Thermochimica Acta, 163 (1990) 257-262
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

THERMAL AND DIELECTRIC PROPERTIES OF THE SOLID SOLUTIONS $(RbCN)_{1-x}(KCN)_x$ AT LOW TEMPERATURES*

T. SHOUDA[1], T. MATSUO[1], H. SUGA[1] and F. LUTY[2]

[1]Department of Chemistry and Microcalorimetry Research Center, Faculty of Science, Osaka University, Toyonaka, Osaka 560 (Japan)

[2]Department of Physics, University of Utah, Salt Lake City, Utah 84112 (USA)

SUMMARY

The heat capacities of $(RbCN)_{1-x}(KCN)_x$ (x= 0.20, 0.35, 0.50, 0.63 and 0.75) were measured between 13 and 300 K. Anomalies due to structural phase transitions to the high temperature cubic phase were found in all of them. Lambda anomalies due to cooperative ordering of the CN^- dipoles were observed for x=0.50, 0.63 and 0.75. In addition to these phase transitions, anomalies of relaxational origin were found in the temperature region below 60 K. The molecular motion related to the relaxation was detected by dielectric measurement at audio frequencies.

INTRODUCTION

Potassium and rubidium cyanides crystallize in the rock salt structure at 300 K (ref. 1,2). The cyanide ions are orientationally disordered in this structure. At low temperatures, they undergo phase transitions to partially ordered phases. The structural phase transition occurs at 168 K in KCN (ref. 3) and 132 K in RbCN (ref. 4). The low temperature phase is orthorhombic (ref. 5) for KCN and monoclinic for RbCN (ref. 6). At a still lower temperature (83 K), a phase transition to the fully ordered phase occurs in KCN (ref. 3). In RbCN, the electric dipoles are frozen without undergoing further ordering. In a previous calorimetric measurement on RbCN the freezing of the orientational disorder was observed at 30 K as a glass transition which characterized the anomaly as due to increasingly slower approach to the thermal equilibrium at lower temperatures(ref. 7).

In mixed crystals $(RbCN)_{1-x}(KCN)_x$ random strain field arises from difference in the size of the cations ($r(K^+)$= 0.133 nm, $r(Rb^+)$= 0.148 nm) (ref. 8). This static strain field will influence the structural phase transition and dipolar ordering of the CN^- ion as well as the kinetics of the molecular reorientation. In the present paper we report some calorimetric and dielectric properties of the solid solutions $(RbCN)_{1-x}(KCN)_x$, x= 0.2, 0.35, 0.5, 0.63 and 0.75.

0040-6031/90/$03.50

EXPERIMENTAL

The crystals were grown at the Crystal Growth Laboratory of the University of Utah using Kyropoulos technique starting from zone-refined KCN and RbCN. The heat capacities were measured with an adiabatic calorimeter (ref. 9) between 13 and 300 K. The samples were loaded in the calorimeter cell with a small amount of helium gas to promote the thermal equilibration in the cell. Complex dielectric permittivities were measured on the solid solutions $(RbCN)_{0.37}(KCN)_{0.63}$ with a capacitance bridge (General Radio model 1620) and LCR meter (YHP model 4725A) at frequencies between 100 Hz and 1 MHz.

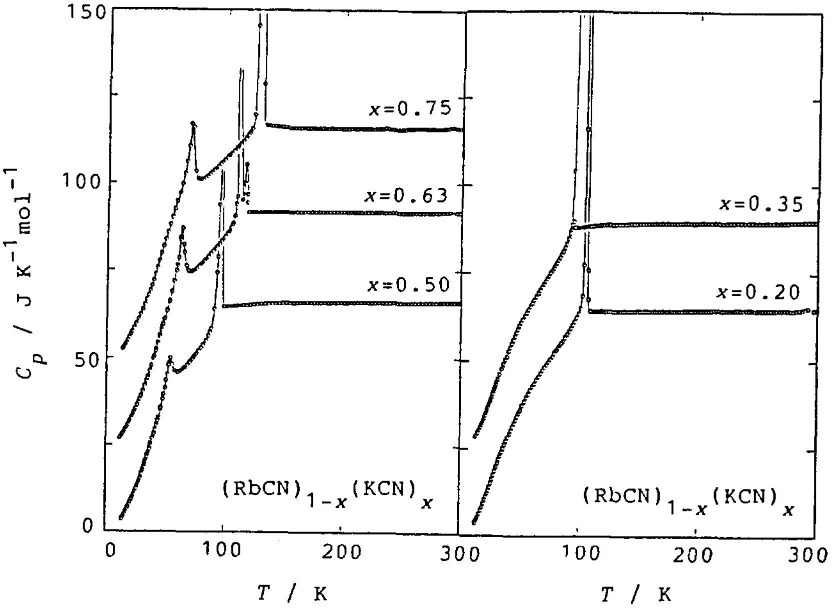

Fig. 1. Heat capacities of $(RbCN)_{1-x}(KCN)_x$. The vertical scale of each curve is shifted from the next by 25 units.

RESULTS AND DISCUSSION

The heat capacities of the five samples are shown graphically in Fig. 1. All the samples have nearly constant heat capacities in the high temperature phase. The low temperature behavior was different for different compositions. The two rubidium rich samples underwent one phase transition whereas the three others (of the potassium rich compositions) underwent two successive phase transitions. Thus rubidium rich and potassium rich samples behaved like neat rubidium cyanide and potassium cyanide, respectively.

$(RbCN)_{0.25}(KCN)_{0.75}$

The transition temperatures were 69.5 and 128.3 K. By analogy with neat KCN, the 69.5 K transition is probably due to the electric dipole ordering. The cyanaide ions underwent further disordering to the cubic phase at the higher transition temperature.

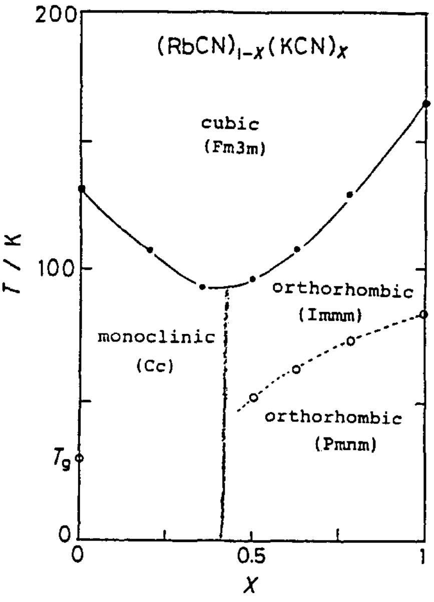

Fig. 2. Phase diagram of RbCN-KCN.

$(RbCN)_{0.37}(KCN)_{0.63}$

The behavior was similar to that of the solid solution with x = 0.75. The transition temperatures were 63.2 and 110.8 K.

$(RbCN)_{0.50}(KCN)_{0.50}$

Two phase transitions occurred at 54.2 and 97.0 K. General temperature dependence of the anomlous heat capacity was similar to that of the previous two solid solutions, although the temperatures of the anomalies were lower than the corresponding ones.

$(RbCN)_{0.65}(KCN)_{0.35}$

This solid solution underwent a phase transition at 93.7 K. It is a first order transition, as the heat capacity anomaly shows. There was no indication of a lambda anomaly at lower temperature. It is likely that the low temperature phase of this solid solution has the same structure (monoclinic) as the low temperature phase of neat RbCN in which the dipolar ordering does not take place for a kinetic reason (ref. 8).

$(RbCN)_{0.80}(KCN)_{0.20}$

This solid solution underwent a first order transition at 105.8 K, but full ordering did not occur. The behavior was the same as that of neat RbCN.

The transition temperatures are plotted in Fig. 2 against the composition. It is interesting that the upper transition temperature has a minimum around x=0.45. This probably means that the orthorhombic ordering and monoclinic ordering are counter-productive to each other.

The transition enthalpy and entropy

The normal heat capacities were assumed to be given by a sum of the Debye and Einstein heat capacity functions. The characteristic frequencies were determined by the least squares fitting to the heat capacity data (for eight degrees of freedom out of nine) and from the vibrational spectrum (for the internal vibration of the cyanide ion). The configurational part (= experimental heat capacity - normal contribution) thus calculated was integrated with the temperature, giving the transition enthalpy and entropy. Figure 3 show the latter quantity for $(RbCN)_{0.5}(KCN)_{0.5}$ as a function of the temperature. The entropy increased in two steps to about 5 $JK^{-1}mol^{-1}$ at the lower transition and then to the limiting value of 15 $JK^{-1}mol^{-1}$. The latter step has a discontinuous part, 3.13 $JK^{-1}mol^{-1}$ in magnitude, due to the first order component. Numerical values of the temperatures, enthalpies and entropies of the transitions are T_1 = 54.2 K, ΔH_1 = 0.30 $kJmol^{-1}$, ΔS_1 = 5.6 $JK^{-1}mol^{-1}$ and T_2 = 97.0 K, ΔH_2 = 1.33 $kJmol^{-1}$, ΔS_2 = 11.0 $JK^{-1}mol^{-1}$. The entropy change ΔS_1 is compararable with $R\ln2$ = 5.76 JK^{-1} mol^{-1} implied by the structural model that the cyanide ions are dipole-ordered in the low temperature phase and dipole-disordered in the intermediate phase. ΔS_2 is related to $R\ln4$ = 11.53 $JK^{-1}mol^{-1}$ by a structural model in which the cyanide ions are eight-fold disordered in the high temperature phase in accordance with the cubic symmetry and two-fold disordered in the intermediate phase. The entropy changes of the other solid solutions could be interpreted in a similar way relating the experimental data to the number W of the allowed orientations for a cyanide ion in each of the phases through the Boltzmann relation $S = R\ln W$.

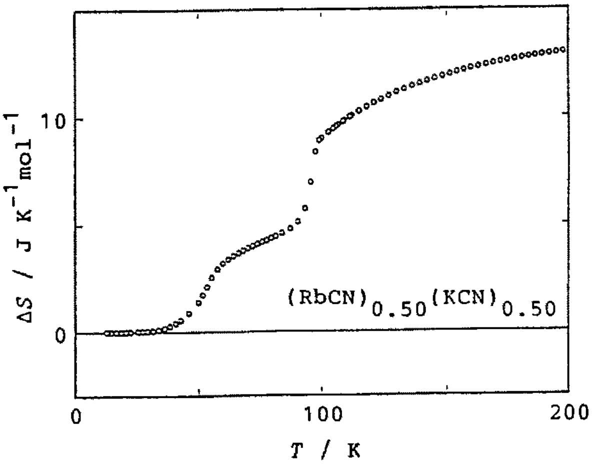

Fig. 3. Excess entropy of $(RbCN)_{0.50}(KCN)_{0.50}$.

Calorimetric and dielectric relaxations

All of the samples exhibited exothermic relaxation in the calorimetric experiment in the temperature range between 20 and 60 K. In order to examine the relaxation more closely, the sample $(RbCN)_{0.50}(KCN)_{0.50}$ was quenched from 70 K to 45.2 K and kept there in an adiabatic condition while the temperature

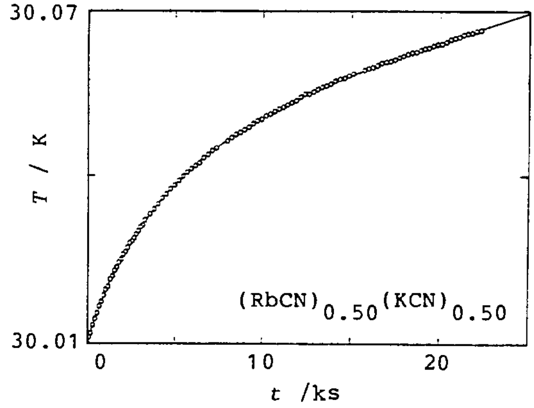

Fig. 4. Spontaneous heating of $(RbCN)_{0.50}$-$(KCN)_{0.50}$.

was recorded. As shown in Fig. 4, the temperature increased rapidly at first and approached a constant value later. The curve suggested an exponential time dependence. However, it turned out that a modified exponential function (ref. 10)

$$T(t) = A + Bt - C\exp(-(t/\tau)^{\beta})$$

reproduces the data very closely. Here, $(A - C)$ is the initial temperature at $t = 0$, B a constant drift rate (due to residual heat leakage), C the amplitude of the relaxation, τ the relaxation time and β the Kohlrausch-Williams-Watts constant ($1 \geq \beta > 0$). The last parameter describes deviation of the relaxation from a simple exponential form (for which $\beta = 1.0$). The best fit value of β was 0.70 in this case.

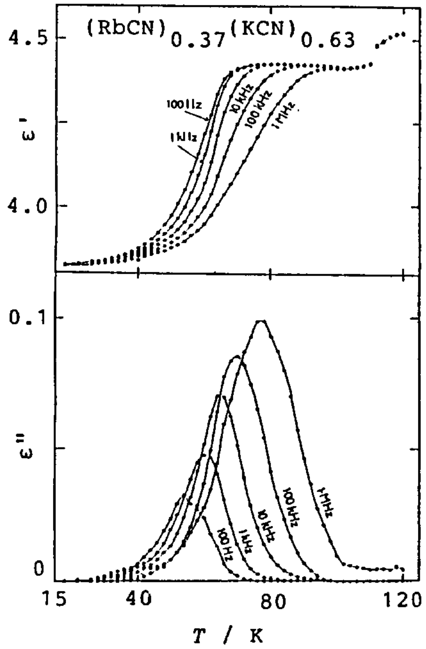

Fig. 5. Dielectric constants of $(RbCN)_{0.37}(KCN)_{0.63}$

Delectric constants (real and imaginary parts) of $RbCN)_{0.37}(KCN)_{0.63}$ are plotted in Fig. 5. There is a discontinuity of ε' at the upper transition temperature but both ε' and ε" are continuous at the lower transition temperature. The magnitude of the dispersion 0.6 (Δε'= 4.4 - 3.8) is approximately equal to the dispersion in neat RbCN (ref. 4) in which all the CN^- dipoles equally participate in the orientational polarization. The activation energy of the dielectric relaxation time was 15.1 $kJmol^{-1}$ which is also comparable with those of neat KCN and RbCN.

The total energy involved in the exothermic drift (Fig. 4) was 1.4 $Jmol^{-1}$.

The dipolar ordering energy is equal to the enthalpy of the lower transition, 300 J mol^{-1}. The ratio of the two energies, 0.005, is a measure of the fraction of the CN^- ions involved in the thermal relaxation. There was another temperature region of anomalously large exothermic drift. It occurred between 45 and 55 K for $x = 0.50$. The drift rate was as large as 100 μW in terms of the heat generation, where less than 1 μW was expected from the heat leakage. Similar exothermic effects were found in other samples. The mechanism of this relaxation is not understood now.

A conclusion drawn from the dielectric and calorimetric relaxations is that although they may have the same molecular origin, fractions of the ions involved in them are very different. At the temperature where the calorimetric relaxation occurred, the dipolar ordering of the cyanide ions was close to completion and only a small fraction of them were able to reorient themselves.

REFERENCES

* Contribution No. 20 from the Microcalorimetry Research Center.

1 D. L. Price, J. M. Rowe, J. J. Rush, E. Prince, D. G. Hinks and S. Susman, J. Chem. Phys., 56 (1972) 3697.

2 Structure Reports (1942-1944), Vol. 9, International Union of Crystallography, 1955, pp. 140.

3 H. Suga, T. Matsuo and S. Seki, Bull. Chem. Soc., 38 (1977) 1115.

4 Y. Kondo, D. Schoemaker and F. Luty, Phys. Rev., 19 (1979) 4210.

5 J. M. Rowe, J. J. Rush and E. Prince, J. Chem. Phys., 66 (1977) 5147.

6 Structure Reports (1942-1944), Vol. 9, International Union of Crystallography, 1955, pp. 142.

7 T. Shimada, T. Matsuo, H. Suga and F. Luty, J. Chem. Phys., 85 (1986) 3530.

8 R. D. Shannon, Acta Crystallogr., A32 (1976) 751.

9 T. Matsuo and H. Suga, Thermochim. Acta, 88 (1985) 149.

10 G. Williams and D. C. Watts, Trans. Faraday Soc., 66 (1970) 80.