PHYSICOCHEMICAL PROPERTIES OF LANTHANIDE(III) IODIDE SPECIES FORMED IN AND ABOVE MOLTEN SALTS

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ABSTRACT

Composition and temperature dependence of the Raman spectra of the molten LnI3-CsI (Ln= Ce, Dy, Ho) mixtures have been measured. The changes of the vibrational modes upon melting the polycrystalline compounds Cs3LnI6 and Cs3Dy2I9 have also been measured. The spectral data suggest that, as for other LnX3-AX (Ln: lanthanide, A: alkali, X: F, Cl, Br) binaries, the six-fold coordination around the lanthanide is preserved at all compositions, including pure LnI3 melts, where a loose network-like structure is formed. The electronic absorption spectra of vapors over solid HoI3 and molten HoI3-CsI, 50:50 mol% mixtures have been recorded at different temperatures. Using the literature vapor pressure data for HoI3(s), the molar absorptivity and the oscillator strength of the Ho3+ 4f<-4f (5G6<-5Ig) hypersensitive transition have been calculated. The obtained values are compatible with the low symmetry semi-trigonal structure for the HoI3(g) species. The spectra of vapors in equilibrium with the 1:1 binary liquid mixture show the presence of two bands, which are assigned to the 5G6<-5Ig transition of two different holmium species. One is associated with the HoI3(g) and the other with a caesium-holmium iodide vapor complex with an anticipated CsHoL stoichiometry.

INTRODUCTION

The structural and thermodynamic properties of molten trivalent rare earth metal halides (LnX3, X=Cl, 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 (as a melt) 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. Furthermore reactions (corrosion) of the halide melts and vapors with the lamp envelope (i.e. polycrystalline alumina) have been...
observed. Thus it appears that the melt and the vapor structure and stoichiometry are rather important for understanding the chemistry inside the lamp.

Detailed Raman spectroscopic measurements on a series of rare earth-alkali halide mixtures LnX₃-AX (X= F, Cl, Br; A= alkali metal) (2,3) indicate that the spectral behavior and structure of these melts are very similar especially in the dilute in rare earth halide mixtures. In general two polarized bands P₁ and P₂ and two depolarized bands D₁ and D₂ appear in the spectra. The P₁ band remains practically unchanged with composition and its frequency is associated to Ln-X vibration of six-fold coordinated species. The P₂ band shifts continuously to higher frequencies with increasing LnX₃ composition and is attributed to the formation of a weak network in the melt composed of distorted halide-sharing octahedra. Rather different is the behavior of the ScI₃-CsI (4) and ScCl₃-ACl (5,6) systems where multispecies equilibria involving ScCl₇⁺, ScX₅⁻, Sc₂X₉⁻ and ScX₄⁻ appear to predominate the melt structure.

Studies of the electronic absorption spectra of lanthanide ions participating in high temperature metal halide melts and metal halide vapor complexes are rather limited (7-9). Systematic temperature dependence measurements of the absorbance and molar absorptivity of the hypersensitive 4f→4f transitions can be used to establish the thermodynamics of vaporization and the structure of the vapor species present (e.g. ref. 7). High temperature mass spectrometric studies of the HoI₃ (10) and HoI₃-CsI (11) systems have established the presence, the equilibrium partial pressure and the thermodynamic functions of the HoI₃, Ho₂I₆ and CsHoI₄ vapor species. Vapor pressure data are also available for the HoI₃ solid (12) while the phase diagram of the binary CsI-HoI₃ has been reported and critically evaluated (13).

In the present work, the molten lanthanide iodide systems LnI₃-CsI (Ln=Ce, Dy, Ho) are investigated by Raman spectroscopy and the results are discussed in terms of the melt structure. Electronic absorption spectroscopic measurements of the vapors over solid HoI₃ and molten HoI₃-CsI are also presented. The results are briefly discussed in terms of vapor species present and their structure.

**EXPERIMENTAL**

**Sample preparation**

All materials used in this work are very hygroscopic and were handled in an inert atmosphere glove box having a water vapor content of less than 1 ppm. Caesium iodide (Fluka, 99.99%) was dehydrated by heating gradually up to 300 °C under vacuum for several hours. Cerium(III), dysprosium(III) and holmium(III) iodide (APL Engineered Materials Inc., 99.99%) were firstly heated gradually up to 500°C under dynamic vacuum for several hours; the products obtained were subsequently purified by sublimation/distillation while heating up to 950°C in sealed fused silica tubes at a temperature gradient.

The optical cells used were made of fused silica tubing and before use, they were carefully cleaned, rinsed with hydrofluoric acid/water, flamed and degassed by...
evacuating white hot. Calculated amounts of the chemicals were transferred into the cells, which were then placed on a vacuum line and sealed with a butane/oxygen torch.

Instrumentation for Raman and UV/VIS electronic absorption measurements

The experimental setup for Raman measurements at elevated temperatures has been described before (4). The 514.5 and 647.1 nm lines of an Ar ion and a Kr ion (Spectra Physics 2020) lasers were used and the spectral resolution was 2 cm$^{-1}$ for solid and 4 cm$^{-1}$ for liquid samples.

The experimental setup for measuring high temperature absorption spectra from the gas phase, is presented in Fig. 1. A modified UV/VIS/NIR spectrophotometer (Perkin Elmer Lambda 900), operated in the reverse mode: light $\rightarrow$ gas sample cell $\rightarrow$ monochromator $\rightarrow$ detector $\rightarrow$ amplifier $\rightarrow$ recorder, has been used. The sample cell and oven have been mounted externally with suitable fiber optics and required optics. A Perkin Elmer Transfer optics (B220-5302) allows the sample beam to be directed exterior to the transmission sample compartment to the cell via a monofiber. A second monofiber is provided collecting the light, which passes through the cell. Remote measurements can be thus achieved. The two quartz fiber optic cables, operated at the wavelength range: 220-1100 nm, especially manufactured by Hellma, had the following characteristics: 1.5 m long, having collimating lens with OD 18 mm, optimizined at 450 nm.

Figure 1. High temperature UV/VIS electronic absorption setup.

A 45 cm long Thermocraft furnace was used to record spectra at high temperatures. To prevent condensation on the cell's windows, the furnace is constructed in three sections: the central part and the two ends, each controlled separately. The cylindrical optical cells (quartz glass Spectrosil Q from STARNA GMBH) containing the samples were placed in an Inconel metallic holder, which smoothed temperature gradient along the cells. Three thermocouples were used to monitor the cell temperature, one at each end and one at the center of the cell holder. During the absorption measurements the temperature at the ends have been maintained about 15 °C higher than that at the center of
the cell. All external compartments were positioned on an optical table and were carefully aligned using optical-rails and micropositioners. This configuration eliminates most thermal radiation by the hot cell and furnace and allows the use of long optical cells (up to 15 cm).

RESULTS AND DISCUSSION

a. Raman spectra of melts

Typical Raman spectra of the CeL-CsI system at different composition are shown in Fig. 2. Similar were the dysprosium system spectra as well as the spectra of the HoL-CsI, 50:50 mol% system. Like in most cases studied before (2,3), the two bands P1 and P2 are present. The P1 band is associated with the octahedral species "LnL3" while the P2 band shows the expected shifting character moving to higher frequencies with increasing Ln content. No changes occur with temperature variation. In fig. 3 we compare the reduced isotropic spectra of the ~50% composition for systems involving bromides and iodides. The spectra appear to be "isostructural" indicating that as in the cases of bromides (3) the iodides also form a network-like structure of halide bridged "LnI6" octahedra.

![Figure 2. Composition dependence of the Raman spectra of the CeL-CsI system.](image1)

![Figure 3. Reduced Raman spectra of the ~50 mol% mixtures Ln11X3-AX.](image2)

The Raman spectra of polycrystalline compounds Cs5LnI6 (Ln=Ce, Dy) and Cs3Dy2I9 were measured from room temperature up and above their melting point. The spectra for the Cs5CeI6 and Cs3Dy2I9 compounds are shown in fig. 4. Similar were the spectra of the corresponding Cs3DyI6 compound. The crystalline Cs5LnI6 (Ln=Ce, Dy) compounds are presumably isomorphous having isolated LnI6\(^{3-}\) ionic species with the Ln in a distorted...
octahedral coordination like in the case of Cs$_3$ScCl$_6$ (5) and Cs$_3$FeCl$_6$ (14). It appears that upon melting these compounds the LnI$_6^{3-}$ vibrational modes of the solid are transferred into the melt. There are also similarities in the solid-liquid spectra of the Cs$_3$Ln$_2$I$_9$ compounds. The intensities of the P$_1$ and P$_2$ bands observed in the liquid spectra of both compounds were not affected by temperature (see e.g. the liquid spectra in fig. 4b) indicating that these bands are associated with the same melt substructure which excludes equilibria between different species like those found in refs (4) and (5).

Temperature dependence of the Raman spectra of solid and molten HoI$_3$-CsI, 50:50 mol% mixture, has also been obtained. The melt’s spectra show similarities (Fig. 3) to the spectra of the LnI$_3$-CsI (Ln= Ce, Dy) and the LnX$_3$-KX (Ln: lanthanide, X: Cl, Br) binaries (1), indicating that the predominant coordination of the Ln in all these systems is octahedral.

![Figure 4. Temperature dependence of the Raman spectra of the Cs$_3$CeI$_6$ (a) and Cs$_3$DyI$_9$ (b) compounds.](image)

**b. Spectrophotometric investigation of vapors**

UV/VIS electronic absorption spectra of the vapors above solid HoI$_3$ and molten HoI$_3$-CsI, 50:50 mol% mixture have been measured at different temperatures.
Figure 5. Electronic absorption spectra of vapors over HoI₃(s); inset: the Ho³⁺ hypersensitive transition of the [HoI₃] vapor species at different temperatures.

b.1. HoI₃(g)

Figure 5 shows the 4f→4f (^5Ge→^5I₈) hypersensitive band of holmium triiodide vapor species at various temperatures. The molar absorptivity εₖ at a specific wavelength λ can be determined from the measured absorbance A, and the available vapor pressure p data (12) according to Eq. [1]:

\[ \varepsilon_k = \frac{(A,RT)}{(p)} \]

where R is the gas constant, T the absolute temperature and l is the optical path length. The calculation of the oscillator strength for the hypersensitive absorption band was based on the Eq. [2]:

\[ f_{exp} = 4.32 \cdot 10^{-6} \int \varepsilon(\tilde{\nu})d\tilde{\nu} \]

where \( \varepsilon(\tilde{\nu}) \) is the molar absorptivity at energy \( \tilde{\nu} \) (cm⁻¹). Experimentally, the integral \( \int \varepsilon(\tilde{\nu})d\tilde{\nu} \) is calculated from the area of the absorption band. The determined values are:

\[ \varepsilon_{467}[\text{HoI}_3(g)] = (420±30) \text{ L mol}^{-1} \text{ cm}^{-1} \] and \[ f_{467}[\text{HoI}_3(g)] = (5.6±0.6) \times 10^{-4}. \] These values of ε and f for Ho³⁺ appear to be the highest of all known 4f transitions in other lanthanides.

Generally the intensity of the hypersensitive transitions decreases with increasing symmetry of the ligands around the lanthanide ions. Thus for the Ho³⁺ ion in distorted HoCl₆³⁻ octahedra formed in molten salts (8), the ^5Ge→^5I₈ transition has a molar absorptivity of ~20 L mol⁻¹ cm⁻¹ and an oscillator strength of ~2 \times 10⁻⁶. As the symmetry is lowered to the semi-trigonal HoCl₃(g) the oscillator strength increases to ~2 \times 10⁻³ (9). An enhancement of the intensity is also expected with increasing ligand polarizability. Thus for the semi-trigonal vapor species NdBr₃ and NdI₃ the molar absorptivity / oscillator

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strength values are (15) 116 L mol\(^{-1}\) cm\(^{-1}\) / 3.3 \(10^4\) (at 1468 K) and 345 L mol\(^{-1}\) cm\(^{-1}\) / 5.35 \(10^4\) (at 1360 K) respectively.

In other words the calculated molar absorptivity and oscillator strength of the HoI\(_3\) vapors confirm the low symmetry (C\(_{3v}/D\(_{3h}\)) for the vapor species and exclude more symmetric molecular structures (e.g. dimmers composed of bridged tetrahedra).

b.2. CsHoI\(_4\)(g)

The spectra of the vapors formed over molten CsI-HoI\(_3\) show (Fig. 6) the characteristic strong absorption band of CsI (at ~320nm) and two other bands (at 460 and 467nm) assigned to the \(^5G\_6\rightarrow^7I\_8\) transition of two different Holmium species. This latter absorption band (of HoI\(_3\) vapor species) appears as a shoulder on the side of a new and rather intense band doublet at ~ 460 - 462 nm (Fig. 7a) which is assigned to a Cs-Ho-I vapor complex. It is more likely (11) that the vapor complex formed has the CsHoI\(_4\) stoichiometry, which at elevated temperatures establishes equilibrium of the form

\[
\text{CsHoI}_4(\text{g}) \leftrightarrow \text{CsI}(\text{g}) + \text{HoI}_3(\text{g})
\]

Figure 6. Electronic absorption spectra of vapors over HoI\(_3\)-CsI (1:1) mixture at different temperatures.

The molar absorptivity was determined as follows: an optical cell having known volume was filled with a small amount of mixture to ensure that all of the added material would be in the vapor phase at the temperature of the measurement. When almost constant absorbance was reached all the chemicals were vaporized (see fig. 7a, temperatures 1223 - 1298 K). The determined values are: \(\varepsilon_{460}[\text{CsHoI}_4(\text{g})] = 220\) L mol\(^{-1}\) cm\(^{-1}\) and \(f_{460}[\text{CsHoI}_4(\text{g})] = 2.8 \times 10^4\). These values are about 50% lower than the corresponding values of the HoI\(_3\)(g) indicating a higher symmetric field around the Ho\(^{3+}\) and thus supporting the presence of the "HoI\(_4\)" tetrahedra in the vapor molecule.
Figure 7. (a) Absorption spectra of the \( ^5G_6 \rightarrow ^5I_3 \) Ho\(^{3+} \) transition from the vapor over HoI\(_3\)-CsI. (b) Calculated vapor pressure of CsHoI\(_4\) over solid (11) and liquid HoI\(_3\)-CsI mixture.

Based on the molar absorptivity measurements the vapor pressure of the Holmium vapor complex over molten HoI\(_3\)-CsI has been calculated as:

\[
\log(p/\text{atm}) = -(7970 \pm 140)(K/T) + (5.23 \pm 0.13) \quad [4]
\]

(for the temperature range 900-1250 K), as presented in Fig. 7b. The same figure shows the vapor pressure literature data (11) over the solidified molten mixture.

From the known vapor pressure of HoI\(_3\) we can estimate the volatility enhancement \( \rho \) (16), due to the vapor complexation with CsI according to equation:

\[
\rho = \frac{p_c}{p_s} \quad [5]
\]

where \( p_c \) is the partial pressure of the Cs-Ho-I vapor complex and \( p_s \) the vapor pressure of the solid HoI\(_3\) at the same temperature (12). It was found that \( \rho \approx 50 \) at 1000 K and \( \rho \approx 2 \) at 1250 K.

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