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Studies on thermal hysteresis of KNO_3 by thermo-Raman spectroscopy

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Abstract

In this work, the polymorphic phase transformations of KNO_3were studied by thermo-Raman spectroscopy in a dynamical thermal process with a heating rate of 5°C min^{-1} from 30°C to 170°C and then cooling down to 30°C at the same rate. Three distinct phase transformations were detected. The characteristic spectrum for each phase was identified. The nature of each phase transformation was investigated in detail through the studies on spectral variation, intensity, intensity variation and shift in band position. In addition, the intensity variation of the ν_1 mode at 1042 cm^{-1} clearly revealed thermal hysteresis involved in the phase transformation of KNO_3. Furthermore, the thermal hysteresis of each phase was also obtained from the ν_3 mode in the range from 1341 to 1354 cm^{-1}.

Keywords: KNO_3; Phase transformations; Thermal hysteresis; Thermo-Raman spectroscopy

1. Introduction

Both differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are used to study the thermodynamic properties in the phase transformation of solid samples in a thermal process. But it is difficult to derive direct information about the phases involved in transformation. Raman spectroscopy has been widely used to study the phase transformation through either the appearance of new bands or disappearance of the existing bands during phase transformation. Raman spectra measured successively in a dynamical thermal process is called thermo-Raman spectroscopy. It can provide valuable information for the in situ investigation of composition change and phase transformation in solid samples because of the possibility of collecting Raman spectra in situ on a timescale of seconds and on a temperature scale of one degree with the availability of CCD detector [1–7].

Ionic nitrates received considerable attention recently because of their tendency to form distortional phases, which may be due to rotational or positional disorder of the nitrate group. Under atmospheric pressure, KNO_3 exhibits an interesting phase sequence depending upon the dynamic thermal process. It has an aragonite structure (phase II) at room temperature. When heated, it undergoes a transformation around 130°C to a rhombohedral structure (phase I). On cooling from some high temperature, e.g., 170°C,

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KNO_3 in phase I passes through ferroelectric phase (phase III) before reverting to phase II. The successive phase transformation in KNO_3 continues to be the subject of intense research activity because of the possibility to use this material in its ferroelectric phase for fabrication of nonvolatile random access memory devices.

The polymorphic phase transformations in KNO_3 were investigated by many methods [8–13]. The hysteresis effect in KNO_3 in terms of intermediate phase in the reversible transformation was studied earlier by DTA [14]. The internal Raman modes of KNO_3 were reported earlier [15–19]. The successive phase transformations in single crystal KNO_3 were also studied using Raman spectroscopic techniques [15,16,18]. Although Balkanski et al. [15] reported the Raman data for a complete phase-transformation cycle, the scan rate during the heating and cooling process was not maintained constantly. The phase III to phase II transformation temperature of KNO_3 and the range of stability of ferroelectric phase (phase III) were found to be depending heavily on cooling rate [20]. In this investigation, the successive phase transformations of KNO_3 in a dynamical thermal process from 30°C to 170°C and back to 30°C with 5°C min^{-1} heating/cooling rate were studied by thermo-Raman spectroscopy. The phase transformations could be demonstrated by the variation in the Raman spectra. Special attention was paid to correlate the modes observed in the ferroelectric phase (phase III) with the corresponding modes in other phases. Intensities of dominant internal modes of KNO_3 measured during the thermal processes were used to demonstrate distinctively the transformation temperature, transformation width, temperature range and also the thermal hysteresis of each phase exhibited by KNO_3.

2. Experimental

Raman scattering was excited with an argon ion laser (Spectra Physics) operating at 514.5 nm with a power of 50 mW. Since the occurrence of phase transformation depends heavily on experimental conditions, the spectral data were collected under the same experimental conditions used for thermal analysis. The sample was placed in TGA (Perkin-Elmer TGA6). The scattered radiation was collected at right angles, analyzed by a 0.5 m spectrophotometer (Spex) and detected by a CCD camera (Princeton Instruments, 1024 × 1024 pixels). Spectra were taken with an exposure time of 12 s successively such that each spectrum covered 1°C in the thermal cycle. The positions of the spectral bands were calibrated using argon spectral lines. The resolution was about 3 cm^{-1}.

The DSC curve of KNO_3 was measured in a flow of N_2 with a heating rate of 5°C min^{-1} from 30°C to 170°C and then cooling down to 30°C at the same rate using a Seiko I DSC-200 differential scanning calorimeter. The above experimental conditions were maintained while measuring TGA curve using Perkin-Elmer TGA6 and the Raman spectra. Analytical grade KNO_3 used in this investigation was from Merck and was used as such.

3. Results and discussion

3.1. Thermo-Raman spectroscopy

An isolated NO_3^- has D_{3h} symmetry. It has four distinct vibrational fundamental modes $\nu_1(A_1')$, $\nu_2(A_2'')$, $\nu_3(E')$ and $\nu_4(E'')$ at 1054, 841, 1383 and 715 cm^{-1}, respectively [21]. For Raman spectrum only three bands are observable at 1054, 1383 and 715 cm^{-1}. D_{3h} symmetry of NO_3^- may be destroyed and the bands shift and split as that in KNO_3. In this work, the internal modes observed in the Raman spectra from 400 to 1500 cm^{-1} were measured for the phase transformations in KNO_3.

3.1.1. Typical spectra

In this work, three typical spectra were found and are shown in Fig. 1. The positions of the intense Raman bands observed in these typical spectra are listed in Table 1 along with their assignments [15,19]. Spectra measured at 30°C, 164°C and 86°C (spectra (a)–(c) in Fig. 1) represented the characteristic spectra for phase II, phase I and phase III, respectively. A strong and a medium band appeared around 1042 and 703 cm^{-1} belonged to the totally symmetric ν_1 and the doubly degenerate ν_4 modes of NO_3^-, respectively. Unfortunately, the shifts of these two bands during the phase transformations were small and difficult to resolve. The bands for ν_3 mode in the range from 1310 to 1460 cm^{-1} were enlarged and are shown in the

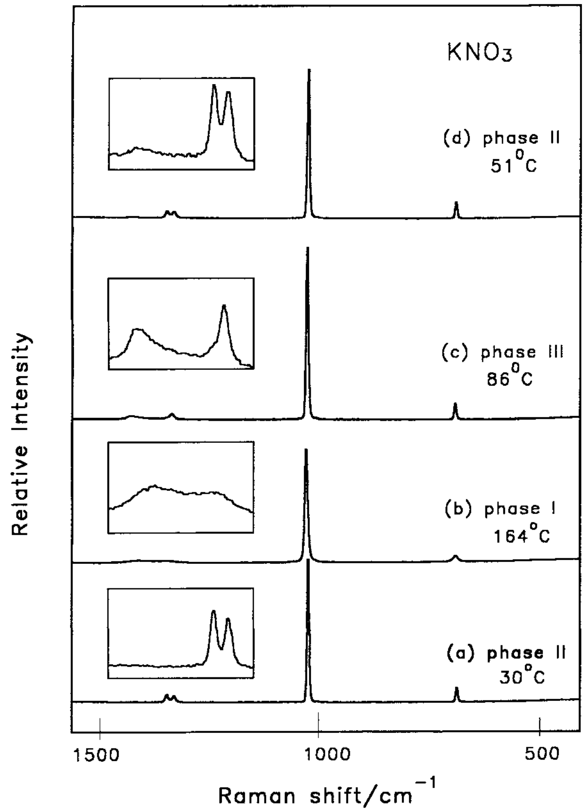

Fig. 1. Typical Raman spectra of KNO_3 for (a) phase II (at 30°C), (b) phase I (164°C), (c) phase III (at 86°C) and (d) spectrum at 51°C. The inserts are the Raman bands of ν_3 mode in the range from 1310 to 1460 cm^{-1}.

inserts. It changed greatly and was used to show the phase transformations.

Spectrum as shown in Fig. 1(d) represented the reverting of KNO_3 back to phase II at 51°C after heated to 170°C. The spectrum was the same as that shown in Fig. 1(a) except a small hump appeared at 1414 cm^{-1} and a slight increase in intensity of the band at 1341 cm^{-1} compared to the band at 1354 cm^{-1}. Those indicated the co-existence of phase III with phase II.

3.1.2. Variation in spectra

The variation of ν_3 band revealed the phase transformation distinctively. It was used to show the phase transformations in this work. Figs. 2–4 show the spectral variations in the range from 1310 to 1460 cm^{-1} for ν_3 mode of NO_3^- in the thermal cycle. The variations in the spectra measured from 128°C to 137°C clearly demonstrated the transformation from phase II to phase I as shown in Fig. 2. The changes were the disappearance of the doublet at 1341 and 1354 cm^{-1} of phase II and the appearance of two broad bands at 1345 and 1414 cm^{-1} of phase I. The phase transformation started at 129°C and ended around 136°C. The rapid disappearance of the bands at 1341 and 1354 cm^{-1} clearly indicated the sharp transformation nature.

The next spectral variations were observed from 118°C to 111°C during the cooling process as shown in Fig. 3. The most pronounced variations were the appearance of a sharp band at 1345 cm^{-1} and a broad band at 1414 cm^{-1}. The transformation temperature was in the range from 116°C to 112°C. In this temperature range, phase I was replaced by phase III. The short transformation width observed for this transformation revealed the fast transformation nature.

The spectral variations observed in the next temperature interval from 85°C to 69°C during the cooling process are shown in Fig. 4. The third transformation was manifested as a gradual modification in the Raman spectra, starting around 83°C by the appear-

Table 1
Band positions of KNO_3 (in cm^{-1})

30°C[a] (phase II)	164°C (phase I)	86°C (phase III)	51°C[b] (phase II)	Assignment[c]
	1414	1414	1414	
1354			1354	ν_3 of NO_3^-
1341	1345	1345	1341	
1042	1045	1045	1041	ν_1 of NO_3^-
703	703	702	702	ν_4 of NO_3^-

[a] Purchased sample, before thermal process.
[b] Mainly in phase II but with some phase III.
[c] From Refs. [15,19].

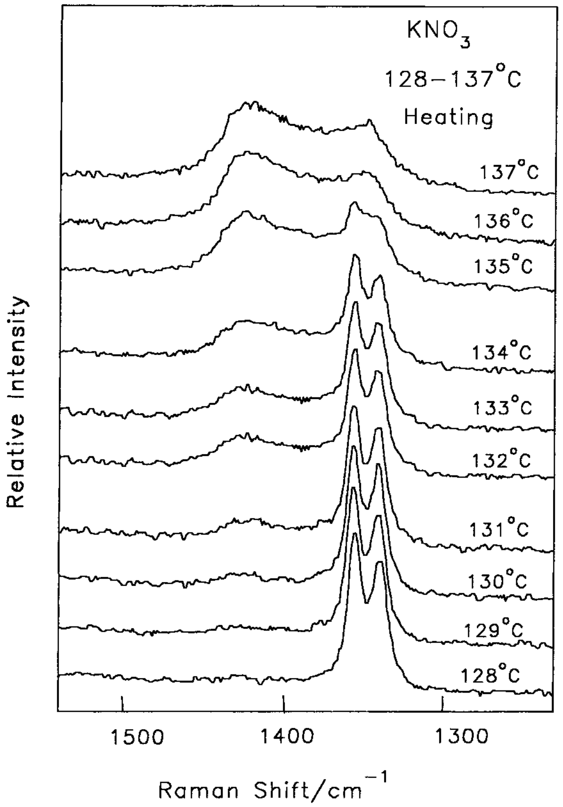

Fig. 2. The thermo-Raman spectra of KNO_3 from 128°C to 137°C (transformation from phase II to phase I) during the heating process.

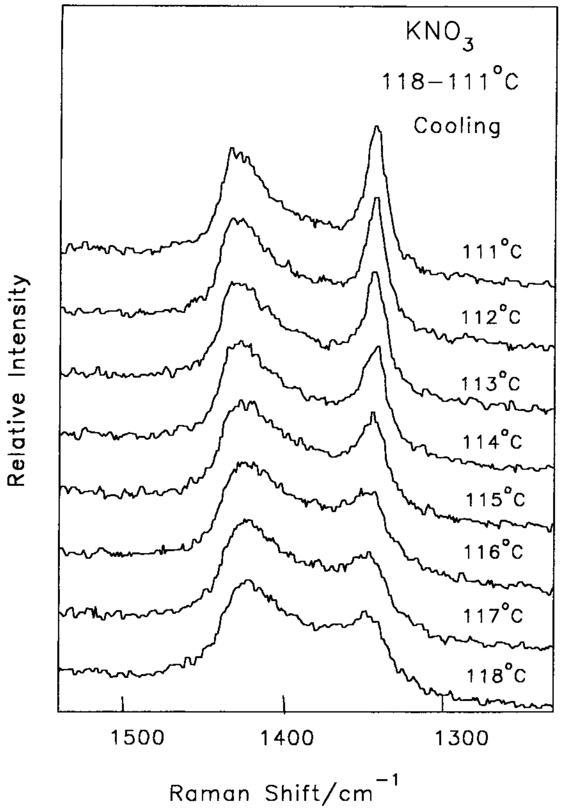

Fig. 3. The thermo-Raman spectra of KNO_3 from 118°C to 111°C (transformation from phase I to phase III) during the cooling process.

ance of a hump at 1354 cm^{-1} on the shoulder of the band at 1345 cm^{-1}. The spectral change was that the sharp single band was replaced by a doublet and the band at 1414 cm^{-1} became weak. At 69°C, a small hump at 1414 cm^{-1} still existed. In addition to that, the intensity of the band at 1341 cm^{-1} was slightly higher than that of the band at 1354 cm^{-1}. This indicated that the transformation to phase II was not completed yet. This broad hump diminished gradually and disappeared around 40°C. This transformation was estimated as from 83°C to 40°C with the major change from 83°C to 69°C. The phase III to phase II transformation appeared to be sluggish compared to other two transformations.

3.1.3. Intensity and intensity variation

Thermo-Raman spectra not only can identify the phase but also can show how the amount of each species varies through its band intensity during a dynamical thermal processes. The intensity and the intensity variation of the band at 1042 cm^{-1} during both heating and cooling process are shown in Fig. 5. As shown in Fig. 5(a), the intensity of the band at 1042 cm^{-1} jumped to a higher value at 136°C during the heating process. It revealed the transformation from phase II to phase I. During the cooling process, it increased sharply from 116°C to 112°C for the transformation from phase I to phase III. For further cooling, it started to decrease from 83°C to the temperature about 40°C with a rapid decrease from 83°C to 69°C. This was the transformation of phase III to phase II. The small temperature intervals for the phase transformations from phase II to phase I and from phase I to phase III demonstrated the sharp transformation nature. However, the gradual decrease in intensity of this band from 83°C to 40°C implies that

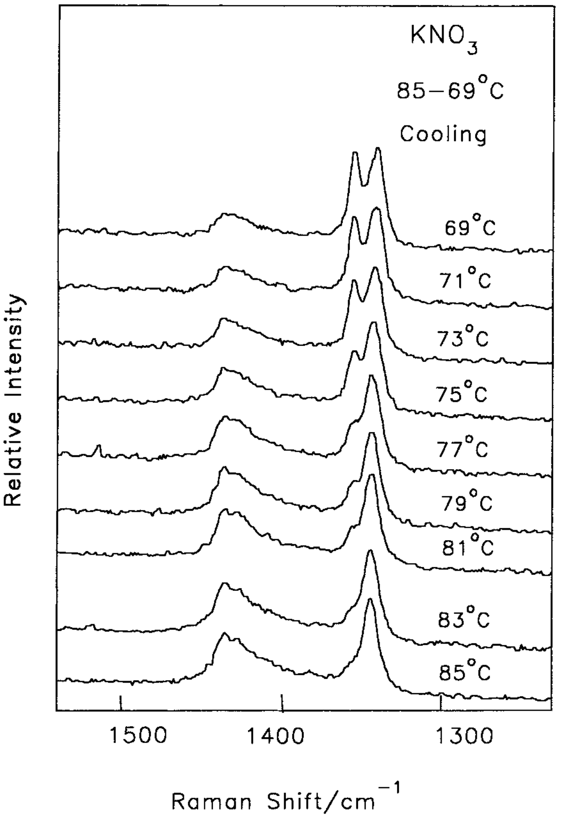

Fig. 4. The thermo-Raman spectra of KNO_3 from 85°C to 69°C (transformation from phase III to phase II) during the cooling process.

the transformation from phase III to phase II occurred sluggish.

The derivative of the intensity of the dominant band can provide some clues about the temperature at which the transformation begins and completes and particularly the maximum transformation rate. Fig. 5(b) shows the derivative for the intensity of the band at 1042 cm^{-1} during both the heating and cooling processes. The derivative curve indicated a peak at 134°C during the heating process corresponding to the maximum rate of the transformation from phase II to phase I. During the cooling process, a peak was observed at 114°C. It revealed the transformation from phase I to phase III. On further cooling, a dip at 72°C superimposed on a shallow broad baseline from 83°C to 40°C was noticed. Of course, it was the transformation from phase III to phase II. The maximum transformation rate was at 72°C. The intensity and its derivative of the band at 703 cm^{-1} showed a similar variation.

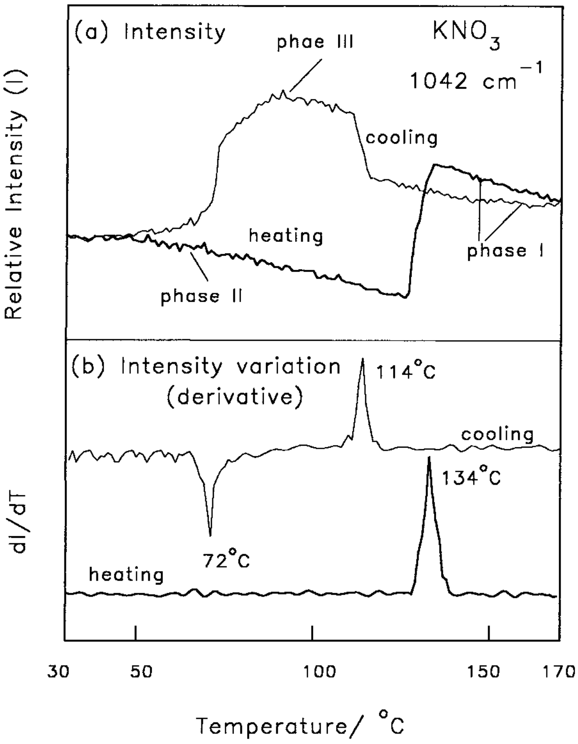

Fig. 5. The (a) intensity and (b) intensity variation (dI/dT) of the strong band around 1042 cm^{-1} during the heating and cooling cycle.

The earlier photoacoustic [10] and infrared [13] studies could not detect the phase III to phase II transformation of KNO_3 and even calorimetric techniques require high sensitivity to detect this transformation. But in the present thermo-Raman studies, all the three phase transformations could be detected distinctively by the intensity variation of the band at 1042 cm^{-1} as shown in Fig. 5(b).

3.1.4. Thermal hysteresis

The Raman spectra of KNO_3 for the three phases in the range from 1310 to 1460 cm^{-1} are different as shown in the inserts in Fig. 1. Then the amounts of these three phases could be calculated based on the intensities of their characteristic bands. For simplicity, during a transformation from one phase to another, it is reasonable to set the amount of the third phase to be zero. The variations of these phases are shown in

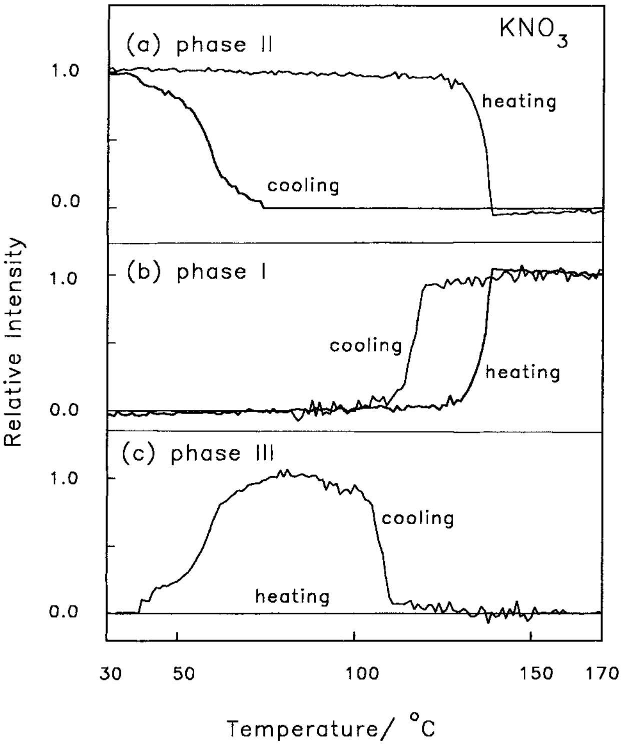

Fig. 6. Thermal hysteresis of (a) phase II, (b) phase I and (c) phase III during the heating and cooling cycle.

Fig. 6. It could demonstrate the variation in the amount of each phase. The intensity variation of the doublet observed around 1341 and 1354 cm^{-1} depicted the variation on the amount of phase II and is shown in Fig. 6(a). During the heating process, its intensity began to fall at 129°C and vanished after 136°C. This implies the disappearance of phase II. During the cooling process, that doublet started to reappear at 83°C with a gradual increase in intensity. The increase became slow after 69°C and the doublet recovered around 40°C.

The intensity variation of two broad bands at 1345 and 1414 cm^{-1} of phase I is shown in Fig. 6(b). During the heating process, these two bands appeared at 129°C and their intensity increased to high value at 136°C corresponding to the appearance of phase I. While cooling, its intensity began to drop at 116°C and vanished after 112°C, which indicated the disappearance of phase I.

The intensity variation of the bands at 1345 and 1414 cm^{-1} of phase III shown in Fig. 6(c) clearly demonstrates the behavior of phase III. During the heating process, it did not present. While in cooling process, it appeared at 116°C and increased until all samples transformed to phase III around 112°C. On further cooling, its intensity started to fall at 83°C, diminished fast at about 69°C and then gradually decreased to vanish around 40°C. Its pure phase was found only from 112°C to 83°C. It would be important because phase III of KNO_3 in thin film was found to be one of the promising raw materials in the construction of nonvolatile random access memory devices.

Thermal hysteresis in KNO_3 studied earlier by DTA showed peak/dip for the three phase transformations. In this thermo-Raman spectroscopic study, the intensity variation of the band at 1042 cm^{-1} showed the thermal hysteresis (Fig. 5(b)) just as those reported by DTA studies [14]. Furthermore, each phase could be detected distinctively, therefore the thermal hysteresis for each phase could be obtained individually as shown in Fig. 6.

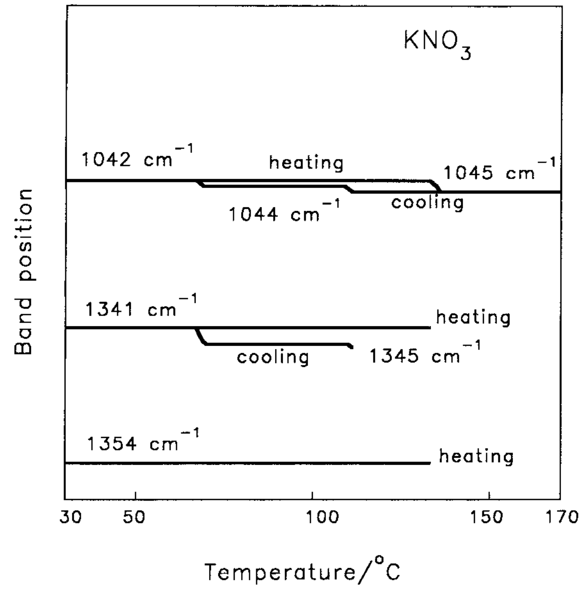

Fig. 7. The shifts of the band positions of the band around 1354, 1341 and 1042 cm^{-1} during the heating and cooling cycle.

3.1.5. Shifts in band positions

The band positions are used to identify the phase and they are also sensitive to phase transformation. Although the band shifts are small for the internal modes in phase transformations, the positions of the bands around 1042, 1340 and 1354 cm^{-1} were measured and are shown in Fig. 7. The band position of the ν_1 mode appeared at 1042 cm^{-1} for phase II remained constant till 129°C and shifted to 1045 cm^{-1} at 136°C for phase I during the heating process. On cooling, this band remained at 1045 cm^{-1} down to 115°C for phase I but afterwards it shifted to 1044 cm^{-1}for phase III. On further cooling to 83°C, it shifted gradually to 1042 cm^{-1} for phase II. These small changes in the band position of ν_1 mode during the phase transformation from phase I to phase III clearly indicated that the local environment of NO_3^- was not disturbed much during this transformation.

The band positions of the doublet remained at around 1341 and 1354 cm^{-1} during the heating process up to 135°C then the doublet disappeared because phase I has only two very broad and weak bands. During the cooling process, a band appeared at 1345 cm^{-1} at 116°C, this clearly indicated the transformation to phase III from phase I. On further cooling to 83°C, this band gradually shifted towards 1341 cm^{-1} for phase II. In the meantime, the band at 1354 cm^{-1} (only for phase II) recovered after 83°C at the same position (the figure cannot show it). The above investigation on the shifts in the band positions of the bands at 1042, 1341 and 1354 cm^{-1} clearly illustrated all the three phase transformations and the transformation temperatures.

3.2. TGA/DSC

The curve of TGA did not show any appreciable weight loss throughout the entire heating and cooling cycle. DSC showed one endothermic and one exothermic process at 131°C and 120°C in the heating and cooling processes, respectively. Thermo-Raman data showed the transformations from phase II to phase I and phase I to phase III were around 134°C during the heating and around 114°C during the cooling process, respectively. DSC curve showed a broad but weak signal in the temperature interval between 85°C to somewhere between 45°C and 35°C corresponding to the transformation of phase III to phase II. This might indicate that the enthalpy involved in this transformation was small. However, a distinct Raman spectral variation was observed for this transformation from 83°C down to 40°C. The thermo-Raman spectra showed an advantage that all the variations in the transformations could be detected distinctively from the beginning to the end in a dynamic way.

4. Conclusion

In this work, thermo-Raman spectroscopic studies on KNO_3 were performed in the frequency region corresponded to the internal modes of NO_3^- as a function of temperature in a dynamical thermal process heating from 30°C to 170°C and then cooling down to 30°C at a rate of 5°C min^{-1}.

The spectra in the range from 1310 to 1460 cm^{-1} showed all the three phase transformations distinctively. The spectra in that range revealed three variations for three phase transformations which were in the temperature ranges from 129°C to 136°C, 116°C to 112°C and 83°C to 40°C. The intensity study for the band at 1042 cm^{-1} during the entire heating and cooling cycle clearly revealed the thermal hysteresis of KNO_3. In addition, the intensity variation (derivative of the intensity) showed three distinct peak/dip for the phase transformations. The sharp natures of transformations from phase II to phase I and from phase I to phase III and the sluggish transformation nature of phase III to phase II were confirmed. The intensities of the weak bands in the range from 1310 to 1460 cm^{-1} demonstrated the presence of each phase therefore the thermal hysteresis for each phase during the thermal cycle could be obtained individually. The stability and the existence temperature range of the ferroelectric phase (phase III) of KNO_3 should be important for its uses. During the cooling process, pure ferroelectric phase existed from 112°C to 83°C. The coexistence of phase III with phase II was also found from 83°C down to 40°C.

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