Raman study of $[Ru(bpy)(CN)_4Mg(H_2O)_5]\cdot H_2O$ crystal at high pressure

Anastasia DELTSIDI (Aristotle University of Thessaloniki, Greece),
Pantelis TELIORIDIS (Aristotle University of Thessaloniki, Greece),
Dimitra KOUSKOUKI (Aristotle University of Thessaloniki, Greece),
Olga KARABINAKI (Aristotle University of Thessaloniki, Greece),
Antonios HATZIDIMITRIOU (Aristotle University of Thessaloniki, Greece),
Theodore LAZARIDES (Aristotle University of Thessaloniki, Greece),
John ARVANITIDIS (Aristotle University of Thessaloniki, Greece),
Dimitrios CHRISTOFILOS, (Aristotle University of Thessaloniki, Greece)

Abstract

$[Ru(bpy)(CN)_4]^{2-}$, where bpy denotes 2,2′-bipyridine, is a luminescent anionic Ru(II) complex with pronounced solvatochromic behavior, enabling substantial tuning of its absorption and emission spectra in different solvent environments [1]. Luminescent coordination polymers, where metal ions or clusters are connected by bridging ligands into extended networks, can be prepared by combining this complex anion with various mono- and divalent metal cations, including alkali and alkaline-earth cations such as K^+, Na^+, Li^+, Cs^+, Ca^{2+}, Sr^{2+}, and Ba^{2+}[1,2,3].

In this work, we report on a high pressure Raman study of crystalline $[Ru(bpy)(CN)_4Mg(H_2O)_5]\cdot H_2O$. Yellowish crystals were obtained when reacting the appropriate salts, following previously reported preparation routes [1]. Single crystal X-ray diffraction (sc-XRD) data can be indexed using a disordered P2/c structural model, where the expected polymeric connectivity is disrupted, due to partial occupancy of $Mg(H_2O)_5$ units bonded to cyanido groups on both trans positions to the bipyridine nitrogen atoms with equal occupation factors. Raman spectra were excited at 785 nm, to minimize any absorption or luminescence contributions, and recorded using a LabRAM HR spectrometer. Pressure was applied using a membrane diamond-anvil cell. Daphne 7676 oil, solidifying at ~5 GPa at room temperature, was used as the pressure transmitting medium (PTM) and pressure was determined using the ruby fluorescence method.

The ambient pressure Raman spectrum is rich in features. External lattice modes and low-frequency internal modes of the molecular complex dominate the spectral region below 300 cm^{-1}. The intermediate-frequency region, extending up to 1700 cm^{-1}, contains peaks associated mainly with internal vibrational modes of the complex, while bands observed in the 2000-2200 cm^{-1} range are assigned to C≡N stretching modes [3,4,5]. Ar or N_2 atmosphere or vacuum, lead to a rapid and clearly visible change in crystal colour, often accompanied by a change in sample texture. The Raman spectra are strongly modified, in a similar manner in all cases, particularly in the low-frequency and C≡N stretching regions. These changes are attributed to desorption of water molecules, as previously reported for related materials [3].

Upon compression, most Raman bands shift to higher frequencies, consistent with bond stiffening under volume contraction. Abrupt spectral changes are observed already at ~0.2 GPa, indicating a pressure-induced structural modification. They are most pronounced in the cyanido-stretching region, where relatively broad bands are replaced by stronger and narrower features, and in the low-frequency lattice-mode region, where the spectral profile changes substantially. The high-pressure phase persists up to the maximum attained pressure of 1 GPa in this experiment and reverts to the ambient-pressure phase upon decompression. In a subsequent experiment up to ~5 GPa, additional spectral changes were observed between 3.3 and 4.1 GPa. The affected spectral regions are again the cyanido-stretching and low-frequency lattice-mode. The C≡N stretching Raman peaks become broader and asymmetric, suggesting a phase with a larger number of crystallographically or chemically inequivalent cyanido groups. Upon decompression, this second high-pressure phase persists down to ambient pressure inside the cell.

Both pressure-induced transformations are expected to be distinct from those observed at ambient pressure associated with the water desorption. However, the detailed structure determination of the studied system by XRD under different environments and high pressure is essential for clarifying the nature of the observed structural modifications.

References

1. T. Lazarides, T. L. Easun, C. Veyne-Marti, et al., J. Am. Chem. Soc. 129, 4014 (2007).
2. J. Q. Liu, Z. D. Luo, Y. Pan, et al., Coord. Chem. Rev. 406, 213145 (2020).
3. S. Hattori, T. Nagai, A. Sekine, et al., Dalton Trans. 51, 1474 (2022).
4. B. Minaev, V. Minaeva, G. Baryshnikov, et al., Mol. Simul., 37, 670 (2011).
5. H. Adams, W.Z. Alsindi, G.M. Davies, et al., Dalton Trans., 39 (2006).