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$NaNO_2 + NaNO_3$ Phase Diagram: New Data from DSC and Raman Spectroscopy

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The binary phase diagram of sodium nitrite and sodium nitrate is currently not well-understood because four earlier determinations of this binary system resulted in considerably different conclusions. Two works classify the system as eutectic and two as a continuous solid solution type, together with different sub-solidus curves. New Raman measurements and differential scanning calorimetry data on solidified mixtures of different compositions have provided support for a simple eutectic diagram with a solidus at 230 °C ranging from 0.25 to 0.80 in mole fraction of sodium nitrate. A sub-solidus transition was detected close to 183 °C and a second one close to 160 °C. The latter was considered to be related to the nitrite component and probably arose from the ferroelectric to antiferroelectric or paraelectric transition of sodium nitrite. The change of slope of the maxima of some Raman lines with temperature also gave support to these transitions.

Introduction

Phase diagrams are extremely useful, summarizing as they do an immense amount of information. However, when the past literature contains two or more determinations on the same system that differ fundamentally, a dilemma of choice occurs; which diagram, if any, is correct? It is unsatisfactory and unscientific to merely choose the most recent publication because our scientific ancestors were not necessarily inaccurate, nor are more contemporary workers always correct. Some further data are then desirable, which might serve to test certain of the earlier observations and eventually allow a more correct phase diagram to be produced.

Such problems can occur even with binary systems made up of single, well-known salts, for example, sodium nitrite and sodium nitrate. In the latter case, the system has been the subject of several investigations, four of which were examined in sufficient detail to merit consideration here (i.e., Bruni and Meneghini[1], Bergman et al.,[2] Kosyakov et al.,[3] and Zamaly and Jemal;[4] see Figure 1panels A to D, where the original published phase diagrams are reproduced with permission). These were largely determined by thermal measurements. However, though the position of the liquidus may be readily measured by this technique, the position of the solidus and particularly of any sub-solidus curves are more difficult to determine. The latter seems not to have been even considered by some investigators.

With the present binary salt system of $NaNO_2$ and $NaNO_3$ although each of the diagrams are really quite dissimilar to the others, there is fairly general agreement about the broad position of the liquidus, but with various differences, for example, the peritectic at 276 °C of Kosyakov et al.[3] and a possible transition only (2 to 4) °C above the eutectic temperature.[2,4]

Moreover the broad assignment of this system as a eutectic or as an example of continuous solid solutions is not agreed upon with Bruni and Meneghini[1] and Kosyakov et al.[3] considering it the latter while the investigations of Bergman et al.[2] and Zamaly and Jemal[4] labeled this system as an eutectic. As a consequence, there is disagreement as to the extent of the horizontal part of the solidus and thus of the consequential gradients of the parts of the solidus joining this horizontal to the melting points of the pure salts.

In addition the solid-state transition at 157 °C claimed by Bergman et al.[2] as that of sodium nitrite is probably related to the transformation of the pure salt, given as 165 °C by Satyamurthy et al.[5] and as 162 °C by Hartwig and others.[6−8] Bergman et al.[2] did not assign the second transition found at 175 °C, but Zamaly and Jemal[4] reported a 1:1 compound only stable between 177 °C and 229 °C for which they determined an orthorhombic structure by high-temperature X-ray diffraction.[9]

Experimental Section

Chemicals. Analytical grade high-purity sodium nitrate and sodium nitrite (Merck) were dried, and eight different mole ratios were made up by mass, mixing the dried salts and melting in a furnace prior to examination.

DSC. The melting temperatures and enthalpies of $NaNO_2$ + $NaNO_3$ as well as the eight mixtures of the salts were determined by differential scanning calorimetry (DSC) using a Seiko DSC320 instrument. The measurements were performed up to 350 °C using air as the purge gas (100 mL/min) with a heating ramp of 5 °C/min. Sample size was approximately 4 mg. The melting points were determined as peak temperatures. The temperature and enthalpy were calibrated using melting of pure Sn (99.999 %, $t_m = 232.0$ °C) and pure Pb (99.9999 %, $t_m =$ 327.5 °C) samples. Values are given as the average of three determinations.

Raman Spectroscopy. Spectra were measured with a DILOR-XY spectrometer with both macro- and microscope entrances. Spectra were excited with Ar^+ ion laser light (about 1 W of power at a wavelength of 514.5 nm). The Rayleigh scattering was mostly filtered off, by use of a Kaiser holographic

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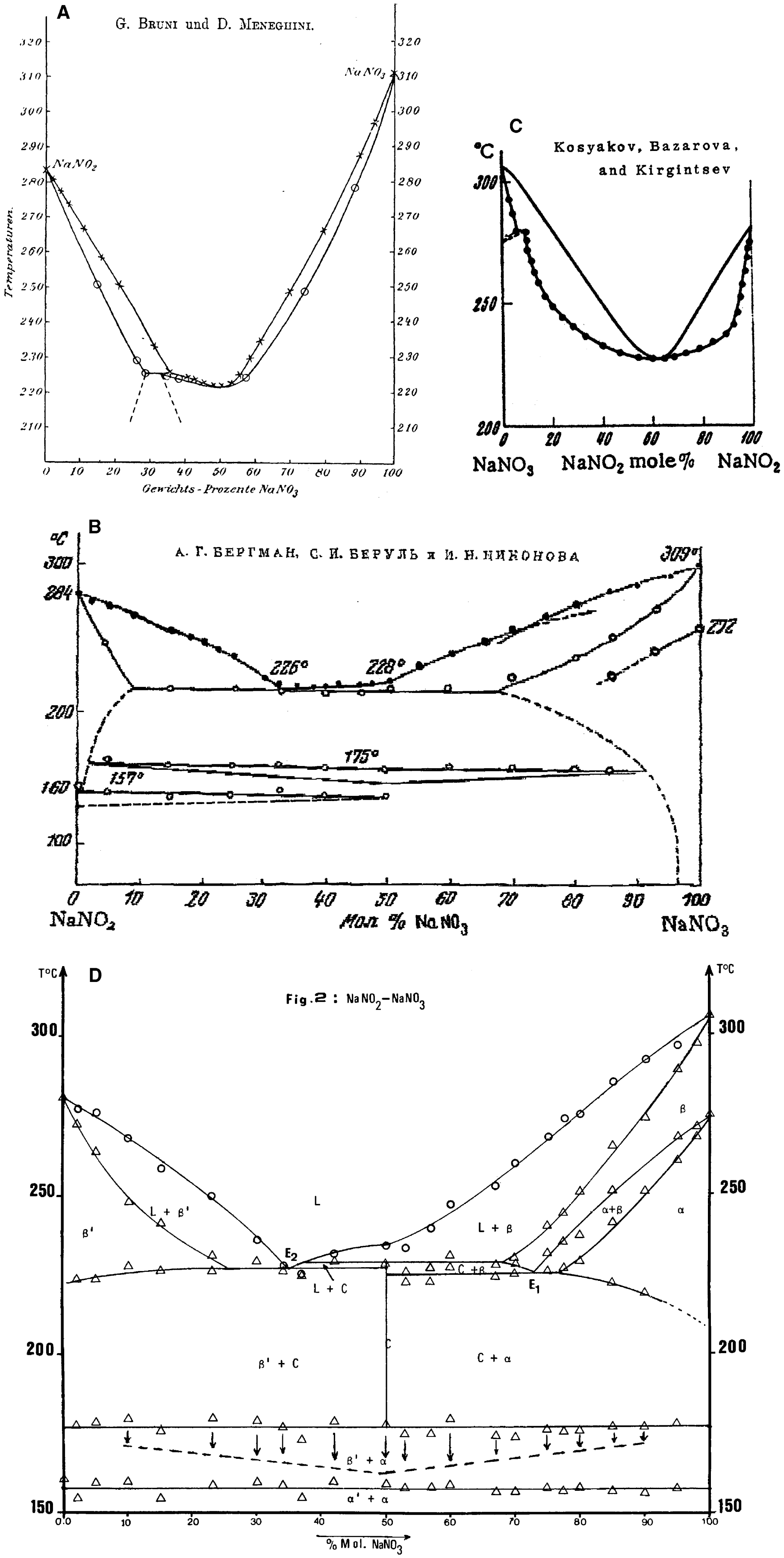

Figure 1. Previous determinations of the $NaNO_2$ + $NaNO_3$ phase diagram from the original papers: A, from Bruni and Meneghini;[1] B, from Bergman et al.;[2] C, from Kosyakov et al.[3] (reprinted with permission from Plenum Pulishing Corp.); and D, from Zamaly and Jemal[4] (reprinted with permission from *J. Soc. Chim. Tunis.*).

Table 1. Thermic Events of the Sodium Nitrite + Sodium Nitrate System According to This DSC Study and the Literature[11−17]

	$NaNO_2$ pure component		$X(NaNO_3) = 0.50$		$NaNO_3$ pure component	
endothermic event	t/°C	ΔH/(kJ/mol)	t/°C	ΔH/(kJ/mol)	t/°C	ΔH/(kJ/mol)
solid state transition	164.6 ± 1 (max)	1.09 ± 0.1	159.4 ± 1 (max)	0.54 ± 0.1	275.7 ± 1 (max)	2.09 ± 0.1
	164[11,12]				276[11,12,14]	
	165.95 heating[15]	1.76[11,12]			276.5[13]	0.73 ± 0.63[11,12]
	~167[16]	(3.7[13])			276.85 heating[15]	(3.9[14])
		17.39[15 a]				19.77[15 a]
solid state transition			183.6 ± 1 (max)	6.95 ± 0.1		
melting	282.9 ± 1 (max)	14.57 ± 0.1	230.5 ± 1 (max)	9.66 ± 0.1	307.8 ± 1 (max)	14.74 ± 0.1
	281[11,12]				307[11,12,16]	14.86[11,12]
	279[16]	13.98[11,12]				14.6[14]
		15.3[16]				15.34 ± 0.18[17]

[a] Possibly the sum of the solid-state transformation and the melting.

SuperNotch-Plus filter (with a cutoff of approximately 200 cm^{-1}). The Raman light was dispersed onto a liquid nitrogen-cooled CCD detector by use of a grating with 1800 lines per millimeter in a single spectrograph (800 mm focal length) or in another spectrograph with a much shorter focal length and a grating with 600 lines per millimeter. In both cases, the slits were set to 100 μm corresponding to a spectral resolution of about (4 to 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 sometimes obtained. 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 color scale was 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 elsewhere.[10]

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

The DSC study showed each of the pure components to have two endothermic events on their heating curves (see Figure 2A,B and also Table 1). The first in each case was a solid-state transition reported in the literature at 164 °C with an enthalpy change of (1.76 ± 0.63) kJ/mol for sodium nitrite and 276 °C with (0.73 ± 0.63) kJ/mol for sodium nitrate,[11,12] although earlier workers gave higher values (i.e., (3.7[13] and 3.9[14]) kJ/mol). On the DSC curves, the enthalpy changes were (1.09 ± 0.1) kJ/mol and (2.09 ± 0.1) kJ/mol, respectively, while the onset temperatures for these transitions were (154 ± 1) °C for sodium nitrite and (257 ± 1) °C for sodium nitrate, with the maxima at 164.6 °C and 275.7 °C, respectively (± 1 °C). The onset temperatures for the *melting* endotherms were at (263 ± 1) °C for sodium nitrite and at (299 ± 1) °C for sodium nitrate with enthalpies of (14.57 ± 0.1 and 14.74 ± 0.1) kJ/mol, while the temperatures of the maxima were (282.9 ± 1 and 307.8 ± 1) °C, which compare with literature values of 281 °C, 13.98 kJ/mol and 307 °C, 14.86 kJ/mol, respectively.[11,12] Evidently for the particular experimental procedures adopted here, the maximum temperatures were considerably closer to the literature values and therefore considered the more accurate and were used for the endothermic events in the binary system.

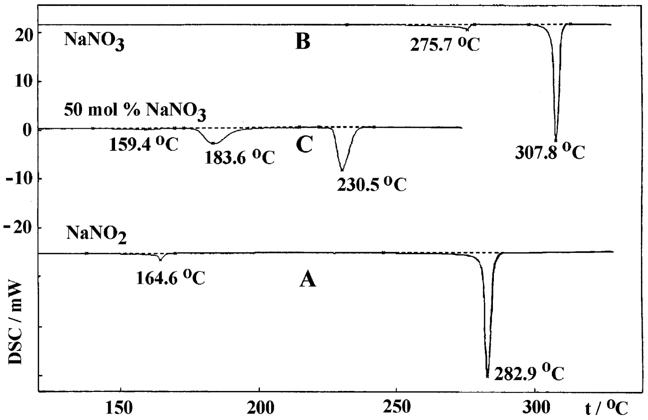

Figure 2. Differential scanning calorimetry curves: A, for pure $NaNO_2$; B, for pure $NaNO_3$; and C, for the equimolar mixture of $NaNO_2$ and $NaNO_3$.

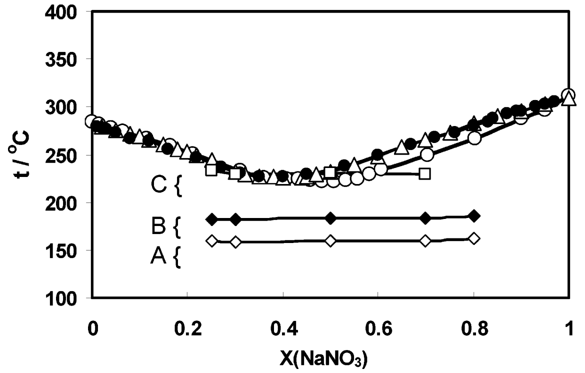

Figure 3. Revised $NaNO_2$ + $NaNO_3$ phase diagram: curves A−C this work. Curve A is the ≈159 °C sub-solidus (◇). Curve B shows the ≈183 °C sub-solidus (◆). Curve C is the ≈230 °C solidus (■). For comparison, liquidus curves from literature are also included: ●, ▲, and ○ from refs 1 to 3, respectively.

Eight binary mixtures of sodium nitrite and sodium nitrate of composition from 0.25 ± 0.01 to 0.80 ± 0.01 in $X(NaNO_3)$ in our experiments showed three endothermic events in the heating curves (see, e.g., Figure 2C) with the maximum temperature of the lowest one averaging (159 ± 1) °C over the whole of this range (see Figure 3), although with decreasing enthalpy toward the mixtures richer in nitrate (see Figure 4A, in which the size of the enthalpy change at each composition is plotted), thus suggesting that the transition would be undetect-

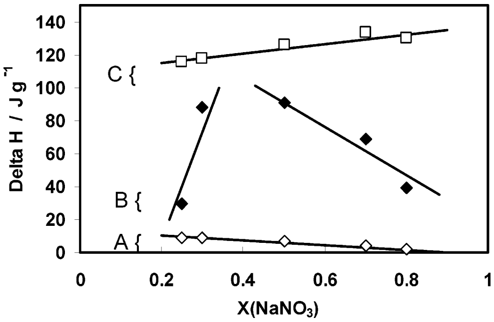

Figure 4. Enthalpy change values for the $NaNO_2 + NaNO_3$ phase diagram found in this work. Curve A shows the 159 °C sub-solidus transformation values (◇). Curve B shows the 183 °C sub-solidus values (◆). Curve C shows the ≈230 °C solidus values (■).

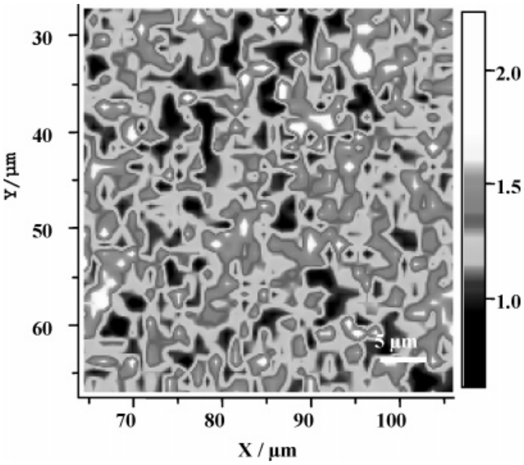

Figure 5. Raman mapping of a sample of $X(NaNO_3) = 0.41$. The sample was melted and solidified in contact with a heat conducting aluminum tube at a cooling rate of 0.1 °C/h in the stationary furnace. The solid was sectioned at 90° to the tube axis and ground. The Raman mapping was based on 40 × 40 spectra providing the intensity ratio for the bands seen at ≈1329 cm^{-1} ($NaNO_2$) and ≈1068 cm^{-1} ($NaNO_3$). White areas are mostly $NaNO_2$, and dark areas are mostly $NaNO_3$. 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.

able above $X(NaNO_3)$ = about 0.85 and that it derived from the nitrite component. This is satisfactorily close to the temperature of 157 °C given by Bergman et al.,[2] who however considered the transition to extend only to a $X(NaNO_3)$ of about 0.50.

The second endotherm of the mixtures did not vary much with composition, averaging a temperature of 183 °C for all the compositions, but with enthalpies that increased in both directions toward the minimum melting point (eutectic temperature; see Figure 4B). This is much like the second transition given by Bergman et al.[2] The third melting endotherm of our thermograms averaged at (230 ± 1) °C, indicating a horizontal solidus extending at least from (0.30 ± 0.01 to 0.65 ±0.01) in $X(NaNO_3)$ with a reasonably constant melting enthalpy (see Figure 4C). Bergman et al.[2] and Zamaly and Jemal[4] have proposed a horizontal solidus extending from (0.06 to 0.68) and (0.23 to 0.73), respectively, in $X(NaNO_3)$ while Kozyakov et al.[3] reported a considerably curved solidus, and Bruni and Meneghini[1] showed an undulating solidus.

It was considered in this work that the temperature of the end of the third endotherm was determined by the thermal conductivity of the molten salts; therefore, it was *not* an indication of the liquidus as has sometimes been claimed. However because of the relative agreement of the earlier publications,[1,2] the liquidus was accepted as that determined by these previous investigations, who despite their other disagreements do put forward broadly the same liquidus position, within ± 3 %, which is likely to be the experimental uncertainty. Their values are therefore also plotted in Figure 3. Thus the phase diagram resulting from the present work is that of an eutectic system and in broad terms resembles more those of Bergman et al.[2] and Zamaly and Jemal[4] rather than those of the other two investigations, who reported continuous solid solutions.

Further support for the system being a eutectic arises from a room temperature Raman mapping of a slowly cooled, sectioned,

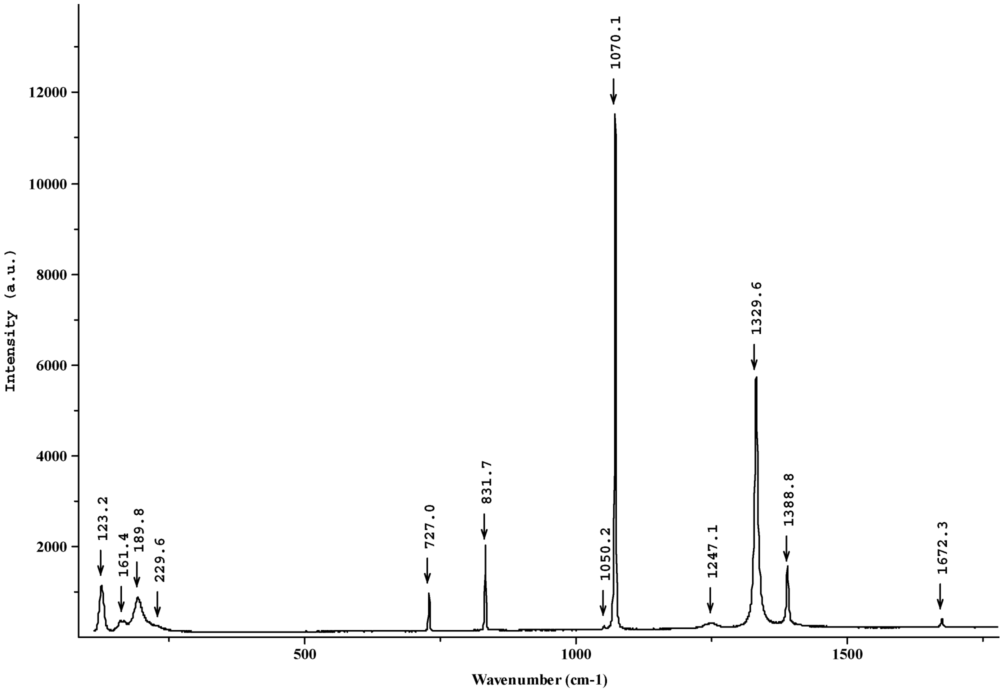

Figure 6. Raman spectrum (intensity in arbitrary units vs wavenumber/cm^{-1}) of a sample of $X(NaNO_3) = 0.41$ at room temperature, 22 °C. Obtained with a pre-double monochromator filter, a laser power of 800 mW at 514.53 nm, and a counting time of 30 s × 2. The microscope objective was 50×.

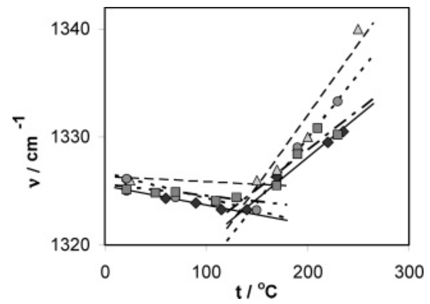

Figure 7. Plot vs temperature of maxima positions of the Raman band at about 1340 cm^{-1} of the following $NaNO_2/NaNO_3$ mole ratios: —, ◆, 90/10; ▲, ···, 50/50; —•—, ●, eutectic; - - -, ■, 30/70. Trend lines are included for each composition.

and polished mixture of X($NaNO_3$) = 0.41 ± 0.01 (Figure 5), which showed a conglomerate structure of alternating, roughly spherical, grains of nitrite-rich and nitrate-rich solid solutions[18] that would be formed as the molten mixture separated at the eutectic temperature into these components. On further lowering of the temperature, the 1:1 compound forms,[9] and this gives rise to the light grayy areas shown in Figure 5. However because this is a solid-state reaction, it does not go to completion at the cooling rate used. In contrast to this Raman map, the eutectic mixture would have shown a uniform composition of X($NaNO_3$) equal to 0.41 ± 0.05 had it arisen from the cooling of a system of continuous solid solutions. Any subsequent separation of phases at lower temperatures in the solid state, as postulated by Bruni and Meneghini,[1] would have been too slow a process to give the conglomerate structure found here. Furthermore, there was no indication from Raman spectroscopy of a structural change at any temperature near the melting point.

However by Raman spectroscopy on a homogeneous solid of X($NaNO_3$) equal to 0.41 ± 0.01 (the eutectic), at a series of temperatures up to the melting point, we found further evidence of a lower temperature solid-state transition. A typical spectrum is shown in Figure 6. The band at ≈1330 cm^{-1}, attributed to the symmetric bending vibration of the nitrite anion, when plotted against temperature showed discontinuous changes in slope between 150 °C and 160 °C, as did the same band for the 0.90/0.10, 0.50/0.50, and 0.30/0.70 nitrite/nitrate mole ratio compositions (Figure 7 and Table 2). This obviously gives support to the presence of the first solid-state transition. The other bands in Figure 6 showed more regular changes in position with temperature. The higher temperature solid-state transition also received some, but not conclusive, support (see later). These results, including the solidus previously determined by Bergman et al.[2] and considered to be the most reliable of the previous results, are collected in a new phase diagram (Figure 8). The discontinuity in the liquidus given by Bergman et al.[2] (≈3 °C above the eutectic temperature) is proposed as a peritectic arising from the 275 °C transition of pure sodium nitrate (see Figure 1C,D). The exact positions of the these sub-solidii points are not known (they are only given graphically in their paper), but they are represented as accurately as possible in Figure 8.

The transition at 159 °C extending from the sodium nitrite side is probably associated with that found by Hartwig et al.,[6] who studied the changing position of the Raman bands of pure sodium nitrite with temperature and found a distinct change of slope of the plot for the (830 and 1240) cm^{-1} bands centered at the ferroelectric to paraelectric transition (Curie temperature l63 °C, Neel temperature 164 °C), though the change began some 5 °C lower and terminated about 5 °C higher, somewhat reminiscent of the two transitions found here at more dissimilar temperatures by DSC in the nitrite/nitrate system. The 1330 cm^{-1} band (also attributed to the symmetric bending vibration of the pure nitrite) showed much less change of frequency though the line width greatly increased.[5] It is suggested that this transition of pure sodium nitrite gives rise to an eutectoid in the two-component system, indicated here by lines beginning at 159 °C, but because of lack of data the situation is not very clear. Satyamurthy et al.[5] however reported their ferro- to para-electric transition peak at a temperature of 165 °C, and Kamimoto[16] has published a curve that shows a transition at around 167 °C.

The 183 °C transition found here is probably the same as those reported previously at 175 °C[3] and 177 °C[4] (the difference perhaps to be attributed to slighly less pure components). However this transition with a maximum enthalpy found to be at or near the 1:1 composition does agree well with the enthalpy changes found by Zamaly and Jemal,[4] which can be attributed to the orthorhombic pseudohexagonal 1:1 compound $Na_2(NO_3\text{-}NO_2)$ found with X-ray powder diffraction data obtained at 200 °C by Zamaly and Jemal.[4] However, the decomposition of this

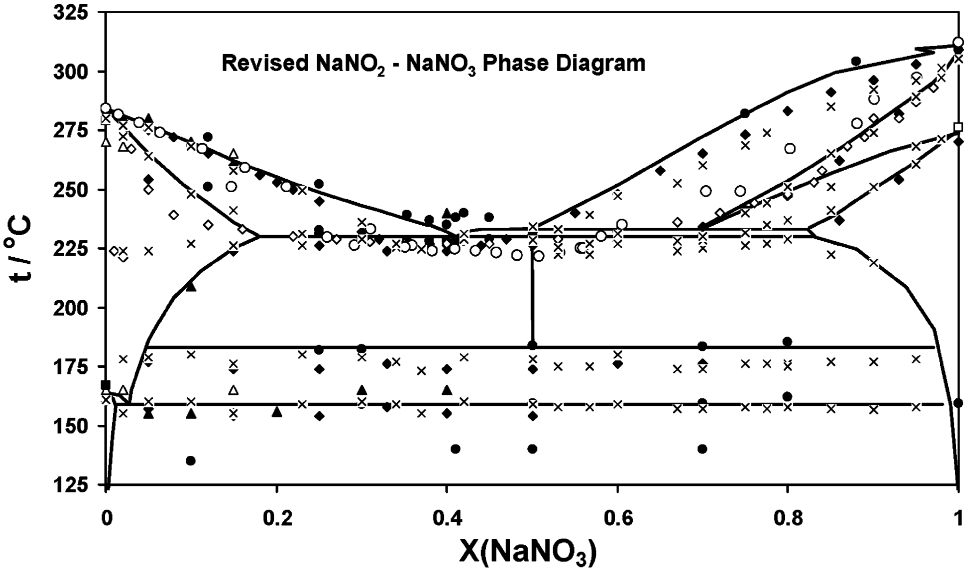

Figure 8. Revised $NaNO_2 + NaNO_3$ phase diagram. Code: ○, Bruni and Meneghini;[1] ◆, Bergman et al.;[2] ◇, Kosyakov et al.;[3] ×, Zamaly and Jemal;[4] △, Satyamurthy et al.;[5] ■, Kamimoto;[16] ▲, Phatak and Darshane;[19] ●, this work.

Table 2. Experimental Transition Temperatures (in °C) Obtained in This Work in Dependence of Composition

composition, X($NaNO_3$)	solid-state transition *t*/°C	solid-state transition *t*/°C	solidus transition *t*/°C	liquidus transition *t*/°C
0.00			282.9	284
0.10	≈140[a]			
0.12			251	272
0.25		183	231	
0.25		181.7	232.6	252
0.30	158.8	182.1	229.1	
0.35			228	239
0.38			228	237
0.40			228	235
0.41	≈145[a]		228	238
0.42			228	240
0.45			229	238
0.50	≈145[a], 159.4	183.7	230.5	
0.70	≈145[a], 159.5	183.4	230	
0.75			241	282
0.80	162	185.4		
0.88				304
1.00	159.2		275	309

[a] Temperature determined by Raman spectroscopy (Figure 7).

postulated compound at around (177 to 183) °C shows this compound to have very little stability. Accordingly, the driving force for the formation is not large, and the phase therefore would be formed even more slowly as the samples were cooled below 230 °C.

Additional evidence that we have noted for the 1:1 compound formation is the observation that on slow cooling below 230 °C, clear and completely transparent crystals were formed, which suddenly became an opaque white solid at around 183 °C.

By contrast with the 160 °C transition, that at 183 °C had only an inconsistent effect on the Raman bands. Only one plot out of five showed breaks in the frequency versus temperature curves. These were the eutectic composition ($X(NaNO_3) = 0.41$) for the band at 1065 cm^{-1}, the $X(NaNO_3) = 0.10$ composition for the bands at (1330, 1260 and 725) cm^{-1}, and the $X(NaNO_3) = 0.70$ composition for the bands at (1065 and 825) cm^{-1}. The other reported transitions at 205 °C by Satyamurthy et al.[5] and at around 210 °C by Phatak and Darshane[19] for some $NaNO_2/NaNO_3$ mixtures, $X(NaNO_3) = 0.10$ or 0.20, had no support from our thermal or Raman measurements and were therefore not used in drawing the revised phase diagram (Figure 8).

Acknowledgment

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