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ON LEAD FLUORIDE PHASE TRANSITIONS

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ABSTRACT

By means of a triple heat bridge method α - and β-PbF_2 heat capacity was measured within 360 - 720 K. We also calculated enthalpies of phase transitions, which within the experimental errors coincide with the values determined using a quantitative DTA method. A small value of β-PbF_2 disordering entropy calculated on the basis of these data indirectly proves a relatively low degree of anion sublattice disordering.

INTRODUCTION

A specific feature of superionic conductors, to which β-PbF_2 belongs, is a considerable increase of ionic conductivity at a certain temperature, which is substantially lower than of the compound melting. This is explained by a phase transition of a disordering type, i.e. "melting" of one of the crystal sublattices with the formation of a quasi-liquid /I,2/. This model is based on a high value of the phase transition entropy comparable with the melting entropy /3/. Recently, however, there were published papers, which show that β-PbF_2 anion sublattice disordering degree reaches only some per cent and they explain an anomalously high conductivity of PbF_2 by high mobility of anion vacancies /4,5/. Determination of PbF_2 heat capacity in the region of its phase transitions provides an important information in favour of a definite point of view. Up to the present time, however, reliable data on PbF_2 heat capacity above room temperature and enthalpies of its phase transitions are missing in the literature.

RESULTS AND DISCUSSION

The aim of this paper was to determine PbF_2 heat capacity of α- and β-modifications within 360 - 720 K by means of a triple heat bridge (THB) method with an error not exceeding 3 %, and also to determine PbF_2 phase transitions enthalpies, using a dynamic differential calorimetry (DDC) method.

α-PbF_2 heat capacity dependence on the temperature reveals

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two anomalies with their maxima at 608 ± I and 7I8 ± I K. The first of them is due to α-PbF_2 $\dashrightarrow$ β-PbF_2 irreversible transition, and the second one is caused by reversible λ-type transition of β-PbF_2. This is confirmed by the results of a high temperature X-ray analysis and repeated experiments with same sample.

Within 360 - 536 K temperature dependence of α-PbF_2 heat capacity is close to a linear one and is expressed by the following equation:

$$C_p\ (\pm 0.43) = 70.I3(\pm 0.52) + I2.46(\pm I.03)\cdot I0^{-3}T,\ J/mol.K.$$

Hence $C_{p\ 298.I5}(\alpha\text{-}PbF_2) = 73.8 \pm 2.2$ J/mol.K.

Within 360 - 5I0 K β-PbF_2 heat capacity dependence on the temperature is also close to a linear one and is described by the equation:

$$C_p(\pm 0.5I) = 64.58(\pm I.2I) + 30.58(\pm 2.76)\cdot I0^{-3}T,\ J/mol.K.$$

Then $C_{p\ 298.I5}(\beta\text{-}PbF_2) = 73.7 \pm 2.2$ J/mol.K.

Errors in determination of the heat capacity are evaluated by a confidence interval with 0.95 probability.

From the heat capacity data by integrating $C_p(T)$ dependence in the region of the phase transitions we calculated enthalpies of α-PbF_2 $\dashrightarrow$ β-PbF_2 transition : $\Delta H\ (\alpha \rightarrow \beta) = I.5I \pm 0.I3$ kJ/mol. Unfortunately the upper temperature limit of THB apparatus did not allow to investigate β-PbF_2 anion sublattice disordering process to the end. Therefore we evaluated only approximately enthalpy of the second transition : ΔH (disord.) = 4.2 kJ/mol.

The results of determination of lead fluoride phase transitions enthalpies by means of DDC method and those obtained from the heat capacity data satisfactorily coincide.

Thus small values of the enthalpy (and entropy) of β-PbF_2 anion sublattice disordering, obtained by different methods, are considerably less than the enthalpy (and the entropy) of PbF_2 melting. This fact gives an indirect confirmation of a comparatively low degree of β-PbF_2 anion sublattice disordering, but not its "melting".

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