

Structure Evolution of Energetic Material LLM-105 Under High Pressure

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Abstract

Recently, 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) has been widely studied on its high pressure structure properties both theoretically and experimentally, but with no universal agreement. This work investigates the structure evolution of LLM-105 crystal under high pressure up to 32 GPa by Raman spectroscopy. The results display that there exist two phase transitions occurring at 10 and 17 GPa, respectively. This conclusion is consistent with the previous theoretical calculation. With further loading above 17 GPa, the broadening of Raman peaks and the peak shifted to high wavenumber mean that the LLM-105 had a tendency to evolve to amorphous state. Moreover, two different crystal growth directions in the LLM-105 twin crystal are identified by using Raman spectra.

1 Introduction

As a latent candidate of energetic material, 2,6-diamino-3,5-dinitropyrazine-1-oxide ($C_4H_4N_6O_5$ Lawrence Livermore Molecule No. 105, LLM-105) is attracting considerable attention due to its low sensitivity and high energy density.¹ The energy and sensitivity of this material are between those of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB).^{2,3} In addition, this material has been found to be good performance on high-sensitive force sensor.⁷ Many theoretical works investigated the structure evolution of LLM-105 under high pressure.⁴⁻⁶ Using periodic density functional theory (DFT) calculations, Wu *et al.*⁴ theoretically predicted that LLM-105 a series of phase transitions exists at 8, 17, 25 and 42 GPa. While, Manaa *et al.*⁵ employed dispersion-corrected DFT calculations to study the hydrostatic compression of crystal LLM-105 up to 45 GPa and suggested that there is no evidence for

structural phase transition or chemically induced transformation up to this pressure. Stavrou *et al.*⁶ concluded that LLM-105 with the ambient phase remains stable up to 20 GPa through a combined experimental and first-principles study. So far, the results from different theoretic groups are controversial each other and few experimental data are reported for the phase transformation of LLM-105 under high pressure. It is worth further exploring the structure evolution of LLM-105 under high pressure.

In this work, based on the investigation of the basic properties of LLM-105, the structure behaviors of LLM-105 crystal powder is studied under high pressure up to 32 GPa by Raman spectroscopy combined with diamond-anvil cell.

2 Experiments

The morphology of sample was characterized by using scanning electron microscope (SEM). Thermal stability was analyzed by thermal gravimetric analysis and differential scanning calorimetry (DSC). The high pressure is generated by diamond anvil cell (DAC) setup. The sample and ruby (as a pressure calibrator) were put into the DAC with 400 μm diameter culets. To radially restrict the pressurized sample, a stainless steel gasket was preindented to a thickness of 60 μm , and then, the sample chamber (a hole with 150 μm diameter) was drilled by a spark eroder (BETSA, MH20M). Raman spectra were recorded by an integrated laser Raman system (LABRAM HR, Jobin Yvon) with a confocal microscope, a stigmatic spectrometer, and a multichannel air-cooled CCD detector with resolution of 1 cm^{-1} . The 785 nm laser was used as the excitation source at a power level of about 8 mW to avoid any possible laser-induced damage. All spectra were recorded in the backscattering geometry at room temperature. The pressure was recorded by the ruby R_1 luminescence line. No transmitting medium was used in the high pressure experiment to avoid the possible influence.

3 Results and Discussion

The LLM-105 crystal shows a brilliant yellow rods. The SEM images show that LLM-105 is a regular oblique prismatic micro-crystal with smooth surface and good crystallinity, the grain size is about 20 to 50 μm as show in Fig. 1. The sample contains two morphologies, one is rods and the other is cross-rods which regard it as twin crystals.

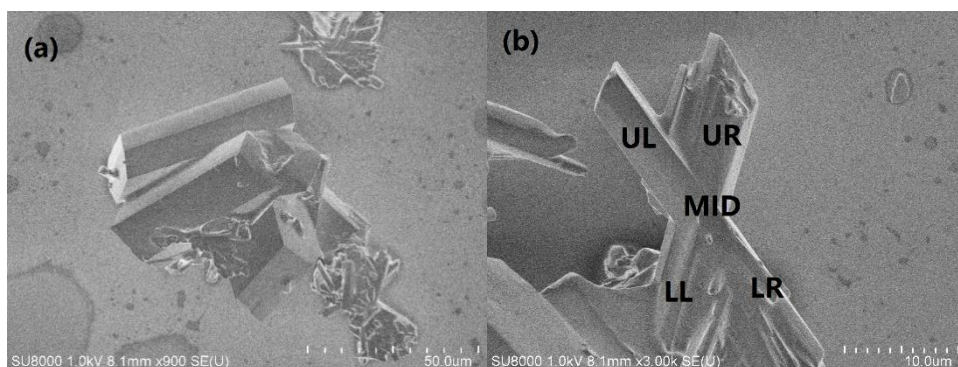


Figure 1. SEM images of LLM-105 powder crystals. (a) rods. (b) twin crystals.

The structure properties for one cross-rod were evaluated by using the Raman spectra at five different positions as shown in Fig.1. The Raman vibration modes at 100 cm^{-1} , 670 cm^{-1} , 1440 cm^{-1} in different

positions of UL(upper left), MID (middle), LR (lower right) are different from those of UR (upper right), LL (lower left) as seen in Fig.2. This indicates that there are two different crystal growth directions in the twin crystal though their differences are small. To avoid possible influence caused by the differences of twin crystal, well-formed samples were selected for following experiments

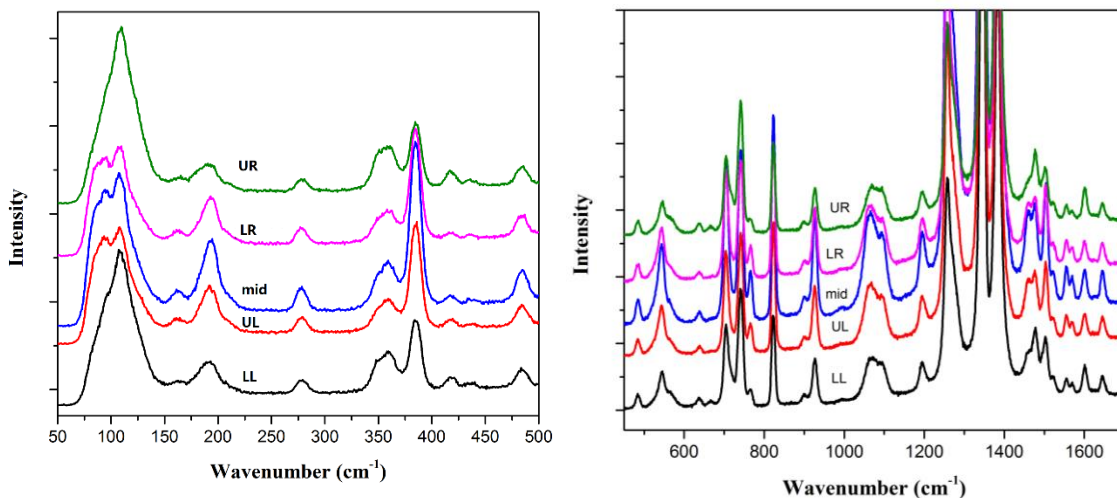


Figure. 2 Raman spectroscopy of twin crystal at five different positions as marked in Fig. 1(b).

The thermal gravimetric analysis (TGA) measurement shows the thermolysis temperature range of LLM-105 is 265°C~360°C. The differential scanning calorimetry (DSC) result shows the exothermic peak is about 357°C. The decomposition temperature is 357°C which agrees with the literature⁹.

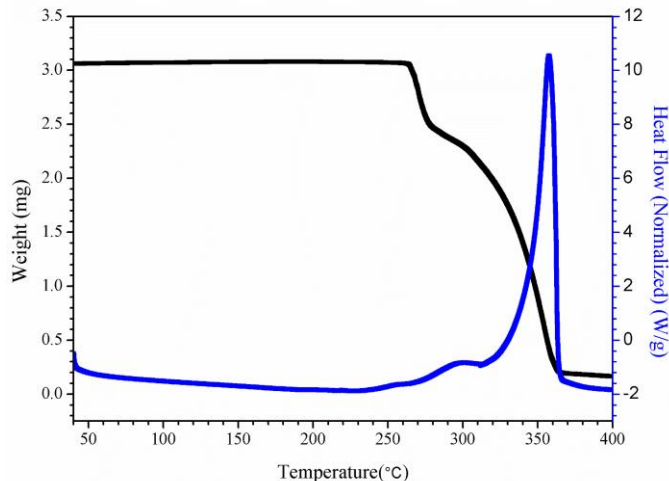


Figure 3. TGA and DSC results

In Fig. 4, selected pressure dependent Raman spectroscopy of LLM-105 are presented. The phase transition is often accompanied by a change in Raman vibration pattern.^{10,11} From ambient pressure to 32 GPa, the frequency and linewidth of all Raman-active phonons almost linearly change with pressure. As the pressure increases, the Raman peak broadens obviously above 17 GPa, indicating that the crystallinity of LLM-105 crystal becomes lower. When the pressure is loaded about 10 GPa, a new Raman vibration mode appears at 686 cm^{-1} , a Raman vibration peak splits at 116 cm^{-1} and the Raman vibration peak disappears at 100 cm^{-1}

as shown in Fig.4. These phenomena reveal that structural phase transition occurred from α -phase at ambient to a β -phase at high pressure. This result almost agrees with the theoretical calculation by Wu *et al.*⁴, they predicted there exists a phase transition at about 8 GPa. And in the vicinity of 17 GPa, the Raman peak at 380 cm^{-1} disappeared, and the Raman peaks broadened to some extent, indicating that the crystal developed further to the amorphous phase and the structural phase transition might occur from β -phase to another high pressure γ -phase. This consequence is also consistent with the theoretical calculation of Wu *et al.*⁴. Because the Raman signal strongly attenuated, the possible phase transition is difficult to identify at higher pressure.

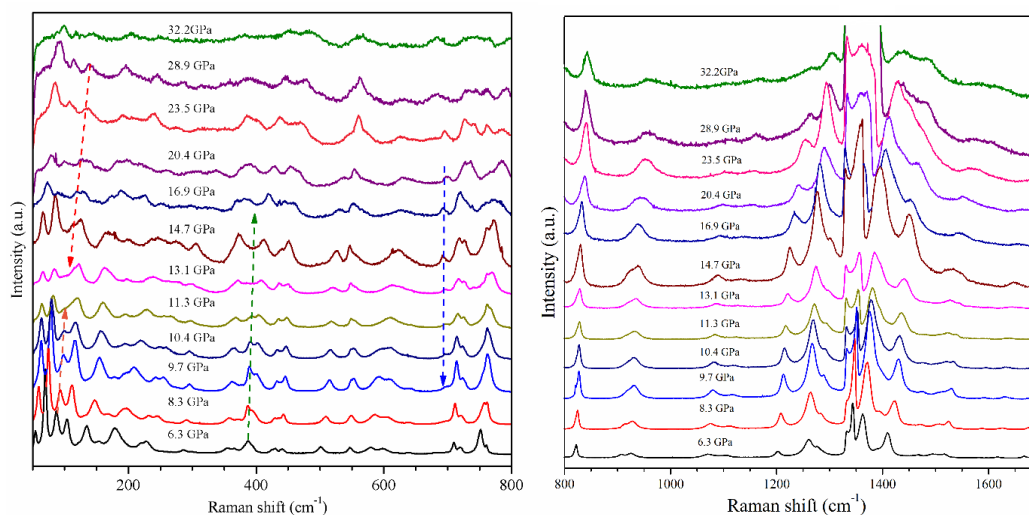


Figure. 4. Raman spectroscopy of LLM-105 under high pressure

4 Conclusion

Two different crystal growth directions in the LLM-105 twin crystal are identified by Raman spectra. The structure evolution behavior of LLM-105 under high pressure was studied. It was found that the Raman signal of LLM-105 was broadened at high pressure (especially after 17 GPa), and the peak shifted to high wavenumber, which indicated that the sample had a tendency to evolve to amorphous state. There exist two phase transformations at 10 and 17 GPa, separately.

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As the paper is only just over 4 pages (6 page limit) please consider adding more detail. Have any other laboratories performed similar experiments to those described? If so, please give details and references. Why do you believe that some of the theoretical predictions are not in agreement with your experimental observations?