Structural phase transition of Cu$_3$N under high pressure

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**A B S T R A C T**

We performed the high-pressure angle-resolved X-ray diffraction experiments on Cu$_3$N up to 36.0 GPa. It was found that a crystal structure phase transition begins to take place at $\sim$5.5 GPa on Cu$_3$N. Under high pressure, Cu$_3$N transforms to a new simple tetragonal structure denoted by $[\text{Cu}(1)\text{Cu}(2)\text{N}]_{1+x/3}$, because parts of Cu and N ions occupy the vacant sites in the crystal lattice. In this structure, Cu(1) and Cu(2) denote the primal Cu position and the vacant position in ReO$_3$ type Cu$_3$N, respectively. The content $x$ is increasing with pressure, indicating that the phase transition is a gradual change. When pressure is greater than 12 GPa, $x$ keeps 1 up to the maximum pressure, so Cu$_3$N completely transforms to a body-center tetragonal structure, where the N sites are filled with $1/3$ N ions.

1. Introduction

Cu$_3$N adopts the anti-ReO$_3$ type structure at ambient pressure, with the space group $Pm-3m$ [1]. The Cu and N ions are in the 3c positions (0.5, 0.5, 0) and 1b position (0.5, 0.5, 0.5), i.e. the X-site and the B-site of ABX$_3$ type cubic perovskite, respectively. Six Cu ions form an octahedron around one N ion. The two neighboring NCu$_6$ octahedra connect each other through the Cu ion in the corner and form a three-dimensional crystal lattice. Comparing with the normal ABX$_3$ type perovskite, there is no ion in the 1a position (0, 0, 0), i.e. the A-site of Cu$_3$N, which will enable rotations of NCu$_6$ octahedra. Cu$_3$N decomposes into Cu and N$_2$ at about 300–470 °C [2–4]. The decomposition temperatures are much lower than those of most nitrides, indicating that it is relatively easy for Cu$_3$N to be subjected to pressure modification. Therefore, it is expected that some crystal structure changes will take place in Cu$_3$N upon compression.

In the previous paper, we performed the *in situ* high-pressure energy-dispersive X-ray diffraction experiment on Cu$_3$N, and found that a crystal structure phase transition happens at $\sim$5.0 GPa [5]. But it is difficult to distinguish the structure of new high-pressure phase, because the synchrotron energy limitation does not allow us to collect more diffraction peaks of the sample. Wosylius et al. have found that Cu$_3$N transforms to a body-center tetragonal structure under high pressure [6]. However, they did not give the transitional structure between the ambient phase and the high-pressure phase [6]. This mediate structure is also of importance to the origin of phase transition for Cu$_3$N. In this paper, we report the high-pressure structural evolution of Cu$_3$N based on the diamond anvil cell (DAC) technique by using the in situ high-pressure angle-resolved X-ray diffraction experiment with synchrotron radiation.

2. Experimental details

The Cu$_3$N sample used in this experiment is the business product purchased from Alfa Aesar Company, with the purity of 99.5%. The *in situ* high-pressure angle-resolved X-ray diffraction experiment for Cu$_3$N was carried out at room temperature at the Advanced Photon Source (APS), with the wavelength of incident X-ray 0.3676 Å. The sample was loaded into the sample chamber in the T301 stainless steel gasket. The pressure on the sample was measured by using the ruby fluorescence method [7]. Silicone oil, which can generate a fine quasi-hydrostatic pressure environment within the pressure range in this study, was used as the pressure-transmitting medium [8,9]. Diffraction patterns were collected on a Mar345 image plate reader up to 36 GPa. The recorded images were integrated using the program Fit2D [10].

3. Results and discussion

Fig. 1(a) shows the spectra of angle-resolved X-ray diffraction (XRD) results of Cu$_3$N at various pressures. There also are two weak diffraction peaks of CuO impurity, as indicated with asterisks.
in Fig. 1(a). Comparing with the normal structure of Cu$_3$N, the difference in relative peak intensity is attributed to the distortion of sample that was compressed before loaded into the cell. According to the peaks intensity evolution, there is a crystal structure phase transition beginning at \( \sim 5.5 \) GPa. When the pressure is greater than 12 GPa, Cu$_3$N completely becomes the high-pressure phase. So there are two phases for Cu$_3$N up to 36 GPa. Region in 5.5–12 GPa is a mediated process. The results are consistent with those of energy-dispersive X-ray diffraction experiment [5]. In Ref. [5], we assumed a structure with the space group Im3 as the high-pressure phase of Cu$_3$N, mainly considering the similar structure with ReO$_3$ that transforms to a new structure with the space group Im3 under high pressure [11]. However, the properties of Cu$_3$N are different from those of ReO$_3$. Like most transition metal oxides, the ReO$_6$ octahedron in ReO$_3$ is steady, because of the strong Re–O ionic bond. The crystal orbital-overlap population (COOP) shows that the Cu(1)–N bond is weak in Cu$_3$N [12]. In Cu$_3$N, there should be the similar weak Cu–N bond. The weak interaction between Cu and N ions in Cu$_3$N is consistent with the low decomposition temperature [2–4]. In fact, the small Cu$^{+}$ ion radius and large N$^{3-}$ ion radius are not suited for forming octahedron [13]. Cu$^{+}$ ion, as a monovalent d$^{10}$ ion, is prone to shift in the crystal lattice due to its high mobility [12]. Thereby the NCu$_6$ octahedron in Cu$_3$N may collapse in some special conditions, e.g. high-temperature, high-pressure, ion substitution.

Under high pressure, parts of Cu$^{+}$ ions in Cu$_3$N occupy the 1a position (0, 0, 0), i.e. the A-site, and parts of N ions occupy the 3d positions (0.5, 0, 0). These Cu and N ions are denoted by Cu(2) and N(2), respectively, which are distinguished with the Cu(1) and N(1) ions that are in the original positions. The form between 5.5 and 12 GPa should be denoted by [Cu(1)Cu(2)$_2$]N$_{1+3/3}$, where x is the occupation of Cu ions in the Cu(2) site. According to the XRD patterns, the ions reconstructing results in that the new form adopts a simple tetragonal structure, with the space group P4/mm. In this new structure, Cu(1) ions occupy the 1c position (0.5, 0.5, 0) and 2e positions (0.5, 0, 0.5), N(1) ion occupies the 1d position (0.5, 0.5, 0.5), Cu(2) ion occupies the 1a positions (0, 0, 0), and N(2) ions occupy the 1b position (0, 0.5, 0) and 2f positions (0, 0.5, 0). Fig. 2(a) and (b) show the schematic views of crystal structure of the anti-ReO$_3$ type and the simple tetragonal structure, respectively. The diffraction intensity of N ions is weaker than that of Cu ions, so the diffraction of Cu ions is the main contribution to the whole XRD pattern of Cu$_3$N. The new transitional phase is a metal, confirmed by Yang et al. through the in situ high-pressure measurements of resistance versus temperature using DAC technique recently [14].

In Ref. [6], the authors thought that there is a mixed phase of cubic and tetragonal in the pressure range of 5–8 GPa. However, they did not provide any X-ray diffraction patterns and the pressure dependencies of unit cell volume for cubic and tetragonal structures in this region. Fig. 1(b) shows the detailed XRD of Cu$_3$N in the 2\( \theta \) range of 8°–12° at 5–12 GPa, which is our experimental results. It is very obvious that the peak at about 9.7° shifts to low diffraction angle with the increasing pressure. The peak at about 11.2° also shifts to low diffraction angle, although the movement is not obvious. If Cu$_3$N is a mixed phase of cubic and tetragonal above 5 GPa, the two peaks should shift to high diffraction angle with pressure. The simple tetragonal structure with the space group P4/mmm is a suitable candidate of high-pressure phase for Cu$_3$N, indicated by the XRD at 5–12 GPa. Although the unit cell volume is increasing with pressure, the number of ions is also increasing. Hence the volume per one Cu$_3$N formula is decreasing, as mentioned in the following discussion.

When the pressure is greater than 12.8 GPa, all the Cu(2) positions are filled with Cu ions. So the new high-pressure phase crystallizes into a body-center tetragonal structure, with the space group I4/mmm [6]. The Cu and N ions occupy the 2a positions (0, 0, 0) and 2b positions (0, 0, 0.5), respectively. In this structure, the N positions are filled with 1/3 N ions, with the disordered arrangement in the crystal lattice. The high-pressure phase could be denoted by Cu$_3$N$_{4/3}$. The XRD pattern of the new high-pressure phase is similar to that of the face-center-like structure of Cu ions. Fig. 2(c) shows the schematic view of body-center tetragonal structure of Cu$_3$N. In the new high-pressure phase, one can find a "face-center" tetragonal structure within the green bold line range in Fig. 2(c), with the \( \sqrt{2}a \)-axis parameter of the body-center tetragonal one. The crystal structure of the high-pressure Cu$_3$N is very similar to Ag$_3$N that crystallizes into a face-center cubic.
structure [15], with the space group Fm-3m. For the ambient anti-ReO$_3$ type Cu$_3$N, six Cu ions surround one N ion, and there are two N ions in the neighbor of one Cu ion. Under high pressure, the coordinated number of Cu ions around N ion does not change. It seems to six N ions surround one Cu ion in the high-pressure body-center tetragonal phase. But, considering to the 1/3 occupation of N ions, the actual coordinated number of N ions is also equal to 2, like that in the ambient phase. Therefore, the phase transition of Cu$_3$N under high pressure does not influence the coordinated numbers of Cu and N ions.

We performed the structural refinement to identify the new phase with Rietveld method by using GSAS program package [16], in order to study the pressure effect on the structural properties of Cu$_3$N down to the atomic level. Fig. 3 shows the typical refining results for the XRD patterns at 3.16, 7.03 and 26.8 GPa, with the fitted residuals $R_{wp}$ factors 2.04%, 2.75%, and 2.96%, respectively. For the transitional phase, the $x$ in [Cu(1)$_x$Cu(2)$_{1-x}$]N$_{1+2/3}$ is increasing with pressure. The weakness and vanishing of some peaks in XRD patterns are consistent with the increasing $x$. When pressure is greater than 12.8 GPa, Cu$_3$N becomes the high-pressure phase, indicated by the $x$ value of 1.

Fig. 4 shows the pressure dependencies of unit cell volume for Cu$_3$N, where the $V_C$, $V_P$, and $V_T$ are denoted by the unit cell volume of the original anti-ReO$_3$ structure, the transitional simple tetragonal structure, and the high-pressure body-center tetragonal structure, respectively. Fig. 4 can be viewed as three regions, which are corresponding to the above-mentioned three structures. In Region I (0.86–5.5 GPa), $V_C$ is decreasing with the increasing pressure. In Region II (5.5–12.0 GPa), $V_P$ is increasing with pressure, due to the increasing Cu and N ions in one unit cell. The inset shows the pressure dependencies of lattice parameter $a_P$ and $c_P$, and content $x$ in Region II. The three values are increasing with pressure. When the pressure is greater than 12.0 GPa (Region III), $V_T$ is decreasing with pressure, implying that Cu$_3$N completely becomes the high-pressure phase at about 12.0 GPa. In fact, the volume per Cu$_3$N is more meaningful than the unit cell volume in the relationship of volume and pressure. In the three regions, the volume per Cu$_3$N is equal to $V_C$, $V_P/(1 + x/3)$, and $3V_T/2$, respectively, as shown in Fig. 4. With the increasing pressure, the volume per Cu$_3$N is decreasing. Comparing with the low-pressure cubic phase, there is a volume collapse of about 21% for the high-pressure body-center tetragonal phase, which is close to that in Ref. [6]. However, considering the intermediate transitional phase, the volume per Cu$_3$N is approximately continuous in our experimental pressure range.

The solid lines in Fig. 4 are the fitting results for the low-pressure cubic phase and high-pressure body-center tetragonal phase using the second-order Birch equation of state (EoS) [17]. With $B'_0$ fixed as 4, we obtained the ambient pressure isothermal bulk modulus $B_0$ of 78(6) and 130(8) GPa for the cubic and tetragonal phases, respectively. The fitted unit cell volume $V_0$ of the two phases is shown in Fig. 4. The experimental (open circle) and fitted (line) X-ray diffraction patterns for Cu$_3$N at 3.16, 7.03 and 26.8 GPa. The asterisk indicates the weak diffraction peak of CuO impurity.
forms at ambient condition is equal to 55.6(2) and 29.8(2) Å³, respectively. So the fitted lattice parameter $a_{0}$ of the cubic phase is 3.817(5) Å, which is approximately equal to the value in Ref. [2]. For the high-pressure phase, the unit cell volume of the hypothetical face-center tetragonal structure is equal to 59.6(4) Å³, being less than that of 83.40(6) Å³ for Ag$_3$N [15].

There are two sorts of mechanisms of crystal structure phase transition: displacive transition and reconstructive transition. In the high-pressure phase of Cu$_3$N, the ions are reconstructive comparing to the ambient phase. However, the formation of high-pressure phase undergoes the ion displacing evolution within the mediated phase. Hereby the phase transition of Cu$_3$N under high pressure includes the two processes of displacive and reconstructive changes. When the pressure releases to ambient, the high-pressure body-center tetragonal phase transforms to the mediated simple tetragonal phase, indicated by the emergence of weak (d) peak [5]. Parts of Cu and N ions will return to their original positions with the pressure release. So the phase transition, which is a complex path, is not completely reversible while unloading pressure. When the pressure is released to ambient, the resistance does not return to the original value at ambient pressure [5]. This phenomenon can be explained by the incompletely recover of phase transition. In fact, the resistance can recover to the primary value through several months after pressure release, which indicates that the transition from the high-pressure phase to ambient phase for Cu$_3$N may be a long-term process. All the above-mentioned experimental and theoretic results support our hypothesis that Cu$_3$N transforms to a new body-center tetragonal structure with the 1/3 occupation of N ions, through a transitional simple tetragonal structure. However, there are some unclear questions to resolve, for example, the reason for ion shift and the path of ion movement. Under higher pressure, Cu$_3$N may transform to other new phases, such as A$_{15}$N type structure, CsCl type structure, and so on. Therefore, we will perform other experiments to figure out the mechanism of phase transition and attempt to find the other possible new phases of Cu$_3$N in future.

4. Summary

In summary, the structural evolution with the pressure of anti-perovskite nitride Cu$_3$N has been investigated through the in situ high-pressure angle-resolved X-ray diffraction experiment. Cu$_3$N transforms to a new simple tetragonal structure denoted by [Cu$_1$(1$_{1}$Cu$_2$)$_{2}$]N$_{1+\frac{x}{3}}$ from $\sim$5.5 GPa, due to the displacive and reconstructive processes of Cu and N ions under high pressure, and completely becomes the high-pressure phase of body-center tetragonal structure above 12 GPa, where the occupation of N ions is equal to 1/3.

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References


Fig. 4. The pressure dependencies of volume for Cu$_3$N. The inset shows the pressure dependencies of lattice parameters $a_{0}$ and $c_{0}$, and the content $x$ in Region II. The solid lines are the fitting results according to the second-order Birch equation of state (EOS).