Mass Spectrometric Study of the Ln-LnI_3 (Ln = La, Ce) Systems

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In most cases lanthanide halides are considered as dielectric materials. There are however some exceptions such as La, Ce, Pr, Nd, Gd diiodides with electron configuration of [Xe] $6s^0 5d^1 4f^{n-1}$. Such compounds are electric conductors and can be characterized by the formula $Ln^{3+}(\bar{e})(I^-)_2$.

The synthesis of lanthanide diiodides requires knowledge on their high temperature behavior. In particular, the thermal stability and vapor composition are of interst.

This work deals with the *in situ* synthesis of the lanthanum and cerium diiodides by the reaction [1]:

$$2LnI_{3(l)} + Ln_{(s)} \rightarrow 3LnI_{2(l)}$$

inside the Knudsen cell with simultaneous mass-spectrometric examination of the vapor composition over the Ln-LnI_3 reaction system with initial mass ratio of Ln and LnI_3 in the mixture as 1:7.43.

The research has been performed by Knudsen effusion mass spectrometry technique. The sector type mass spectrometer MI1201 modified for high-temperature studies was used. It works in electron ionization (*EI*) and thermionic emission (*TE*) regimes which allow investigating both the neutral and charged gas phase species. The mass spectra recorded are given in Table 1.

Table 1. The ions in the mass spectra for vaporization of the Ln-LnI_3 (Ln = La, Ce) systems

Object	Regime	Temperature range, K	Identified ions
LaI_3	*EI*	860 – 1020	La^+, LaI^+, LaI_2^+, LaI_3^+, $La_2I_4^+$, $La_2I_5^+$
	TE	880 – 1020	I^-, LaI_4^-, $La_2I_7^-$, $La_3I_{10}^-$, $La_4I_{13}^-$
La-LaI_3	*EI*	890 – 1300	La^+, LaI^+, LaI_2^+, LaI_3^+, $La_2I_3^+$, $La_2I_4^+$, $La_2I_5^+$
	TE	1140 – 1290	I^-, LaI_3^-, LaI_4^-, $La_2I_7^-$
CeI_3	*EI*	920 – 1120	Ce^+, CeI^+, CeI_2^+, CeI_3^+, $Ce_2I_6^+$
	TE	930 – 1220	I^-, CeI_4^-, $Ce_2I_7^-$
Ce-CeI_3	*EI*	910 – 1290	Ce^+, CeI^+, CeI_2^+, CeI_3^+, $Ce_2I_3^+$, $Ce_2I_4^+$, $Ce_2I_5^+$, $Ce_2I_6^+$

The temperature dependences of the ion currents for *EI* regime are shown for LaI_3 (Fig.1, *a*) and La-LaI_3 (Fig.1, *b*). The presence of the two evaporation stages for the system (Fig.1 *b*) was determined. The similar dependence was observed for the Ce-CeI_3 system as well.

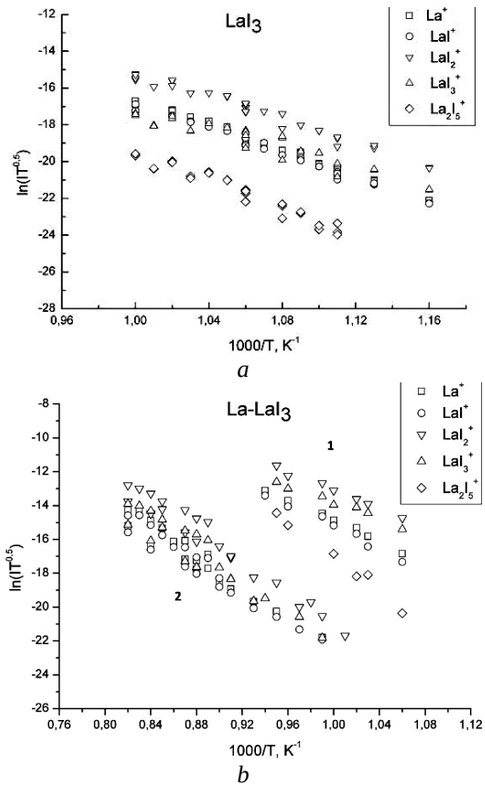

Fig.1 The temperature dependences of the ion currents for *EI* regime: LaI_3 (*a*), La-LaI_3 (*b*)

The evidence for the formation of LnI_2 comes from the mass spectra comparison at these two stages (Fig.2). The second stage indicates the temperature interval in which disproportionation reaction takes place with high rigor.

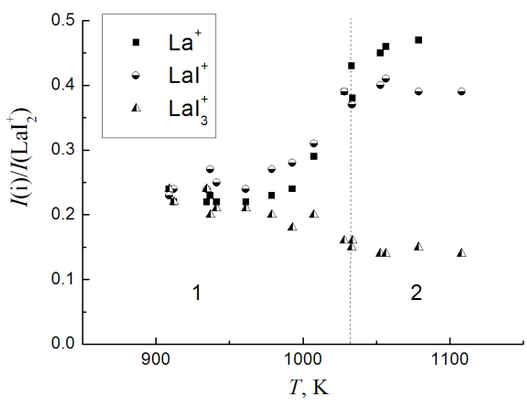

Fig.2 The temperature dependences of the ion current ratios for the La-LaI_3 system

[1] **J. D. Corbett and A. Simon**, Lanthanum Diiodide // Inorganic Syntheses: Nonmolecular Solids. Editors: Donald W. Murphy, Leonard V. Interrante, V. 30, P. 17-19 (1995)

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