

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

J. J. Curry, E. G. Estupiñán, W. P. Lapatovich, A. Henins, S. D. Shastri et al.

Citation: *Appl. Phys. Lett.* **100**, 083505 (2012); doi: 10.1063/1.3687171

View online: <http://dx.doi.org/10.1063/1.3687171>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v100/i8>

Published by the [American Institute of Physics](http://www.aip.org).

Related Articles

Quartz crystal microbalance based on passive frequency to voltage converter
Rev. Sci. Instrum. **83**, 025107 (2012)

Measurements of beam current density and proton fraction of a permanent-magnet microwave ion source
Rev. Sci. Instrum. **82**, 113505 (2011)

Magnetic quartz crystal microbalance: Magneto-acoustic parameters
J. Appl. Phys. **110**, 013905 (2011)

Frequency-shift vs phase-shift characterization of in-liquid quartz crystal microbalance applications
Rev. Sci. Instrum. **82**, 064702 (2011)

Flash radiography with 24 GeV/c protons
J. Appl. Phys. **109**, 104905 (2011)

Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT



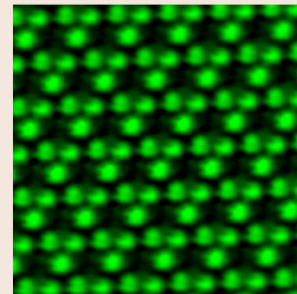
**ASYLUM
RESEARCH**
The Technology Leader in SPM/AFM

Register Now at
www.asylumresearch.com

Free AFM Webinar February 22 Register Now

“Smaller and Quieter: Ultra-High Resolution AFM Imaging”

With Jason Cleveland, AFM pioneer,
inventor and Asylum Research co-founder



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

J. J. Curry,^{1,a)} E. G. Estupiñán,² W. P. Lapatovich,³ A. Henins,¹ S. D. Shastri,⁴ and J. E. Hardis¹

¹National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA

²Osram Sylvania Inc., Beverly, Massachusetts 01915, USA

³Independent Consultant, 51 Pye Brook Lane, Boxford, Massachusetts 01921, USA

⁴Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

(Received 9 November 2011; accepted 1 February 2012; published online 22 February 2012)

Total vapor-phase densities of Dy in equilibrium with a DyI₃/InI condensate and Tm in equilibrium with a TmI₃/TlI 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 complexes^{1,2} 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/TlI was studied by Foosnaes⁸ over the range of 1100 K–1180 K using optical absorption spectroscopy and by Knapstad, Østvold, 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/TlI 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/TlI, 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

^{a)}Electronic mail: jjcurry@nist.gov.

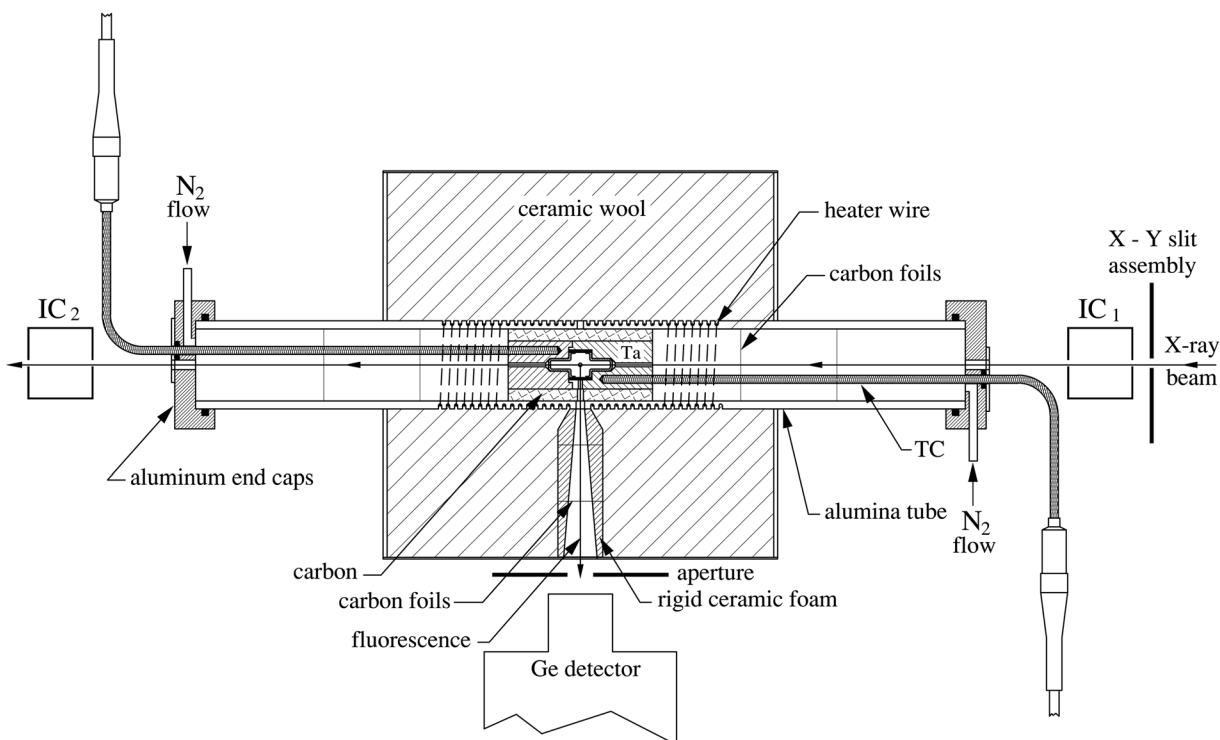


FIG. 1. Schematic of the experiment for measuring vapor-phase densities with x-ray induced fluorescence. IC₁ and IC₂ are upstream and downstream ionization chambers for non-perturbatively measuring the photon flux in the x-ray beam. TC indicates thermocouple.

bonding or valence ionization. Thus, we determine the total density of atoms n of a particular atomic number Z

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

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

$$p_Z = n_Z kT = kT \sum_i c_{Zi} M_i, \quad (2)$$

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 DyI₃ and TmI₃ have been reported previously.¹¹ The mixed salt systems DyI₃/InI and TmI₃/TlI were chosen because the mono-iodides InI and TlI are commonly known throughout the lighting industry to enhance the total vapor densities of DyI₃ and TmI₃, 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

TABLE I. Details of observed vapor cells.

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

^aAlso contains 670 Pa of Ar.

^bSome data previously reported in Ref. 11.

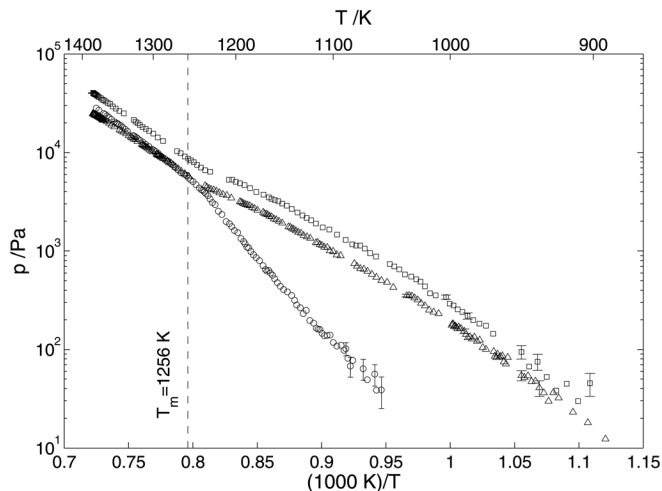


FIG. 2. Measured total vapor-phase densities of Dy over DyI₃/InI (cell 3 → □, cell 4 → △) compared to that over pure DyI₃ (cell 1 → ○). Statistical uncertainties are shown by vertical error bars for a few representative points. At higher temperatures, uncertainties are insignificant on the scale of the plot. The dashed vertical line indicates the tabulated melting temperature of pure DyI₃ (Ref. 12).

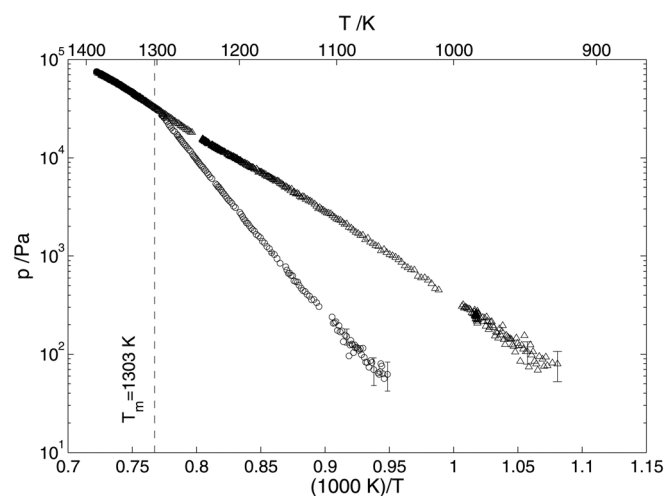


FIG. 3. Measured total vapor-phase densities of Tm over TmI₃/TII (cell 8 → Δ) compared to that over pure TmI₃ (cell 5 → ○). Statistical uncertainties are shown by vertical error bars for a few representative points. At higher temperatures, uncertainties are insignificant on the scale of the plot. The dashed vertical line indicates the tabulated melting temperature of pure TmI₃ (Ref. 12).

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 (□'s and Δ's) relative to that over the pure DyI₃ salt (○'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,^{8–10} 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 volatilized at 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

of one cell to another due to variations in placement during insertion into the oven and to shifting of oven parts over time as a result of thermal cycling. Studies with cell A3 (Xe) indicate such errors are usually limited to less than ±20%, although there is no reason it cannot be larger. Such difficulties will be resolved in the next generation of measurements by the use of an internal standard within each cell.

Measurements of the TmI₃/TII system are shown in Figure 3 and display characteristics similar to those seen in the DyI₃ and DyI₃/InI systems.

The uncertainties discussed above notwithstanding, the present measurements quantify vapor enhancements in the mixed metal-halide salt systems DyI₃/InI and TmI₃/TII 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.

The authors thank the management of Osram Sylvania for supporting this project and our colleagues Joanne Browne, Victor Perez, Jeff Neil, Michael Quilici, and John Kelso for their expert technical assistance. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

¹K. Hilpert, *J. Electrochem. Soc.* **136**, 2099 (1989).

²J. W. Hastie, *Advances in Molten Salt Chemistry* (Plenum, New York, 1971), Chap. 5, p. 225.

³W. P. Lapatovich and J. A. Baglio, in *Proceedings of the 9th International Symposium on the Science and Technology of Light Sources*, edited by R. S. Bergman (Cornell University, Cornell University, 2001), paper 026:I.

⁴C. Hirayama, P. M. Castle, C. S. Liu, and R. J. Zollweg, *J. Illum. Eng. Soc.* **6**, 209 (1977).

⁵R. Lorenz, *Light. Res. Technol.* **8**, 136 (1976).

⁶E. Fischer, *J. Appl. Phys.* **47**, 2954 (1976).

⁷S. Boghosian and G. N. Papatheodorou, *Handbook on the Physics and Chemistry of Rare-Earths* (Elsevier, Amsterdam, 1996), Chap. 157, p. 435.

⁸T. Foosnaes, "Gas complexation of neodymium halides," Ph.D. dissertation, University of Trondheim, Trondheim, Norway, 1979.

⁹B. Knapstad, T. Østfold, and H. A. Øye, *Acta Chem. Scand.* **A41**, 98 (1987).

¹⁰M. Ohnesorge, "Untersuchungen zur hochtemperaturchemie quecksilberfreier metallhalogenid-entladungslampen mit keramischem brenner," Ph.D. dissertation, Forschungszentrum Jülich, 2005.

¹¹J. J. Curry, E. G. Estupiñán, A. Henins, W. P. Lapatovich, and S. D. Shastri, *Chem. Phys. Lett.* **507**, 52 (2011).

¹²S. Hansen, R. Steward, J. Getchius, and T. Brumleve, *Supplement to Vapor Pressure of Metal Bromides and Iodides* (APL Engineered Materials, Inc., Urbana, IL, 2000).