

Article



Investigation of Mn²⁺-Doped Stearic-Acid Through XRD, Raman, and FT-IR, and Thermal Studies

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Abstract: In this research, we investigated the influence of Mn^{2+} ions on the packing in stearic acid (SA) crystals through the use of Raman spectroscopy, X-ray diffraction (XRD), and Fourier transform infrared (FT-IR) spectroscopy. The crystals investigated were obtained utilizing the slow evaporation methodology in a hexane solution under varying manganese (Mn) concentrations sourced from MnSO₄ 5H₂O (0.5, 1.0, 1.5, 2.0, 4.0, and 6.0%). XRD studies indicated that all SA crystals were grown in the B_m form (monoclinic), favoring the *gauche* conformation in molecular packing. Additionally, crystalline lattice modifications were observed through Raman spectral changes in the low-vibrational energy region. Variations in the intensities and Raman shifts in two lattice vibrational modes, centered at approximately 59 and 70 cm⁻¹, revealed that two types of hydrogen bonds are distinctly affected within the crystalline lattice. Furthermore, the unit cell parameters (*a*, *b*, *c*, and β) were determined via Rietveld refinement, and their behavior was analyzed as a function of Mn concentration. The results indicated that Mn²⁺ ions exert a strain and deformation effect on the unit cell. Lastly, differential scanning calorimetry (DSC) was employed to evaluate the thermal stability of the B_m form of SA crystals.

Keywords: Doping fatty acid crystals; Polymorphism in fatty acids; X-ray diffraction; Rietveld refinement; Raman and FT-IR spectroscopy

1. Introduction

The study of new materials plays an important role in science and technology. One way to obtain a new material is through doping with substances of different properties, e.g., combining organic and inorganic systems [1,2], which can form compounds with unique features. Generally, these compounds are used in various technological applications, with the purpose of optimizing the properties of their constituents. Given this, eutectic mixtures of fatty acids (FAs) have been used in carbon-based nanostructures for applications in several strategic fields [3,4].

Saturated FAs can be used as precursors in synthesizing strategic materials to improve their chemical and physical properties [4–7]. FAs are common organic compounds in



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Polymorphism is a phenomenon intrinsic to the specific physical and chemical properties of materials in their crystalline solid state, induced by different ways of molecular packing. This characteristic is commonly observed in diverse organic compounds, including FAs, amino acids, proteins, and paraffin [13–15].

Regarding chain parity, the polymorphic forms A_1 , A_2 , A_3 , A_{-super} , C, $B_{o/m}$, and $E_{o/m}$ have been observed in even-chain standard FAs. In contrast, the forms A', B', C', and D' are characteristic of odd-chain counterparts [16–20], where the subscript symbol "o/m" represents orthorhombic/monoclinic symmetry. The literature reports that even FAs can undergo phase transformations in which all their polymorphic forms transition to the C form, which is more stable under ambient conditions [16–20].

Overall, FA polymorphism arises from the possible molecular arrangements adopted within the unit cell, depending on the disposition and configurations of the O–H···O hydrogen bonds through a pair of molecules forming centrosymmetric $R_2^2(8)$ patterns, known as dimers [21,22]. Therefore, the molecules are packed in the crystalline lattice to form dimers, which can adopt either the all-*trans* or *gauche* conformation, as shown in Figure 1a,b.



Figure 1. Organizational structure of dimers in the (**a**) all*-trans* and (**b**) *gauche* conformations for the SA crystal lattice.

Currently, diverse polymorphic phases or forms have been assigned to saturated FAs (both odd and even), including stearic acid (SA, C18:0, $C_{18}H_{35}O_2H$) [23,24]. Due to its polymorphic characteristics, many structures can be observed, as mentioned above, even for saturated FAs. This phenomenon plays a central role in various applications, such as the production of cosmetic products and detergents, and as an excipient material in pharmaceutical drugs due to its soft texture [8,9,21–26].

In our research, manganese sulfate pentahydrate (MnSO₄ 5H₂O) was used in the doping process of SA crystals. This inorganic compound is a precursor of manganese-based materials [27] and forms several hydrates, including monohydrate, tetrahydrate, pentahydrate, and heptahydrate. In an aqueous solution, manganese sulfate dissociates, forming Mn²⁺ and sulfate ions. By modifying crystalline materials with ions like manganese, it is possible to improve these crystals' chemical stability and combined properties, broadening their potential applications. For instance, Mn²⁺-doped materials are promising for detecting ionizing and particle radiation as effective luminescence detectors [27–33].

In this work, we investigated the influence of Mn^{2+} ions on the crystalline lattice and thermal properties of SA. The crystals were grown with varying Mn^{2+} concentrations of $MnSO_4$ 5H₂O (0.5, 1.0, 1.5, 2.0, 4.0, and 6.0%) in a solution containing stearic acid dispersed in hexane. The effects of Mn^{2+} ions on the SA crystalline structure were investigated using

XRD, Raman and FT-IR spectroscopy, and DSC techniques. Additionally, Rietveld's method was applied to refine the XRD patterns and obtain the lattice parameters as a function of Mn concentration. DSC measurements were performed to analyze the thermal stability of the obtained crystals, suggesting a possible application of doped crystals in advanced systems that require greater thermal and structural control.

2. Materials and Methods

2.1. Growth of Stearic Acid Crystals

The stearic acid sample was purchased from Argos Chemistry Industry, with a guaranteed purity exceeding 99%. The crystals were grown using the slow evaporation technique, utilizing a solution of SA + MnSO₄ 5H₂O + hexane. This solution was prepared by dissolving the required quantity of SA (pH close to 6) in a standardized volume of 30 mL, followed by the addition of MnSO₄ 5H₂O in varying mass percentages (0.5, 1.0, 1.5, 2.0, 4.0, and 6.0%). The addition of SA was performed considering the solubility of the fatty acid in hexane. Furthermore, the solutions were subjected to mechanical agitation for 5 h and filtered to eliminate excess acid and impurities. The resulting solutions were placed in an isolated chamber at a controlled temperature of 298 K. After two weeks, single SA crystals containing Mn^{2+} ions were obtained as tiny transparent platelets.

2.2. XRD, Raman, FT-IR, and DSC Techniques

The polymorphic phases were characterized using X-ray powder diffraction (XRPD) analysis. A Rigaku powder diffractometer with Bragg–Brentano geometry was utilized to record the XRPD patterns. Radiation with a wavelength of $\lambda = 1.54056$ Å (Cu-K_{α 1}) was employed, operating at an electrical voltage of 40 kV and an electrical current of 25 mA. Measurements were conducted over a 2 θ range of 5–50° using a step-scan procedure (with a step size of 0.02° step size) and a counting time of 1 s per step. The XRD patterns of the grown crystals were refined using Rietveld refinement with the GSAS program [34].

A Jobin Yvon T64000 spectrometer equipped with a nitrogen-cooled charge-coupled device (CCD) detection system was utilized to record the Raman spectra. The spectral resolution was maintained at 2 cm⁻¹, with excitation provided by an argon-ion laser operating at the 514.5 nm line. An Olympus microscopic lens with a 20.5 mm focal length and a numerical aperture of 0.35 was employed to focus the laser onto the sample's surface.

FT-IR spectra were recorded using powdered crystal samples in the transmittance mode over the spectral range of 100–3000 cm⁻¹. A Nicolet 5ZPX FT-IR spectrometer was employed, equipped with an A225/Q Platinum attenuated total reflectance (ATR) accessory and an RT-DLa TGS wide-range MIR-FTIR detector featuring a 6 mm aperture. This setup facilitated measurements down to 100 cm⁻¹ with a spectral resolution of 4 cm⁻¹ for 220 scans.

Differential scanning calorimetry (DSC) analysis was conducted using a Netzsch Instrument (DSC 204 F1—Phoenix) with a liquid nitrogen cooling accessory. Approximately 3 mg of each sample was analyzed over a temperature change from 303 to 373 K, with a heating rate of 5 K/min.

3. Results and Discussion

3.1. Growth, XRD, and Rietveld's Refinement Studies

The XRD patterns of $MnSO_4$ 5H₂O, pure SA (C form), and Mn^{2+} -doped SA crystals were recorded over a 2 θ range of 5–50°, as illustrated in Figure 2. A comparative analysis between the experimental and theoretical patterns was conducted to facilitate a more comprehensive interpretation of the results obtained for the Mn^{2+} -doped crystals.



Figure 2. XRD patterns of Mn^{2+} -doped SA crystals compared to the theoretical patterns of both the B_m and C forms and the experimental pattern of the MnSO₄ 5H₂O phase in the $2\theta = 5-50^{\circ}$ angular range.

Several changes in the crystallographic planes were observed due to the presence of Mn^{2+} ions, with the main modifications occurring at angles lower than $2\theta = 27^{\circ}$. From Figure 2, when the theoretical diffraction pattern of the C form [35] is compared with the Mn^{2+} -doped SA patterns, a significant difference can be noted between them. On the other hand, a strong qualitative correlation was observed with the theoretical pattern of the B_m form. Therefore, it was verified that all patterns of the Mn^{2+} -doped crystals correspond to the B_m polymorphic phase, classified within the $P2_1/a$ (C_{2h}^5) space group of monoclinic symmetry, containing four molecules in the unit cell (Z = 4).

The structure of the grown crystal with the 0.5% concentration was identified as belonging to the B_m form, with its unit cell parameters, according to the literature, being a = 5.598 Å, b = 7.397 Å, and c = 49.440 Å, with $\beta = 117.24^{\circ}$ [36].

A significant similarity between the diffraction patterns of the Mn²⁺-doped crystals is noticed, indicating that the phases are common, as shown in Figure 2. However, all peaks are shifted to higher angles, with the colored rectangles in the figure highlighting the noticeable changes. For concentrations between 1.5% and 2.0%, a slight jump occurs in the behavior of the diffraction peaks. Above 2%, all peaks shift slightly but without anomalous behavior, up to the highest concentration.

In addition, the Rietveld method was applied to determine the cell parameters as a function of Mn concentration in the SA crystals. Figure 3 exhibits the effect of Mn^{2+} ions on each of the lattice parameters, including the cell volume. Interestingly, the cell dimensions (*a*, *b*, *c*, and β) exhibit nonlinear behavior. The parameters *a* and *b* increase as the Mn concentration increases from 0.5% to 2.0%, whereas *c* and β decrease. However, for concentrations above 2.0%, their behavior remains almost constant.



Figure 3. Cell parameters vs. Mn concentration plot for the SA crystals.

Conversely, the behavior of the cell volume closely resembles that of the smaller cell parameters (*a* and *b*), suggesting a considerable increase in volume due to the compression exerted by the Mn^{2+} ions, which preferentially occurs along the direction of the *c* parameter. This behavior can be explained by the expansion in the *a* and *b* parameters, which is responsible for a notable increase in the lateral dimensions of the monoclinic cell.

X-ray diffraction (XRD) patterns for different Mn^{2+} concentrations were obtained from samples carefully ground into fine powder before measurements to minimize preferential orientation effects. This procedure ensured a random distribution of crystallites, reducing the influence of specific alignments that could intensify certain diffraction peaks. Furthermore, the data obtained were analyzed using Rietveld refinement, which considers possible variations in peak intensity resulting from residual preferential orientation effects. The results confirmed that the similarity in the XRD patterns reflects the structural preservation of the B_m form of the SA crystal at all concentrations, evidencing the stability of the crystalline structure rather than distortions caused by sample alignment.

Regarding the behavior of the cell parameters, it is noteworthy that doping with Mn^{2+} ions in the crystalline structure induces strain or deformation, effectively promoting contraction along the *c*-direction and expansion along the *a*- and *b*-directions. Moreover, with the introduction of Mn^{2+} ions above 0.5%, it was observed that the structure associated with the B_m phase (monoclinic) is preserved at all concentrations studied herein. It can also be noted that the presence of Mn^{2+} ions in the crystal lattice promotes polymorphic control of the crystalline phase of SA without causing any change in symmetry. Conversely, the deformation-induced effect results in a volume expansion of the unit cell, increasing by approximately 2%, after which it remains almost constant.

3.2. Raman Spectroscopy Studies

Raman measurements were performed for $MnSO_4$ 5H₂O, pure SA, and Mn^{2+} -doped SA crystals in the range of 20–3000 cm⁻¹, as shown in Figures 4 and 5. The Raman spectra of all samples are presented to facilitate a straightforward comparison among them. Firstly, the spectral range between 20 and 1000 cm⁻¹ is analyzed. The wavenumber values below 200 cm⁻¹ (Figure 4a) correspond to the spectral region of the crystal lattice modes. In this region, some alterations in the wavenumbers are observed due to the increase in Mn concentration.



Figure 4. Raman spectra of Mn^{2+} -doped SA crystals compared to the spectra of $MnSO_4$ 5H₂O and pure SA crystals (C form) in the ranges of (**a**) 20–300 cm⁻¹ and (**b**) 300–1000 cm⁻¹.



Figure 5. Raman spectra of Mn^{2+} -doped SA crystals compared to the spectra of $MnSO_4$ 5H₂O and pure SA crystals (C form) in the ranges of (**a**) 1000–1700 cm⁻¹ and (**b**) 2800–3000 cm⁻¹.

An interesting behavior is observed in the two intermolecular modes centered at 59 and 70 cm⁻¹ (Figure 4a, marked by orange arrows), which exhibit a completely different behavior compared to the other modes. These two modes shift and tend to converge as the Mn concentration increases, eventually overlapping near 2.0%. Above 2.0%, these modes maintain their displacements, with the first mode exhibiting a blueshift and the second undergoing a redshift, as highlighted by the dashed rectangle in Figure 4a. Additionally, the two orange arrows at 0.5% and 6% indicate the main modifications in the intensities and displacements of both wavenumbers due to Mn^{2+} ions within the crystal lattice.

The behavior of the Raman wavenumbers associated with the modes recorded at 59 and 70 cm⁻¹ as a function of Mn concentration is displayed in Figure 6. Interestingly, changes in the positions of other vibrational modes were not observed, indicating that Mn^{2+} contributes to maintaining the B_m form of the SA crystal structure. As shown in Figure 6, the behavior of both modes exhibits a nonlinear evolution with a common inflection point

occurring near 1.7%, as indicated by the filled square in the figure. However, the two modes display different displacements: the first undergoes a significant Raman shift to higher wavenumbers, with $\delta \omega = 13 \text{ cm}^{-1}$ (blueshift), while the second shifts to lower wavenumbers, with $\delta \omega = -10 \text{ cm}^{-1}$ (redshift). This behavior can be explained by changes in the strength of intermolecular bonds within the crystalline lattice and, consequently, in the hydrogen-bonded dimers due to the pressure exerted on the unit cell.



Figure 6. Wavenumber vs. Mn concentration plot for the lattice modes initially observed at 59 and 70 cm^{-1} .

A similar pressure-induced effect on hydrogen bonds has been observed in the lattice vibrations of L-ascorbic acid crystals under hydrostatic pressures of up to 5.9 GPa [37]. In this study, the modes at 59 and 70 cm⁻¹ are coupled with distinct hydrogen bonds. Additionally, anomalous behavior of low-wavenumber modes associated with lattice vibrations has been recorded in amino acid crystals, including α -L-glutamic acid [38], likely due to hydrogen bond coupling. This suggests that high-pressure experiments could further clarify the behavior of hydrogen bonds within the crystalline environment.

In the 300–1000 cm⁻¹ spectral range, as shown in Figure 4b, modes related to chain motions were observed. Modes between 200 and 600 cm⁻¹ were assigned as skeletal modes [35]. In this study, the following modes were observed: 341, 372, 405, 443, 502, 556, and 571 cm⁻¹, associated with δ (CCC) and/or δ (CCO) vibrations. These modes did not change their profiles with increasing Mn concentration. Generally, in the range from 800 to 1000 cm⁻¹, the rocking vibrations of CH₂ units are observed.

The differences between the C and B_m forms in this spectral region are related to the number of modes [39]. In the C form, only two modes around 892 and 909 cm⁻¹ were observed in the same spectral range [40]. On the other hand, the B_m form showed a higher number of well-defined modes, appearing at approximately 763, 786, 817, 847, 865, 890, 908, and 943 cm⁻¹, suggesting a considerable influence of the *gauche* conformation on the motions of CH₂ units [39]. As illustrated in Figure 4b, in this spectral region, the Raman spectra of Mn²⁺-doped SA crystals present several modes and vibration band profiles that are very similar across all concentrations used in this study.

For higher wavenumber values between 1000 and 1700 cm⁻¹, the Raman spectrum of the crystal exhibits modes related to internal vibrations, including carbonyl motion, as shown in Figure 5a. In the 1000–1200 cm⁻¹ range, modes were observed at approxi-

mately 1061, 1098, 1128, and 1172 cm⁻¹, which are identified as CC single-bond stretching (ν (CC)) [40]. The intense band centered at 1295 cm⁻¹ is classified as a CH₂ twisting vibration, while the modes near 1370, 1404, 1416, 1440, 1461, and 1472 cm⁻¹ correspond to CH₂ deformations [40]. Notably, no changes were observed in these Raman-active bands with increasing Mn concentration.

An important feature can also be noted from the characteristics of a broad doublet (broadband) with low intensity located at 1637 and 1650 cm⁻¹. These modes are assigned as vibrations of the C=O unit, stretching vibrations, which remain unaffected by the presence of Mn²⁺ ions in the crystalline lattice.

The spectral range of higher wavenumbers ($2800-3000 \text{ cm}^{-1}$), primarily associated with stretching motions of CH₂ and CH₃ units [39], is displayed in Figure 5b. The Raman data suggest that no changes in these vibrational motions occur due to the presence of the dopant. This behavior suggests that Mn²⁺ ions do not directly influence each molecular unit but occupy an interstitial position within the crystal lattice.

3.3. FT-IR Spectroscopy Studies

FT-IR spectroscopy experiments were conducted in the 100–4000 cm⁻¹ spectral region on MnSO₄ 5H₂O, pure SA, and Mn²⁺-doped SA crystals. Figures 7 and 8 present a comparative analysis of the IR absorption spectra. The purpose of measuring IR-active modes lies in the fact that the C_{2h} factor group of the monoclinic system has an inversion center (C_i), which dictates the selection rule between the irreducible representations of the Raman- and IR-active modes, i.e., they are distinct, as reported elsewhere [39,40]. This section aims to determine whether doping affects the IR absorption bands.



Figure 7. IR spectra of Mn^{2+} -doped SA crystals compared to the spectra of $MnSO_4$ 5H₂O and pure SA crystals (C form) in the ranges of (**a**) 100–500 cm⁻¹ and (**b**) 500–1000 cm⁻¹.

Subtle distinctions between the spectra of the C form and the Mn^{2+} -doped polymorphic phases can be noted, as illustrated in Figure 7. One spectral difference is associated with the band recorded at approximately 386 cm⁻¹, which appears only in the IR spectrum of the C form, as pictured in Figure 7a. In the spectra corresponding to the doped crystals, no modifications in the IR absorption spectra were observed across all Mn concentrations, even at the highest doping level. Moreover, the IR-active bands of MnSO₄ 5H₂O were not detected in the spectra of the Mn²⁺-doped SA crystals.



Figure 8. IR spectra of Mn^{2+} -doped SA crystals compared to the spectra of $MnSO_4$ 5H₂O and pure SA crystals (C form) in the ranges of (a) 1000–1800 cm⁻¹ and (b) 2700–3000 cm⁻¹.

In the 500–1000 cm⁻¹ region, many modes corresponding to chain vibrations can be observed [39], as shown in Figure 7b. The doublet located around 719 and 730 cm⁻¹ is associated with the rocking vibrations of CH₂ units, and no changes in this motion were observed with increasing Mn concentration.

Figure 8a presents the IR spectrum in the $1150-1350 \text{ cm}^{-1}$ range, characterized by regularity in the spacing of bands attributed to the wagging, rocking, and twisting motions of methylene groups. This spectral detail, referred to in the literature as band progression [20], indicates that the B_m form is exclusive to the Mn²⁺-doped crystals. These absorption bands appear as regular, well-spaced modes for the C form, whereas this regularity is absent in the B_m form. This phenomenon arises from the unique configuration of carboxylic groups in the *gauche* conformation.

A doublet associated with carbonyl (C=O) motion appears near 1690 and 1712 cm⁻¹ (marked by a rectangle), resulting from the overlap of symmetric and antisymmetric vibrations within the dimers. It is important to highlight that the characteristics of these modes vary depending on the specific form of each fatty acid [39]. In the spectrum, these modes appear as a superposition in the C form, indicating in-plane motion. Conversely, a clear separation is observed in the B_m form, suggesting out-of-plane motion.

The behavior of carbonyl modes remains unchanged with increasing Mn concentration, indicating that Mn²⁺ ions do not interact with the polar portion of the SA molecule. This observation aligns with the behavior of the Raman-active doublet associated with carbonyl motion. Table 1 provides the IR modes of the doublet as a function of Mn concentration, showing that their frequencies remain constant. This constancy indicates that Mn²⁺ ions do not directly interact with SA molecules, as they do not influence carbonyl vibrations. The results suggest only probable pressure exerted by Mn²⁺ ions on the unit cell.

The IR absorption spectra corresponding to higher wavenumbers are displayed in Figure 8b. The results reinforce the hypothesis that Mn^{2+} ions do not interact with the CH₃ groups of SA molecules, as no changes were observed in the motions associated with CH₂ and CH₃ units of the nonpolar portion.

Carbonyl IR-Active Modes			
Mn Concentration (%)	Wavenumber Range (cm $^{-1}$)		
C form	1682–1700		
B _m form: 0.5	1690–1712		
B_m form: 1.0	1690–1712		
B_m form: 1.5	1690–1712		
B_m form: 2.0	1689–1712		
B_m form: 4.0	1690–1712		
B_m form: 6.0	1690–1713		

Table 1. Behavior of the carbonyl IR-active mode of SA crystals as a function of Mn concentration obtained from the IR absorption bands.

Although $MnSO_4$ 5H₂O is known to be poorly soluble in nonpolar solvents such as hexane, specific strategies were implemented to ensure the availability of Mn^{2+} ions in the system. The salt was introduced as a fine powder into a solution of SA dispersed in hexane, forming a suspension that allowed the partial dissociation of Mn^{2+} ions at the solid–liquid interface. The polar groups of the SA molecules facilitated the interaction of Mn^{2+} ions with the crystal matrix, even in a predominantly nonpolar medium. Furthermore, the system was maintained under continuous and controlled temperature conditions, promoting prolonged contact between Mn^{2+} ions and SA molecules during crystal growth [41,42]. These conditions allowed the effective incorporation of Mn^{2+} ions into the SA crystal structure, as evidenced by XRD and Raman analyses.

3.4. DSC Studies

DSC measurements were performed to analyze the phase transformations from the B_m form to the C form (both with monoclinic symmetries) that occur at high temperatures, as reported in the literature [20]. As shown in Figure 9, the DSC curves of the Mn^{2+} -doped samples reveal characteristic peaks in the 327–335 K temperature range, as indicated by the red arrow. This value is close to that reported for the phase transformation from the B_m form to the C form in SA crystals, as described in the literature [20]. These results confirm our hypothesis that the B_m polymorphic phase is preserved for all samples, even with increasing Mn^{2+} ion concentrations in the crystal lattice. The complete thermal analysis data are presented in Table 2.



Figure 9. DSC analyses of the Mn²⁺-doped SA samples measured in the 300–390 K temperature interval.

Melting of SA Crystals						
Mn Concentration (%)	Onset (K)	Peak (K)	Endset (K)	Width (K)		
0.5	342.3	345.5	347.1	3.2		
1	342.3	345.6	347.2	3.4		
1.5	342.2	344.5	346.0	2.6		
2	342.3	345.3	347.0	3.3		
4	342.0	344.7	346.1	2.7		
6	342.1	345.2	347.2	3.3		
Transformation from the B _m form to the C						
Mn Concentration (%)	Onset (K)	Peak (K)	Endset (K)	Width (K)		
0.5	328.9	331.1	334.4	4.1		
1	327.5	330.3	333.1	4.3		
1.5	328.0	330.8	334.3	4.7		
2	327.8	331.1	334.3	4.7		
4	327.9	330.6	333.7	4.2		

Table 2. Onset, peak, and endset values of Mn²⁺-doped SA crystals.

The peaks highlighted in Figure 9 by a red arrow correspond to the thermal events associated with the phase transformation of SA crystals from the B_m form to the C form, as identified by differential scanning calorimetry (DSC). Although the peaks appear visually similar at different Mn^{2+} concentrations, more detailed analyses reveal subtle variations in the onset temperatures and enthalpies of these transitions, indicating changes in the internal dynamics of the crystal structure.

These thermal events reflect the rearrangement of hydrogen-bonded dimers within the SA crystal lattice, which is characteristic of this phase transformation. The consistency of these peaks across all Mn²⁺ concentrations analyzed demonstrates that Mn²⁺ doping does not interfere with the polymorphic transition mechanism of the SA crystal, preserving its structural stability even at higher dopant levels.

4. Conclusions

XRD, Raman, and IR absorption analyses provided detailed insights into the behavior of the SA crystal structure upon incorporating Mn²⁺ ions. The presence of Mn²⁺ ions in the crystal structure was studied at various concentrations, only revealing selective modifications in the crystalline environment. These changes were clarified through Raman spectroscopy, particularly by examining the behavior of lattice modes near 59 and 70 cm⁻¹, which were associated with two distinct types of hydrogen bonds being affected. XRD studies indicated that the introduction of Mn^{2+} ions into the crystalline structure of SA preserved the B_m phase, in which all molecules, through hydrogen-bonded dimers, exhibit a gauche conformation across all concentrations. The pressure-induced effect caused by Mn^{2+} ions resulted in strain or deformation of the unit cell. Specifically, a contraction occurred along the *c*-axis, while expansion was observed along the *a*- and *b*-axes. This phenomenon demonstrates the potential to maintain the polymorphism of SA crystals through doping with Mn²⁺ ions, regardless of the Mn concentration. These findings enhance the fundamental understanding of SA crystal behavior under chemical doping and open new avenues for tailoring material properties through controlled dopantinduced modifications.

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