Thermochimica Acta, 88 (1985) 497-500
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

Note

HEAT CAPACITY AND ENTHALPY OF PHASE TRANSITIONS OF α- AND β-MODIFICATIONS OF LEAD FLUORIDE

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(Received 14 December 1984)

It is known that at room temperature lead fluoride exists either as a thermodynamically stable orthorhombic modification (α-phase, $PbCl_2$-type), or as a metastable cubic one (β-phase, CaF_2-type). The high-temperature β-modification possesses a high fluoride-ion conductivity comparable with that of melts at temperatures far below its melting point, which allows it to be used as a solid electrolyte [1,2].

Until recently, the high fluoride-ion conductivity of β-PbF_2 was associated with the process of complete disordering of the fluoride-ion sublattice (called "sublattice melting"). Such a disordering should be accompanied by a considerable entropy change and the authors [3] provided a transition entropy value equal to 16.5 J mol^{-1} K^{-1} which is comparable with the melting entropy of PbF_2. At present, however, papers exist in which the high conductivity of β-PbF_2 is associated with an anomalously high mobility of the anion vacancies, and they show that the disordering degree of the anion sublattice is considerably less than 100% [4].

There are also reports [5] in which lead fluoride was investigated by means of DTA, dilatometry and X-ray analysis. On the basis of the above results the authors conclude that PbF_2 exists not in two, but in five different polymorphic modifications, transitions among which take place at temperatures of 613, 733, 833 and 993 K.

Therefore, a direct investigation of PbF_2 heat capacity is of great interest since the available data on high-temperature heat capacities and enthalpies of lead fluoride phase transitions [6,7] differ significantly.

METHODS

Suprapur PbF_2 was used, which was previously dried and annealed in vacuum at about 473 K for 30 h. X-ray analysis showed that the sample contained only the low-temperature α-form. For investigation by DTA, samples were also prepared according to ref. 5 by means of treating lead carbonate with concentrated hydrofluoric acid.

0040-6031/85/$03.30

The experimental determination of PbF_2 heat capacity was made using a triple heat bridge (THB) method [8]. The error in the determination of heat capacity did not exceed 3%. Heating rate was 2.2 K min^{-1}. Copper of 99.95% purity was used as a reference. Copper heat capacity values were taken from ref. 9. (In our calculations we accepted that the atomic weight of copper was 63.546, molecular weight of lead fluoride was 245.19, and 1 cal = 4.184 J.)

The investigations by quantitative DTA were conducted using an apparatus of original construction [10].

RESULTS AND DISCUSSIONS

Experimental results on heat capacity investigations are shown in Fig. 1.

As one can see from Fig. 1, within the 360–720 K temperature range, there are two anomalies of heat capacity of lead fluoride with maxima at 608 ± 1 and 718 ± 1 K.

The first anomaly is due to the α-$PbF_2 \rightarrow \beta$-PbF_2 transition and the second is caused by a structure disordering of cubic β-PbF_2. This is also confirmed by our high-temperature X-ray investigations.

Within the range 360–586 K, the temperature dependence of α-PbF_2 heat capacity is almost linear and is expressed by the following equation

$$C_p(\pm 0.43) = 70.13(\pm 0.52) + 12.46(\pm 1.03) \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

During the reheating of the sample the first maximum (at 608 K) is missing, which proves that the $\alpha \rightarrow \beta$ transition is irreversible. In the region of the second maximum (at 718 K) C_p values practically completely coincide with those obtained during initial heating. Thus, the second transition is reversible. We also investigated β-PbF_2 samples which were kept at room

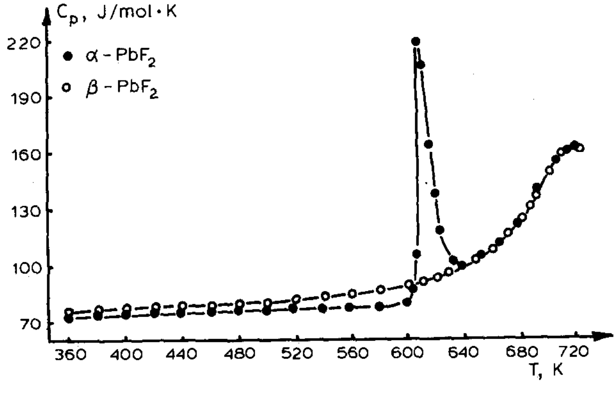

Fig. 1. Heat capacity of α- and β-modifications of lead fluoride.

temperature for approximately 3 months. For this purpose we used the THB method and revealed that in this case an anomaly of heat capacity with a maximum at 608 K was present, though the corresponding heat capacities in the region of the maximum were considerably less than those for the initial α-PbF_2. This is evidently due to the slowly proceeding transition of the β-form, which is thermodynamically unstable, into α-PbF_2.

For the β-modification of lead fluoride within the range 360–510 K, the temperature dependence of its heat capacity is expressed by the following equation

$$C_p(\pm 0.51) = 64.58(\pm 1.21) + 30.58(\pm 2.76) \times 10^{-3} T \text{ J mol}^{-1} \text{ K}^{-1}$$

By integrating the $C_p(T)$ dependence in the region of the first maximum we found the enthalpy value for the $\alpha \rightarrow \beta$-PbF_2 transition: 1.51 ± 0.13 kJ mol^{-1}. Unfortunately, the upper temperature limit of the THB apparatus did not allow the second transition to be fixed completely, but the temperature at which the heat capacity reaches its maximum (718 K) was determined reliably enough. This made it possible to evaluate the value of the enthalpy of the β-PbF_2 anion sublattice disordering approximately, which amounted to ~ 4.2 kJ mol^{-1}.

PbF_2 thermal behaviour was also investigated by the quantitative DTA method (from room temperature to 1073 K; dry argon atmosphere; sample heating rate, 5 K min^{-1}). Thermograms recorded during the sample heating process showed only two endothermal effects; one (irreversible) beginning at 603 ± 5 K and the second (reversible) proceeding from 673 to 788 K. Unlike the results of ref. 5, we found no other effects either for PbF_2 suprapur or PbF_2 synthesized as in ref. 5.

According to DTA, the enthalpy of lead fluoride phase transitions are: ΔH (α-$PbF_2 \rightarrow \beta$-PbF_2) = 1.42 ± 0.21 kJ mol^{-1}; ΔH (disordering) = 4.48 ± 0.54 kJ mol^{-1}.

Thus, one can see a satisfactory coincidence of values of lead fluoride phase transition enthalpies obtained from the THB and quantitative DTA methods.

The small value of the cubic β-PbF_2 disordering enthalpy leads to a small value of this process entropy which is essentially less than the melting entropy of lead fluoride. This fact can serve as an indirect confirmation of the relatively low degree of fluoride anion sublattice disordering in β-PbF_2.

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