890
0 0 15	108	0.26220	0.26224
1 1 0	42	0.30714	0.30705
1 1 3	7	0.31788	0.31754
1 1 6	3	0.34904	0.34900
0 0 18	38	0.37759	0.37762
1 1 9	3	0.40164	0.40145
2 0 2	3	0.41399	0.41406
2 0 5	10	0.43802	0.43853
1 1 12	34	0.47488	0.47488
0 0 21	14	0.51398	0.51399

[a] d_{cal} was calculated on the basis of the hexagonal unit cell, $a = 0.36094(4)$ nm, $c = 2.9292(4)$ nm.

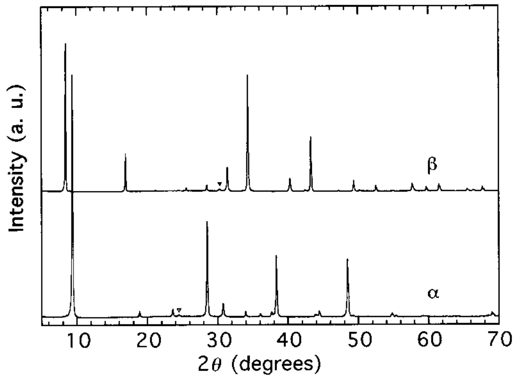

Figure 4. XRD patterns of α- and β-HfNI. The reflection peaks due to the contamination of NH_4I in the α-form sample and HfO_2 in the β-form sample are marked by ▽ and ▼, respectively.

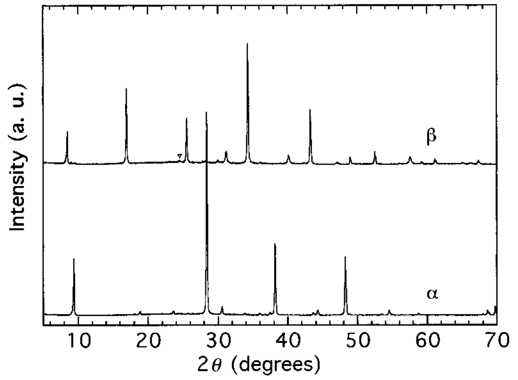

Figure 5. XRD patterns of α- and β-ZrNI. A reflection peak due to the contamination of NH_4I in the β-form sample is marked by ▽.

3. Results and Discussion

α-HfNBr was treated under a high-pressure condition of 3 GPa at 900 °C for 1 h. The XRD patterns of the samples before and after the treatment are given in Figure 3, and the diffraction data are listed in Tables 2 and 3, respectively. α-HfNBr has an orthorhombic unit cell of $a = 0.41129(8)$ nm, $b = 0.35586(9)$ nm, and $c = 0.86383(17)$ nm. After the high-pressure treatment, the diffraction peaks of the sample can be indexed on the basis of a hexagonal unit cell of $a = 0.36094(4)$ nm, and $c = 2.9292(4)$ nm. Both polymorphs exhibited layer structured characteristics and showed a preferred orientation with the basal plane. Therefore the XRD patterns had strong (00*l*) reflections but weak (*hkl*) reflections in the intensities. We observed only $-h + k + l = 3n$ reflections for the high-pressure treated sample, indicating that the unit cell was rhombohedral. The iodide crystals α-MNI (M = Zr, Hf) could also be transformed into the β-polymorphs. The XRD patterns for the HfNI and ZrNI systems are shown in Figures 4 and 5, respectively. The iodide crystals required a higher pressure of 5 GPa for the transformation to the β-form. The lattice parameters determined for the new β-forms obtained in this study are listed in Table 4, together with the lattice parameters of the other crystals so far reported.

The β-forms of ZrNI, HfNBr, and HfNI were obtained for the first time in this study by using high-pressure conditions. Figure 6 shows the lattice parameters of all of the β-polymorphs as a function of the ionic radius of the halogen ions. The ionic radii were taken from the table of Shannon.[19] Note that the lattice

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Table 4. Lattice Parameters and Theoretical Densities (d) of α- and β-MNX (M = Zr, Hf; X = Cl, Br, I)

	α-form				β-form			
	a, nm	b, nm	c, nm	d, g cm^{-3}	a, nm	c, nm	d, g cm^{-3}	ref
ZrNCl	0.408	0.352	0.857	3.79	0.3606	2.7666	4.49	7, 9
ZrNBr	0.4121	0.3597	0.8796	4.77	0.3635	2.9261	5.50	7, 2
ZrNI	0.4106(3)	0.3739(2)	0.9457(1)	5.31	0.37184(4)	3.1345(3)	6.16	this study
HfNCl	0.41307	0.34974	0.8070	6.49	0.3573	2.7678	7.42	4
HfNBr	0.41129(5)	0.35586(5)	0.8638(1)	7.15	0.36094(4)	2.9292(4)	8.21	this study
HfNI	0.41067(9)	0.36944(5)	0.9382(1)	7.45	0.36880(3)	3.1328(2)	8.63	this study

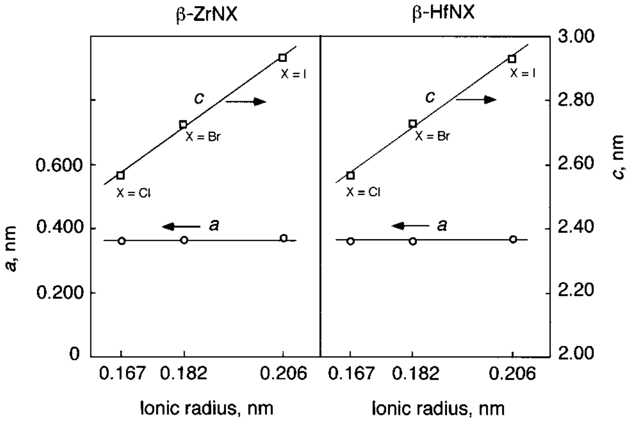

Figure 6. The lattice parameters of β-MNX (M = Zr, Hf; X = Cl, Br, I) as a function of the ionic radius of the halogen ion (X).

parameter c of the axis perpendicular to the basal plane increases linearly with the increase of the ionic radius, while the parameter a of the axis in plane is not influenced by the ionic radius. Figure 7 depicts schematic structural models of the two kinds of double metal nitride layer (α- and β-forms) with halogen ions. In the case of the β-form, it is reasonable to assume that the lattice parameter a in plane 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 centers of the hexagonal rings of the double M−N networks, and the distance between adjacent halogen ions in the layer corresponds to the lattice parameter a. Therefore, if the lattice parameter in plane is larger than or close to twice the ionic radius of the halogen ion, the M−N plane can accommodate the halogen ions. However, in the case of the iodides, the ionic radius (0.206 nm) is too large to fit in M−N networks ($a/2 = \sim 0.18$ nm), and thus the iodide ions should be so compressed as to fit this network by high pressure to form the β-form. In β-HfNBr, the ionic radius of bromine is almost critical (Shannon's ionic radius of Br^- = 0.182 nm, $a/2 = \sim 0.18$ nm); the α-form can be easily transformed to the β-form at a lower pressure (3 GPa) than that required for the transformation of the α-form of the iodide crystals. In β-MNCl (M = Zr, Hf), the parameter $a/2$ ($\sim$0.18 nm) is larger than the ionic radius of Cl^- (0.167 nm); the treatment at elevated temperature can activate the rearrangement of the M−N networks from the α- to the β-type. The theoretical densities calculated on the basis of the lattice parameters are listed in Table 4, which indicates that the β-forms have higher densities than the α-forms. Evidently, the β-forms should be characterized as high-density forms of the α-forms rather than as high-temperature polymorphs. The β-form is compressed in plane by about 25% compared to the corresponding α-form.

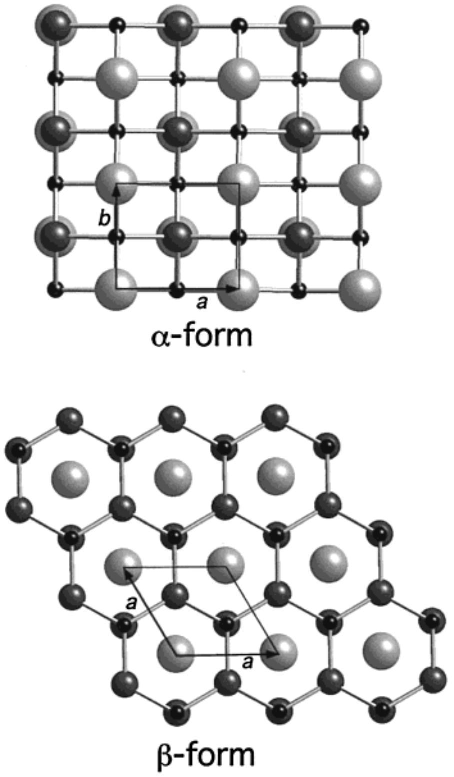

Figure 7. Downward projection of the two-dimensional M−N networks of α- and β-MNX with halogen ions (X, large spheres): M, small black spheres; N, medium size dark gray spheres.

Now we have all kinds of combinations of the β-form for MNX (M = Zr, Hf; X = Cl, Br, I). The influence of halogen ions on the T_c of the electron-doped nitride layers is now under investigation, and the results will be reported elsewhere. There are a large number of layer structured mixed-anion compounds MXY.[1] Those adopt mainly four kinds of layered structures, FeOCl, PbFCl, YOF, and SmSI types. It will be interesting to study the high-pressure transformation between these structures to develop new layer structured compounds with interesting electrical and magnetic properties. From a viewpoint to develop new high-T_c superconductors in relation with the electron-doped β-ZrNCl and β-HfNCl, systematic studies to prepare β-TiNX (X = Cl, Br, I) should be made, since all of the titanium nitride halides adopt only the FeOCl-type structure under ambient pressure.

Acknowledgment. This study has been supported by Grant-in-Aid of the Ministry of Education, Science, Culture, and Sports, Japan.

IC991058L