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Sublimation enthalpies of gadolinium and thulium triiodides and formation enthalpies of the molecules LnI_3, Ln_2I_6, and Ln_3I_9 (Ln = Gd, Tm)

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ABSTRACT

The sublimation of solid gadolinium and thulium triiodides was studied by Knudsen effusion mass spectrometry. The partial vapor pressures [atm] of the monomer and dimer molecules were determined as: $\ln p(GdI_3) = -(32.31 \pm 0.18) \times 10^3/T + (21.38 \pm 0.21)$ for 777–946 K; $\ln p(Gd_2I_6) = -(38.07 \pm 0.42) \times 10^3/T + (24.49 \pm 0.47)$ for 843–946 K; $\ln p(TmI_3) = -(31.84 \pm 0.25) \times 10^3/T + (21.88 \pm 0.29)$ for 760–965 K; and $\ln p(Tm_2I_6) = -(38.23 \pm 0.27) \times 10^3/T + (25.71 \pm 0.43)$ for 799–965 K. In addition, the trimers Gd_3I_9 and Tm_3I_9 were detected in very small fractions. On the basis of a joint analysis of all available data in literature, the sublimation enthalpies [kJ mol^{-1}] at 298.15 K are recommended as 283 ± 9 (GdI_3), 336 ± 16 (Gd_2I_6), 366 ± 50 (Gd_3I_9), 276 ± 3 (TmI_3), 330 ± 6 (Tm_2I_6), and 354 ± 50 (Tm_3I_9). The standard formation enthalpies [kJ mol^{-1}] of the gaseous species at 298.15 K are −341 ± 9 (GdI_3), −912 ± 16 (Gd_2I_6), −1506 ± 50 (Gd_3I_9), −344 ± 5 (TmI_3), −909 ± 7 (Tm_2I_6), and −1506 ± 50 (Tm_3I_9).

1. Introduction

A wide range of technological applications of lanthanide halides require the knowledge of their basic physicochemical properties. Among these, the vapor pressure and thermodynamic parameters of vapor species are of special interest and great importance for high-temperature processes. A well-known example is the metal halide lamp. Salt mixtures, iodides and bromides including lanthanide halides, improve the performance of these light sources [1]. The thermodynamic properties of lanthanide halide molecules, especially those of lanthanide iodides, are rarely studied. They ask for further investigation and deeper analysis. This work reports sublimation studies of GdI_3 and TmI_3 by high temperature mass spectrometry (KEMS). It continues our line of research with previous contributions on PrI_3 [2], LaI_3 [3], and CeI_3 [4].

Hirayama and co-workers were the first who studied mass spectra of the saturated vapor [5,6] and measured the total vapor pressures over solid GdI_3 and TmI_3 by the Knudsen effusion mass loss (KEML) technique [7]. As they concluded from the analysis of mass spectra and ion appearance energies, these compounds sublime congruently in the form of monomer molecules LnI_3 (Ln = Gd, Tm). Hence, the thermodynamic parameters for the reaction $LnI_3(s) = LnI_3(g)$ were derived from their mass spectrometric and KEML data. In contrast, Dettingmeijer and Dielis [8] stated that the dimer species Tm_2I_6 is present in a large amount (about 40% at 1000 K) in the vapor of TmI_3. These authors observed the di-Ln ions $Tm_2I_n^+$ (n = 3–5) and assumed that a significant fragmentation of the dimer produces the mono-Ln ions TmI_n^+ (n = 0–2). Accordingly, they applied this assumption to treat their vapor pressure data obtained by the KEML method and gave the partial pressures and thermodynamic parameters for the molecules TmI_3 and Tm_2I_6. Struck and Feuersanger [9] confirmed the existence of Tm_2I_6 in the vapor over TmI_3, but they did not agree with the quantitative interpretation of the mass spectra suggested in Ref. [8]. Karwath et al. [10] used the same method and reported the partial pressures and sublimation parameters of thulium triiodide in the form of monomer and dimer species. Piacente et al. [11] and Brunetti et al. [12] (the same group) applied the torsion effusion technique to measure the vapor pressure over GdI_3 and TmI_3. They processed their data on the total vapor pressure assuming that the vapor consists of monomers only. They estimated that the neglect of dimers in amount of up to 10% introduces an error which does not exceed their experimental uncertainty. Later on, Giricheva et al. [13] determined the dimer fraction for GdI_3 by mass spectrometry as 2.8% at 1100 K. Recently, Curry et al. [14] reported the pressure measurements for TmI_3 in the range of 10^2–10^5 Pa by X-ray induced fluorescence.

The parameter values reported in literature for the sublimation

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Table 1
Mass spectra of GdI_3 and TmI_3 [% of the maximum intensity] and the ion appearance energies *AE* [eV] (reported in parentheses with an estimated uncertainty of ± 0.5 eV). Temperature *T* [K], ionization energy *E* [eV].

	GdI_3			TmI_3			
	this work	Ref. [5]	Ref. [13]	this work	Ref. [6]	Ref. [8]	Ref. [9][a]
T	875	943	1100	936	913	970	not
E	40	28	50	40	28	28	specified
Ln^+	49	47	32	54	51	35	8
	(17.5)	(17.0)		(15.4)	(16.1)		(15.2)
LnI^+	34	66	27	27	37	28	27
	(14.1)	(13.5)		(12.0)	(12.4)		(12.1)
LnI_2^+	100	100	100	100	100	100	88
	(10.7)	(10.1)		(9.8)	(10.5)		(10.5)
LnI_3^+	16	69	41	7	50	72	100
	(9.3)	(9.2)		(8.5)	(9.2)		(9.6)
$Ln_2I_3^+$	–			0.3		2	
$Ln_2I_4^+$	–			2		8	0.6
$Ln_2I_5^+$	5		11	6		16	3
	(9.7)						(9.8)
$Ln_3I_8^+$	0.01			0.01			

[a] The relative ion current intensities were extracted from Fig. 2 in Ref. [9].

enthalpies of gadolinium and thulium triiodides are quite scattered. They require a critical analysis on the basis of a common set of thermodynamic functions in order to obtain reliable values. Moreover, the fraction of dimers and other complex species in the saturated vapor over GdI_3 and TmI_3 should be verified and their thermodynamic parameters determined.

2. Experimental

A commercial magnetic type mass spectrometer MI1201 modified for high-temperature studies was used. Vapor species were ionized by electrons emitted from a filament-type tungsten cathode. The electrons' energy could be varied in a range of 3–150 eV. The registration system consisted of a secondary electron multiplier Hamamatsu R595 (with a gain of 10^6 at 1500 V) and a picoammeter Keithley 6485 (with 10 fA resolution and 20 fA typical RMS noise). It allows to measure ion currents down to 10^{-18} A. Further details on the apparatus and experimental procedure were described earlier [15–18]. Samples of GdI_3 and TmI_3 were synthesized from Gd (99.9%, Reacton), Tm (99.99%, Stanford materials corp.), and iodine (> 99.8%, sublimed, Merck). The bulk metal was broken to 2–3 mm size pieces. With one percent excess of iodine, the elements were sealed in an evacuated silica ampoule (typically 20 g total weight) and slowly heated to 700 °C or 750 °C for GdI_3 or TmI_3, respectively. After the reaction was completed, typically in two weeks, the ampoule was opened and the excess iodine removed under vacuum. The product was sealed in a silica ampoule under vacuum again and sublimed at 800 °C for purification. This procedure results in oxygen-free, crystalline GdI_3 and TmI_3 of the BiI_3 crystal structure. The phase purity was verified by powder X-ray diffraction. The chemical purity is > 99.9% due to the purification by sublimation. Since rare earth iodides are strongly hygroscopic, all syntheses were done under strictly dry and oxygen-free conditions in sealed ampoules or glove boxes (M. Braun, Munich) with O_2 and H_2O < 0.2 ppm. The samples were loaded at atmospheric pressure into molybdenum effusion cells, which were found to be inert with respect to lanthanide iodides, with a vaporization to effusion area ratio of about 400. Promptly, the cells were installed into the mass spectrometer and evacuated. The contact with air was minimized to a few minutes. In order to safely remove the adsorbed moisture due to the short air contact, the samples were kept in a vacuum of ~10^{-1} Pa at a temperature of ~150 °C for several hours before the experiments were started.

3. Results

3.1. Mass spectra interpretation

The sublimation of GdI_3 and TmI_3 was studied in the temperature ranges of 777–946 K and 760–965 K, respectively. The recorded mass spectra are presented in Table 1. The compositions of mono-Ln ions with the most intense LnI_2^+ ion are in agreement with those of Refs. [5,6,8,13] as well as with other lanthanide triiodides [2–4]. A somewhat different mass spectrum for TmI_3 [9] with dominating TmI_3^+ ions was seemingly recorded at lower ionization energy (not specified). The doubly charged ions Ln^{++}, LnI^{++}, and LnI_2^{++} (not shown in Table 1) were also detected in a total amount of about 7%; this fact agrees with our earlier observations for LaI_3 [3], CeI_3 [4], and PrI_3 [2]. All mono-Ln ions are mainly formed from LnI_3 molecules, as it is supported from the analysis of their appearance energies *AE*, see Table 1, and the temperature dependency of the product of ion current and temperature *IT*, as exemplified for TmI_3 in Fig. 1. The *AE* values were calculated from the measured ionization efficiency curves (exemplified for TmI_3 in Fig. 2) by the linear extrapolation and vanishing current methods; the averaged values are given in Table 1. The energy scale in Fig. 2 was corrected by the ionization energy of HI (10.386 ± 0.001 eV [19]); the correction value was found to be 2.4 eV. The di-Ln ions, see Table 1,

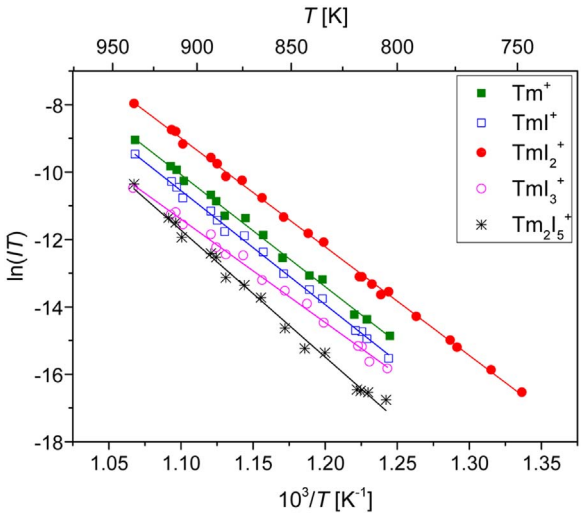

Fig. 1. Temperature dependence of the ion currents for TmI_3.