High Pressure Behavior of Mercury Cyanamide HgCN$_2$

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Abstract. Using the diamond anvil cell technique, angle-dispersive X-ray diffraction and Raman spectroscopy were employed to study the high pressure behavior of mercury cyanamide. Its decomposition under pressure starts at 1.9 GPa and is not completed even up to 10 GPa. The decomposition product α-Hg transforms to β-Hg during 7–10 GPa, while the C/N residual is not detectable by X-ray diffraction. The zero pressure bulk modulus of mercury cyanamide is estimated as 38.5 GPa.

Keywords: High pressure; Angle dispersive X-ray diffraction; Raman spectroscopy; Mercury cyanamide; Mercury

The structures of 11th and 12th group metal cyanamides were systematically studied at ambient conditions by using X-ray and neutron diffraction, recently, and the cyanamides display a rich degree of various crystal structures, depending on the cations present [1–3]. However, the high pressure behavior of cyanamides is unknown up to now. In addition to some general interest in the high pressure behavior of metal cyanamides, the C–N bond inside these compounds is of special interest in a number of fields with implication for low compressibility materials [4, 5]. In particular, polymerizing the CN_2^{2-} units could open a versatile access to three dimensional C/N networks. The research on phase transition and decomposition behavior of cyanamide using *in situ* high pressure techniques offers us an opportunity to study the intrinsic characteristics of C–N bonding and to gain insight concerning the decomposition dynamics of cyanamide under high pressure conditions.

Experimental

$HgCN_2$ was prepared by double conversion of $HgCl_2$ with sodium cyanamide in aqueous solution. Its crystal structure (orthorhombic, Pbca) has been determined using X-ray powder data and refined by combined profile fits using X-ray and neutron diffraction data [1, 3]. The high pressure experiments were carried out at room temperature in a diamond anvil cell (DAC) apparatus, in which the mixture of ethanol and methanol (4:1) was used as pressure transmitting medium, while the ruby fluorescence method was used for pressure calibration [6]. Raman spectra were collected by a Jobin-Yvon LabRAM laser microscope Raman system using CCD detector with excitation line 6328.17nm (He–Ne laser). The angle-dispersive X-ray powder diffraction experiments (wavelength 0.3738 Å) in a DAC were performed at the beamline ID30 of European Synchrotron Radiation Facility (ESRF, Grenoble, France). Diffraction patterns were recorded on an image plate and then converted to the intensity versus 2θ diffraction angle by using the program FIT2D [7].

Results and Discussion

Raman spectroscopy

The Raman spectra of the sample under high pressure is shown in Fig. 1. It was expected that the intensities of the two Raman modes, i.e. δ mode of the C–N bond and v_s mode of the Hg–N bond [3], decrease with increasing pressure, and almost disappear as pressing up to 9.8 GPa. Both Raman modes show a trend to soften as a function of pressure. These results imply that the bonds between Hg–N and C–N become weaker under high pressure than at ambient
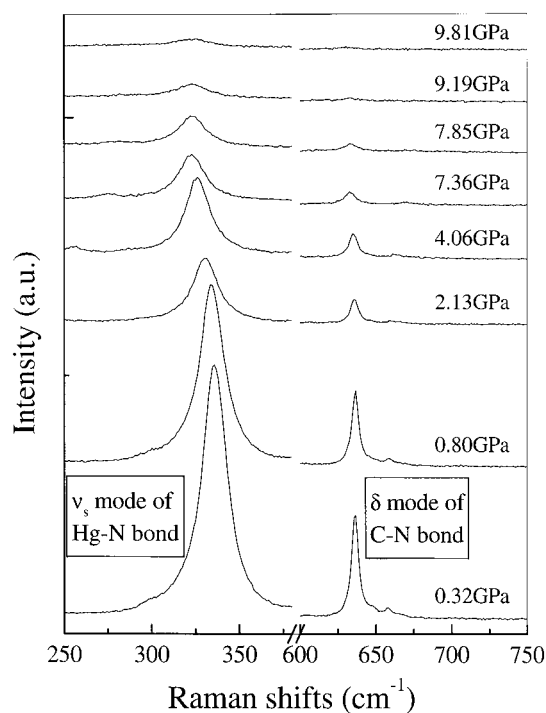
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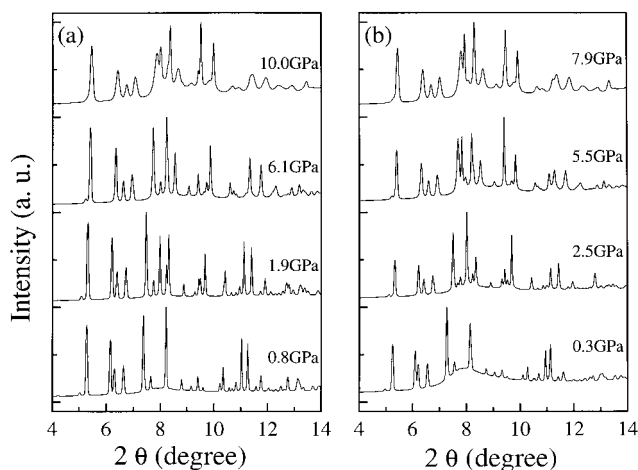e-mail: martin@jansen.mpi-stuttgart.mpg.de

Fig. 1 Raman spectra of HgCN$_2$ upon compression.

Fig. 2 XRD patterns of HgCN$_2$ during compression (a), and decompression (b).

Fig. 4 The lattice parameters of α-Hg and β-Hg as a function of pressure (right), and their relative ratio and total ratio compared to HgCN$_2$ remained in sample during increasing pressure process (left).
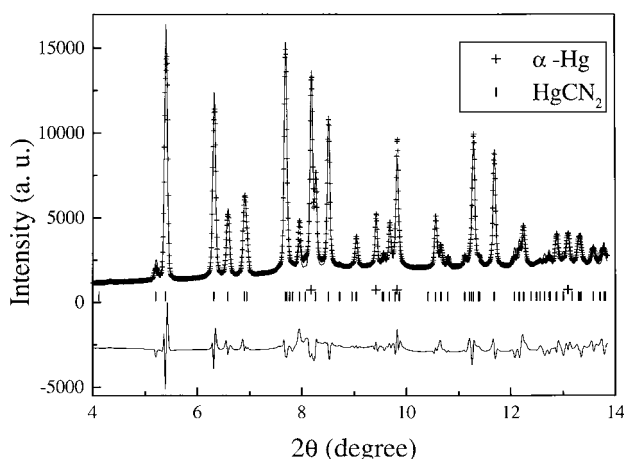

Fig. 3 Observed, calculated, and difference XRD profile of a sample at 5.1 GPa (increasing pressure), in which α-Hg and HgCN$_2$ coexist.

Fig. 5 Pressure dependence of lattice parameters and unit cell volume of HgCN$_2$ with increasing pressure.

conditions. The intensities of these Raman peaks recover in the decompressing process.

X-ray diffraction analysis: Fig. 2 (a) and (b) show the typical XRD patterns of the sample under various pressure conditions during compressing and decompressing processes, respectively. At increasing pressure to 1.9 GPa, additional diffraction peaks appear while the diffraction peaks of HgCN$_2$ keep stable. The new peaks can be indexed as α-Hg, this indicates the pressure induced decomposition of HgCN$_2$ to happen at about 1.9 GPa. However, the decomposition proceeds slowly, and does not finish even as the pressure reaches 10 GPa. The product of decomposition should consist of mercury and C–N remnants. The possibility of some of C–N double bonds converting to single bonds and then forming a C–N single bond network under high pressure is the interesting point to check. However, only mercury could be observed in the diffraction patterns. The C–N remnants may have formed an amorphous network which has no obviously new Raman active modes.

Using the program GSAS [8], the Rietveld refinements were carried out for all of these diffraction patterns. Fig. 3
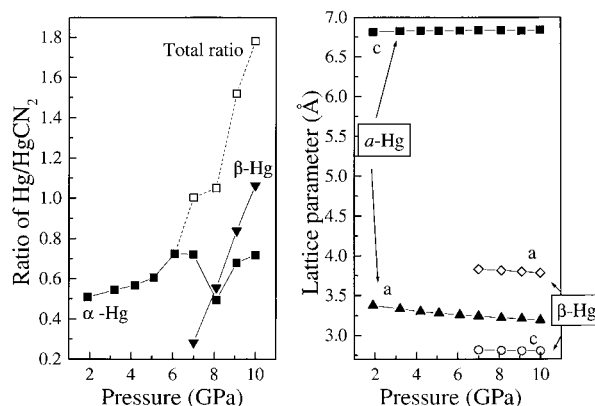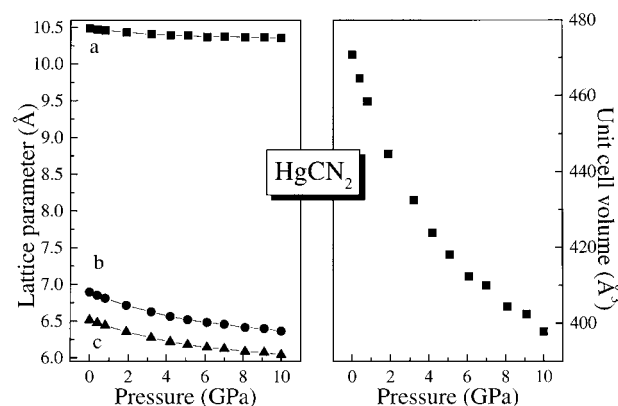
shows a typical refinement result of the powder pattern at 5.1 GPa at compression. At these conditions two phases (HgCN$_2$ and α-Hg) coexist, and the two phase refinement converged to R$_p$ = 6.2%, R$_{wp}$ = 7.9%. In the pressure range of 7.0 GPa to 10 GPa, α-Hg (rhombohedral, *R-3m*) partly transforms to β-Hg (tetragonal, *I4/mmm*). This phase transition should happen at 3.7 GPa for pure mercury [9]. The delay of this phase transition may be attributed to small amounts of impurities of carbon and nitrogen resulting from the decomposition. Fig. 4 shows the lattice parameters of the two modifications of mercury as a function of pressure, and their relative and total ratio compared to the residual cyanamide phase. When pressure was released to 0.3 GPa (Fig. 2), only diffraction lines of HgCN$_2$ could be observed and all reflection peaks of mercury had disappeared. This is attributed to a melting of mercury at high pressure, which is also noticeable from a higher background in the XRD patterns as compared to the initial powder diagrams.

The lattice parameters of HgCN$_2$, and the corresponding unit cell volume change with pressure are illustrated in Fig. 5. Neglecting the decomposition occurring at 1.9 GPa, the equation of state for mercury cyanamide could be fitted according to second order (K$_0'$ = 4) Birch equation [10]. The zero pressure bulk modulus (K$_0$), estimated as

38.5 GPa, indicates mercury cyanamide to be a very soft compound.

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