A Raman Spectral Study of Crystalline Strontium Nitrite Monohydrate

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Abstract

The Raman spectra of the vibrational modes of pyroelectric $Sr(NO_2)_2 \cdot H_2O$ crystal had been studied from 80 to 420K. The main internal vibration modes are found to be constructed by three vibration modes of the nearly free NO^-_2 ions. The interaction between water molecules and NO^-_2 inos strongly couple with each other and result coupled peaks around the water main peaks.Three anomalous points or phase transitions in the temperature range of 130-135k, 185-190k, and 235-240k were seemly observed by observing the temperature dependent Raman spectra, which have not been investigated by x-ray diffraction in the previous work. We also confirm the dehydrating of $Sr(NO_2)_2 \cdot H_2O$ crystal at around 412k by both Raman and IR spectra.

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I. Introduction

The crystal structure of a pyroelectric $Sr(NO_2)_2 \cdot H_2O$ crystal at room temperature has been investigated by x-ray diffraction [1] and found to be a monoclinic structre with space group $P2_1$ and four formulas in the unit cell. The lattice constants of the unit cell at 295k are : a=12.5831(4)Å, b=8.94941(15) Å, c =4.4860(2) Å, and B=99.111 (4)°. A neutron diffraction [2] study of the structure of $Sr(NO_2)_2 \cdot H_2O$ was also been carried out at 294, 100, and 20k. The crystal structure yields with that of taken by x-ray diffraction at 295k, and found the monoclinic structure were maintained at these three temperatures. In $Sr(NO_2)_2 \cdot H_2O$ crystal, each lattice cell was observed to contain two isolated Sr^{++} ions which is surrounded by seven NO^-_2 ions and one water molecule. In different temperature, the average distance between ions were found undergoing a nonlinear thermal expansion. For $Ba(NO_2)_2 \cdot H_2O$ crystal, it was found undergoing a reversible phase transition at 350k followed by formation of a hemihydrate at about 425-435k and dehydration [3] at 455k. Whereas the phase transition of $Sr(NO_2)_2 \cdot H_2O$ was not found before onset of dehydration [4] at 412k. In the present work, a Raman spectrum of the $Sr(NO_2)_2 \cdot H_2O$ polycrystal was taken from 80 to 420k. It was found that the main spectrum of its lattice modes and internal modes was maintained in the same configuration throughout the whole temperature range. However, there appeared apparently three phase transition in the temperature range 130-135k, 185-190k, and 235-240k, which have not been determined by x-ray and neutron diffraction, was discovered. The dehydration of $Sr(NO_2)_2 \cdot H_2O$ crystal was confirmed at around 412k by both Raman and IR spectra.

II Experimental

Strontium Nitrite Monohydrate [$Sr(NO_2)_2 \cdot H_2O$] is a monoclinic crystal at room temperature. It is made from 4.00g Silver Nitrite ($AgNO_2$) and 3.456g hydrated Strontium Chloride ($SrCl_2 \cdot 6H_2O$) dissolved in 30ml-40ml deionic distilled water. The saturated solution was stirred in a closed container for 120 hours. The Silver Chloride precipitate was then filtered out from the solution. By evaporating the filtered solution to dryness at room temperature, the white Strontum Nitrite Monohydrate powders were obtained. The samples were then loaded into the quartz cell under dry nitrogen atmosphere and placed in an Oxford Instruments DN 1714 variable temperature liquid nitrogen cryostat. The temperature sensor is a standard 100 ohm platinum resistor mounted on the inside of a heat exchanger. The heat exchanger is also fitted with a heater for temperature varying operation in conjunction with a DTC – 2 temperature controller and the temperature resolution is nearly 0.1k.

Raman spectra were obtained using standard 90° scattering configuration. The exciting source was a Coherent Innova 90 - 4 Ar^+ ion laser, operating at 0.4 to 0.5w on the 5145 or 4880 Å lines. Scattered light was analyzed using a J.Y. Ramanor U 1000 double monochromator and detected with a chilled RCAC31034A-02 photomultiplier tube and Spex DPC-2 digital photometer. The output pulses were then fed to an IBM-PC computer for data storage, subsequent processing, and display on an X-Y plotter. Frequencies reported here are estimated to be accurate to ± 1 cm^{-1} for shart features. Periodic calibration checks were made using the known wavelengths of laser line or other non-lasing plasma lines.

Ⅲ Results and Discussion

The observed Raman spectra will be discussed following the natural separation of modes into (intramolecular) modes and lattice (intermolecular) modes. The vibration modes of the NO^-_2 ions are the main modes in the internal vibration spectrum. They consist modes of the symmetric stretching vibration, $\nu_1 = 1342\ cm^{-1}$, the symmetric bending vibration, $\nu_2 = 848\ cm^{-1}$ and the asymmetric stretching vibration, $\nu_3 = 1245\ cm^{-1}$. All these modes are Raman active in the Raman spectra, but ν_1 and ν_3 become inactive in the infared spectra. The lattice vibrational modes contain approximately 26 peaks whereas the 128, 151 and 324 cm^{-1} peaks are those that will be discussed particularly and are labeled as ω_1, ω_2 and ω_3 respectively.

The Raman spectra of the vibration modes of $Sr(NO_2)_2 \cdot H_2O$ crystal had been taken from 80 to 420k as shown in Fig.1. Comparison with the Raman spectra, it was noticed that there were no new modes appearing in the entire temperature region. When the temperature approaches to room temperature, some modes gradually merge together under the anharmonic effect. At low temperature, splitting modes can be clearly seen existing with the symmetric stretching vibration ν_1 spectra, and it gradually merges with ν_1 when room temperature is reached. At about 400k, the shape of the spectrum becomes blurred in both lattice and internal vibraion modes.

The internal vibration modes, ν_1, ν_2 and ν_3, that appears above 400 cm^{-1}, were found to follow the vibration modes of the free NO^-_2 ion. This strongly indicates a weak interacion between Sr^{++} amd NO^-_2 ions. However, the interaction between water molecules and NO^-_2 ions does strongly couple with each other and results coupled peaks ($\nu_{1\text{-}1}$, $\nu_{1\text{-}2}$, $\nu_{2\text{-}1}$, $\nu_{2\text{-}2}$, and $\nu_{3\text{-}2}$) around the main peaks. The mode frequency deviations of the coupled peaks to the main peaks were 24.4, 23.6 cm^{-1} for

ν_1 families and 6.7, 3.9 cm^{-1} for ν_2 families. The frequency deviation in ν_2 families were found to be asymmetric. It can be concluded that the crystalline water molecule exerts an asymmetric perturbation effect on the asymmetric bending vibration mode of nitrite ions. Whereas, a nearly symmetric perturbation effect on the symmetric bending vibration mode, ν_1, was observed. A new mode ν_{3-2} produced under the effect of asymmetry became apparent when the temperature exceeds 115k. However, there was no ν_{3-1} mode observed. The reason of this extremely asymmetric effect cannot be interpreted from the present message of the relationship of the spectrum intensity and temperature. The mode frequencies of lattice vibration exhibits a gradually softening phenomena from low to high temperature. This could be due to the lattice expanding in heating and the vibration frequencies decrease as the temperature is increased. The width of the spectrum frequency is found to increase gradually with the temperature and can be attributed to be the anharmonic effect exerted on the lattice during heating [5,6].

The intensity of the Raman spectrum is predominantly determined by the ground state population and the cross secion of scattering. The intensity of the peaks verses temperature is plotted in Fig. 2. The intensity of both lattice and internal vibration modes decreases exponentially with the temperature. Few anominal jump or phase transition in the temperature range 130-135k, 185-190k, 235-240k were observed. From the view point of Boguslawski model [7], the increasing in temperature makes the atoms or ions undergoing asymmetric anharmonic vibration in the pyroelectric lattice. Therefore, different structured pyroelectric materials shoulds have anomalous change in the ground state population and the scattering cross section due to the effect of atomic anomalous displacement. It also can be said that at certain character temperature, there exist certain anomalously stable states in the lattice structure.

When the sample is heated to 400k, it becomes hard to analyze the spectral shape further. The full scale of the photometer is changed and the spetra of lattice vibration and internal vibration are shown in Fig.3. When the temperature is raised to 420k, the intensity of the Raman spectra increases abruptly. Holding this temperatuare for 90 mins, and then cooling the sample to room temperature (300k), a completely different spectrum is scanned. This niw spectra belongs to $Sr(NO_2)$. It means that the crystalline water of strontium nitrite monohydrate is removed at 400-420k, and the precise temperature from the former worker by measuring its heat capacity is 412k [4].

Besides, comparing the infrared spectra of the high temperature heated sample with that of the ordinary strontium nitrite monohydrate at 1500-4000 cm^{-1} in Fig.4, it is discovered that the internal vibration mode of water molecule has disappeared. This proves that the crystalline water in strontium nitrite monohydrate has been removed. At the same time, the $\nu_{1\text{-}1}$, $\nu_{1\text{-}2}$, $\nu_{2\text{-}1}$, $\nu_{2\text{-}2}$, and $\nu_{3\text{-}2}$ modes which belong to the $Sr(NO_2)_2 \cdot H_2O$ have disappeared from the internal vibraion mode spectra of $Sr(NO_2)_2$. This fact may give an evidence to our conclusion that $\nu_{1\text{-}1}$, $\nu_{1\text{-}2}$, $\nu_{2\text{-}1}$, $\nu_{2\text{-}2}$, and $\nu_{3\text{-}2}$ modes are new modes produced by the coupling of water molecule with internal vibration modes.

IV Summary

The Raman spectra of the vibrational modes of $Sr(NO_2)_2 \cdot H_2O$ crystal had been studied from 80 to 420k. The main internal vibration modes was found to be constructed by the nearly free NO^-_2 ions. This indicates the interaction between Sr^{++} ion and the NO^-_2 ions is relatively weak. However, the interaction between water molecules and NO^-_2 ions did strongly couple with each other and resulted coupled peaks around the main peaks. Three anomalous points or phase transitions in the

temperature range of 130-135k, 185-190k, 235-240k were observed which have not been investigated by x-ray diffraction in the previous work. The further study in the anomalous points on phase transition is under investigation. We also confirm the dehydrating of $Sr(NO_2)_2 \cdot H_2O$ crystal at around 412k by both Raman and IR spectra.

Acknowledgement

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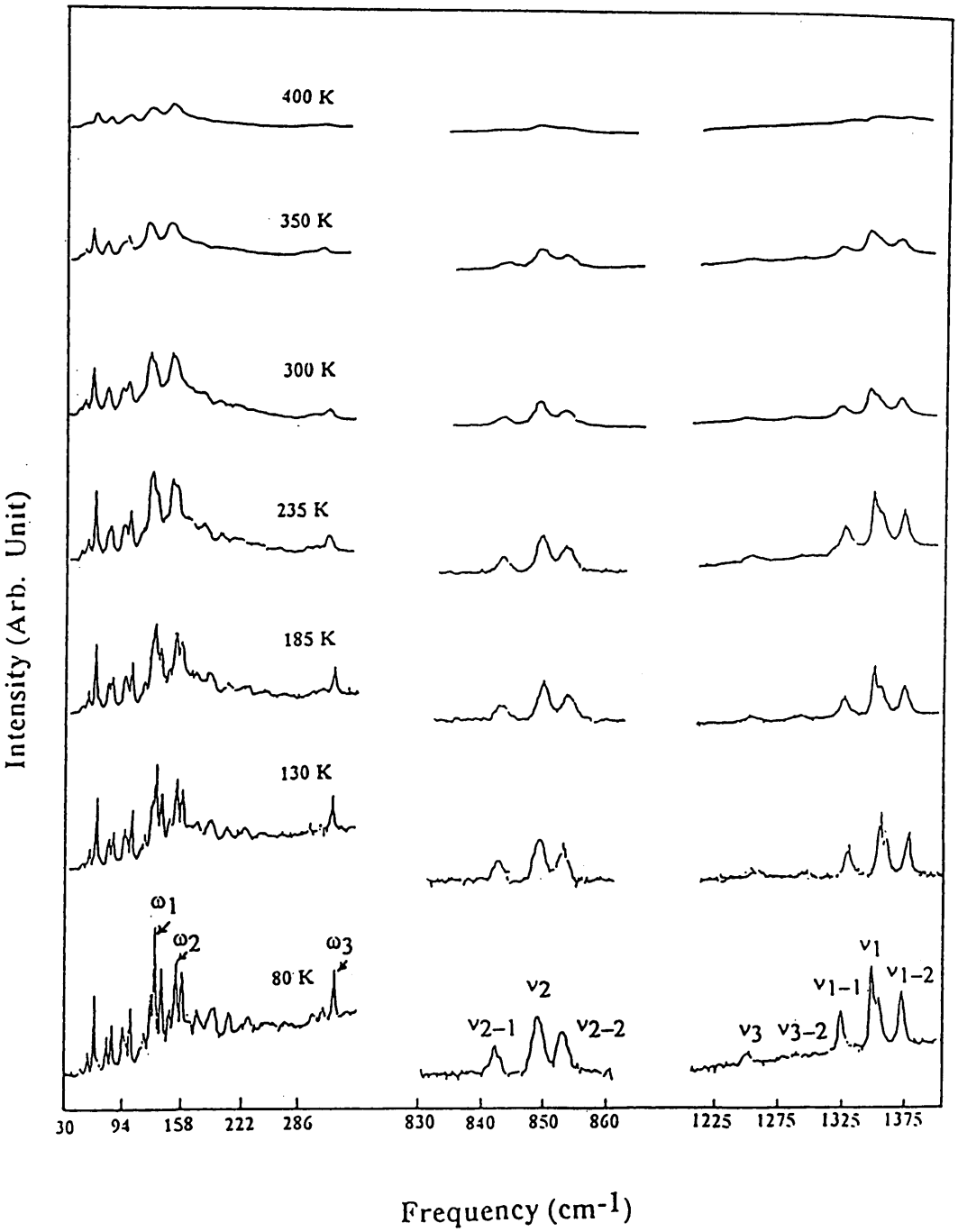

Fig.1. The Raman spectra of lattice and internal vibration mode frequencies at 80-400k.

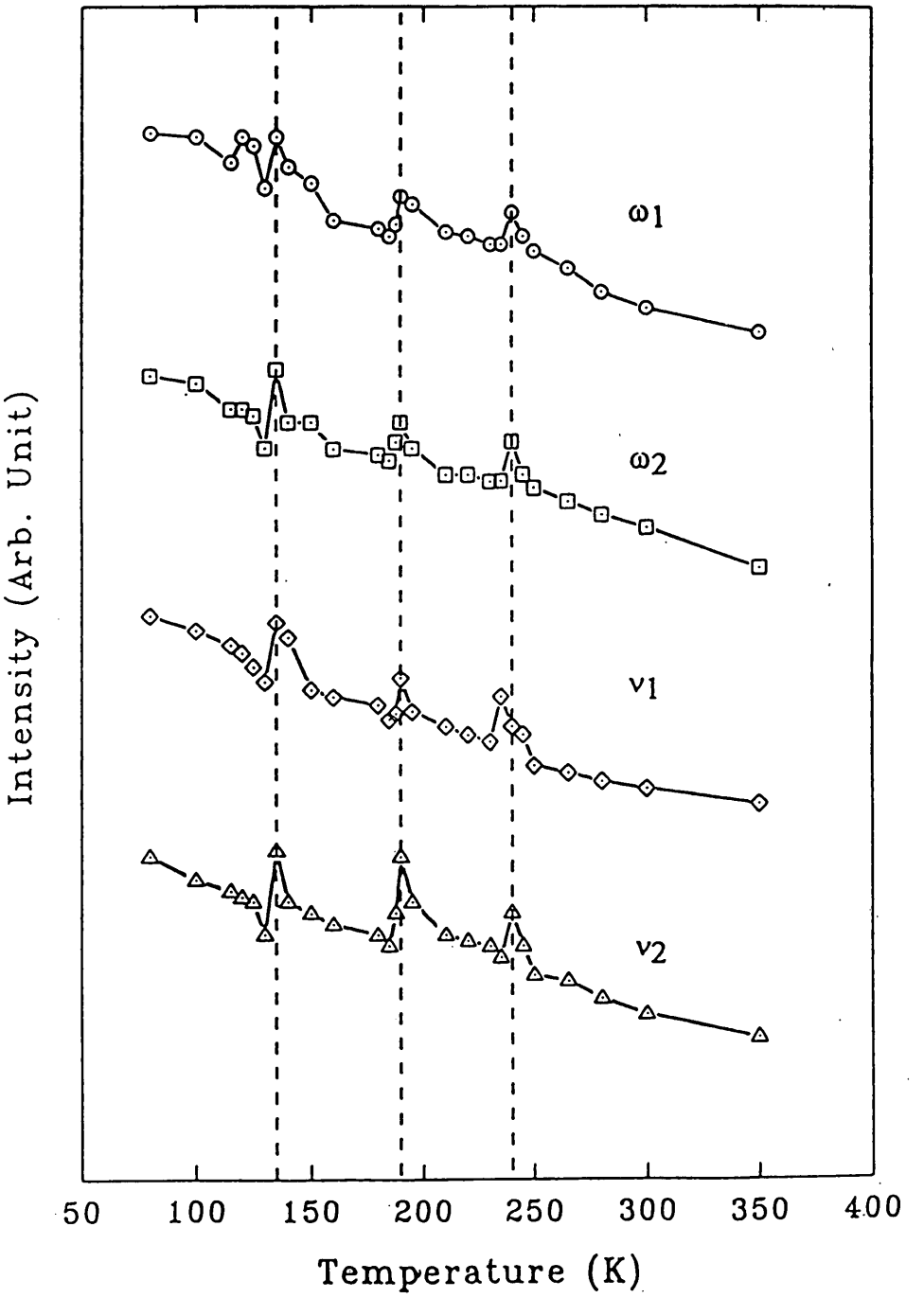

Fig.2. The temperature dependence of intensity of modes ω_1, ω_2, ν_1, and ν_2.

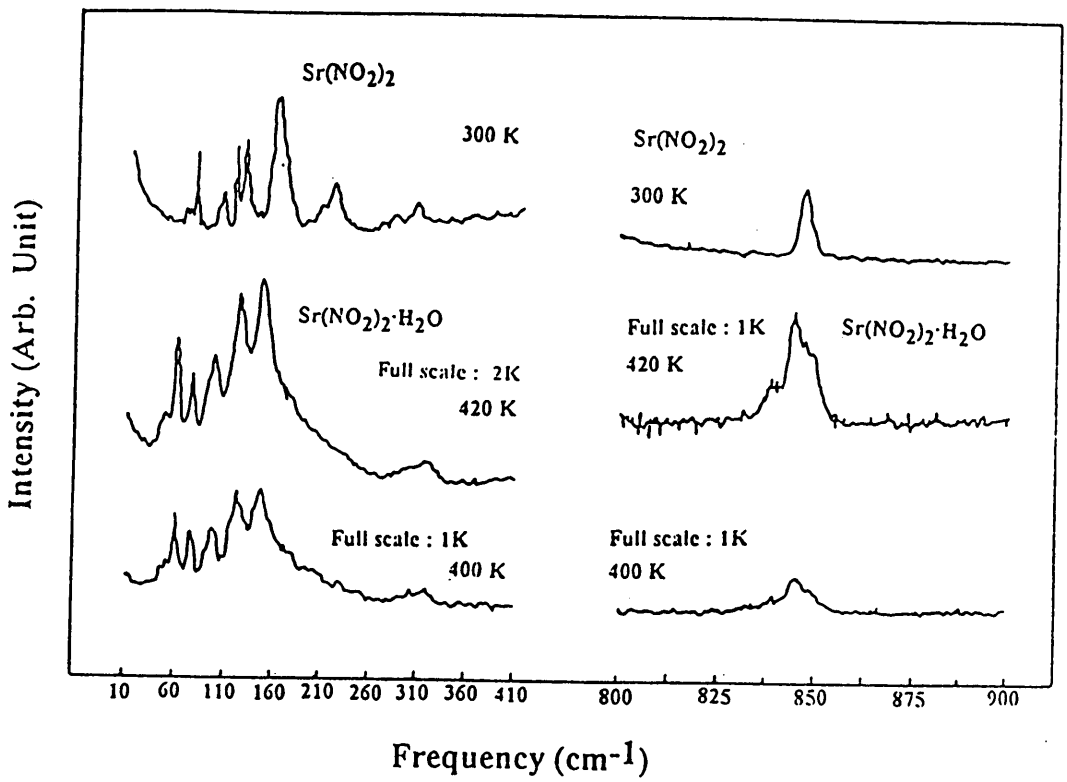

Fig.3. The Raman spectra of lattice and internal vibration mode in the procedure of crystalline water dehydrated.

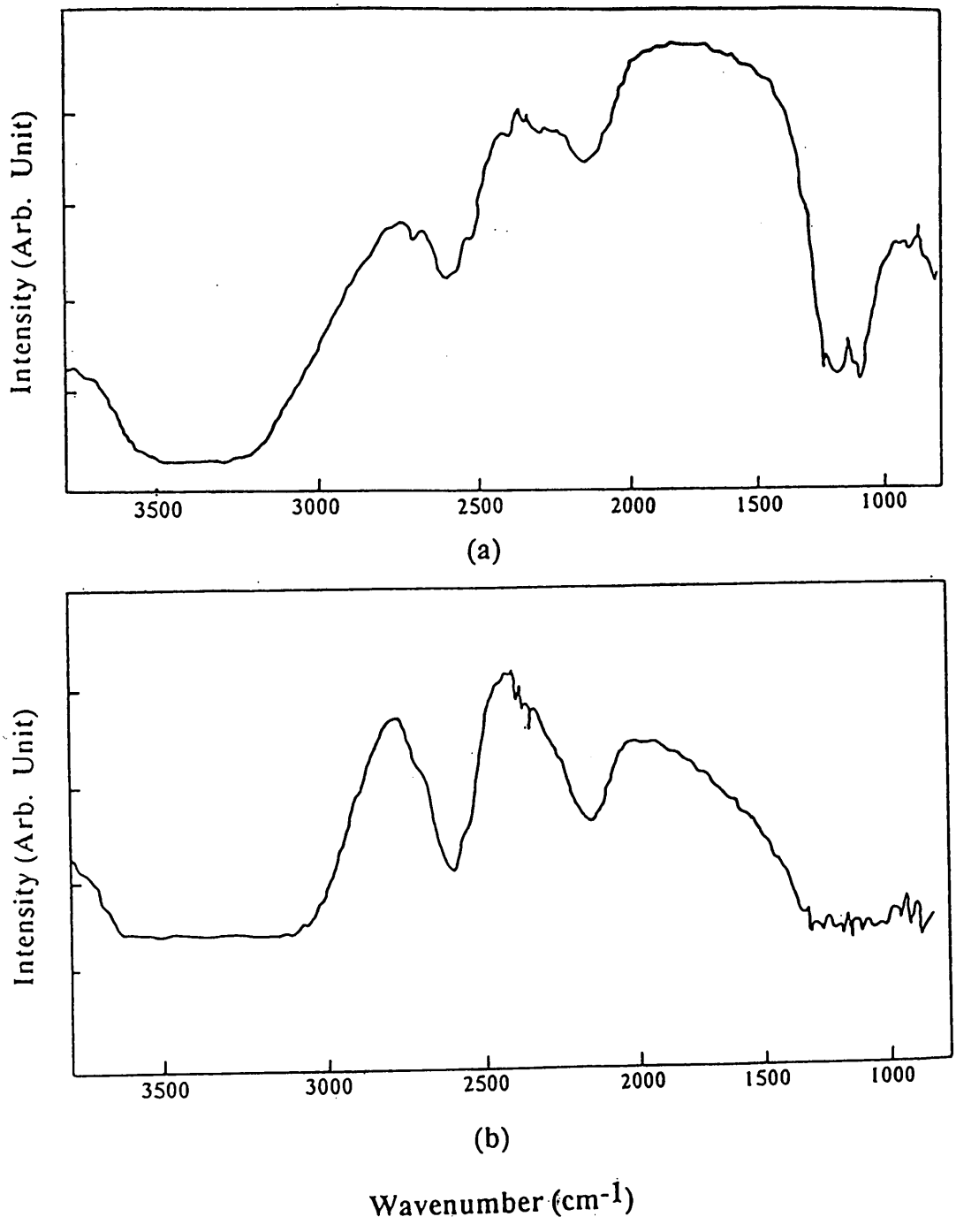

Fig.4. The infarared spectrum before (a) and after (b) the crystalline water is dehydrated.

晶形單水亞硝酸鍶之拉曼光譜研究

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摘 要

利用拉曼（Raman）散射方法，對焦熱電晶體 $Sr(NO_2)_2 \cdot H_2O$ 之分子振動光譜做了詳細之變溫研究，晶體之分子內振動模式乃由近似自由 NO^-_2 離子之三個模式組成，晶體內水分子與 NO^-_2 離子相互作結果，使得水分子之主振動模式附近有偶合之模式，在三個溫度範圍(130-135K，185-190K 及 235-240K)內由變溫之拉曼光譜圖可以看出有可能存在相變化之現象，這個結果由前人之 X 光光譜圖並沒有發現過。此外，本實驗結果(拉曼及紅外光)確認該晶體之潮解機制發生於 412K 左右。

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