The NaNO$_3$/KNO$_3$ system: the position of the solidus and sub-solidus

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The existing evidence for the nature of the phase diagram for the binary system sodium nitrate–potassium nitrate is reviewed and in particular whether the system is of the continuous solid solution type, as has often been stated in the last 80 years, or whether this system is of the eutectic type as was earlier believed and has again been asserted recently. Additional evidence from Raman spectroscopy and Raman mapping on the 50 : 50 mol% (minimum melting point) composition is now presented, supporting the eutectic classification. Abrupt changes in wavenumber, or in the wavenumber–temperature gradient of five Raman bands indicate a solid-state transition at about 115 °C and are attributed to a phase transition in KNO$_3$-rich areas. On a fast cooled sample, Raman bands attributed to sodium nitrate-rich and potassium nitrate-rich areas were found to persist up to and slightly beyond the melting point, and although their wavenumber-positions converged, the apparent single band could still be resolved into the two bands which could be attributed to the Na-rich and K-rich areas. On cooling, the reverse change took place quickly. Measurements with the initially slow cooled sample, where these areas were bigger, showed that the spectral bands reverted to the room-temperature wavenumber values, after holding at 22 °C for only 60–90 min.

Introduction

The system NaNO$_3$/KNO$_3$ is probably the most studied of the binary salt systems, but the details of the phase diagram are not yet agreed. In particular whether, as is generally thought, it is an example of continuous solid solutions, or whether it is an eutectic system. Support for the former stems principally from two investigations[1,2] both of which were experimentally flawed.

A complete review of earlier work is necessarily long since there were 21 papers published between 1857[3] and 1955[4] and there have been at least as many since then. Thus the following is selective. The early reports[3,5–8] all indicated a eutectic system with the minimum melting point at the 50 : 50 mol% composition, while later papers until very recently, interpreted the data as indicating continuous solid solutions, though Freeth[9] rapidly responded that this was unlikely on theoretical grounds. A critical review of the NaNO$_3$/KNO$_3$ phase diagram and thermal transformations in the pure components are given in refs. 10–12

Those and later papers have all been much influenced by the data of Briscoe and Madgin[2] who reported a heavily curved solidus. Regrettably their experimental procedures were not suitable, since they cooled their salt mixtures below the liquidus temperatures and scraped off the deposited crystals for analysis. Unfortunately these crystals were only drained by raising them "some 4.5 cm above the surface of the melt". They claimed, optimistically, that the crystals "could scarcely have retained, after drainage, any very large proportion of included mother liquor". This, of course, ignores the melt which would necessarily be held by surface tension and viscous forces and which would have solidified away from the melt.

Recent work[13] has shown that crystals filtered under vacuum on a glass frit for four hours while kept above the melting point of the salt mixture in an electric resistance furnace, still contained large amounts of the melt, at least equal weights of melt and crystals. Analysis of the whole, crystals and melt as by Briscoe and Madgin,[2] would of course indicate compositions much nearer to those of the liquidus than those of the crystals alone, thus indicating an incorrect solidus.

Later papers appear not to have considered this experimental difficulty and have generally accepted the very curved solidus reported, with its implication of a continuous solid solution, despite a series of redeterminations of the solidus chiefly by differential scanning calorimetry (DSC),[14–19] which suggested that the solidus was really quite flat and that it extended ever nearer towards the pure components, Fig. 1. These extended horizontals have mostly been interpreted as indicating continuous solid solutions. Indeed two papers[15,17] included calculated solidus curves based on regular solution theory which were claimed to support the continuous solid solution theory, even though the calculated solidus was much more curved, deviating as much as 30 °C from the experimental line.

The other frequently cited evidence for continuous solid solutions in this system is the work of Kofler[1] who after a study of mixtures across the phase diagram, using a hot stage optical microscope, reported that he saw no differentiation into discrete solid solutions. Regrettably he gave no information on the optical magnifications used, nor of his etching technique. Even in the best optical microscope it is not possible to resolve structures, *e.g.* such as separations of discrete solid solutions of colourless components, smaller than about 1 micrometer. Therefore Kofler[1] cannot claim to have proven solid solubility by the mere absence of any microscopically visible structures.
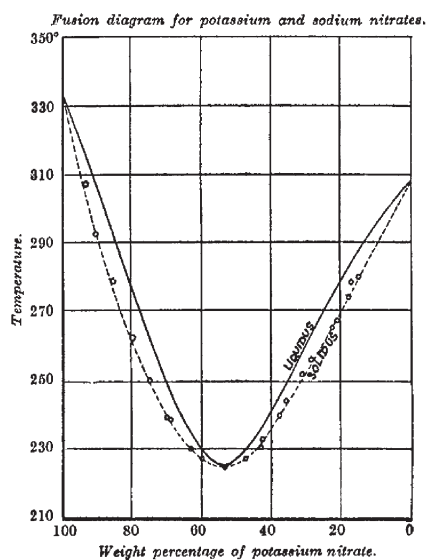
More recent measurements of the electrical conductivity of the solidified 50 : 50 mol% composition[21,22] and of the melting enthalpy[23,24] have however suggested that the solid has an eutectic structure of alternating areas of sodium nitrate-rich and potassium nitrate-rich composition. Raman mapping at room temperature[25] has recently confirmed this hypothesis, but left open the possibility that continuous solid solutions might be formed at higher temperatures.
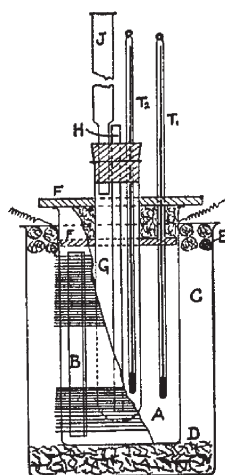
Structures

To assist the following discussion we summarise some essentials on the nomenclature of the phases of the pure components:

NaNO$_3$

NaNO$_3$ crystallises *at room temperature* in the trigonal $R\bar{3}c$ (D_{3d}^6) space group[26] with $Z = 2$ (Z = number of formula units in the cell). This phase is referred to in the following as Na*II*, which is an ordered calcite structure. At temperatures higher than ~276 °C[18] NaNO$_3$ undergoes a second order phase transition into a structure of average trigonal $R\bar{3}m$ space group, with $Z = 1$ (referred to as Na*I*,

Fusion diagram for potassium and sodium nitrates.

Briscoe & Madgin (1923)

Kofler (1955) [Tamman & Ruppelt 1931]

Schmelzdiagramm NaNO₃-KNO₃. ● Eigene Meßpunkte; + Punkte nach *Briscoe* und *Madgin*; ○ Punkte nach *Tammann* und *Ruppelt*.

Fig. 3. Experimental DSC data for NaNO₃–KNO₃.
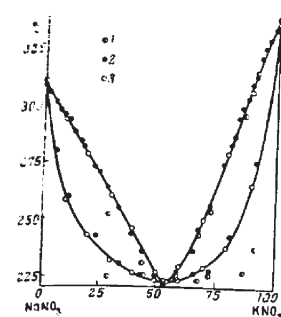
Kramer & Wilson (1980)

Rogers & Janz (1982) [Bergman & Berul 1952]

Fig. 1. Fusibility diagram of the system NaNO₃ — KNO₃ according to the data of: 1) Tamman; 2) Bergman and Berul'; 3) Kofler [8].

Kirgintsev & Kosyakov (1968)

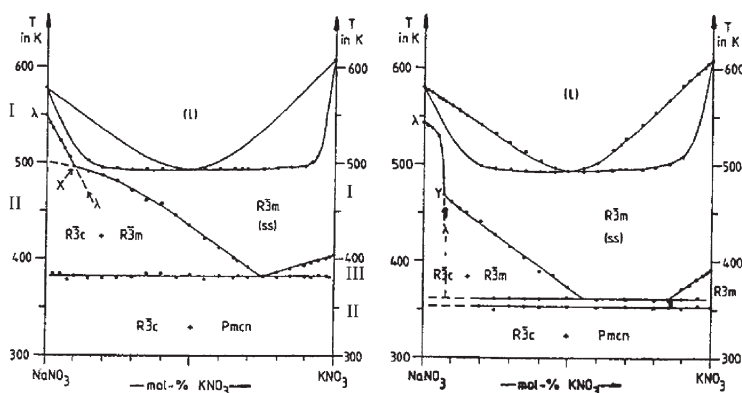Fig. 2. Phase diagram for the system NaNO₃–KNO₃ (DSC, heating rate 10 K min⁻¹).

Greis et al. (1985)

Xu & Chen (1999)

Fig. 1 Phase diagrams from the literature,[20] and the apparatus used by Briscoe and Madgin.[2]

a disordered calcite structure),[27,28] until it melts at about 307 °C. At low temperatures, below ~260 K, NaNO₃ adopts another phase.[29]

KNO₃

At *room temperature* KNO₃ has the orthorhombic *Pmnc* (D_{2h}^{16}) space group with $Z = 4$,[30] (referred to as K*II*). Above ~128 °C[31–33] it adopts the rhombohedral $R\bar{3}m$ (D_{3d}^5) space group, with $Z = 3$ (1 per primitive cell) (referred to as K*I* or α, also of disordered calcite structure).[31] On cooling from above 180 °C K*I* does not change directly to K*II*, but transforms *via* a third ferroelectric phase,[34] stable at ~124 to ~110 °C, referred to as K*III*, belonging to the rhombohedral, polar, space group $R\bar{3}m$ (C_{3v}^5) with $Z = 3$ (1 per primitive cell).[32,33,35]

Raman

The Raman spectra of the pure NaNO₃ and KNO₃ salts, forming the system investigated here, are well known,[36] and have been studied also *vs.* temperature[37] and pressure[38,39] and as single crystals.[40,41] The unperturbed nitrate ion is a triangular planar species of D_{3h} symmetry with four fundamentals: v_1(A′₁, Raman active at ~1050–1070 cm⁻¹), v_2(A″₂, only IR active at ~830 cm⁻¹), v_3(E′, Raman and IR active at ~1380 cm⁻¹), and v_4(E′, Raman and IR active at ~715 cm⁻¹).[36,42] The band positions depend somewhat on the cation and the crystal phase, see *e.g.* experimental data on nitrates.[43–45] Theoretical treatments of the vibrations have also been carried out.[46,47]

More importantly in connection to this work, a Raman spectroscopic study of the NaNO$_3$/KNO$_3$ system[45] has recently been published which makes available the data in the first author's PhD thesis,[48] produced under the supervision of the late Prof. M. H. Brooker at the Memorial University of Newfoundland. Xu[48] reported that the solids produced by quenching melts of compositions close to equimolar melts ($0.5 < X$(KNO$_3$) < 0.80, where X is mole fraction) were mixtures, perhaps of Na*I* and K*I*, which Devlin[49] had found by Raman spectroscopy to be slightly different, even though X-ray diffraction (XRD) had suggested that they were of the same space group ($R\bar{3}m$). This apparent higher symmetry may have arisen from averaging. A more detailed argument by Xu[48] suggested "the Raman bands indicated an admixture of very small particles of Na*II* and K*III*" and different structures would suggest only limited solid solutions. In principle sodium and potassium cations would not normally be expected to form continuous solid solutions because of their very different sizes (Na 95, K 133 pm). Xu[48] further proposed limits on the solid solutions of about X(KNO$_3$) $= 0.20$ for Na*I* and 0.90 for K*I*, in fact similar to those suggested 100 years earlier by Hussink.[7] Interestingly the XRD pattern of equimolar NaNO$_3$/KNO$_3$ had earlier been reported as different from either of the pure salts at the same temperature of 200 °C.[17] Xu commented that a noteworthy feature of the Raman bands of the intermediate compositions[45,48] was their broadness and smoothness when compared with those of the more extreme compositions. Xu further suggested that this arose because of a "phase separation on a few hundred to a few thousand nanometer scale". By using Raman mapping the present authors have shown that this separation is in fact an eutectic structure of the conglomerate type[25,50] with the phases of this order of size and the Raman bands also comparatively broad.

It was considered that Raman mapping which shows the spatial relationship of two or more different compositions in sections taken across solidified salt melts, if undertaken at varying temperatures, would contribute towards the resolution of the uncertainties outlined above, in particular the existence or otherwise of the solid state transformation (sub-solidus line) reported by Bergman and Berul,[51] Rogers and Janz[52] and Greis *et al.*[19] It would similarly be expected to elucidate whether continuous solid solutions were formed across the central part of the phase diagram, or alternatively whether there was a conventional eutectic system. Fortunately there has always been agreement that the minimum melting point was close to 220 °C with a composition of 50 : 50 mol%.

Experimental

The principle of confocal Raman microscopy (mapping) is based on the automatic successive recording of Raman spectra from many points (or pixels) of a flat sample surface, prepared by various cooling regimes, sectioned, ground and polished, by use of a motorized microscope table, and from these spectra a Raman mapping is computed, based on band intensities at specific wavelength intervals.[50]

The compounds of "*pro analysi*" quality were dried, weighed out in the specified proportions, ground together and melted in 10-mm inner diameter Pyrex tubes drawn out to a point at their lower ends. Two methods of heating and cooling were employed. Firstly in a temperature controlled furnace to produce slow cooled specimens, where the tube was slowly pushed downwards from a heated section at a rate of 5 mm h^{-1}. Visual inspection showed the molten eutectic to initially solidify to a transparent/translucent solid which turned white and opaque on further cooling. Secondly small quantities were heated and quickly cooled in the LINKAM temperature controlled microscope stage (HP891/TP93).[53]

The slow cooled solidified eutectics were broken out of their container tubes and transverse sections ground with paraffin, on a metallurgical polishing machine with, successively, P220 and 1200 Carborundum papers and finally a lap impregnated with 0.25 µm diamond paste. The best results were obtained when lubricating with paraffin, washed off with *n*-pentane. Other lubricants (ethylene glycol, water) and washing liquids (acetone) were tried but resulted in dissolution of more of the salt surface.

Raman spectra were measured with a DILOR XY CCD spectrometer with both macro and microscope entrances. Spectra were excited with Ar$^+$ ion laser light of about 1 W power at 514.5 nm wavelength. The Rayleigh line was filtered off by using a Kaiser holographic SuperNotch-Plus filter (approximately 200 cm^{-1} cutoff). The Raman light was dispersed onto a liquid-nitrogen cooled CCD detector by use of a 1800 lines mm^{-1} grating in an 800 mm focal length single spectrograph, or in a second spectrograph with a much shorter focal length and a grating with 600 lines mm^{-1}. In both cases the slits were set to 100 µm corresponding to a spectral resolution of about 4–5 cm^{-1}. Calibration of wavenumber scales to an accuracy of ± 1 cm^{-1} could be done with neon lines superimposed on the spectra; if not calibration errors as large as 30 cm^{-1} were often obtained.[54] The spot size was generally 1 µm and a 40×40 matrix of points was normally used. Spectral and image files were collected as ".tsf" and ".tvf" format files with the DILOR Labspec program. The microscope table was controlled by the software. Raman band areas were calculated by the software without the background. Mappings were smoothed from pixel to pixel and an artificial colour scale added to obtain better Raman imaging. Band positions were found with the software without any smoothing, employing mixed gaussian–lorentzian band shapes and built-in baseline correction procedures. Other details are given in the figure captions or have been given previously.[55]

The Raman signal strength was found to vary considerably from spot to spot for most samples, because of the sensitivity of the focus adjustment and lack of flatness at high microscope magnification; *i.e.* the sample was often partly out of focus. Thus, instead of using the absolute signal to compose the mappings, it was found that better images could be obtained by using the ratio of selected bands. For points out of focus both bands decreased in the same manner but the ratio was invariant though subject to noise.

Results and discussion

A small pellet of equimolar sodium nitrate/potassium nitrate was placed on a gold foil dish in the LINKAM temperature-controlled hot-stage. Because of the small quantity of salt and the configuration of the LINKAM, the actual rate of solidification was quite high despite the slow rate at which the temperature ramp was set. Raman spectra using an approximate 2 µm diameter spot were obtained on this solid sample at various lower temperatures, both in cooling and heating modes. Representative spectra are shown in Fig. 2. At the higher temperatures the most intense (v_1) band appeared to be single, whereas at lower temperatures it split into two bands. The v_4 (~720 cm^{-1}) band and a number of minor bands were little changed with temperature, but the v_3 band (1390 cm^{-1}) though initially a single band was accompanied by two more slightly lower energy bands at lower temperatures.

A typical Raman mapping result is shown in Fig. 3. It clearly showed that there was considerable segregation of the components, although under the optical microscope polished surfaces were virtually featureless. The same segregation features were seen for other Raman mappings of this and other systems. Here, in Fig. 3, the two chemical components were gathered into rather irregular, probably very roughly spherical masses, of about 0.5 to 5 µm across, with compositions ranging from high in sodium nitrate to high in potassium nitrate, both with smaller concentrations of the other constituent, though without large areas approximating to equimolar mixtures.

The roughly circular areas seen in Fig. 3 may perhaps best be described as a "conglomerate" structure (to adapt the geological term). It is of some interest that Ubbelohde in his book *The Molten State of Matter*[56] used the word "conglomerate" to describe solid salt eutectics, though without citing any evidence or literature reference.

Some preliminary SEM studies[25] suggest the "ground" surface of a solid eutectic (NaNO$_3$/KNO$_3$) shows close packed roughly spherical masses also measuring up to 5 µm across. The cross sections found in this work could well arise from sectioning randomly through such close packed irregular sized spherical lumps.
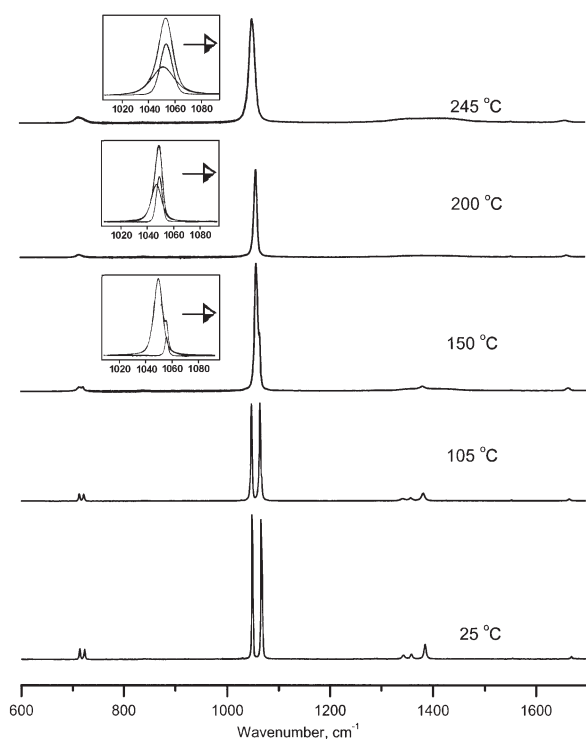
Fig. 2 Spectra of a 50 : 50 mol ratio NaNO₃/KNO₃ sample solidified on the LINKAM hot-stage and reheated. The top curve is for the molten drop.
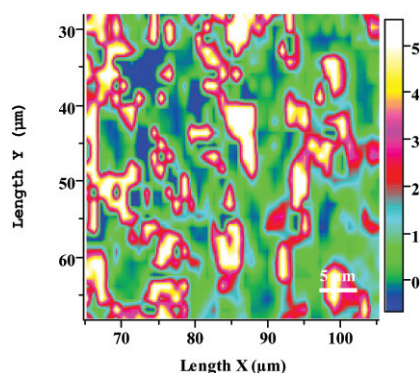

Fig. 3 Raman microscope mapping of a 50 : 50 mol ratio sample of NaNO₃/KNO₃. The sample was melted and solidified by pushing it out of the furnace at a rate of 5 mm h⁻¹. The Raman mapping was based on bands seen at ~1068 and ~1050 cm⁻¹, due to NaNO₃-rich and KNO₃-rich areas, respectively. The pixel size and spatial resolution were 1 μm, obtained with a 100 × objective, a 180 μm confocal hole, a 100 μm slit width, excited with 200 mW of 514.5 nm of Ar ion laser light. Each pixel was exposed twice for 1 s and averaged, followed by an automatic cosmic-ray spike-removal procedure in the software.

At room temperature a Raman map of a sample solidified on the LINKAM hot-stage was obtained (Fig. 4), which showed a 'conglomerate' eutectic structure of alternating sodium-rich and potassium-rich roughly rounded areas of up to 3 μm diameter. This 'conglomerate' structure consisted of smaller areas than was previously found in sections from a slow cooled sample (Fig. 3), largely because of the more rapid way of solidification.

On heating and cooling the drop sample in the LINKAM it was found that the spectra became stable in quite short times (*ca.* 20 min). At temperatures above 150 °C the main band became single but asymmetrical (Fig. 2), and could be resolved into two symmetrical bands which became progressively closer together. Indeed at temperatures below the melting point, where continuous solid solutions have been postulated, it was not possible to obtain a satisfactory Raman map from those two bands. However the two bands could still be clearly distinguished at these temperatures and even at just above the melting point (sample kept 5 °C above the melting point for 15 min), probably due to slow homogenisation because of the high viscosity. On cooling to room
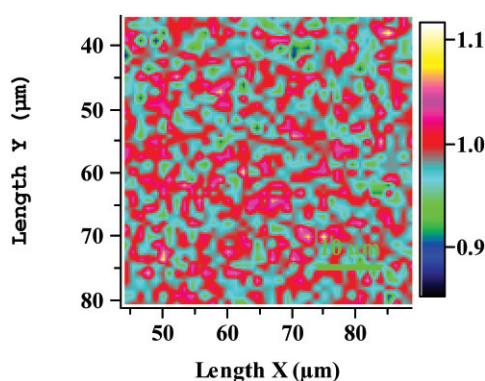

Fig. 4 Raman microscope mapping of a 50 : 50 mol ratio sample of NaNO₃/KNO₃, melted and solidified on the LINKAM hot-stage at a rate of 0.1 °C min⁻¹. The Raman mapping was carried out in the same way as in Fig. 3.

temperature when the apparently single band at high temperature reassumed its low temperature twin form, there was no indication of any new band which might be attributed to a homogeneous solid solution which might be supposed to have formed at around the melting point. A much smaller band could also be resolved from the apparent single band (at about 1046 cm⁻¹). This and the small band already noted at about 1030 cm⁻¹ are considered to arise from nitrate anions with one oxygen-18 atom. Wavenumber values at room temperature quoted by Brooker *et al.*[33,57,58] for pure nitrates are NaN¹⁶O₃ ~1068 cm⁻¹, NaN¹⁸O¹⁶O₂ ~1049 cm⁻¹, KN¹⁶O₃ ~1050 cm⁻¹, and KN¹⁸O¹⁶O₂ ~1030 cm⁻¹.

A band position wavenumber *vs.* temperature plot, showed a change of slope at around a temperature reading of 125 °C for the "1030", "1050" and "1070" bands suggesting a change of structure, but the true temperature of change was somewhat lower since the equimolar mixture apparently melted at 240 °C according to the thermocouple in the LINKAM. However, the fact that two bands persisted up to the melting point and reverted to original values on cooling, and after refocusing on a Na-rich area, or alternatively on a K-rich area, the two Raman bands showed that both sodium-rich and potassium-rich areas existed and that a single solid solution was not formed.

Further support for this conclusion was obtained when Na-rich and K-rich areas were picked out in the slow cooled (Fig. 3) samples at room temperature and spectra obtained from both areas at temperatures up to just below, but not above, the melting point on heating. These showed similar features to the samples cooled in the LINKAM (Fig. 2) but with a small but consistent shift in wavenumber towards either the pure sodium nitrate band or the pure potassium nitrate band, respectively. Cooling such samples from below the melting point to room temperature, caused the bands to return to their original positions over 60–90 min with the formation of isopiestic points (Figs. 5 and 6). This reversal was so fast at room temperature as not to be attributable to the diffusion of cations from a continuous solid solution into separate sodium-rich and potassium-rich areas, and therefore provided additional evidence for the alternative eutectic theory.

Besides the change of slope noted above, it was found that the "1340" and "1360" bands had disappeared at around 125 °C, giving more support to the suggestion of a phase change around 115 °C which is close to the phase change earlier suggested by the earlier authors[51,52] and also fairly close to the constant temperature eutectoid line proposed by Kofler[1] at 105°C, though the heavily curved sub-solidus line also proposed by him was not supported. In addition the sub-solidus lines suggested by Greis *et al.* were not supported by these results, but they are in any case likely to be less accurate because they were derived from DSC measurements obtained at heating and cooling rates of 10 °C min⁻¹ which the present results show is much too fast for even an approximate approach to equilibrium to be established and this is illustrated by the considerable differences between the phase diagrams they derived from their heating and cooling results. Xu and Chen[45] somewhat perversely
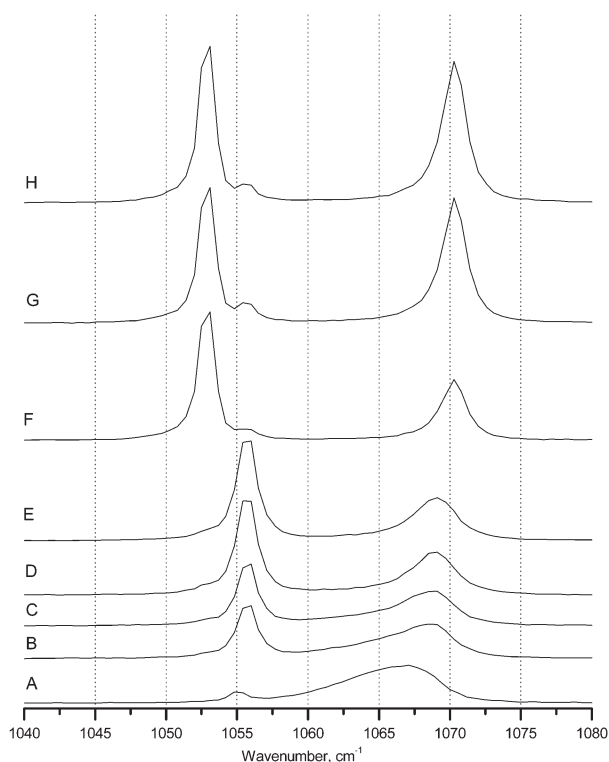
Fig. 5 Spectra of Na-rich area of a 50:50 mol ratio sample of NaNO$_3$/KNO$_3$ cooled to 22 °C after heating to 220 °C. Time increasing from curve A to curve H (60 min).
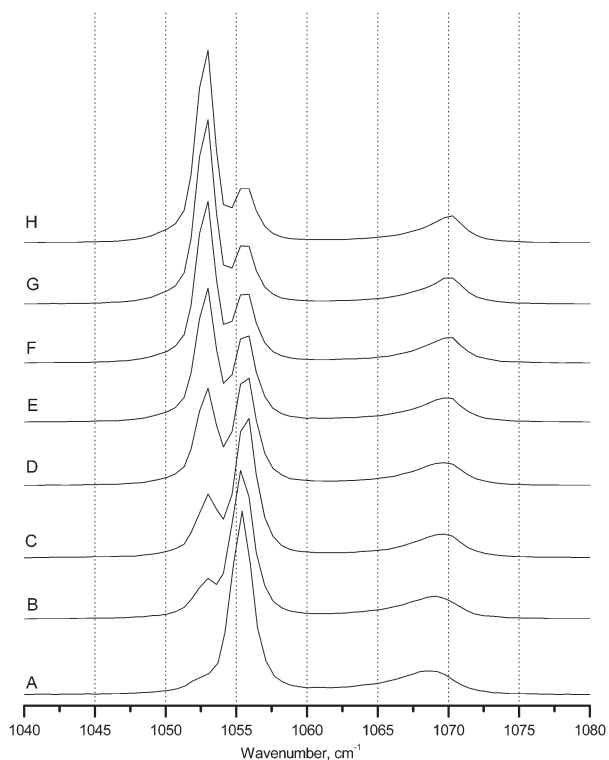

Fig. 6 Spectra of K-rich area of a 50:50 mol ratio sample of NaNO$_3$/KNO$_3$ cooled to 22 °C after heating to 220 °C. Time increasing from curve A to curve H (90 min).

interpreted their Raman results in terms of the cooling diagram which is almost certainly less accurate.

By careful adjustment of the notch filter, used to reduce the light scattered by the Rayleigh process, the low energy lattice modes were examined, showing a band of moderate intensity at room temperature at 189 cm^{-1} (Fig. 7, curve A) and a weak band at around 126 cm^{-1}. These bands showed small shifts to slightly lower frequencies at about 105 °C (Fig. 7, curve B). At higher temperatures, at 150 and 175 °C (curves C and D), new bands
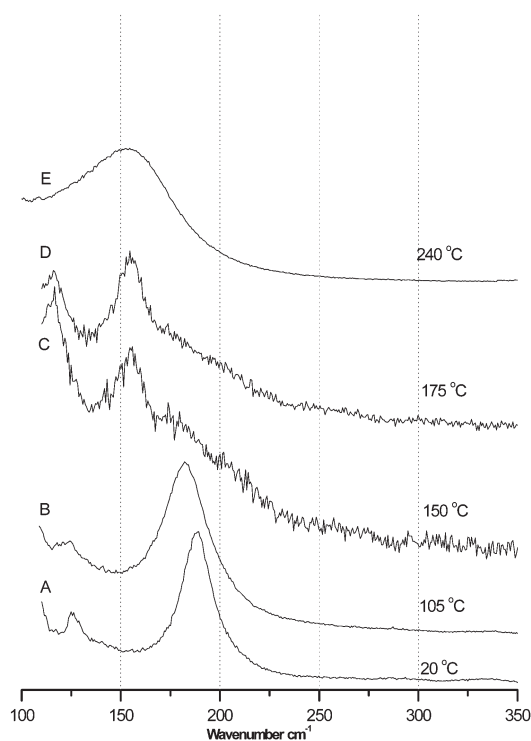

Fig. 7 Spectra of a 50:50 mole ratio sample of NaNO$_3$/KNO$_3$ in the low wavenumber range at increasing temperatures (for curves C and D the focusing was not optimal).

probably due to the KII → KI transition were seen at 158 cm^{-1} and around perhaps 120 cm^{-1} (perhaps deformed somewhat by the notch filter). Bands at these positions have also been observed by Xu.[48] A broad band at about 155 cm^{-1} remained in the melt spectrum at 240 °C (Fig. 7, curve E).

Conclusion

Abrupt changes in slope in the band maximum wavenumber position and wavenumber-temperature gradients of five Raman bands of 50:50 mol% NaNO$_3$/KNO$_3$ indicated a solid state transition at around 115 °C. The persistence up to the melting point of bands close to those of the pure nitrates, with small shifts probably due to small amounts of solid solution, indicated that a continuous solid solution across the whole phase diagram was not formed, as has been widely thought. Indeed the speed with which the band shifts with increasing temperature were reversed on cooling to 22 °C indicated the hypothesis that diffusion of ions from a high-temperature solid solution, back to a conglomerate structure of separate Na-rich areas and separate K-rich areas was not credible. Thus the long standing assumption that the sodium nitrate–potassium nitrate system forms continuous solid solutions, apparently in defiance of the usual rule of too dissimilar ion sizes and of recent measurements indicating an eutectic structure, must now be abandoned in favour of an ordinary eutectic structure. This is the position that was held for the first 50 years of investigation of this system, which was then abandoned as a result of inaccurate experimental results.

Finally it may be said that the theory of solid solution for inorganic compounds has been developed using simple halides and oxides as models, where the ions can safely be considered as spherical. It should therefore not be too much of a surprise to find that disc shaped nitrate ions do not necessarily follow all the generalisations and rules derived for purely spherical ions.

Acknowledgements

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