

Physicochemical Properties Of Lanthanide(III) Iodide Species Formed In And Above Molten Salts

A. Chrissanthopoulos and G.N. Papatheodorou

Institute of Chemical Engineering and High Temperature Chemical Processes-FORTH and Department of Chemical Engineering, University of Patras, P.O.Box 1414, GR-26504, Patras, GREECE

The structural and thermodynamic properties of molten trivalent rare earth metal halides (LnX_3 , $\text{X}=\text{Cl}, \text{Br}$) and their binary compounds with alkali halides (AX) have been investigated rather extensively⁽¹⁾. Studies of binaries containing high-melting lanthanide iodides are limited, mainly due to experimental difficulties. The practical interest for studying these mixtures arises from their use as additives in high-intensity-discharge mercury lamps. In these lamps the dissociation of metal halides in the high temperature arcs and the recombination on the wall is a repeated procedure. Iodides are more suitable for this cycle as they have higher vapor pressures and lower decomposition temperatures than chlorides and bromides. It is very important to know the structure of the melt in order to fully understand and describe the vapor species and their chemistry inside the lamp.

An UV/VIS spectroscopic investigation of the vapor phase above solid HoI_3 and liquid $\text{HoI}_3\text{-CsI}$, 50:50 mol% mixture is undertaken. For both systems the absorption spectra of the vapor phase have been measured at different temperatures. Using the literature vapor pressure data for $\text{HoI}_3(\text{s})$ the molar absorptivity and the oscillator strength of the $\text{Ho}^{3+} 4f \leftarrow 4f$ ($^5\text{G}_6 \leftarrow ^5\text{I}_8$) hypersensitive transition have been calculated as $\epsilon_{467}[\text{HoI}_3(\text{g})] = (420 \pm 30) \text{ l mol}^{-1} \text{ cm}^{-1}$ and $f_{467}[\text{HoI}_3(\text{g})] = (5.6 \pm 0.6) 10^{-4}$ respectively. Like most LnX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) vapors at high temperatures, a trigonal planar D_{3h} symmetry is anticipated for the $\text{HoI}_3(\text{g})$. In support of this are the high values of ϵ and f for the hypersensitive transition which support strong deviation from highly symmetric coordinations. Actually the measured values of ϵ and f for Ho^{3+} appear to be the highest of all known $4f$ transitions.

The spectra recorded from vapors over the $\text{HoI}_3\text{-CsI}$ binary liquid mixture are shown in Fig. 1a. The bands seen are assigned to the $^5\text{G}_6 \leftarrow ^5\text{I}_8$ transition of two different Holmium species. The shoulder band at 467nm is that of the $\text{HoI}_3(\text{g})$ while the set of the two bands at 460 and 462nm are associated with the caesium-holmium-iodide vapor complex with an anticipated CsHoI_4 stoichiometry. Based on these measurements the vapor pressure of the Holmium vapor complex over molten $\text{HoI}_3\text{-CsI}$ has been calculated as presented in Fig. 1b. The same figure shows the vapor pressure literature data⁽²⁾ over the solidified melt mixture.

Temperature dependence of the Raman spectra of solid and molten $\text{HoI}_3\text{-CsI}$, 50:50 mol% mixture, have been obtained. The spectra are similar with the spectra of the solid and liquid phases of the DyI_3/CsI system and of the liquid LnX_3/AX (Ln : lanthanide, A : alkali, X : Cl, Br) binaries⁽¹⁾, indicating the formation of a weak network melt structure of halide bridged distorted octahedral units.

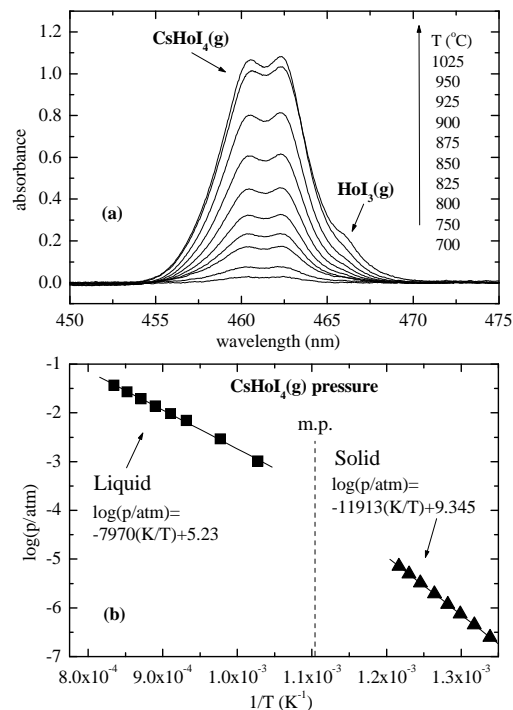


Fig. 1. (a) Absorption spectra of the $^5\text{G}_6 \leftarrow ^5\text{I}_8$ Ho^{3+} transition from vapor over HoI_3/CsI . (b) Vapor pressure of CsHoI_4 over solid and liquid HoI_3/CsI mixture.

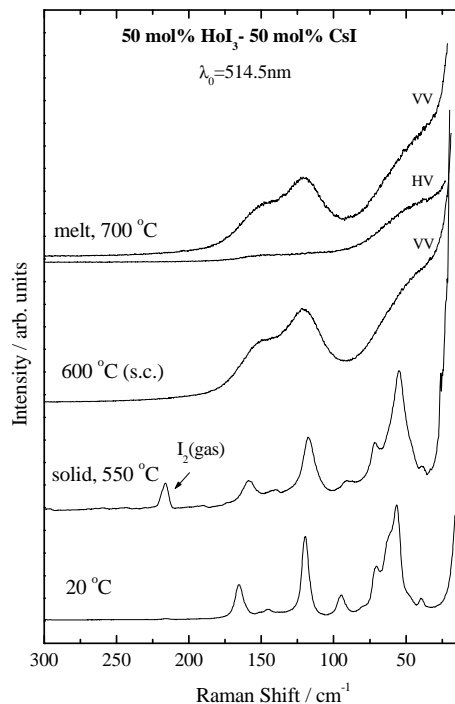


Fig. 2. Raman spectra of the CsI/HoI_3 equimolar solid and liquid mixture.

References

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