PHRD AND RAMAN SPECTROSCOPY ANALYSIS OF THE Zn (II) COORDINATION POLYMER BASED ON 1,2,4,5-CYCLOHEXANTETRACARBOXYLATE

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Introduction

In the reliable description of the structure of coordination polymers, it is important to jointly evaluate the long-range order and local metal-ligand bonds in the crystal lattice. Powder X-ray diffraction (PXRD) provides information on the crystallinity level, diffraction reflections, and spatial ordering of the sample, while Raman spectroscopy allows for the determination of vibrations associated with carboxylate groups, the organic skeleton, and metal-oxygen bonds of the ligand [1-2]. 1,2,4,5-cyclohexane tetracarboxylate is a multi-donor and conformationally flexible ligand that can bind to Zn (II) ions in various coordination modes to form ordered coordination structures [3-4]. Therefore, in this work, the crystalline properties of the Zn (II) coordination polymer based on 1,2,4,5-cyclohexane tetracarboxylate were studied using PCRD, and the state of local bonding was studied using Raman spectroscopy, and the results were analyzed structurally in relation to each other [5].

PXRD analysis

The X-ray diffraction profile of the Zn (II) coordination polymer powder based on 1,2,4,5-cyclohexane tetracarboxylate was analyzed in the range of 2θ 2-60°. On the diffraction pattern, characteristic diffraction maxima are observed in the regions of approximately 9.1, 10.5, 16.6, 24.7, 33.6, and 51.5. ° The presence of narrow and high-intensity reflexes indicates that the sample has a well-crystallized and ordered crystal

structure (Fig. 1).

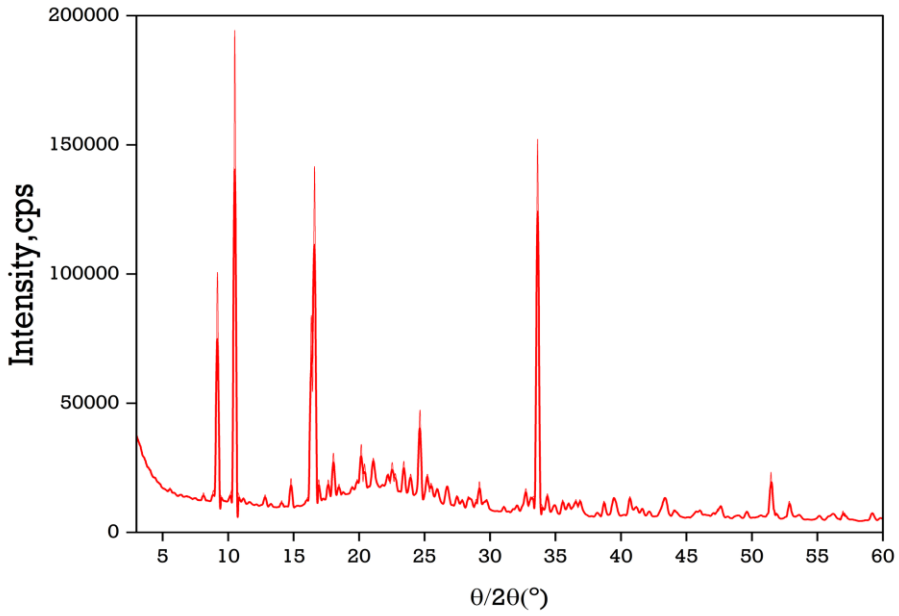


Figure 1. PXRD diffractogram of the Zn (II) coordination polymer based on 1,2,4,5-cyclohexane tetracarboxylate.

The strong reflexes observed in the low-angle region indicate the presence of ordered structural fragments in the crystal lattice corresponding to relatively large periodicity distances. A strong reflection around 33.6° reflects the intense diffraction response of the crystalline phase along certain crystallographic planes. The PCRD results characterize the long-range crystal arrangement of the sample; for a rigorous assessment of phase purity, it is advisable to compare the experimental profile with the simulation PCRD calculated from single-crystal structural data.

Raman spectroscopic analysis

Characteristic signals were observed in the Raman spectrum of the Zn (II) coordination polymer at 3521, 3036, 1536, 1238, 999, 801, 548, and 254 cm−1 (Fig. 2).

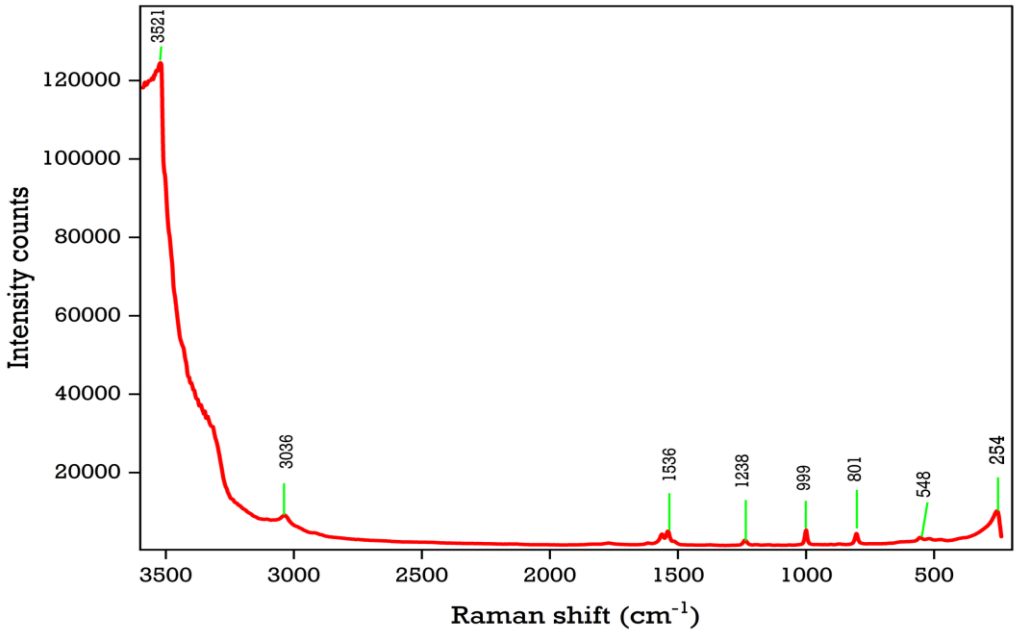


Figure 2. Raman spectrum of Zn (II) coordination polymer based on 1,2,4,5-cyclohexane tetracarboxylate.

The signal in the high-frequency region of the spectrum at 3521 sm^{-1} is associated with O-H valence oscillations, which is explained by the presence of water molecules and hydrogen-bonded O-H groups in the crystal structure. The signal at 3036 sm^{-1} corresponds to C-H vibrations in the organic skeleton of the ligand. The characteristic Raman signal in the 1536 sm^{-1} region is associated with oscillations of coordinated carboxylate groups. This signal supports the deprotonation of the carboxyl groups in the ligand and their coordination interaction with Zn (II) centers. Changes in carboxylate oscillations in Zn (II) -polycarboxylate systems are one of the important spectroscopic features of metal-ligand coordination. The signal at 1238 sm^{-1} can be associated mainly with vibrations of C-O and C-C-O fragments. Raman signals in the 999 and 801 sm^{-1} regions reflect the skeleton and deformation vibrations of the cyclohexane ring and carboxylate fragments. The observation of these signals indicates that the organic ligand skeleton is preserved within the coordination polymer. The low-frequency region of the spectrum is of particular importance in describing metal-ligand

interactions. The signal around 548 sm^{-1} is associated with vibrations of Zn-O coordination bonds. A strong low-frequency signal at 254 sm^{-1} most likely refers to metal-oxygen coordination fragments and collective vibrations of the crystal lattice.

The results of PXRD and Raman spectroscopy are complementary. Narrow and intense reflections on the PXRD diffractogram indicate the crystalline order of the coordination polymer, while carboxylate groups in the Raman spectrum and signals corresponding to low-frequency Zn-O vibrations support local coordination bonds between Zn (II) centers and oxygen donor atoms. Thus, PCRD characterizes the long-range order in the crystal structure, while Raman spectroscopy allows for a comprehensive assessment of the structural properties of the compound, characterizing the local oscillation properties of metal-ligand bonds.

CONCLUSION

The structural properties of the Zn (II) coordination polymer based on 1,2,4,5-cyclohexane tetracarboxylate were studied using PCRD and Raman spectroscopy. The clear and high-intensity reflexes observed on the PXRD diffractogram showed that the sample has a well-crystallized and ordered structure. In the Raman spectrum, carboxylate vibrations were recorded at 1536 sm^{-1}, ligand skeleton signals at 1238, 999, and 801 sm^{-1}, as well as low-frequency metal-ligand vibrations at 548 and 254 sm^{-1}. The consistency of PCRD and Raman data indicates the presence of coordination bonds between Zn (II) centers and oxygen donor atoms of the carboxylate ligand, as well as the compatibility of the crystal and local structures of the resulting coordination polymer.

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