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Observation of vapor pressure enhancement of rare-earth metal-halide salts in the temperature range relevant to metal-halide lamps

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Total vapor-phase densities of Dy in equilibrium with a DyI3/InI condensate and Tm in equilibrium with a TmI3/TII condensate have been measured for temperatures between 900 K and 1400 K. The measurements show strong enhancements in rare-earth vapor densities compared to vapors in equilibrium with the pure rare-earth metal-halides. The measurements were made with x-ray induced fluorescence on the sector 1-ID beam line at the Advanced Photon Source. The temperature range and salt mixtures are relevant to the operation of metal-halide high-intensity discharge lamps. © 2012 American Institute of Physics. [doi:10.1063/1.3687171]

Formation of molecular complexes1,2 in metal-halide (MH) vapors is an important phenomenon in MH high-intensity discharge (HID) lamps. Vapor-phase complexing between a low vapor pressure salt and a high vapor pressure salt can lead to strong enhancement in the presence of the former in the vapor over the mixed system. This effect is exploited to improve luminous efficacy and color-rendering of MH-HID lamps because it results in an increase in the density of metal atom radiators in the discharge.3–5

The metal-halide vapor in a MH-HID lamp is created by evaporation from a mixed salt condensate whose temperature is typically in the range of 1100 K–1400 K. The vapor temperature is strongly inhomogeneous across the lamp and can exceed 4000 K in the discharge core. In addition, plasma and fluid effects exert a strong influence on the local content of the vapor with the so-called "de-mixing" effects being commonly exhibited.6 Nevertheless, the vapor immediately in contact with the condensate looks much like a vapor in equilibrium with a condensed phase. Thus, there is great interest in measurements of vapors in equilibrium with mixed salt condensates at temperatures in the range of 1100 K–1400 K.

The difficulties inherent in working and making accurate measurements at temperatures exceeding 1100 K has greatly limited the number of vapor-phase studies directly applicable to MH-HID lamps. An extensive review of existing work on rare-earth vapors including hetero-complexing was given by Boghosian and Papatheodorou.7 This included only one system combining a trivalent rare-earth iodide with a Group IIIA mono-iodide: NdI3/TII was studied by Foosnaes8 over the range of 1100 K–1180 K using optical absorption spectroscopy and by Knape, Knapstad, Øystvold, and Øye9 over the range of 950 K–1150 K using a boiling point method and condensate analysis. Also of relevance to the present work is the more recent contribution of Ohnesorge10 who made measurements on several binary salt systems including the DyI3/InI and DyI3/TII systems, both over the temperature range of 800 K–1000 K. Ohnesorge used Knudsen cell effusion mass spectroscopy.

This letter presents the measurements of vapor-phase densities over two mixed-salt systems, DyI3/InI and TmI3/TII, for the temperature range of 900 K–1400 K. These measurements show the enhancement of both Dy and Tm in the vapor compared to pure DyI3 and pure TmI3 systems.11

The data presented here were obtained during a 96-h proof-of-principle demonstration at the Advanced Photon Source using x-ray induced fluorescence (XRIF) on the sector 1-ID beam line. A description of the method, along with data for the pure salt systems DyI3 and TmI3, has been given by Curry et al.11 Figure 1 is a schematic of the experimental apparatus, with the sector 1-ID x-ray beam indicated by a horizontal line. The beam was mono-energetic with a photon energy of either 61 keV or 86 keV (see Table I) and a photon flux on the order of 1011 s−1 in a 0.5 × 0.5 mm2 cross section. The flux was continuously monitored by ionization chambers (ICs) before and after the vapor cell containing the salts.

Each salt system was contained in a sealed polycrystalline alumina cell, which was further contained by a tantalum jacket used to control scattered x rays and to provide a more uniform temperature distribution on the cell. Small holes in the tantalum allowed for entrance and exit of the x-ray beam, insertion of two thermocouples, and escape of K-shell characteristic fluorescence induced in the vapor by the x-ray beam. The latter was observed perpendicular to the beam by a solid-state energy-resolving Ge detector. The strength of measured fluorescence was related to vapor-phase densities by substituting, for the vapor cells, a cell filled with a known density of Xe.

The spectral signature of characteristic fluorescence provides an unambiguous identification of the atom from which it is emitted. Furthermore, the magnitude of a characteristic fluorescence feature is proportional to the number of emitters, and with suitable calibration, absolute number densities can be obtained. Neither the energy nor the intensity of K-shell characteristic fluorescence is significantly affected by chemical...
bonding or valence ionization. Thus, we determine the total density of atoms $n$ of a particular atomic number $Z$

$$n_Z = \sum_i c_{Zi} M_i,$$  \hspace{1cm} (1)

because the XRIF signal is a summation over all molecular species $M$ multiplied by the appropriate stoichiometric number $c_Z$. Vapor pressures corresponding to total densities are defined as

$$p_Z = n_Z k T = k T \sum_i c_{Zi} M_i,$$  \hspace{1cm} (2)

where $k$ is Boltzmann’s constant and $T$ is the measured temperature of the vapor. The parameter $p_Z$ will be referred to as the vapor pressure corresponding to the total density of element $Z$. This pressure differs from a sum of partial pressures when $c_{Zi} > 1$ for any $i$.

Five different salt mixtures, chosen for their relevance to MH-HID lamps, were examined with XRIF over a temperature range of 900 K (or lower) to 1400 K. The details of those mixtures are given in Table I. Results for pure DyI$_3$ and TmI$_3$ have been reported previously.$^{11}$ The mixed salt systems DyI$_3$/InI and TmI$_3$/TlI were chosen because the mono-iodides InI and TlI are commonly known throughout the lighting industry to enhance the total vapor densities of DyI$_3$ and TmI$_3$, respectively, although that enhancement has never been quantified in the temperature range relevant to metal-halide lamps. The molar ratios investigated (Table I) were chosen for their relevance to MH-HID lamps.

Possible systematic errors in these measurements are discussed by Curry et al.$^{11}$ Because only proof-of-principle

![FIG. 1. Schematic of the experiment for measuring vapor-phase densities with x-ray induced fluorescence. IC$_1$ and IC$_2$ are upstream and downstream ionization chambers for non-perturbatively measuring the photon flux in the x-ray beam. TC indicates thermocouple.](image)

**TABLE I.** Details of observed vapor cells.

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Quantity</th>
<th>Beam energy (keV)</th>
<th>Cell no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DyI$_3$$^{a,b}$</td>
<td>10.3 mg</td>
<td>86</td>
<td>1</td>
</tr>
<tr>
<td>DyI$_3$/InI$^a$</td>
<td>11.8/0.72 mg</td>
<td>86</td>
<td>3</td>
</tr>
<tr>
<td>DyI$_3$/InI$^a$</td>
<td>12.5/0.71 mg</td>
<td>61</td>
<td>4</td>
</tr>
<tr>
<td>TmI$_3$$^{a,b}$</td>
<td>8.9 mg</td>
<td>86</td>
<td>5</td>
</tr>
<tr>
<td>TmI$_3$/TlI$^a$</td>
<td>8.8/0.63 mg</td>
<td>86</td>
<td>8</td>
</tr>
<tr>
<td>Xe</td>
<td>670 Pa</td>
<td>61 and 86</td>
<td>A3</td>
</tr>
</tbody>
</table>

$^a$Also contains 670 Pa of Ar.

$^b$Some data previously reported in Ref. 11.

![FIG. 2. Measured total vapor-phase densities of Dy over DyI$_3$/InI (cell 3→□, cell 4→Δ) compared to that over pure DyI$_3$ (cell 1→○). Statistical uncertainties are shown by vertical error bars for a few representative points. At higher temperatures, uncertainties are insignificant on the scale of the plot. The dashed vertical line indicates the tabulated melting temperature of pure DyI$_3$ (Ref. 12).](image)
The enhancement may well be due to the formation of temperature to a factor of 2 or less near the melting point of a temperature of 1000 K. It decreases monotonically with pronounced at lower temperatures, being a factor of 10–20 at $D\text{ and } L$.

That position is difficult to maintain from the measurement cell and tantalum jacket relative to the fluorescence detector. Resonance intensities are sensitive to the position of the vapor errors in measurements from different cells. Observed fluorescence from the pure salt in cell 1. Both of these suggest systematic errors, despite the fact that the cells are nominally quite similar than those from cell 4 across the whole range of temperatures exceeding 1000 K.

The results from cell 3 are consistently about 50% larger than those from cell 4 across the whole range of temperatures, despite the fact that the cells are nominally quite similar. In addition, those from cell 4 dip slightly below those from the pure salt in cell 1. Both of these suggest systematic errors in measurements from different cells. Observed fluorescence intensities are sensitive to the position of the vapor cell and tantalum jacket relative to the fluorescence detector. That position is difficult to maintain from the measurement measurements have been conducted, the magnitudes of these errors are not yet sufficiently characterized.

Figure 2 shows the measured enhancement of the total Dy density in the vapor over the mixed DyI3/InI system ($\square$'s and $\Delta$'s) relative to that over the pure DyI3 salt ($\bigcirc$'s).

The enhancement in the Dy content of the vapor is most pronounced at lower temperatures, being a factor of 10–20 at a temperature of 1000 K. It decreases monotonically with temperature to a factor of 2 or less near the melting point of DyI3. The enhancement may well be due to the formation of the vapor-phase hetero-complex InDyI4, in analogy with other rare-earth trihalide—Group IIIA salt systems, which augments the normal vapor pressure of DyI3 over the pure salt. These XRIF measurements are not capable of directly measuring the balance of molecular species. The magnitude and temperature dependence of the enhancement is quite likely dependent on the limited dose of InI in the cells, as the entire dose is expected to be volatized at temperatures exceeding 1000 K.

The uncertainties discussed above notwithstanding, the present measurements quantify vapor enhancements in the mixed metal-halide salt systems DyI3/InI and TmI3/TlI at temperatures above 1100 K. Enhancement is strongest at low temperatures, decreasing as temperature increases up to the melting point. Above the melting temperatures of the salts, enhancement is clearly much weaker. This is likely the result of dilution or depletion of the mono-iodide. Further studies may show that different molar ratios and/or salt quantities may be used to fine tune the enhancement over particular temperature ranges.

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