SHORT COMMUNICATIONS

A Jump Change in the Sublimation Coefficient of the PrBr$_3$ Single Crystal at the Polymophic Transition Point

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Abstract—The sublimation of praseodymium tribromide under Knudsen and Langmuir conditions was studied by high-temperature mass spectrometry over the temperature range 804–957 K. During sublimation from the open surface of a single crystal, the sublimation coefficient of PrBr$_3$ changed abruptly at the polymorphic transition point (UCl$_3$-type low-temperature polymorph–PuBr$_3$-type high-temperature polymorph, $T = 934 \pm 3$ K). The change was reproducible in the heating–cooling cycles.

INTRODUCTION

The electronic and thermodynamic properties of lanthanide halides with a UCl$_3$ structure have received much attention in view of the potential application of these compounds as effective scintillation materials [1]. In particular, scintillators based on PrBr$_3$ and PrBr$_3$: Ce^{3+} attract special attention [2]. In order to grow single crystals of the required size, data on the high-temperature properties of praseodymium tribromide such as the thermal expansion coefficient α_T and saturated vapor pressure p are necessary.

Recent neutron diffraction study [3] showed the α_T value to be strongly anisotropic. Expansion along the hexagonal *a* axis was ~3.5% over the range from 2 K to the melting point ($T_m = 963$ K). Along the *c* axis, 0.15% expansion was observed over the range 2–450 K; expansion changed into 0.4% compression over the range 450–963 K. Work [3] also provided evidence in support of the previous data [4] on the possibility of a polymorphic transition of PrBr$_3$ at temperatures near the melting point. According to differential scanning calorimetry measurements and subsequent structural analysis [3], the low-temperature phase existed up to the melting point when heated at a rate of 5 K/min. Near this point, lines of the high-temperature phase appeared in the diffraction pattern. When cooled at a rate of 2 K/min, PrBr$_3$ melt became supercooled and crystallized at ~946 K in the form of the high-temperature phase with a PuBr$_3$-type structure; the phase transition to the low-temperature polymorph with a UCl$_3$ structure was observed at 930 K.

Recently, we studied [5] the pressure and composition of saturated vapor over crystalline PrBr$_3$ using high-temperature mass spectrometry (the Knudsen method combined with mass spectrometric analysis of evaporation products). The temperature-programmed dependence of p(PrBr$_3$) did not show indications of any phase transition. It should, however, be noted that obtaining reliable information about polymorphic transitions is problematic in effusion sublimation studies because of sample smallness, the spread of the experimental p(PrBr$_3$) values, and small enthalpies of phase transitions.

On the other hand, practical aspects of growing single crystals require not only thermodynamic but also kinetic data on sublimation. For this purpose, in addition to measurements under Knudsen conditions, we studied sublimation of PrBr$_3$ in the Langmuir mode from the open surface of a single crystal. This paper reports comparative results of measurements in both modes.

EXPERIMENTAL

This work was performed on an MI-1201 magnetic mass spectrometer (<90°, radius of curvature 200 mm) modified for high-temperature studies. Details of the apparatus and experimental procedure are given in [6].

In the Knudsen mode, PrBr$_3$ powder was evaporated from a molybdenum effusion cell with a ratio between the cross section area of the cell and the effusion orifice area of ~400. In the Langmuir mode, the PrBr$_3$ single crystal was fixed in a molybdenum holder; the (001) face of the crystal (3 × 3 mm) was exposed to sublimation (the face was obtained by cleaving the crystal immediately before mounting the evaporator in the mass spectrometer). The molecular vapor components were analyzed under electron impact ionization conditions. The mass spectra were measured using the ioniz-
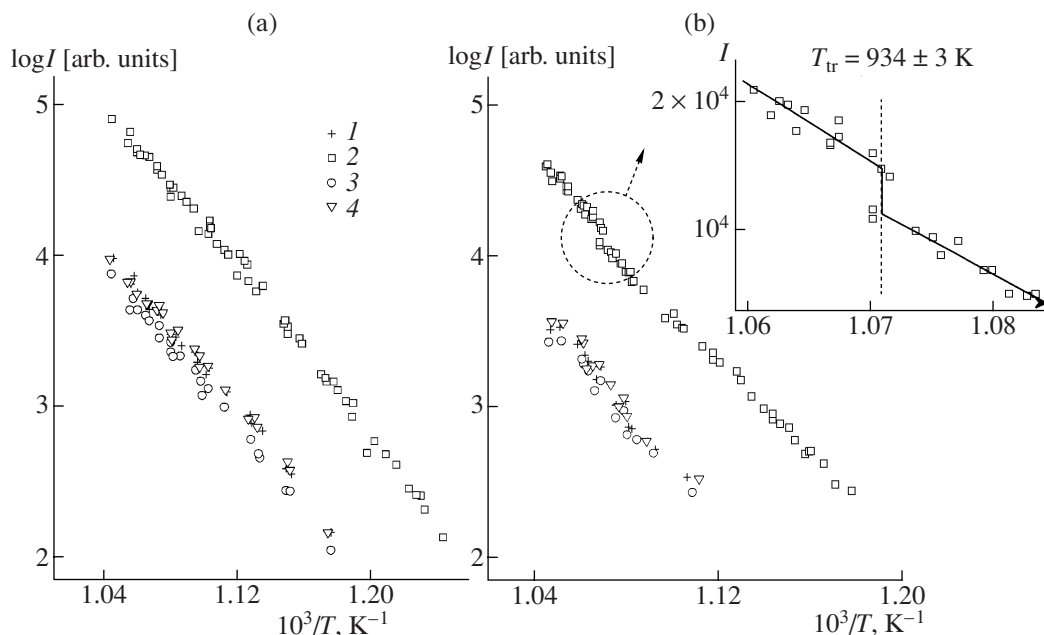
Temperature dependences of ion currents in the electron impact mass spectra in the (a) Knudsen and (b) Langmuir modes; (*1*) Pr$^+$, (*2*) PrBr$_2^+$, (*3*) PrBr$^+$, and (*4*) PrBr$_3^+$.

ing electron energy $E_e = 70$ eV and cathode emission current $I_e = 1$ mA.

The PrBr$_3$ sample (99.99%) was synthesized by the known NH$_4$Br procedure [7, 8] described in [6]. The PrBr$_3$ single crystal was grown from praseodymium tribromide powder placed in sealed quartz ampules by the Bridgman vertical procedure.

RESULTS AND DISCUSSION

A detailed analysis of the electron impact mass spectra obtained under the conditions of equilibrium sublimation of PrBr$_3$ was performed previously [5]. Here, we only note that the mass spectra obtained in the sublimation of PrBr$_3$ in the Langmuir and Knudsen modes were completely similar as concerns the qualitative compositions of the ions. As shown in [5], the largest contribution to the total ion current formed by the ionization of PrBr$_3$ molecules was made by Ln$^+$, LnBr$^+$, LnBr$_2^+$, and LnBr$_3^+$ ions. We will restrict our consideration to these ions. The temperature dependences of these ion currents in both sublimation modes are shown in the figure.

Our attention will be focused on an abrupt change in the sublimation molecular flow from the single crystal surface (measurements in the Langmuir mode) over the temperature range corresponding to the polymorphic transition of the PrBr$_3$ crystal. This effect is well defined for the most intense ions, PrBr$_2^+$. It is reproduced when single crystals are changed and in heating–cooling cycles. The temperature at which we observed a step in the temperature dependence of the PrBr$_2^+$ ion current was estimated at 934 ± 3 K.

An increase in the sublimation flow from the high-temperature polymorph with a PuBr$_3$ structure compared with the low-temperature polymorph with a UCl$_3$ structure is in agreement with the ratio between saturated vapor pressures of lanthanide tribromides having structures of this type at high temperatures. For example, at equal temperatures, the pressure over LaBr$_3$ and CeBr$_3$ (UCl$_3$ structure) is lower than the pressure over NdBr$_3$ (PuBr$_3$ structure) [9]. The abrupt change in the sublimation flow is evidence of a jump change in the sublimation coefficient α_s of praseodymium tribromide at the polymorphic transition point. This change in α_s is of 27%. As far as we know, this is the first observation of this kind.

The sublimation coefficient is a kinetic parameter. It depends on several parameters that characterize the morphological and defect properties of the crystal surface [10]. The observed jump is most clearly understood in terms of the terrace–ledge–kink (TLK) model of single crystal surfaces [11]. According to this model, the α_s coefficient for sublimation in a vacuum is given by [12]

$$\alpha_s = \frac{d}{\lambda}\tanh\left(\frac{\lambda}{d}\right),$$

where d is the mean displacement of a particle during surface self-diffusion and λ is the mean distance between evaporation steps. The polymorphic transition

causes changes in these parameters because of the structural rearrangement of the surface and redistribution of point defects in the surface region.

To summarize, as distinct from sublimation in the Knudsen mode, sublimation in the Langmuir mode is rather sensitive to various polymorphic transitions that influence the structure and surface properties of crystals. This opens up the possibility of detecting high-temperature polymorphs.

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