

β -MNCl (M = Zr, Hf) 単結晶の高圧合成と構造解析

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Recently, the compounds MNX (M = Zr, Hf; X = Cl, Br, I) have gained considerable interest because of the superconductivity caused by alkali-metal intercalation into the interlayer space. The crystal structure of the β -ZrNCl host lattice has been determined by several groups using powder X-ray or neutron diffraction. The powder sample shows a very strong preferred orientation due to the layer structured nature of the crystals, and the structural data reported by different authors vary largely. During our investigation of the ternary M-N-X system using high-pressure technique, we have obtained the single crystals of β -MNCl (M = Zr, Hf) for the first time. In this work we report their crystal growths and accurate structure determinations.

The single crystals of two kinds of metal nitride halides, β -ZrNCl and β -HfNCl, were grown in sealed Au (or Pt) tubes with the presence of NH_4Cl under a pressure of 3 GPa at 900 °C and 1200 °C, respectively, using a high pressure apparatus (Fig. 1). Their crystal structures were refined on the basis of X-ray four circle diffractometer data. β -ZrNCl crystallizes in a space group $R\bar{3}m$; $a = 3.6046(4)$, $c = 27.672(4)$ Å, and $Z = 6$; $R1/wR2 = 0.0270/0.0751$ for 447 observed reflections and 11 variables. β -HfNCl is isostructural with β -ZrNCl; $a = 3.5767(8)$, $c = 27.711(7)$ Å, and $Z = 6$; $R1/wR2 = 0.0372/0.0979$ for 454 observed reflections. The compounds are isotypic with SmSI and comprise structural slabs $[\text{Cl-M-N-N-M-Cl}]$ (M = Zr, Hf) with close-packed anion layers. Three of those slabs are stacked rhombohedrally in the unit cell along the c -axis and held together by Cl...Cl van der Waals interactions. The metal atoms (M) are placed in the octahedral sites between the Cl and N layers, leading to the overall layer sequence of $\text{Cl}_A\text{M}_c\text{N}_b\text{N}_c\text{M}_b\text{Cl}_A|\text{Cl}_c\text{M}_b\text{N}_a\text{N}_b\text{M}_a\text{Cl}_c|\text{Cl}_b\text{M}_a\text{N}_c\text{N}_a\text{M}_c\text{Cl}_b$ as shown in Fig. 2. The present single crystal data of β -MNCl (M = Zr, Hf) are more accurate than the powder results in the literatures. This is also the first single crystal study on the layered nitride halides MNX (M = Zr, Hf, X = Cl, Br, I).

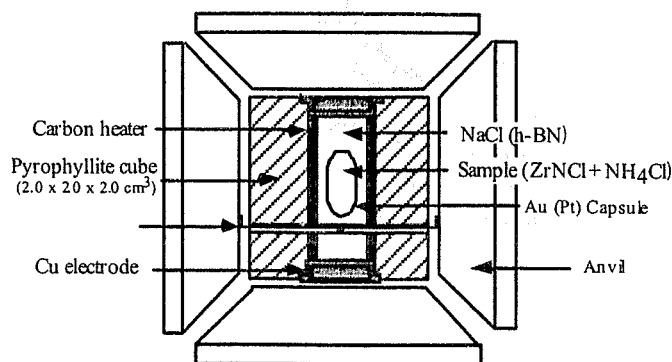


Fig. 1. An assembly used for the high-pressure synthesis

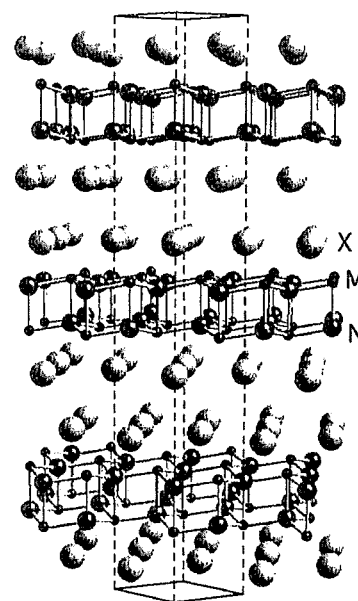


Fig. 2. Schematic structural model of β -MNCl (M = Zr, Hf)