June 2009 Volume 5 Issue 3

Materials Science

Trade Science Inc.

An Indian Journal

Full Paper

MSAIJ, 5(3), 2009 [214-217]

Thermal analyses of $NaNO_3$-$RbNO_3$ pseudo-binary system-differential scanning calorimetry

A.Sadananda chary*, M.V.Madhava Rao, S.Narender Reddy

[1]Department of Physics, Osmania University, Hyderabad, Andhra Pradesh, (INDIA)

E-mail : chary_as@yahoo.co.in

Received: 24th February 2009 ; Accepted: 1st March, 2009

ABSTRACT

The differential scanning calorimetry (DSC) in $Na_xRb_{1-x}NO_3$ pseudo-binary system are presented by varying x from 0 to 1. The formation of an intermediate compound and its effect on the phase transitions of $RbNO_3$ is explained in terms of redistribution of energies involved in various transitions. Corresponding phase diagram is constructed. DSC peak at about 173 C with eutectic composition 0.46 (Na mole fraction) has been attributed to the formation of a congruently melting compound $NaRb(NO_3)_2$. X-Ray Diffracto grams (XRD) indicate the formation of this new compound. DSC peak corresponding to the melting of this compound and XRD lines related to this compound are found to grow with x until it reaches the eutectic composition.

KEYWORDS

Eutectic;
Phase diagram;
Structural phase transition;
Endotherm.

INTRODUCTION

Among all the alkali nitrates, $RbNO_3$ has three distinct structural phase transitions at high temperatures designated as IV-III, III-II, and II-I as we go from room temperature. Of these IV-III (trigonal to CsCl cubic) and II-I (rhombohedral to NaCl cubic) are transitions going from a lower to higher symmetry phase. Contrary to these, we have a sudden fall of conductivity noticed during III-II transition (CsCl cubic to rhombohedral). In an attempt to understand more about the mechanisms involved in these transitions we have decided to study the effect of $NaNO_3$ in $RbNO_3$.

Several alkali nitrates have been studied, with different combinations, in the form of solid solutions[1], glass forming ionic melts[2], eutectics such as $NaNO_3$-KNO_3[3,4], $LiNO_3$-KNO_3[5] and mixed crystals $RbNO_3$ -$CsNO_3$[6]. None of them has considered $RbNO_3$ and $NaNO_3$ in the form of eutectic system. In the present study we attempt to do this. Sharp discontinuities at structural[7] phase transition temperatures were noticed in conductivity[8], dielectric constant[9] etc.. $NaNO_3$ was chosen as the second component from the group of alkali nitrates which is devoid of any major structural phase transition except a very gradual lambda transition at about 272^0C [10]. When two isovalent ionic substances are mixed they may form solid solutions in the whole range or up to certain value of x. As per Osmiable et al.[1] mixing could result in the formation of an intermediate compound $NaRb(NO_3)_2$ coexisting with the individual components in the form of a eutectic mixture. This newly formed compound in the eutectic has homogeneous phase with fixed melting point that is different from those of the constituents. In addition to seeing the effect of this newly formed compound on the melting points, structural phase transitions may also get modified.

EXPERIMENTAL

The eutectic system $Na_xRb_{1-x}NO_3$ was prepared by the following method. The required masses of salts were accurately weighed and dissolved in double distilled water (both the nitrates are highly soluble in water) and the solution thus obtained was warmed to about 50^0C. The powder obtained was ground in an agate mortar and was sieved through mesh (No.240). The quantity of the sample taken is 5 mg and the data was recorded on Du Pont 9900 thermal analyzer with constant rate of heating (10^0C per minute) and some traces were taken on Du Pont 1090 thermal analyzer. The energies of endotherms were recorded automatically by the former instrument, where as they were estimated by measuring the area under the curves using planimeter in the latter. X-Ray diffractograms for various compositions of the system were taken at room temperature on Phillips PW 1730 using CuKα radiation.

RESULTS AND DISCUSSION

Figure 1 shows the DSC curve for pure $RbNO_3$ with endotherms corresponding to IV-III, III-II, II-I transitions and melting at 164^0C, 221^0C, 283^0C and 310^0C respectively. Figures 2 to 6 show DSC for x = 0.05, 0.08, 0.37, 0.46, and 0.87 in the eutectic system of $Na_xRb_{1-x}NO_3$. Figure 7 is the DSC curve for x = 1 (pure $NaNO_3$) which shows no major structural phase transition except at about 272^0C, where it undergoes a very gradual second order phase transition (10). Figure 2 (x = 0.05) exhibits some additional features with respect to those of pure $RbNO_3$ (Figure 1). It can be seen here that IV-III transition is not affected, but III-II is broadened while melting peak merges with II-I transition. However, the melting point of the excess $RbNO_3$ has been lowered and broadened which is known to happen in a eutectic system[11]. There is another distinct endotherm at about 173^0C with energy equal to 12.73 J/g corresponding to the newly formed compound termed as congruently melting compound $NaRb(NO_3)_2$. Figure 3 for x=0.08, reveals that the additional peak observed at 173^0C becomes sharper and the melting point decreases, as a result II-I transition is not observable. Figure 4 (x = 0.37) indicates the obvious missing of III-II transition and only the melting peak of $NaRb(NO_3)_2$ is noticed. IV-III transition (164^0C), be-

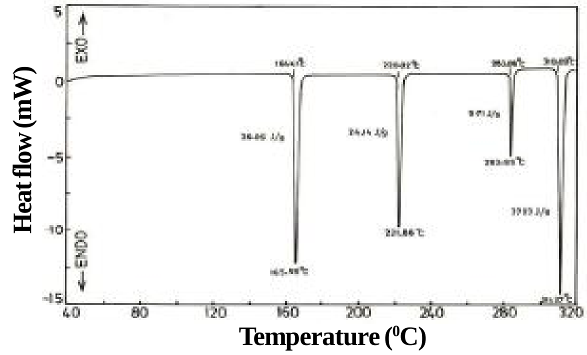

Figure 1: DSC curve for pure $RbNO_3$

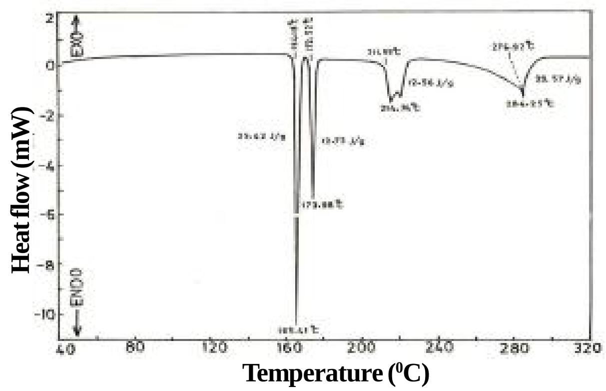

Figure 2: DSC curve for $Na_xRb_{1-x}NO_3$ with x = 0.05

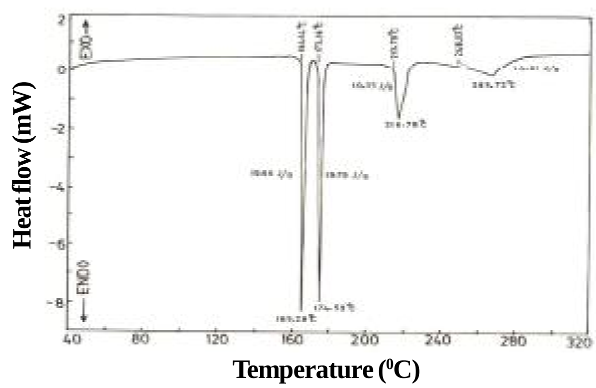

Figure 3: DSC curve for $Na_xRb_{1-x}NO_3$ with x = 0.08

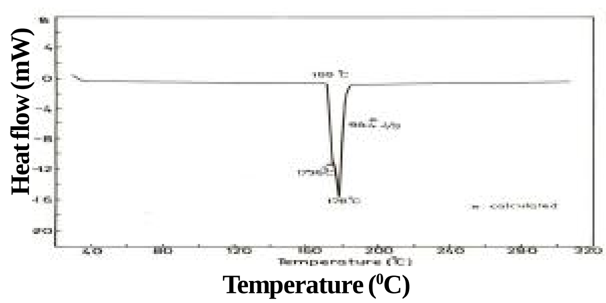

Figure 4: DSC curve for $Na_xRb_{1-x}NO_3$ with x = 0.37

Full Paper

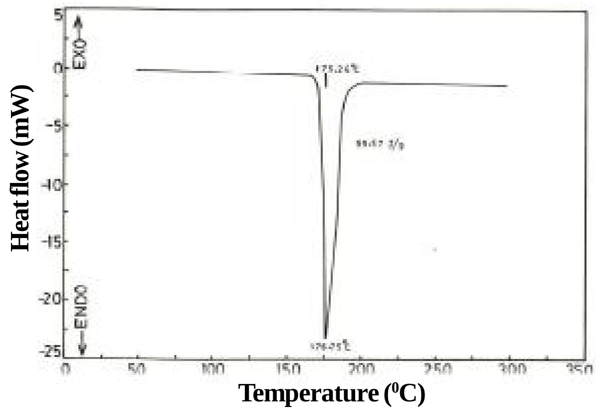

Figure 5 : DSC curve for $Na_xRb_{1-x}NO_3$ with x = 0.46

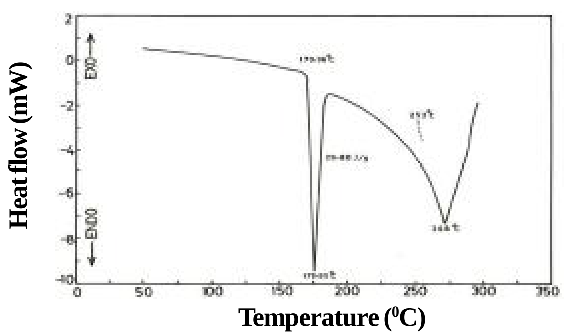

Figure 6: DSC curve for $Na_xRb_{1-x}NO_3$ with x = 0.87

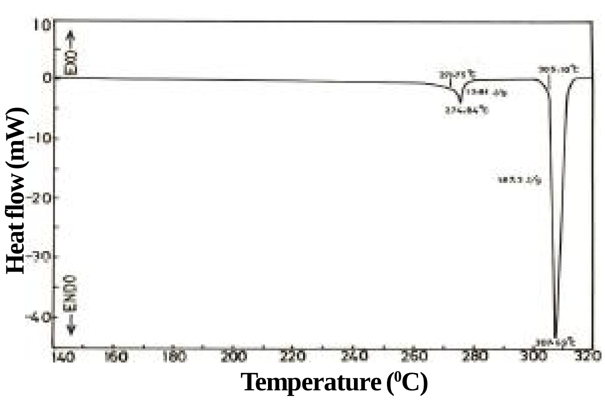

Figure 7: DSC curve for pure $NaNO_3$

ing very close to this peak(173^{0}C), can be seen as a shoulder (shown with arrow mark) since the two peaks are not clearly resolved. The energies for all these compositions were recorded by the instrument itself while that for x = 0.37 was calculated from the area measured using planimeter. Figure 5, for x = 0.46, has a special significance as it has only one peak. This results is in accordance with Hopkin's[12] phase diagram showing the eutectic near 0.45, which seems to be only a rough sketch. Finally, Figures 6 and 7 show DSC for x=0.87 and pure $NaNO_3$ which are on the other side of the eutectic composition. They show the melting endotherms of excess $NaNO_3$ at about 253^{0}C and 305^{0}C, latter being the melting point of pure $NaNO_3$.

TABLE 1 gives the transition temperatures (onset values) and energies involved in each of them. With the help of the above results (taking onset temperatures) we have constructed a phase diagram for this system n the lines of Wiedemann[13]. The energies associated with melting of $NaRb(NO_3)_2$ for x = 0.02, 0.05 and 0.08 are respectively 3.63, 12.73, and 19.79 J/g. We know from the phase diagram (Figure 8) that $RbNO_3$:$NaNO_3$ forms eutectic composition in the mole percent (m/o) ratio 54:46. So, for each value of x the ratio of $NaRb(NO_3)_2$ to the excess $RbNO_3$ can be estimated. Our calculations for other two values of x based on the value of energy for x = 0.02 gave 11.39 J/g and 19.88 J/g respectively for their corresponding peaks. These

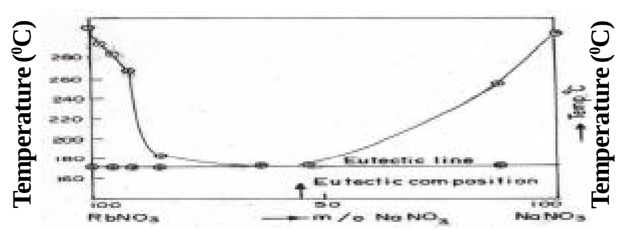

Figure 8: Phase diagram of $RbNO_3$: $NaNO_3$ system

TABLE 1: Transition temperatures and energies in $Na_xRb_{1-x}(NO_3)_2$

Transition temperatures (onset values in degree centigrade)						Energies (J/g)				
X value	IV-III	New Peak	III-II	II-I	Melting	IV-III	New Peak	III-II	II-I	Melting
0	164.41	-	220.92	283.08	310.09	29.09	-	24.14	9.71	37.03
0.02	163.91	171.98	209.11	283.4	293.36	23.21	3.63	16.35	8.08	13.7
0.05	164.18	172.52	211.55	276.92	-	25.42	12.73	16.56	29.57	-
0.08	164.14	173.16	213.7	248.03	-	19.66	19.79	10.35	14.61	-
0.15	164	173	-	-	-	8*	62.22*	8*	-	-
0.37	169	173.5	-	-	-	-	98.4*	-	-	-
0.46	-	175.26	-	-	-	-	99.57	-	-	-
0.87	-	170.36	-	271.75	253**	-	-	-	-	-
1	-		-	-	305.1	-	-	-	13.87	187.3

***Evaluated by using planimeter, **Approximate**

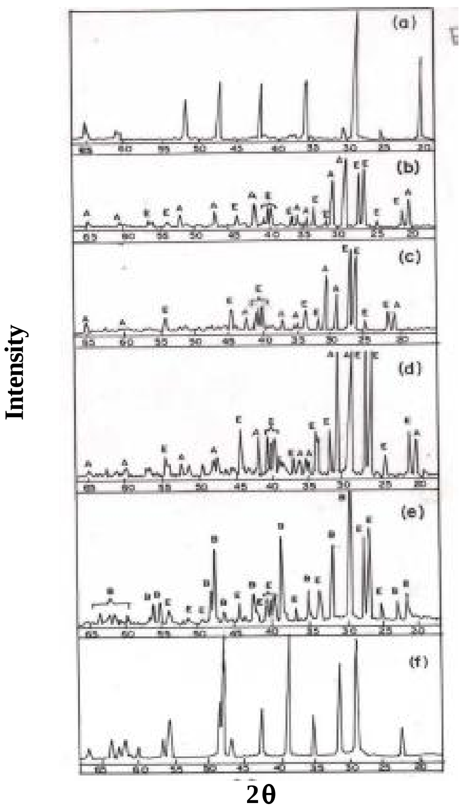

Figure 9: X-Ray diffractograms for $Na_xRb_{1-x}NO_3$(a) x=0(pure $RbNO_3$), (b) x=0.15, (c) x=0.37, (d) x=0.46, (e) x=0.87, (f) x=1(pure $NaNO_3$)

values are in excellent agreement with the above-mentioned recorded values by the instrument. We made similar calculations for IV-III transition based on the estimated value of excess $RbNO_3$ in the eutectic system, and they were also found to be in good agreement with the recorded values.

X-Ray diffractograms of $Na_xRb_{1-x}NO_3$ for x = 0, 0.15, 0.37, 0.46, 0.87 and 1 are shown in figure 9. Though recorded, we have excluded some of XRDs in order to reduce the number of figures. In figures 9(b-d) we see RbNO3 lines and extra lines (neither belonging to $RbNO_3$ nor $NaNO_3$) due to $NaRb(NO_3)_2$. These lines can be seen to grow in intensity with increasing value of x just as the energy of corresponding melting peaks increased in DSC. To distinguish different lines in the diffractograms the $RbNO_3$ and $NaNO_3$ lines are denoted as 'A' and 'B' respectively and lines corresponding to $NaRb(NO_3)_2$ as 'E'[14].

CONCLUSIONS

Addition of isovalent $NaNO_3$ to $RbNO_3$ lead to the formation of a new congruently melting compound $NaRb(NO_3)_2$. Its melting was found to be at about 173^0C which happens to be above IV-III transition of $RbNO_3$. DSC endotherms corresponding to the melting of this compound were found to grow as x increased. The melting peak influences the III-II and II-I transitions and thereby energies involved in them got redistributed. X-Ray diffractograms confirmed the formation of this new compound and lines corresponding to it were also found to grow with increasing x.

ACKNOWLEDGMENTS

The authors wish to thank the Head, Department of Physics, Osmania University, Hyderabad, INDIA.

REFERENCES

[1] Osmiabe, Tiazo Utsunomiya, Yoshio Hoshino; Thermochimica.Acta, **78**, 251-260 **(1984)**.

[2] E.Veliyulin, A.Voronel, H.A.Oye; J.Phys.Condns. Matter., **7**, 4821-4828 **(1995)**.

[3] Kangcheng Xu, Yang Chen; J.Raman.Spectrosc., **30**, 173-179 **(1999)**.

[4] N.B.Singh, A.K.Ojha; Thermochimica.Acta, 390, 67-72 **(2002)**.

[5] Mohamed Guizani Zamali, Mohamed Jemal; Comptes Rendus de l'des Sciences IIC-Chemistry, **112**, 78-789 **(1998)**.

[6] E.A.Secco, Richard A.Secco; Journal of Physics and Chemistry of Solids, **63**, 433-440 **(2002)**.

[7] P.P.Salhotra, E.C.Subba Rao, P.Venkateswarlu; Solid State Commu., **41**, 169 **(1982)**.

[8] A.Sadananda Chary, S.Narender Reddy, T. Chiranjivi; Solid State Ionics, **31**, 27-30 **(1988)**.

[9] A.Sadananda Chary, S.Narender Reddy, T. Chiranjivi; Journal of Materials Science, **24**, 2199-2202 **(1989)**.

[10] E.Mariani, J.Ekstein, E.Rubinova; Czech.J.Phys., **B17**, 552-558 **(1967)**.

[11] T.Daniel; Thermal Analysis, Kogan Page Ltd. London, **(1973)**.

[12] N.M.Hopkin; 'Meller's Comprehensive Treatise on Inorganic and Theoretical chemistry', Longmans, Green and Co. Ltd., **2(3)**, 2249 **(1963)**.

[13] H.G.Wiedemann, G.Bayer; Journal of Thermal Analysis, **30**, 1273-1281 **(1985)**.

[14] Xin Feng, Liyi Shi, Shaofei Wang, Shurui Ma; Solid State Ionics, In Press, **(2009)**.