

Pressure-induced structural evolution of Cu_3N

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Introduction

Cu_3N crystallizes into anti- ReO_3 type structure of space group $\text{Pm}\bar{3}\text{m}$. The Cu atom is in the position of 3d (0.5, 0, 0) and the N atom is in the B-site of normal ABO_3 type cubic perovskite structure, with the atomic position being: 1a (0, 0, 0). Cu_3N can decompose into Cu and N_2 and become conductor from semiconductor at very low temperature [1]. So the Cu_3N films can be used as the write-once optical recording material. Since the lattice mismatch between thin film and substrate always leads to strain, it is important to learn how pressure will affect the structural properties of this functional material. The low decomposition temperature means weak Cu–N bonding, indicating that it is relatively easy for Cu_3N to be subjected to pressure modification.

Methods and Materials

The *in situ* high-pressure X-ray angle-dispersive diffraction experiment was carried out at room temperature at the Advanced Photon Source (APS). The wavelength of incident X-ray was 0.3897 Å. The culet of diamond is 500 μm in diameter and the hole in a T301 stainless steel gasket is 200 μm in diameter. The silicon oil was used as the pressure-transmitting medium, which kept a good hydrostatic pressure environment. The sample was pressed into a pellet and was loaded into the hole. Pressure on the sample was measured by ruby fluorescence.

Results

Fig. 1 shows the spectra of X-ray diffraction (XRD) results of Cu_3N at various pressures. There are ten peaks of the sample, indicated with (a)–(j) in the XRD patterns. The indices of peaks are indicated for Cu_3N at 0.86 GPa. Comparing to the normal structure of Cu_3N , the difference in relative peak intensity is attributed to the distortion of sample that was compressed before loaded into cell. The peak (b), (f), (h) and (i) exist only in the region 0.86–6.18 GPa and almost vanish at 7.03 GPa. The peak (a) and (e) almost vanish at 12.8 GPa. Above 12.8 GPa, no splitting or merging peaks are observed up to 36 GPa.

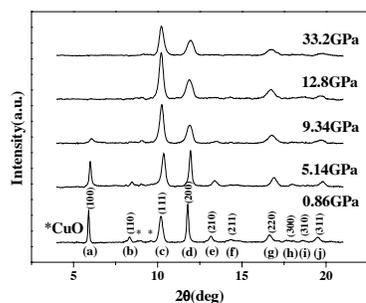


Fig. 1.

The relationships of d-values of peak (a)–(j) versus pressure below 16 GPa are shown in Fig. 2. Some peaks are too weak to fit and calculate the d-values. According to the peak intensity evolution and the d-value change tendency, Fig. 2 can be viewed as three regions. Region I corresponds to low pressure

(0.86–5.5 GPa), where d values are decreasing with increasing pressure, and $d_{(b)}$ is only increasing from 5.14 GPa. In the region from 5.5 to 12.0 GPa, which is denoted Region II, $d_{(c)}$ and $d_{(g)}$ are lightly increasing with increasing pressure, and $d_{(a)}$, $d_{(d)}$, $d_{(e)}$ and $d_{(j)}$ are almost unchanged, indicating that there may be a crystal structure phase transition at ~5.5 GPa. When the pressure is higher than 12.0 GPa denoted with Region III, all the d values are decreasing with increasing pressure, implying Cu_3N becomes the high-pressure phase completely at about 12.0 GPa. So there are two phases for Cu_3N up to 36 GPa. The ambient phase (α -phase) and the high-pressure phase (β -phase) correspond to Region I and III, respectively, and Region II is the mixture of the two phases, which is consistent with the results of X-ray energy-dispersive diffraction experiment [2].

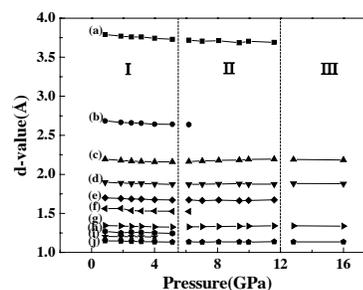


Fig. 2.

Discussion

Under high pressure, parts of Cu ions may shift to the 1b-site of (0.5, 0.5, 0.5) from the 3d-site for the high mobility of Cu^+ as a monovalent d^{10} ion, which forms the Cu_4N -like structure [3,4]. The new form of $\text{Cu(II)}_x\text{Cu(I)}_{3-x}\text{N}$, with Cu(II) in the 1b-site and Cu(I) in the original situation, is a possible candidate of the β -phase. The movement of Cu ions can result in the enlargement of d-values and lattice parameters at ambient pressure [4], so the competition between ion shift and pressure effect induces the unusual change of d-values in Region II. The obvious disappearance or weakness of the peak with mixed even and odd indices is consistent with the fcc-like structure of Cu ions in the new high-pressure phase. Further structural refining will be performed in future to identify the new phase.

Acknowledgments

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