Pressure- and Temperature-Dependent Structural Stability and Photoluminescence properties of LLM-105 Crystal

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New energetic material 2,6-diamino-3,5-dinitropyrazine-1-oxide (C4H4N6O5, LLM-105) maintains its structure stability under high pressure below 30 GPa at room temperature or in the temperature range from 513 K to 5 K with ambient pressure based on the high pressure or the cryogenic XRD patterns. One structural phase transition occurs at about 30 GPa and is confirmed by pressure-dependent Raman and infrared spectra.

The structure of LLM-105 crystal shows anisotropic compressibility under pressure in the order $\beta_b > \beta_a > \beta_c$ and anisotropic thermal expansion in the order $\alpha_b > \alpha_c \approx \alpha_a$. Debye temperature of 1225 K for this crystal is obtained based on the lattice parameters at different pressure or temperature. Raman and infrared spectra at extreme conditions suggest that the structure stability is contributed to the stronger inter- and intra- molecule hydrogen bonding networks within LLM-105 crystal. The symmetric and asymmetric stretching modes of amino groups are coupled and promote the understanding of pressure evolution of LLM-105 crystal. The bond constants of amino groups with different pressure and temperature are also obtained.

For studying the electronic structure evolution process of LLM-105 crystal under high pressure, the experiments of photoluminescence spectroscopy as well as absorption spectroscopy and the DFT calculations were employed. With the pressure increasing, the luminescence of LLM-105 crystal first increases because the hydrogen bond network limits molecular vibration, then over 9.0 GPa, the intensity decreases due to the lower electronic transfer efficiency. Results reveal that the band gap of LLM-105 crystal presents a strong pressure dependence. The high pressure phase transition has also been observed at about 30 GPa with a band gap suddenly decrease again.

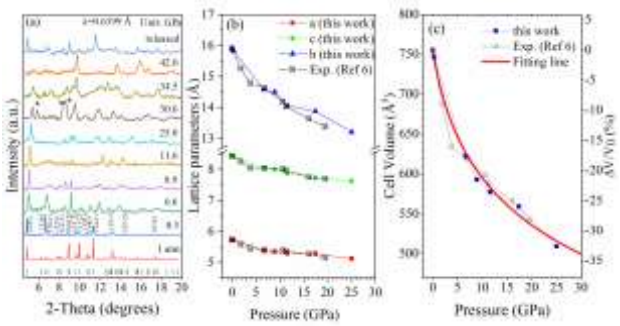

Figure 1. The structure parameters of LLM-105 crystal under high pressure, (a) The synchrotron X-ray diffraction patterns , (b) the lattice constants, and (c) the unit cell volume.

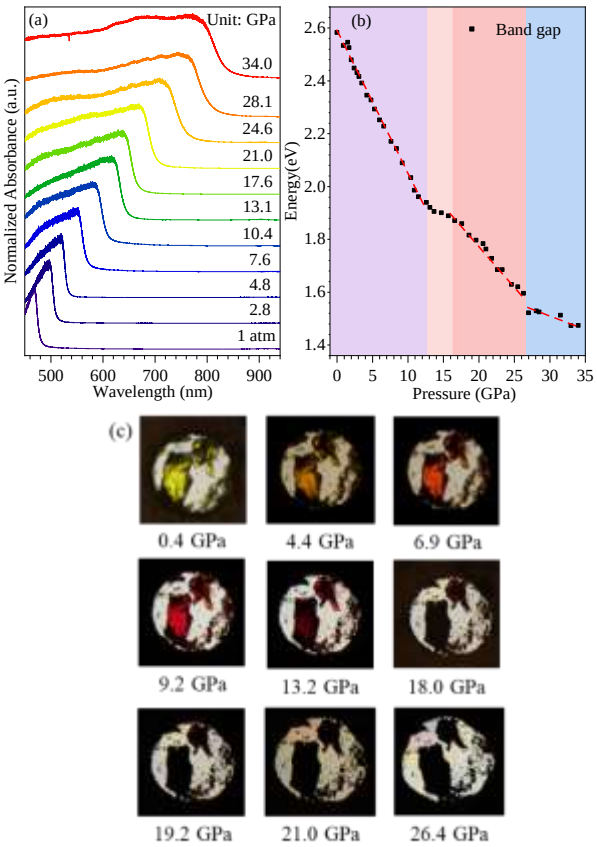

Figure 2. The absorption properties under high pressure. (a) The absorption spectroscopy measured in transmission mode. (c) The microscopic photos of LLM-105 crystal.

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