

PHASE DIAGRAM OF THE $\text{AgNO}_3\text{--CsNO}_3$ SYSTEM

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Abstract

The phase diagram of the binary $\text{AgNO}_3\text{--CsNO}_3$ system was constructed using differential thermal analysis (DTA) technique in the range 300–700 K. The apparatus is described briefly. The results exhibit a congruently melting compound $\text{CsNO}_3\cdot 3\text{AgNO}_3$ ($m.p.=453$ K) characterized by two allotropic varieties α and β , an incongruently melting compound $\text{AgNO}_3\cdot\text{CsNO}_3$ ($m.p.=450$ K) with three forms α' , β' and γ' , two eutectics (16 mol% CsNO_3 , 442 K and 32.5 mol% CsNO_3 , 445 K) and a peritectic (38 mol% CsNO_3 , 450 K). The occurrence of the transitions of intermediates was confirmed by X-ray diffraction at variable temperatures. The phase diagram exhibits also two plateaus at 429 K and 435 K corresponding to the phase transitions of CsNO_3 and AgNO_3 , respectively.

Keywords: cesium nitrate, intermediate compound, phase diagram, silver nitrate

Introduction

Due to their interesting thermal properties, mixtures of alkali metal nitrates have been widely investigated. Moreover, their thermodynamic properties suggest fundamental rules which can be applied to other salts. Because of a certain similarity of silver nitrate to the alkali nitrates, mixtures containing silver nitrate have also been studied [1–10].

The aim of this paper is to establish the phase diagram of $(\text{Ag,Cs})\text{NO}_3$ in the range 300–700 K and to compare the results with other published data.

Experimental

We used simultaneous direct and differential thermal analysis technique. The apparatus was described in more detail in previous papers [3–4]. It consists of a metallic block with two symmetrical cavities for platinum crucibles of 3 g capacity. The external diameter of the block is a few millimeters smaller than the inner tube of the

furnace. This limits the convection current around the test tubes, contributes to the improvement of the heat transfer, and makes the thermal flow propagation more homogeneous. Two quartz tubes surround the crucibles in order to ensure electrical and thermal isolation of the sample and the reference. The sample thermocouple is connected to a potentiometer which is related to a direct current power supply and a Kipp and Zonen recorder. The device is also provided with a highly sensitive 'Keithley 191' multimeter for temperature readings at regular time intervals.

The thermal curves were obtained by recording the imbalance output voltage of the potentiometer and ΔT was simultaneously plotted on the second channel of the recorder.

Heating and cooling rates were less than 2.5 K min⁻¹ for the first cycle and about 1 K min⁻¹ for the next cycles. The measurements were carried out under atmospheric air.

Merck analytical grade nitrates were used: AgNO₃ was of 99.8% purity and CsNO₃ of high purity. They were used without further purification but dried for more than 24 h at 380 K in an oven. The samples were prepared by intimately mixing weighed amounts of AgNO₃ and CsNO₃ powders in a platinum crucible. In order to get homogeneous mixtures without appreciable decomposition, mixtures (2.5 g) were previously melted several times at a temperature a few degrees over the melting point.

An Anton-Paar HTK10 high-temperature camera mounted on the Philips PW 1050/20 goniometer was employed to obtain the diffraction patterns. X-ray diffraction powder method at different temperatures was used with a CuK_α ($\lambda_{\text{CuK}\alpha} = 0.15405$ nm) from room temperature up to 700 K. The experiments were carried out under helium. The thermal sequences and the goniometer $\theta/2\theta$ scanning are computer assisted. A computer program permits also X-ray data acquisition and treatment.

Results and discussion

For pure CsNO₃ values of T_{tr} (transition temperature) and T_{m} (melting temperature) were 427 and 679 K, respectively. These values are in the range of most of the results published previously. T_{tr} reported by Mustajoki [11] and by Flotow *et al.* [12] is 424.7 K and 425.2 K, respectively. They are close to that of Zamali [4] 424 K. Values of Bridgman [13] and Jriri [14] were 426.9 and 427 K, respectively. That of Kazuhiko [15] was higher: 430.4 K. The published values of T_{m} are in the range of 677–687 K [4, 11, 12, 14–19]. Kleppa [20] reported 690.2 K.

For AgNO₃, the temperatures of the transition and melting points were 435.5 K and 484.5 K, respectively. The transition point slightly exceeds the upper limit of the range published previously, 430.2 to 433.2 K [2, 21–28]. The value found by Rhodes [29] is higher: 443 K. However, the melting point is within the range of published values: 481.2 to 485 K [2, 16, 19–23, 26–32]. The T_{m} found by Goodwin and Kalmus is 491 K [33].

The phase diagram of the system AgNO₃-CsNO₃ was drawn at static atmospheric pressure using the results of simultaneous direct and differential thermal analysis data. Regular rates of heating and cooling were about 1 K min⁻¹. The solidus and subsolidus curves were drawn from the results obtained by heating, whereas the liquidus was obtained from cooling curves. A undercooling appeared only for

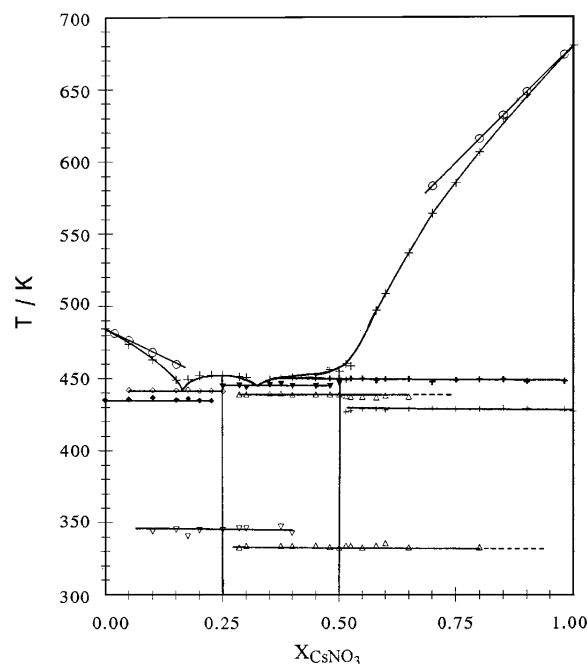


Fig. 1 AgNO₃-CsNO₃ phase diagram; ○ – results from Raoult's law

mixtures having 25 to 55 mol% CsNO₃. This phenomenon decreases by annealing the liquid for up to 24 h, then cooling at a low rate (0.6 K min⁻¹). Figure 1 shows the phase diagram which is characterized by:

- two eutectic mixtures (16 mol% CsNO₃, 442 K and 32.5 mol% CsNO₃, 445 K);
- a peritectic plateau at 38 mol% CsNO₃, 450 K and two other plateaus at 429 and 435 K corresponding to the phase transitions of CsNO₃ and AgNO₃, respectively;
- two intermediates CsNO₃·3AgNO₃ ($T_m=453$ K) and AgNO₃·CsNO₃ ($T_m=450$ K) which have been mentioned previously by other authors [7–9]. CsNO₃·3AgNO₃ is characterized by two allotropic varieties, α and β , whereas AgNO₃·CsNO₃ has three forms, α' , β' and γ' . The phase transition of the first compound occurred at 345 K. Those of the second one at 333 K for the α'/β' transition and at 439 K for the β'/γ' transition.

It has also been reported that there are two eutectics at 17.7 mol% CsNO₃–441.2 K and at 35.3 mol% CsNO₃–439.2 K respectively, and a peritectic point at 49.5 mol% CsNO₃–449.2 K [7–9]. But the phase transitions of these intermediates are not mentioned in the previous publications, there is no crystal data for these compounds and for their crystal systems.

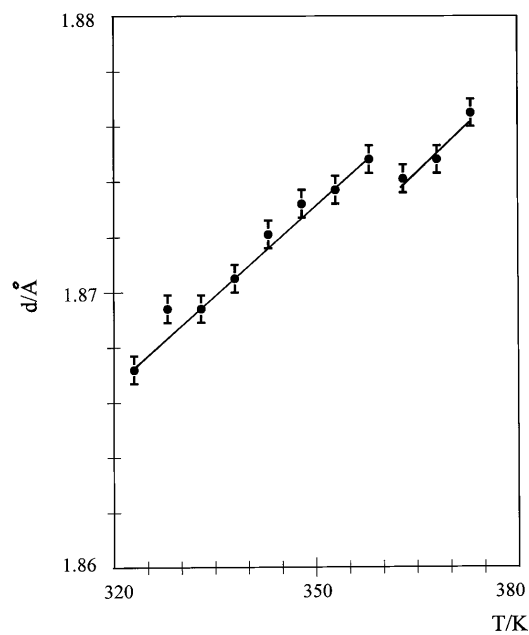


Fig. 2 $d/\text{Å}$ vs. T/K for the 1:3 compound; $\Theta=24.392_5^\circ$ for $T=293\text{ K}$

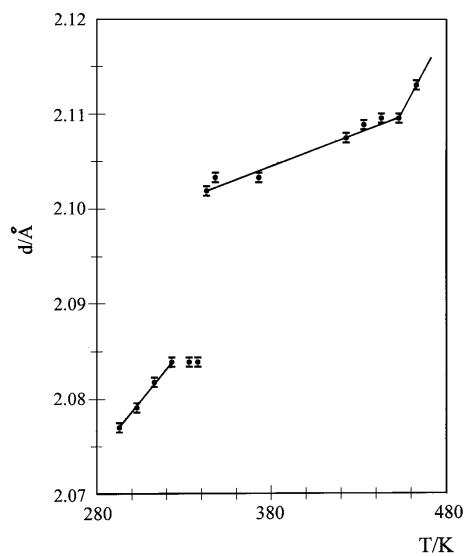


Fig. 3 $d/\text{Å}$ vs. T/K for the 1:1 compound; $\Theta=21.767_5^\circ$ for $T=293\text{ K}$

Comparison of the X-ray diffraction patterns recorded at room temperature for samples with variable molar fraction of CsNO₃ (0.1, 0.25, 0.4, 0.5 and 0.8) with those for pure AgNO₃ and CsNO₃ confirms the existence of the two intermediates.

The existence of the phase transitions for the two intermediates was confirmed by recording high-temperature X-ray diagram for mixtures having 1:3 and 1:1 composition ratio after one hour annealing time. Theoretically, variation of any $d/\text{Å}$ vs. T/K exhibits a deviation or a shift at the transition temperature. Nevertheless the plot of $d/\text{Å}$ for small angles is not decisive because of the scattering of the results. Figures 2 and 3 show the plots of these variations for $\Theta=24.392_5$ degrees for the 1:3 compound and $\Theta=21.767_5$ degrees for the 1:1 compound. One can notice the phase transitions near 360 K for the first compound and near 340 and 450 K for the second. The discrepancy between these temperatures and those obtained by DTA results from the difference in the temperature detection systems in the two devices.

Using Raoult's law, we estimated the liquidus temperature, T , from the following expression:

$$RT \ln X_i = \Delta_f H_i(T_f) \left(\frac{T}{T_f} - 1 \right)$$

where X_i =molar fraction of constituent i (AgNO₃ or CsNO₃) in the liquid state, $\Delta_f H_i(T_f)$ =molar enthalpy of melting of i at his melting temperature T_f .

These quantities are respectively:

$$\Delta_f H_{\text{AgNO}_3}(484 \text{ K}) = 12300 \text{ J mol}^{-1} [28]$$

$$\Delta_f H_{\text{CsNO}_3}(679 \text{ K}) = 12100 \text{ J mol}^{-1} [14]$$

The estimated temperatures were then plotted against the molar fraction of CsNO₃ (Fig. 1:◦). We note that they agree satisfactorily with the experimental data for the molar fraction of CsNO₃ in the ranges 0 to 0.05 and 0.85 to 1.

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