

CHEMICAL THERMODYNAMICS
AND THERMOCHEMISTRY

A Mass Spectrometric Study of the Molecular and Ionic Sublimation of Lanthanum Tribromide

M. F. Butman^a, V. B. Motalov^a, L. S. Kudin^a, A. E. Grishin^a, A. S. Kryuchkov^a, and K. W. Krämer^b

^a Ivanovo State University of Chemical Technology, Ivanovo, Russia

^b University of Bern, Bern, Switzerland

e-mail: butman@isuct.ru

Received October 3, 2006

Abstract—The molecular and ionic composition of vapor over lanthanum tribromide was studied by high-temperature mass spectrometry under the conditions of sublimation from a Knudsen effusion cell and from an open single crystal surface. The partial pressures of LaBr_3 and La_2Br_6 in saturated vapor and the ratio between their sublimation coefficients under free vaporization conditions were determined. The second and third laws of thermodynamics were used to calculate the enthalpies of sublimation of LaBr_3 in the form of monomers and dimers. In ionic sublimation studies, the emission of the Br^- , LaBr_4^- , and La_2Br_7^- negative ions was recorded in both regimes. Studies of the ionic sublimation of LnX_3 single crystals were shown to give reliable data on the thermochemical properties of negative ions.

DOI: 10.1134/S0036024408020040

INTRODUCTION

Lanthanide halides have been attracting the unremitting attention of experimental and theoretical chemists over more than 50 years. The earliest studies of the physicochemical properties of these compounds were performed to answer the demands of nuclear power engineering, nonferrous metallurgy, technologies for the separation and isolation of superpure metals, and some other practical applications. Emphasis was laid in these studies on the rules governing chemical sublimation and saturated vapor pressure determination. The development and perfection of mass spectrometric techniques allowed the complex chemical composition of high-temperature vapors containing diverse molecular and ionic associates to be determined. This stimulated repeated studies of lanthanide halides at the modern stage with the purpose of determining the thermodynamic characteristics of separate vapor components.

Critical reviews of the data on vapor pressures of monomeric LnX_3 molecules were published first by Myers and Graves in 1977 [1] and, more recently, by Oppermann and Schmidt [2]. An analysis of the data available shows that the statistical spread of vapor pressure data p obtained by various methods sometimes reaches one order of magnitude and more. Clearly, the accuracy of values recommended for handbooks can only be increased by increasing the number of mutually consistent results. The thermodynamic characteristics compiled in [1, 2], the enthalpies and entropies of sublimation of LnX_3 , cannot be considered very reliable because of the approximate character of the thermodynamic functions (in particular, reduced Gibbs energies

for calculations according to the third law of thermodynamics) used in the original works for LnX_3 in both gaseous and condensed states (e.g., see [3]). The functions for the gaseous state require recalculations with newly determined molecular constants, in particular, with the use of the data recommended in the review by Kovacs and Konings [4] on the basis of a critical analysis of the results of experimental (spectroscopic and electron diffraction) and theoretical studies of the structure and vibrational spectra of these molecules performed during the past decade. The functions for the condensed state should be calculated anew because of the availability of measurement data on the low- and high-temperature heat capacity components for several LnX_3 compounds obtained using modern calorimetric methods (e.g., see [5]).

Finer effects of the sublimation of LnX_3 compounds related to the determination of the partial pressures of oligomeric (dimeric, trimeric, etc.) molecules also require refinement. First, mass spectrometric measurements were performed for a limited number of objects (the most complete information can be found in [6, 7]). Next, the thermodynamic characteristics of sublimation of oligomers should be revised for the reasons specified above.

As distinct from thermodynamics, the kinetics of sublimation of LnX_3 crystals, that is, sublimation from open surfaces or “free” sublimation, has not been studied at all, although, practically, just the kinetic aspects of vapor formation can be of special interest, in particular, for growing pure and doped LnX_3 crystals extensively used in optical [8] and scintillation [9] devices.

The kinetic sublimation effects can be revealed and correctly described if measurements are performed for LnX_3 single crystals. Methodologically, kinetic studies should be performed jointly with thermodynamic studies to exclude analytic artifacts possible when the results are interpreted on the basis of only the literature data on the thermodynamic characteristics of sublimation. The data on the kinetics of sublimation of cubic ionic crystals obtained by us in [10–13] can be useful for the development of the terrace-ledge-kink (TLK) model (e.g., see review by Chernov [14]) as concerns the influence of morphological and electric surface properties determined by extended and point defects on the rate of vaporization, the composition of sublimation fluxes, and the state of vibrational-rotational excitation of molecules undergoing desorption. We believe that joint studies of the thermodynamic and kinetic characteristics of sublimation of LnX_3 would allow us not only to obtain a more complete physicochemical description of the process at the phenomenological level but also to more clearly and deeply understand the mechanisms of vapor formation for this important group of ionic crystals.

In view of these considerations, we undertook a systematic mass spectrometric investigation of the rules governing the molecular and ionic sublimation of lanthanide tribromides under both equilibrium conditions with the use of the Knudsen effusion method and free vaporization conditions from the open surface of LnBr_3 single crystals (the Langmuir method). These objects of study were selected because the sublimation of lanthanide bromides is currently of considerable interest for the creation of high-efficiency light sources of a new generation, metalhalide lamps [15]. In this work, we report the results obtained for lanthanum tribromide.

EXPERIMENTAL

Measurements were taken using an MI 1201 ($\angle 90^\circ$, radius of curvature 200 mm) commercial magnetic mass spectrometer modified for high-temperature studies.

The thermodynamic characteristics of sublimation were studied by vaporizing LaBr_3 from a molybdenum effusion cell with a ~ 400 ratio between the areas of the cell cross section and effusion orifice (0.3 mm^2). The substance was loaded into the cell from evacuated ampules at atmospheric pressure and dehydrated in a $\sim 10^{-1} \text{ Pa}$ vacuum to remove adsorbed moisture directly in the mass spectrometer at a temperature of $\sim 150^\circ\text{C}$ for several hours.

The temperature of the cell heated by a resistance furnace was measured by a standard W–WRe thermocouple. Thermocouple readings were corrected according to measurements of the melting points of reference substances.

Sublimation from an open surface was studied for $3 \times 3 \times 10 \text{ mm}$ LaBr_3 single crystals fixed in a cylindri-

cal holder made of molybdenum. A $3 \times 3 \text{ mm}$ (001) crystal face was exposed for sublimation. It was cleaved directly before mounting a vaporizer into the mass spectrometer.

The vaporizer and a block for the formation of an ion beam of an original design allowed us to study both the neutral and ionic vapor components in one experiment. The molecular beam was aligned by moving the cell-holder in two mutually orthogonal directions with a bellows mechanism.

The molecular vapor component was analyzed when the source of ions operated under electron impact conditions. Thanks to the presence of a collimator, the medium molecular beam portion was directed into the ionization chamber. The ionization chamber was under a high voltage (3 keV). The ions formed in it were drawn off and focused into a narrow beam by a system of electrostatic lenses. The signal was separated from the background of residual gases using a mobile shutter situated between the cell and ionization chamber. The mass spectra were recorded at an $E_e = 70 \text{ eV}$ ionizing electron energy and an $I_e = 1 \text{ mA}$ emission current from the cathode.

Ionic sublimation was studied similarly with the difference that a high voltage was directly applied to the cell or crystal holder. Ions of the thermal origin formed inside the effusion cell or on the surface of the crystal were then drawn off by a low electric field (10^4 – 10^5 V/m) created between the cell and collimator. A deflecting capacitor placed at the exit of the ion source allowed conditions to be selected for recording the ions drawn off from the inside cell cavity only.

Positive and negative ions could be recorded in one experiment because the current direction in an analyzing electromagnet, Hall probe polarity, and voltages on the cell and electrodes of the ion-optical system could be changed. The time of switching from one mode to another was $\sim 1 \text{ min}$.

After separation according to masses in a magnetic field, ions were directed to the collector and recorded by a secondary electron multiplier combined with an electrometric amplifier. The sensitivity of the recording scheme under the conditions of measurements of the direct current of positive ions was 10^{-17} A . For negative ions, the sensitivity could differ from this value severalfold because of a different mechanism of the ion beam action on the input dynode of the secondary electron multiplier. A high working vacuum (up to 10^{-5} Pa) in the mass spectrometer was created by three magnetic-discharge pumps.

The LaBr_3 samples studied were of a 99.99% purity. They were synthesized using the NH_4Br procedure [16, 17], according to which lanthanum oxide was dissolved in HBr , ammonium bromide was added into the solution in a $\text{La} : \text{NH}_4\text{Br}$ ratio of 1 : 3.5, and the solution was evaporated, the residue ground and heated, first in a flow of argon to 150°C and then slowly in a vacuum to

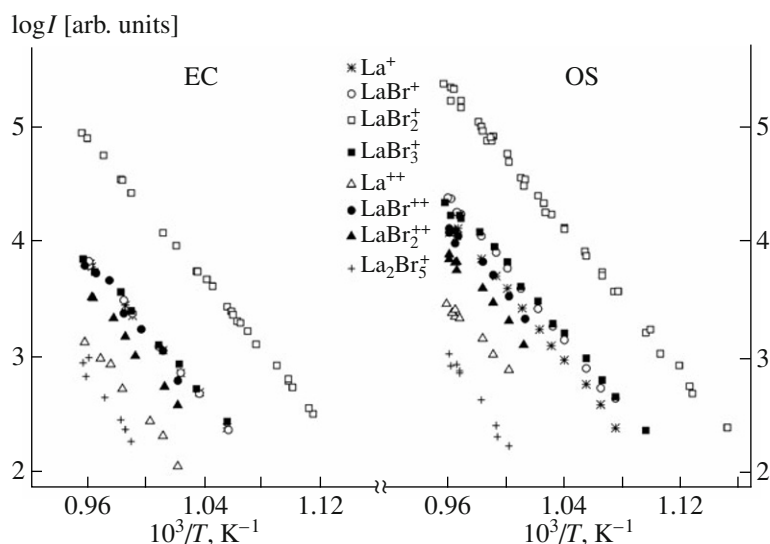
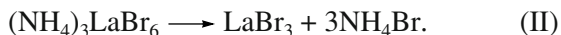
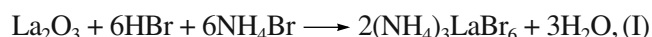


Fig. 1. Temperature dependences of ion currents measured under the conditions of LaBr_3 sublimation from the effusion cell (EC) and open single crystal surface (OS); I is the ion current.

decomposition temperatures $\sim 450^\circ\text{C}$. The overall reactions were



A single crystal of LaBr_3 was grown following the vertical Bridgman method from a lanthanum tribromide powder sealed in quartz ampules. All synthesis and crystal growth manipulations were performed in a dry box.

RESULTS AND DISCUSSION

Molecular Sublimation

Mass spectra. The qualitative composition of the ions recorded in the electron-impact mass spectra over the temperature range 848–1046 K was the same under the conditions of effusion measurements and sublimation from an open single crystal surface. Namely, the ions recorded were La^+ , LaBr^+ , LaBr_2^+ , LaBr_3^+ , La^{++} , LaBr^{++} , LaBr_2^{++} , and La_2Br_5^+ . As distinct from [7, 18], where fragmentation with the formation of double-charged ions was not studied, we found these ions to make a fairly substantial contribution to the total ion current produced in the interaction of the molecular beam of sublimation with an electron beam. The temperature dependences of ion currents are plotted in Fig. 1 in the $\log I - 1/T$ coordinates.

By way of example, the mass spectrum obtained at $T = 954$ K is presented in Table 1; for comparison, mass spectra obtained earlier are also given. In addition, Table 1 contains the appearance energies AE of ions obtained by the linear extrapolation¹ of the near-thresh-

¹ The use of a linear law for double-charged ions, for which a quadratic or some other threshold law is quite probable, is a fairly crude approximation.

old ionization efficiency curve portions with the use of Ag and H_2O as standards for the calibration of the energy scale of ionizing electrons.

An analysis of the coefficients of the linear equation

$$\log I = -A \times 10^3/T + B \quad (1)$$

(Table 2), the AE values, which were in close agreement with those reported in [18], and the shapes of ionization efficiency curves, which did not contain noticeable kinks, led us to conclude that the La^+ , LaBr^+ , LaBr_2^+ , LaBr_3^+ , La^{++} , LaBr^{++} , and LaBr_2^{++} ions were predominantly formed from monomeric LaBr_3 molecules with negligibly small possible fragmentation contributions of La_2Br_6 dimers, which predominantly fragmented to give La_2Br_5^+ ions. This conclusion is in agreement with that drawn in [7, 18]. Small differences between the mass spectra from different works as concerns the ratios between fragment ion currents, which, as is well known, possess excess kinetic energies, is likely a consequence of differences in the geometry of ion sources, mutual spatial orientations of the molecular, electronic, and ionic beams,² and the special features of ion-optical system focusing.

The thermodynamic characteristics of sublimation. The partial pressures of molecules in vapor were calculated using the standard mass spectrometric procedure for electron-impact ionization by the equation

$$p_i = \frac{kT}{\sigma_i^{\text{mol}}} \sum_j \frac{I_{ij}}{\gamma_j a_j}, \quad (2)$$

² In particular, as distinct from [7], where the molecular and ionic beams were mutually orthogonal, they were coaxial in our unit.

Table 1. Electron-impact mass spectra obtained under the conditions of sublimation from the effusion cell (EC) and from the open surface (OS) and ion appearance energies (AE)

Value	T , K	E_e , eV	La^+	LaBr^+	LaBr_2^+	LaBr_3^+	La^{++}	LaBr^{++}	LaBr_2^{++}	La_2Br_5^+	Refs.
I , % (EC)	954	70	8.9	9.1	100	10.3	1.3	7.6	4.1	0.34	[7]
	954	35	10.9	29.3	100	10.3				0.34	
	986	?	20	20	100	6				0.7	
I , % (OS)	954	70	7.2	10.9	100	12.7	2.1	7.7	4.6	0.22	[18]
AP, eV			21.1	15.1	11.0	9.3	33.9	30.7	27.0	11.0	
			19.7	15.1	10.2	9.4					[18]

Note: Mass spectra are given taking into account ion isotopic varieties; the error in appearance energies can be estimated at ± 0.5 eV; I is the relative ion current value.

Table 2. Coefficients of Eq. (1)

Ion	A	B	ΔT , K	N	A	B	ΔT , K	N
	EC conditions				OS conditions			
La^+	15.07 ± 0.12	18.30 ± 0.12	947–1040	8	15.52 ± 0.26	22.07 ± 0.27	931–1041	14
LaBr^+	15.16 ± 0.22	18.40 ± 0.22	946–1041	8	15.98 ± 0.16	22.73 ± 0.16	931–1043	14
LaBr_2^+	15.33 ± 0.07	19.62 ± 0.07	897–1046	25	15.95 ± 0.11	23.66 ± 0.11	868–1046	38
LaBr_3^+	14.50 ± 0.36	17.76 ± 0.36	947–1044	8	14.91 ± 0.27	21.67 ± 0.27	913–1044	15
La^{++}	16.66 ± 0.83	19.14 ± 0.83	978–1044	7	13.57 ± 0.59	19.48 ± 0.57	999–1044	8
LaBr^{++}	15.66 ± 1.02	18.85 ± 1.01	978–1044	7	14.81 ± 0.76	21.35 ± 0.74	988–1042	9

Note: N is the number of measurements.

where k is the sensitivity constant of the instrument (it was determined in a separate experiment with vaporization of silver), T is the temperature of the cell, σ^{mol} is the total ionization cross section of the i th molecule at the working ionizing electron energy (calculated from the ionization cross sections of atoms σ^{at} [19] as $\sigma^{\text{mol}} = 0.75 \sum_j \sigma_j^{\text{at}}$ [20]), $\sum_j I_{ij}/(a_j \gamma_j)$ is the total ion current of ions of all types formed from the i th molecule, a is the coefficient determined by the natural abundance of the isotopes of the elements constituting the ion, and γ is the ion-electron conversion coefficient (it is assumed that $\gamma \sim M^{-1/2}$ [21], where M is the molecular weight of the ion).

The temperature dependences of the saturated vapor pressures p (Pa) of monomeric and dimeric molecules were approximated by the equations

$$\log p(\text{LaBr}_3) = (-15.708 \pm 0.056) \times 10^3/T + (14.894 \pm 0.059), \quad T = 897\text{--}1046 \text{ K}, \quad (3)$$

$$\log p(\text{La}_2\text{Br}_6) = (-20.702 \pm 1.948) \times 10^3/T + (17.364 \pm 1.895), \quad T = 1010\text{--}1044 \text{ K}. \quad (4)$$

The values preceded by \pm are the standard deviations.

The partial pressures of saturated vapor molecules over crystalline lanthanum tribromide are given in Fig. 2 together with the results of the mass spectrometric study performed in [7] and the data [18, 22, 23] on the total vapor pressure. We see that the spread of LaBr_3 vapor pressures reported in the literature substantially exceeds one order of magnitude. The results obtained in this work much better agree with those reported in [22] and the most recent work [18]. Differences in pressure values determined mass spectrometrically are caused by errors in sensitivity constants. Note that the ratio between monomeric and dimeric molecule pressures obtained in this work and [7] closely agree with each other. A similar ratio value, although at one temperature only, was obtained in [18] in auxiliary mass spectrometric studies³ (see Table 1).

The enthalpies of sublimation of LaBr_3 crystals in the form of monomeric and dimeric molecules were determined from the temperature dependence of the partial pressures of saturated vapor components using the procedure for experimental data processing according to the second and third laws of thermodynamics. The thermodynamic functions of LaBr_3 in the condensed state necessary for these calculations were

³The mass spectrum was reported in [18] without specifying experimental conditions.

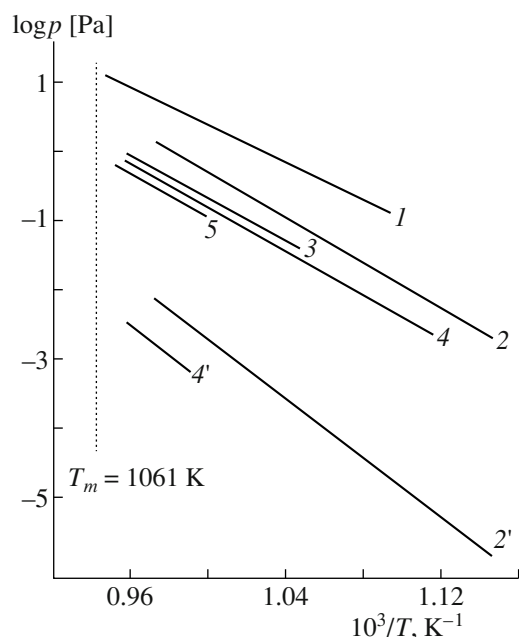


Fig. 2. Temperature dependences of saturated vapor pressure over LaBr_3 : $p(\text{LaBr}_3)$ from (1) [23], (2) [7], (3) [18], and (4) our data; $p(\text{La}_2\text{Br}_6)$ from (2') [7] and (4') our data.

obtained by Bergman (Joint Institute of High Temperatures, Russian Academy of Sciences) [24]. The thermodynamic functions of LaBr_3 and La_2Br_6 in the gas phase were calculated in this work in the rigid rotator-harmonic oscillator approximation. We used the molecular constants of LaBr_3 recommended in [4] on the basis of an analysis of the available experimental and theoretical data. The molecular constants of La_2Br_6 were obtained by Kovacs in ab initio calculations [25]. The reduced Gibbs energy values $\Phi^\circ(T) = -(G^\circ(T) - H^\circ(0))/T$ were approximated by the polynomial [20]

$$\Phi^\circ(T) = a + b \ln x + c \times 10^{-4} x^{-2} + dx^{-1} + ex + fx^2 + gx^3 \quad (x = T \times 10^{-4}), \quad (5)$$

whose parameters are listed in Table 3.

The results of the processing of the totality of experimental data, including literature data, on saturated vapor pressure according to the second and third laws of thermodynamics obtained using a unified set of thermodynamic functions are listed in Table 4.

Table 3. Parameters of polynomial (5)

Compound	$\Phi^\circ(T)$, J/(mol K)						
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>
LaBr_3	599.938	81.8494	-8.28424	0.442156	16.8896	-50.0233	72.3556
La_2Br_6	1107.20	180.665	-17.1836	1.02650	29.3746	-86.8675	125.136
$\text{LaBr}_3(\text{cr})$	106.729	1.13524	134.937	-2.00437	1703.37	-6351.80	13150.3

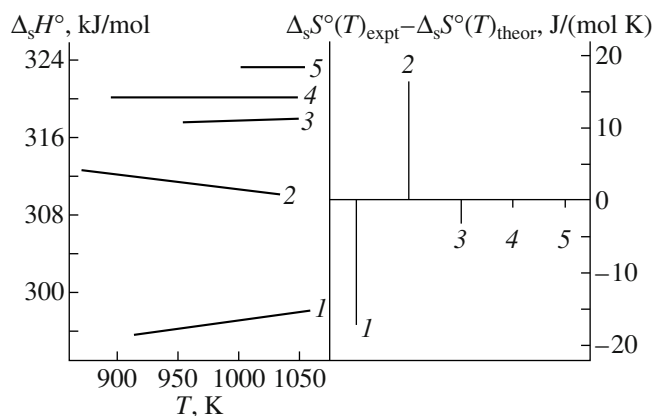


Fig. 3. Analysis of the temperature dependences of $\Delta_s H^\circ(\text{LaBr}_3, 298.15)$ and the difference $\Delta_s S^\circ(\text{LaBr}_3, T)_{\text{expt}} - \Delta_s S^\circ(\text{LaBr}_3, T)_{\text{theor}}$: (1) [23], (2) [7], (3) [18], (4) our data, and (5) [22].

According to a formal analysis of the results, the best agreement of the values obtained using the second and third laws was achieved in [22] and this work. In addition, these values closely agree in [18] and [26]. As concerns the enthalpies of sublimation determined according to the third law of thermodynamics, the value obtained in this work is very close to those reported in [18, 22, 26], whereas this value is substantially lower in [7] and, especially, [23]. A more detailed analysis of the results is based on consideration of the temperature dependence of the enthalpies calculated by the third law, which allows conclusions to be drawn concerning the reliability of the initial experimental data (provided the thermodynamic functions used are quite reliable), and a comparison of the entropies of sublimation determined experimentally according to the second law and calculated theoretically. The results of this analysis are shown in Fig. 3. According to this figure, the values obtained in this work and [18, 22] are more reliable than those reported in [7, 23]. The latter are characterized by noticeable variations in the enthalpy of sublimation depending on temperature and the largest discrepancies in the entropy values.

The enthalpies of sublimation in the form of dimeric molecules calculated according to the second and third laws of thermodynamics (Table 4) agree with each other. Similar agreement is observed for the values reported in [7].

Table 4. Enthalpies (kJ/mol) and entropies (J/(mol K)) of LaBr₃ sublimation in the form of monomeric and dimeric molecules

ΔT , K	N	T_{mh}	Second law			Third law	Refs.
			$\Delta_s H^\circ(T_{\text{mh}})$	$\Delta_s S^\circ(T_{\text{mh}})$	$\Delta_s H^\circ(298.15)$	$\Delta_s H^\circ(298.15)$	
$\text{LaBr}_3(\text{cr}) = \text{LaBr}_3(\text{gas})$							
897–1046	25	958	300.7 ± 1.1	189.5 ± 1.2	319.1 ± 1.1	320 ± 10	This work
855–1045	41	1000	294.7 ± 2.9	185.8 ± 3.8	314.6 ± 2.9	318 ± 10	[18]
873–1029	66	952	309.1 ± 1.1	207.3 ± 1.1	327.2 ± 1.1	311 ± 10	[7]
1305–1526	?	1416	225.3	120.1	323.6	320 ± 10	[26]
1002–1052	6	1027	301.0 ± 4.4	186.6 ± 4.3	321.9 ± 4.5	323 ± 10	[22]
915–1057	3	984	260.8	172.4	280.1	296 ± 10	[23]
$2\text{LaBr}_3(\text{cr}) = \text{La}_2\text{Br}_6(\text{gas})$							
1010–1044	7	1028	396 ± 37	236 ± 36	426 ± 37	451 ± 30	This work
873–1029	66	952	409.9 ± 1.9	262.2 ± 1.6	435.3 ± 1.9	440 ± 30	[7]

Note: The values preceded by \pm are standard deviations for the values calculated by the second law and limiting deviations, including statistical and systematic errors in temperature, pressure, and reduced Gibbs energies, for the values calculated by the third law; T_{mh} is the mean harmonic temperature. In [26], saturated vapor pressure was measured over liquid LaBr₃.

Free sublimation. The mass spectrum recorded under the conditions of Langmuir sublimation is evidence that La₂Br₆ dimeric molecules are also present in the sublimation flux from the open surface of LaBr₃ single crystals. The dimer/monomer concentration ratio is, however, larger in the flux from an effusion orifice than in the free sublimation flux. For instance, at $T = 1050$ K, the $p(\text{La}_2\text{Br}_6)/p(\text{LaBr}_3)$ values are 5.2×10^{-3} and 2.4×10^{-3} , respectively. In other words, the sublimation coefficients of monomers and dimers are different.

It was shown by the method of molecular beams that the probability of the formation of oligomeric molecules from monomers on ionic crystal surface terraces is low [27]. For this reason, surface oligomerization should be localized directly at vaporization steps and result from the coalescence of monomers that migrate along steps. Another mechanism of oligomer formation presupposes their direct detachment as such from kinks, viz., fractures of vaporization steps. A key parameter of both mechanisms is the energy of the detachment of molecules from kinks, which largely determines the activation energy of sublimation too.

The differences in the energy of detachment from kinks on a free surface in sublimation under Langmuir conditions and on a surface which is in dynamic equilibrium with the vapor phase in sublimation under Knudsen conditions can be caused by the special features of morphological surface development and crystal lattice relaxation in the vicinity of kinks. We, however, did not observe such a difference in the energy characteristics. In particular, the activation energies of sublimation of lanthanum tribromide crystals in the form of monomers and dimers determined from the regression coefficients of the dependences

$$\log \left(\sum_j I_j T / (a_j \gamma_j) \right) - 1/T$$

(j : La⁺, LaBr⁺, LaBr₂⁺, LaBr₃⁺, La⁺⁺, LaBr⁺⁺, and LaBr₂⁺⁺)
and

$$\log I_{\text{La}_2\text{Br}_6} T - 1/T$$

were $E_s(\text{LaBr}_3, 971 \text{ K}) = 300.6 \pm 1.8$ kJ/mol and $E_s(\text{La}_2\text{Br}_6, 1026 \text{ K}) = 381 \pm 15$ kJ/mol, respectively. The first value coincides with the enthalpy of monomeric sublimation $\Delta_s H^\circ(958 \text{ K}) = 300.7 \pm 1.1$ kJ/mol. As concerns the second value, the low intensities of the signals of La₂Br₅⁺ ions, the narrow temperature interval of measurements, and, accordingly, larger measurement errors prevent us from reliably putting it in correspondence to the enthalpy of dimeric sublimation 396 ± 37 kJ/mol, although these values can be taken to be equal to within measurement errors.

In terms of the terrace-ledge-kink model of the surface, the free sublimation model [28] predicts that the concentration of particles undergoing sublimation, which are localized close to steps, should virtually be equal to the equilibrium concentration, whereas their concentration on terraces is determined by such a kinetic parameter as the mean displacement of a particle involved in surface self-diffusion d [29],

$$d = r \exp \left(\frac{E_{\text{des}} - E_{\text{diff}}}{2kT} \right), \quad (6)$$

where r is the mean diffusion jump length and E_{diff} and E_{des} are the activation energies of surface self-diffusion on a terrace and desorption from a terrace, respectively. Just the d parameter at the given distance between

Table 5. Ionic sublimation mass spectra measured under effusion cell and open surface conditions

Value	T , K	Br^-	LaBr_4^-	La_2Br_7^-
I , % (EC)	1048	0.022	100	2.9
I , % (OS)	1048	0.0054	100	2.9

Note: Mass spectra are given taking into account ion isotopic varieties.

vaporization steps λ determines the partial sublimation coefficients [30, 31],

$$\alpha_s = \frac{d}{\lambda} \tanh\left(\frac{\lambda}{d}\right). \quad (7)$$

It follows that a smaller (approximately by a factor of 2) α_s value for dimers compared with monomers is likely caused by the special features of surface diffusion, which can be of interest for studies by the method of molecular beams.

Ionic Sublimation

In this work, we for the first time studied the sublimation of ions from the surface of LaBr_3 . As with the thermal emission of ions from lanthanum trifluoride [32] and trichloride [33], we found that lanthanum tribromide sublimates only in the form of negative ions such as Br^- , LaBr_4^- , and La_2Br_7^- (we omit from consideration the emission of positive alkali metal ions observed always, which are present as impurities). The novelty in principle of the present study was measurements of the ionic sublimation of LaBr_3 from both the effusion cell and the surface of a single crystal. The quantitative composition of the ionic beams formed

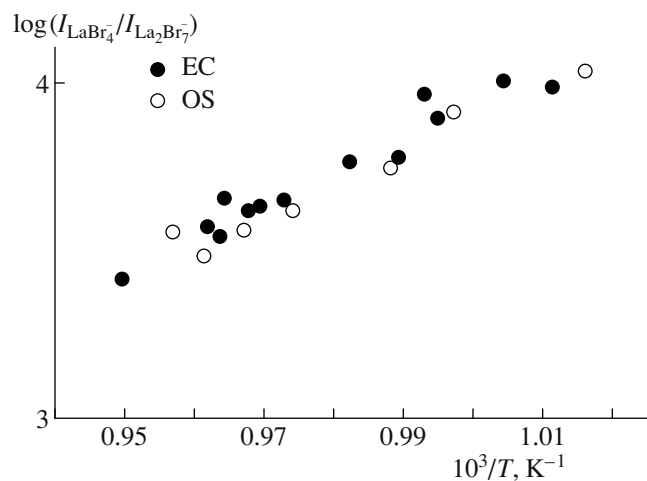
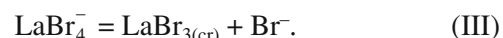


Fig. 4. Dependences of the ion current ratio $I(\text{LaBr}_4^-)/I(\text{La}_2\text{Br}_7^-)$ on the inverse temperature under effusion cell (EC) and open surface (OS) conditions.

under different measurement conditions is presented in Table 5. According to this table, the main difference between the mass spectra is a much lower intensity of the signal of Br^- ions in the flux from an open surface. This result immediately attracted our attention for the following methodological reason.

One of the important applications of high-temperature mass spectrometry is the determination of the thermochemical characteristics of molecular ions in the gas phase that are formed on the surface of ionic crystals under thermodynamic equilibrium conditions [34]. For instance, the enthalpy of formation of LaBr_4^- ions can be determined by studying the heterophase ion-molecular reaction



The systematic error in the equilibrium constant of this reaction calculated from the ion current ratio $I(\text{Br}^-)/I(\text{LaBr}_4^-)$ is related to the problem of the probable contribution of halogen anions formed on the outer effusion cell surface [32, 33]. Studies of ionic sublimation from the surface of a single crystal with the use of a drawing out electrode-collimator fully removes this problem. Another question then, however, arises, namely, can calculations of the equilibrium constant of reaction (III) from the currents recorded under open vaporization conditions be considered justified? In other words, to what extent can the application of the quasi-equilibrium approach to these results be considered correct?

In the first place, it is pertinent to note that the use of the technique of the reversal of drawing out electric field polarity [35] showed that no accumulation of ions on the surface occurred during the time of reversal. This, in particular, excludes consideration of dislocations emerging to the surface of the crystal [36] as sources of bromine anions. For this reason, Br^- anions are in all probability produced directly on the surface and are detached from kinks.

Suppose that the LaBr_4^- and La_2Br_7^- ions are formed by the sequential addition of adsorbed LaBr_3 molecules to the Br^- anion, that is, they are homologues of the $\text{La}_n\text{Br}_{3n+1}^-$ series. Equal ion current ratios $I(\text{LaBr}_4^-)/I(\text{La}_2\text{Br}_7^-)$ at various temperatures under equilibrium and free sublimation conditions then testify to the validity of K_p calculations for reaction (III) from the data obtained under free vaporization conditions. The temperature dependence of this ratio is shown in Fig. 4. We see from this figure that, to within measurement errors, the $I(\text{LaBr}_4^-)/I(\text{La}_2\text{Br}_7^-)$ ratio remains virtually unchanged when we pass from effusion cell to open vaporization conditions.

Another convincing argument is a comparison of the thermodynamic stabilities of LaBr_4^- ions in the gas phase determined experimentally and calculated by quantum-

chemical methods.⁴ The energy of the detachment of the bromine anion from LaBr_4^- was 302 ± 10 kJ/mol at 0 K according to our data. Theoretical density functional theory calculations give 303 kJ/mol. Such a coincidence of the results is evidence that studies of ionic sublimation from LnX_3 single crystals allow reliable data on the thermochemical properties of negative ions to be obtained.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research, project no. 06-03-32496.

REFERENCES

1. C. E. Myers and D. T. Graves, *J. Chem. Eng. Data* **22**, 440 (1977).
2. H. Oppermann and P. Schmidt, *Z. Anorg. Allg. Chem.* **631**, 1309 (2005).
3. L. B. Pankratz, *Thermodynamic Properties of Halides* (U.S. Department Int., Bureau of Mines, Washington, D.C., 1984), Bulletin 674.
4. A. Kovacs and R. G. M. Konings, *J. Phys. Chem. Ref. Data* **33**, 377 (2004).
5. L. Rycerz, E. Ingier-Stocka, B. Ziolk, et al., *Z. Naturforsch., A: Phys. Sci.* **59**, 825 (2004).
6. L. S. Kudin and D. E. Vorob'ev, *Zh. Fiz. Khim.* **79** (8), 1395 (2005) [*Russ. J. Phys. Chem.* **79** (8), (2005)].
7. Cl. Gietmann, K. Hilpert, and H. Nickel, *Thermodynamische Eigenschaften von Halogeniden der Lanthaniden* (Forschungszentrum Jülich, 1997).
8. G. Oczko, L. Macalik, Ja. Legendziewicz, and J. J. Hanuza, *J. Alloys Compd.* **380**, 327 (2006).
9. K. W. Krämer, P. Dorenbos, H. U. Güdel, and C. W. E. van Eijk, *J. Mater. Chem.* **16**, 2773 (2006).
10. M. F. Butman, L. S. Kudin, A. A. Smirnov, and Z. A. Munir, *Int. J. Mass Spectrom. Ion Processes* **202**, 121 (2000).
11. M. F. Butman, A. A. Smirnov, L. S. Kudin, and Z. A. Munir, *Int. J. Mass Spectrom. Ion Processes* **194**, 69 (2000).
12. M. F. Butman, A. A. Smirnov, L. S. Kudin, and Z. A. Munir, *J. Mater. Synthesis Processing* **8**, 93 (2000).
13. M. F. Butman, L. S. Kudin, A. A. Smirnov, and Z. A. Munir, *J. Mater. Synthesis Processing* **7**, 115 (1999).
14. A. A. Chernov, *J. Cryst. Growth* **264**, 499 (2004).
15. T. Markus, U. Niemann, and K. Hilpert, *J. Phys. Chem. Solids* **66**, 372 (2005).
16. G. Meyer and M. S. Wickleder, in *Handbook on the Physics and Chemistry of Rare Earth*, Ed. by K. A. Gschneidner and L. Eyring (Elsevier, Amsterdam, 2000), Vol. 28, Ch. 177, p. 53.
17. G. Meyer, *Inorg. Synth.* **25**, 146 (1989).
18. B. Brunetti, A. R. Villani, V. Piacente, and P. Scardala, *J. Chem. Eng. Data* **45**, 231 (2000).
19. J. B. Mann, in *Recent Developments in Mass Spectrometry*, Ed. by K. Ogata and T. Haykawa (Univ. of Tokyo, Tokyo, 1970), p. 814.
20. *Thermodynamic Properties of Pure Substances: A Handbook*, 3rd ed., Ed. by V. P. Glushko (Nauka, Moscow, 1978–1984), Vols. 1–4 [in Russian].
21. P. W. Gilles, B. R. Conard, R. I. Sheldon, and J. E. Bennet, in *Thermodynamics of Nuclear Materials* (IAEA, Vienna, 1975), Vol. 2, p. 499.
22. V. E. Shimazaki and K. Niwa, *Z. Anorg. Allg. Chem.* **314**, 21 (1962).
23. E. R. Harrison, *J. Appl. Chem.* **2**, 601 (1952).
24. *IVTANTERMO-2006 Database*.
25. A. Kovác, *Chem. Phys. Lett.* **319**, 238 (2000).
26. A. Makhmudmurodov, M. Temurova, and A. Sharipov, *Izv. Akad. Nauk Tadzh. SSR, Otd. Fiz-Mat., Khim. Geol. Nauk* **111** (1), 39 (1989).
27. H. Dabringhaus and H. J. Meyer, *J. Cryst. Growth* **61**, 91, 95 (1983).
28. J. P. Hirth and G. M. Pound, *Condensation and Evaporation: Nucleation and Growth Kinetics* (Pergamon, Oxford, 1963; Metallurgiya, Moscow, 1966).
29. H. J. Meyer and H. Dabringhaus, in *Current Topics in Material Science*, Ed. by E. Kaldis (North-Holland, Amsterdam, 1978), Vol. 1, p. 47.
30. J. P. Hirth and G. M. Pound, *J. Chem. Phys.* **26**, 1216 (1957).
31. T. Surek, G. M. Pound, and J. P. Hirth, *J. Chem. Phys.* **55**, 5157 (1971).
32. A. T. Pyatenko, A. V. Gusarov, and L. N. Gorokhov, *Teplofiz. Vys. Temp.* **19** (2), 329 (1981).
33. M. F. Butman, L. S. Kudin, G. G. Burdukovskaya, et al., *Zh. Fiz. Khim.* **61** (11), 2880 (1987).
34. L. N. Sidorov, M. V. Korobov, and L. V. Zhuravleva, *Mass-Spectrometry Thermodynamic Investigations* (Mosk. Gos. Univ., Moscow, 1985) [in Russian].
35. M. F. Butman and H. Dabringhaus, *Surf. Sci.* **540**, 313 (2003).
36. H. Dabringhaus and M. F. Butman, *Surf. Sci.* **560**, 167 (2004).

⁴These data are now being prepared for publication.