

Studies of Phase Transitions of Chromium Coordination Compounds under High Pressure

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Abstract: In this paper, the high pressure Raman scattering spectroscopy of $\text{Cd}_2(\text{HATr})_4(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ (Cd) was measured by diamond anvil cells (DACs) up to 10GPa. The Raman spectra of Cd at 0GPa was assigned completely. With pressure increased to 6GPa, a new Raman peak appeared and the original C-NH₂ bending vibration mode and N-NH₂ bending vibration mode disappeared, indicating that Cd underwent a phase transition.

Key words: Coordination compound; High pressure; Phase transition; Raman scattering.

1. Introduction

With the rapid development of science and technology, the design and synthesis of new materials and the exploration of new properties and functions of substances have gradually become the most important frontier scientific issues. High pressure science refers to exploring the structure and properties of materials under the conditions of high pressure or ultra-high pressure^[1]. Under high pressure, the atomic distance is shortened, the intermolecular or intramolecular interaction is changed, and the density of matter is increased, which leads to the occurrence of phase transition and the structure and physical properties of materials are changed^[2-4].

Energetic materials are usually made up of strong oxidation and explosive groups, which contain high nitrogen content. Such compounds are easy to decompose or explode when the external stimulation energy exceeds a certain threshold. Energetic materials are often used in the fields of detonators, high energy explosives, rocket propellants, etc. The study of energetic materials have important research value and broad application prospects in national defense and military^[5].

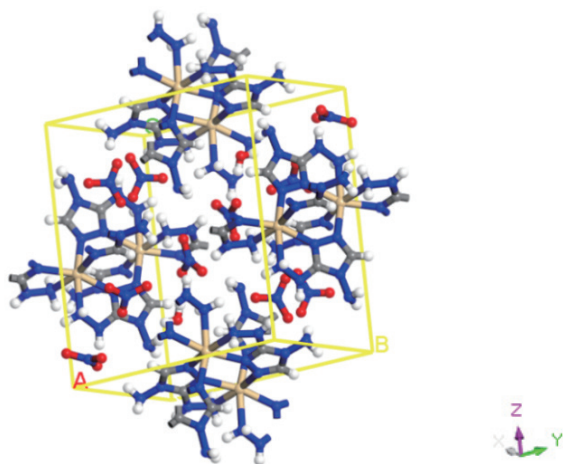


Figure 1. The crystal structure of Cd (red, gray, beige, white and blue represent O, C, Cd, H and N, respectively)

3-hydrazine-4-amino-1,2,4-triazole (HATr) is a class of nitrogen-rich heterocyclic ligands with high enthalpy of formation and dense structure. $\text{Cd}_2(\text{HATr})_4(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ (Cd) is a three-dimensional network coordination compound, which is formed by the coordination of nitrate and water molecules accompanied with the metal Cd as the central cation and HATr as the ligand. The crystal structure of Cd is triclinic P-1 space group, and its crystal structure is shown in Figure^[6,7]. In this paper, the change of the vibration modes of Cd and the relationship between the molecular structure and the pressure are analyzed by in situ Raman scattering spectroscopy in the pressure range of 0 ~ 10GPa.

2. Experimental method

High pressure experiments are performed in a set of diamond anvil cells (DACs) with a diameter of 500 μm . The gasket is a T301 stainless steel sheet. The gasket was drilled a hole with 120 μm in diameter and 60 μm in thickness, which is served as the high pressure sample chambers. The pressure transmitting medium is a mixture of methanol and ethanol with a volume ratio of 4:1. The Raman spectra were measured by Horiba iHR550 spectrometer with Smart Raman Microconfocal module (developed by Institute of Semiconductors, Chinese Academy of Sciences). The wavelength of the excitation light is 532nm. The resolution of the Raman system is about 1 cm^{-1} . The acquisition time of each spectrum is 10s.

3. Results and discussions

In different chemical environments, the vibration mode of the same group have similar characteristic frequencies. The vibration modes of Cd can be analyzed in terms of the corresponding vibrations of HATr and nitrate ions. The Raman spectra of Cd under ambient pressure

are shown in Figure 2.

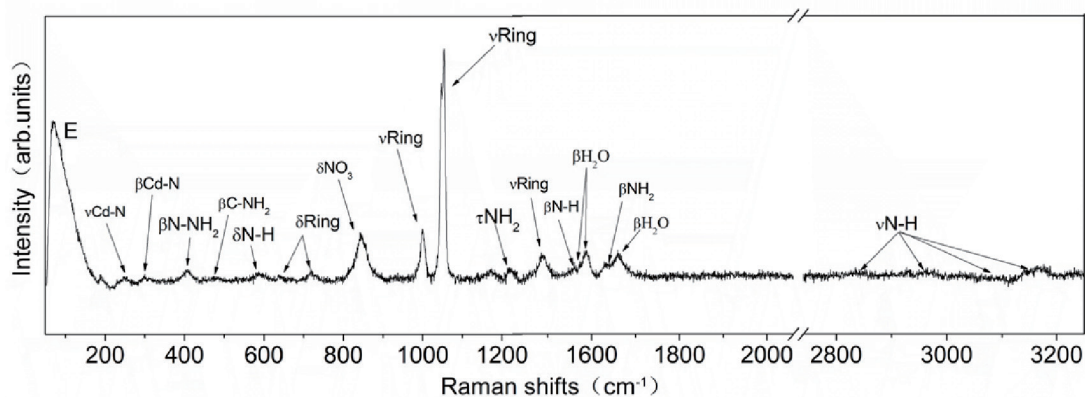


Figure 2. Raman spectra of Cd under ambient pressure.

According to the vibration modes of 1,2,4-triazole and HATr in the literature, the bending vibration of N-NH₂ (βN-NH₂) in Cd appears at 408cm⁻¹, the bending vibration of C-NH₂ (βC-NH₂) appears at 486 cm⁻¹, and the out of plane bending vibration of 1,2,4-triazole (δring) appears at 638 cm⁻¹ and 720 cm⁻¹. The stretching vibration modes of 1,2,4-triazole (νRing) were located at 1000 cm⁻¹ and 1052 cm⁻¹. The twisting vibration of NH₂(τNH₂) appears at 1218 cm⁻¹. The bending vibration of N-H (βN-H) appears at 1558 cm⁻¹. The Raman peak at 1631 cm⁻¹ is the bending vibration of the NH₂ (βNH₂) group, which is consistent with the vibration peak at 1600 ~ 1700 cm⁻¹ in the literature^[8]. The bending vibration of N-H (νN-H) appears at 2800 ~ 3200 cm⁻¹, and the N-H stretching vibration of Cd is 2833 cm⁻¹, 2961 cm⁻¹ and 3163 cm⁻¹, respectively.

In situ Raman spectra of Cd were performed under high pressure up to 10GPa. The Raman spectra were shown in Figure 3(a-d). The diamond (◆) and asterisk (*) represent the appearance and disappearance of Raman peaks, respectively. Raman peaks below 400cm⁻¹ are associated with external vibration modes, and those above 400cm⁻¹ are identified as internal vibration modes. In Figure 3(c), the intensity of 1,2,4-triazole stretching vibration mode at 1488 cm⁻¹ increased at 0.5GPa as marked by upward arrows, indicating that the molecular structure of the 1,2,4-triazole changes from non-planar to planar, which is similar to the phenomenon in Ni₃[(C₂H₅N₃)₆(HO₂)₆](NO₃)₆·1.5H₂O^[9]. At 1GPa, the H₂O bending vibration mode at 1588 cm⁻¹ disappeared, meaning the change of C-H...O hydrogen bond. In Figure 3(d), the N-H stretching vibration mode exhibits redshift below 5GPa, indicating that Cd has weak or moderate strength hydrogen bonds. As the pressure increased to 5GPa, the N-H stretching vibration mode disappeared, suggesting that the original hydrogen bond is broken. When the pressure increased to 6GPa, a new external mode appeared at 242 cm⁻¹ accompanied with the disappearance of the C-NH₂ bending vibration mode and N-NH₂ bending vibration mode, indicating the occurrence of a phase transition. The phase transition may be caused by the distortion of HATr ligand. With increasing pressure, all the Raman peaks move towards high frequencies, indicating that the intermolecular distance decreases under high pressure.

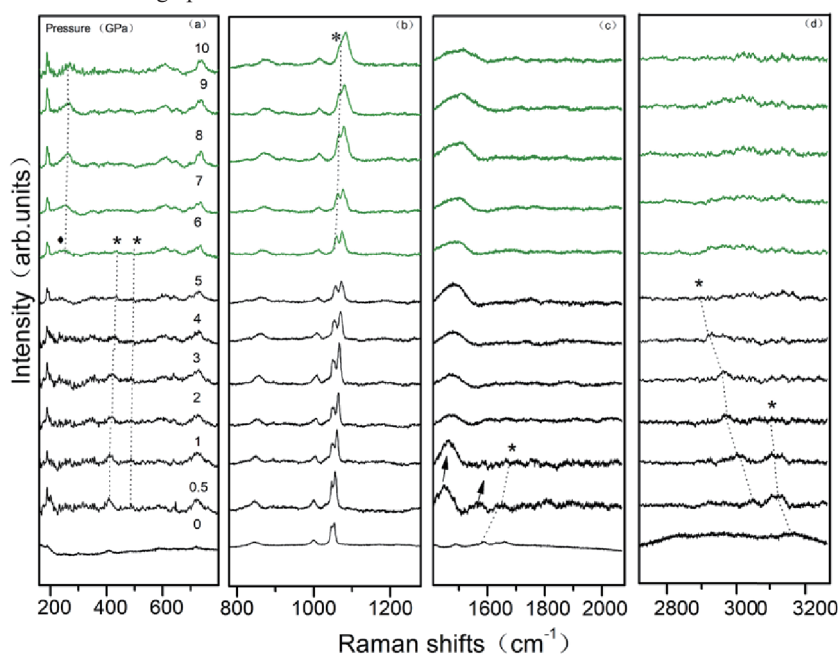


Figure 3. Raman spectra of Cd under high pressure.

4. Conclusion

To sum up, in this paper, the Raman vibration modes of Cd under ambient pressure were assigned. The molecular structure of 1,2,4-triazole in Cd changes from non-plane to plane at 0.5GPa. With the pressure increased to 1GPa, the C-H...O hydrogen bond of Cd has changed, and broke until to 5GPa. When compressed to 6 GPa, the C-NH₂ bending vibration mode and N-NH₂ bending vibration mode disappeared, indicating the phase transition of Cd. The study of Cd under high pressure is helpful to study the influence of pressure on the complex and the change of hydrogen bond, which may be beneficial to the subsequent development of the coordination compounds.

References:

- [1] Zhao D.,Wang M.,Xiao G.,et al.Thinking about the Development of High-Pressure Experimental Chemistry [J]. The Journal of Physical Chemistry Letters, 2020, 11(17): 7297-7306.
- [2] Dahe Xiong. High-pressure Physics Research in the Earth Sciences [J]. Physics,1996,25(4):7.
- [3] Nowok A.,Szeremeta A Z.,Sieradzki A.,et al.Toward the Undiscovered Dielectric Properties of Hybrid Acetamidinium Manganese Formate under High Pressure [J]. The Journal of Physical Chemistry C, 2021, 125(1): 908-914.
- [4] Xiao G.,Geng T.,Zou B.Emerging Functional Materials under High Pressure toward Enhanced Properties [J]. ACS Materials Letters,20,2(9):1233-1239.
- [5] Xiao Y.,Guan Q.,Wang Y.,et al.A Novel Supramolecular Silver Coordination Complex Based on a Triazole Carboxylate Ligand:Synthesis and Fluorescence Sensing of Colchicine and a Series of Nitro Explosives.ChemistrySelect 2019, 4 (45) : 13327-13332.
- [6] Wu J.,Zhang J.,Yin X,et al.Energetic Salts Based on 3-Hydrazino-4-Amino-1,2,4-Triazole(HATr): Synthesis and Properties[J].New Journal of Chemistry,2016,40(6):5414-9.
- [7] Xu C.,Yin X,Jin X,et al.Two Coordination Polymers with 3-Hydrazino-4-Amino-1,2,4-Triazole as Ligand:Synthesis,Crystal Structures,and Non-isothermal Kinetic Analysis [J].Journal of Coordination Chemistry,2014,67(11):2004-15.
- [8] Socrates G.Infrared and Raman Characteristic Group Frequencies:Tables and Charts[M]. John Wiley & Sons,2004.
- [9] Jiang J.,Zhu P.,Li D.,et al.High Pressure Studies of Trimethyltin Azide by Raman Scattering,IR Absorption,and Synchrotron X-ray Diffraction [J].RSC Advances,2016,6(101):98921-98926.

*Brief introduction of corresponding author: Junru Jiang (1990.09.02 –), female, Han nationality, doctoral candidate, master supervisor, research direction: the structure and properties of materials under ambient pressure and extreme conditions.

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