Thermochimica Acta 622 (2015) 82–87

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Mass spectrometric study of molecular and ionic sublimation of lanthanum triiodide

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ARTICLE INFO

Article history:
Received 31 May 2015
Received in revised form 4 September 2015
Accepted 6 September 2015
Available online 21 September 2015

Keywords:
Knudsen effusion mass spectrometry
Lanthanum triiodide
vapor pressure
Sublimation enthalpy
Ion-molecular reactions
Electron work function

ABSTRACT

The molecular and ionic composition of saturated vapor over lanthanum triiodide was studied by Knudsen effusion mass spectrometry. The $(LaI_3)_n$ molecules (n = 1–3) and the $[I(LaI_3)_n]^-$ ions (n = 0–4) were observed. The partial pressures of the molecules were determined and the enthalpies of sublimation, $\Delta_s H^\circ$ (298.15 K) in kJ mol^{-1}, in the form of monomers (304 ± 7), dimers (428 ± 25), and trimers (455 ± 50) were obtained by the second and third laws of thermodynamics. The enthalpy of formation, $\Delta_f H^\circ$ (298.15 K) in kJ mol^{-1}, of the LaI_3 (−376 ± 10), La_2I_6 (−932 ± 25), La_3I_9 (−1585 ± 50) molecules and the LaI_4^- (−841 ± 24), $La_2I_7^-$ (−1486 ± 32) ions were determined. The electron work function, φ_e = 3.5 ± 0.3 eV, for the LaI_3 crystal was calculated from the thermochemical cycle.

1. Introduction

For a long time lanthanide halides have been in the focus of attention of many scientific groups due to their promising light emission [1] and catalytic [2] properties. The thermodynamic information on these compounds is a necessary prerequisite for various technological applications. The investigation of the vaporization plays a key role for the determination of various characteristics of the gaseous species (molecules and ions) such as formation enthalpy, atomization energy, bond energy, ionization energy, electron affinity etc. It is generally accepted that the most reliable data for these quantities are obtained by the Knudsen effusion mass spectrometry (KEMS), which options enable studies of thermodynamic properties of both neutral and charged vapor species [3,4].

Lanthanum triiodide is among those lanthanide halides for which a thorough KEMS study was not performed yet and the ionic vapor constituents were not known so far. The first measurement of the vapor pressure over LaI_3 was carried out by Shimazaki and Niwa [5] using a Knudsen effusion technique. The same method was applied later by Hirayama et al. [6]. In addition the authors of Ref. [6] investigated the vapor composition by time-of-flight mass spectrometry and found the fraction of dimer molecules to be less than 0.5%. A torsion effusion method was applied by Brunetti et al. [7] to determine the total vapor pressure. Note that the variation in the vapor pressure values reported in Refs. [5–7] reaches almost an order of magnitude.

Thus the aim of the present work, which continues our systematic investigations (see e.g. [8–11]) of the molecular and ionic sublimation of lanthanide halides by KEMS, is not only to refine the available thermodynamic data for LaI_3 but to obtain as well new information for previously undiscovered minor vapor species. The use of a modern high sensitive registration system allowed us to expand the detection limits and to measure the partial pressures of oligomeric molecules and a variety of negative cluster ions.

2. Experimental

A single-focusing magnetic sector type mass spectrometer MI1201 modified for high-temperature studies was used. A detailed description and schematic representation of the apparatus were given in Refs. [12,13]. The mass spectrometer was equipped with a combined ion source which enabled measurements in the following two alternative regimes: the electron ionization, *IE* (for the analysis of neutral vapor species), and the thermal ion emission, *TE* (for charged vapor species). In latter case, the ions formed inside an effusion cell by thermal ionization are drawn out from it by an electric field in the magnitude of 10^4–10^5 V/m. The polarity of the high voltage applied to the cell and the ion-optical system electrodes

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http://dx.doi.org/10.1016/j.tca.2015.09.008
0040-6031/

could be changed with respect to the potential of the ground. Thus, ions of both positive and negative charge could be analyzed. Switching from one mode to another is performed automatically and takes about 1 min. The registration system consists of a secondary electron multiplier Hamamatsu R595 (with a gain of 10^6 at 1500 V) and a picoammeter Keythley 6485 (with 10 fA resolution and 20 fA typical RMS noise). It allows to measure ion currents down to 10^{-18} A.

The lanthanum triiodide crystalline sample was synthesized from bulk lanthanum metal (99.9%, Strem) and iodine (p.a., sublimed, Merck) at the University of Bern. With one percent excess of iodine the elements were sealed in an evacuated silica ampoule (typically 20 g total weight) and slowly heated to 1000° K until the reaction was completed (typically two weeks). Afterwards the excess of iodine was removed by heating under vacuum. The product was sublimed in a silica ampoule under vacuum for purification. By this procedure oxygen-free, crystalline LaI_3 of $PuBr_3$ type crystal structure and faint yellow color is obtained. The phase purity was checked by powder X-ray diffraction. The chemical purity is >99.9% (La metal) due to the purification of LaI_3 by sublimation. Since LaI_3 is strongly hygroscopic all synthesis was done under strictly dry and anhydrous conditions in sealed ampoules or glove boxes (M. Braun, Munich) with O_2 and H_2O < 0.2 ppm. The sample was placed into a molybdenum effusion cell with inner diameter of 6 mm and height of 10 mm. The lid of the cell has cylindrical effusion orifice (diameter of 0.3 mm, length of 1 mm). Vaporization-to-effusion area ratio was about 400. The temperature of the cell was measured by a tungsten–rhenium thermocouple with uncertainty ±5 K. The cell was loaded in a glove-box under dry conditions and then transferred into the vaporization chamber of the mass spectrometer and evacuated.

3. Results and discussion

3.1. Neutral vapor constituents

In the *IE* mass spectra the La^+ (18), LaI^+ (15), LaI_2^+ (100), LaI_3^+ (49), $La_2I_5^+$ (0.7), and $La_3I_8^+$ (<10^{-2}) ions, as well as the doubly charged La^{++} (0.5), LaI^{++} (3), and LaI_2^{++} (0.05) ions were registered in the saturated vapor over lanthanum triiodide in the temperature range of 827–978 K. The relative ion currents given in parentheses are exemplified for the temperature of 989 K and the energy of ionizing electrons of 40 eV. The mass spectra were found to be time-independent thereby indicating the thermal stability of the lanthanum triiodide in the temperature range studied.

By analogy with other lanthanide trihalides, see e.g. [11,14,15], the molecular precursors were assumed as follows: (i) the ions with one atom of lanthanum are formed as a result of the direct (LaI_3^+) and dissociative (La^+, LaI^+, and LaI_2^+) ionization of the monomer LaI_3 molecules with negligibly small fragmentation contributions from more complex molecules; (ii) the $La_2I_5^+$ and $La_3I_8^+$ ions are the products of dissociative ionization of the dimer La_2I_6 and trimer La_3I_9 molecules, respectively. The temperature dependence of the ion currents supports this assumption, see Fig. 1.

The partial pressures of molecules (p_j), see Table 1, were calculated according to the conventional procedure using equation:

$$p_j = \frac{k \cdot I \cdot T}{\sigma_j} \quad (1)$$

where k is the sensitivity constant of mass spectrometer (determined in a separate experiment with an Ag as a reference sample; vapor pressure of pure silver was taken from [16]), σ_j is the ionization cross-section of the jth molecule at the working energy of the ionizing electrons (calculated from the experimentally determined atomic cross sections, σ_{at} [17,18], by the equation $\sigma_j = 0.75 \Sigma \sigma_{at}$ [19]), $I_j = \sum_i I_{ij}/(a_i \cdot \gamma_i)$ is the total ion current of ith ion species formed from the jth molecule, a_i is the natural abundance of the measured isotope of the ith ion, γ_i is the ion-electron conversion coefficient of the ith ion ($\gamma_i \sim M^{-1/2}$ [20], where M is the mass of ion), and T is the temperature of the cell. It should be emphasized that the application of the accurate experimental σ_{at} values [17,18] leads to more than two times higher pressures compared to traditionally used Mann's cross-sections [21].

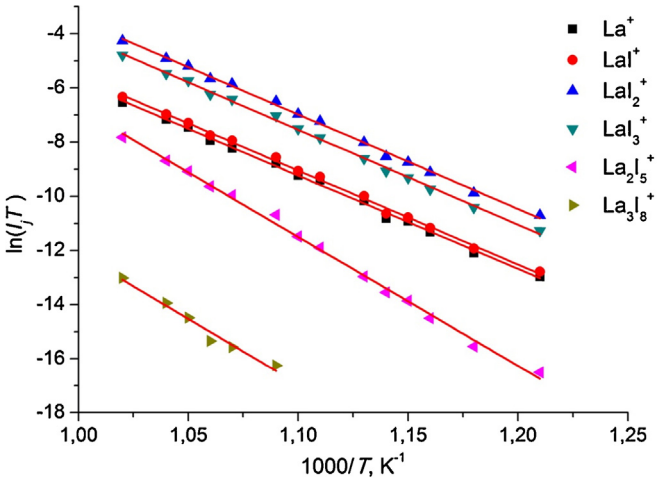

Fig. 1. Temperature dependence of ion currents in the *EI* regime

The temperature dependence of the saturated vapor pressures of the monomer and oligomer molecules was approximated by the equation:

$$\ln p_j = -A \times \frac{10^3}{T} + B \quad (2)$$

The coefficients of Eq. (2) are given in Table 2.

The partial pressures of molecules in the saturated vapor over crystalline lanthanum triiodide from different references are compared in Fig. 2. As it has been previously mentioned and can be seen in Fig. 2, all the data for the monomer molecules are scattered within about one order of magnitude. Our temperature dependence is located between those of Shimazaki and Niwa [5] and Brunetti

Table 1
Partial pressures (Pa) of molecules in the vapor over LaI_3.

LaI_3		La_2I_6		La_3I_9	
T, K	$p_j \cdot 10^3$	T, K	$p_j \cdot 10^5$	T, K	$p_j \cdot 10^6$
905	17	905	6.5	923	0.46
884	7.1	884	2.0	937	1.1
869	3.5	869	0.75	943	1.5
862	2.5	862	0.47	954	2.8
845	1.1	845	0.16	962	4.1
827	0.47	827	0.048	978	10
875	4.7	875	1.1		
910	22				
910	8.9				
921	34				
921	16				
937	65				
937	40				
943	81				
943	54				
953	120				
953	91				
962	170				
962	140				
978	310				
978	330				

The relative standard uncertainty does not exceed 0.5% in temperature and 5% in pressure. Systematic error in pressure may be as high as 100% due to that in molecular ionization cross-sections.