Role of complex halides in metal halide lamps

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Complex vapor compounds of the form $MLnI_4$, where M is an alkali metal ion and Ln is a lanthanide or another trivalent ion, play an important role in metal halide arc lamps. Such compounds may be the dominant species in the vaporization process and increase the density of desired radiative species in discharge medium. Data are reported from a number of such systems obtained by mass spectroscopic, optical adsorption, vapor transport and lamp characteristic measurements.

1. Introduction

In recent years there has been an increased emphasis on the development of lamps with higher efficiency and good color rendering index (CRI). This has led to the exploitation of modifications in the high-pressure mercury lamp via the addition of various metal halides¹⁾. Some of the metal halides which are found in present commercial lamps are DyI_3 , ScI_3 , NaI , SnI_2 , TlI , InI , and LiI . This has resulted in the family of high-intensity discharge (HID) metal halide lamps with good CRI and efficacies as high as 140 lumens/watt (1pw)²⁾, as compared to 50 to 55 1pw with an unsatisfactory bluish color for the pure mercury high-pressure lamp. Not surprisingly, the metal iodides have been most satisfactory as the lamp additives. Three of the more important reasons for this are: (1) the iodides are compatible with silica arc tubes; (2) the iodides are the most compatible of the halides with the tungsten electrodes; and (3) the iodides usually have the highest vapor pressure among compounds of the metals that are suitable as lamp additives. In those HID lamps which contain the covalent iodides, such as indium, thallium, and tin iodides, the quantities of these additives must be limited to control the vapor concentration during lamp operation because of the high vapor pressure of these iodides. However, when the more ionic, less volatile salts are used, such as the alkali and lanthanide iodides, there will nearly always be an excess of the solid or liquid additive. In the latter mixtures, the concentration of the desired radiator in the vapor may be quite low, and any means to increase the vapor pressure tends to improve the lamp efficacy.

In order to effect a significant improvement in the HID lamp, the concentration of the atomic radiator in the electric discharge must be of the

order of at least 10^{15} atoms/cm³ at arc temperatures of 4000~6000 K. Consequently, the vapor pressure of the additive salt in the lamp reservoir, where the temperature is approximately 750°C, must be at least 0.1 torr. Table 1 shows the temperatures at which the vapor pressure is 0.1 and 1 torr for the lanthanide and scandium iodides, as well as sodium iodide. These temperatures were calculated from the vapor pressure equations which we obtained for the pure iodides^{3-6) 14)}.

Table 1 Temperatures at which vapor pressures are 1 and 10^{-1} torr

	1	10^{-1}
LaI_3	857	781
CeI_3	856	777
PrI_3	838	763
NdI_3	840	763
GdI_3	836	764
TbI_3	841	759
DyI_3	839	757
HoI_3	835	762
ErI_3	824	750
TmI_3	815	741
SmI_3	1091	864
ScI_3	664	604
NaI	744	636

It should be noted that a metal halide lamp usually contains a mixture of iodides, with an alkali iodide, such as NaI , nearly always being added as one of the components. When this mixture becomes molten at the lamp reservoir temperature of approximately 730°C, the vapor pressure of the components in this mixture will be proportional to their chemical activities, i.e., $P_i = a_i P_{0i}$, where i refers to the component, a_i the activity, and P_0 is the vapor pressure of the pure component at the reservoir temperature. Because the activity of any component in the molten salt solution is usually less than unity, the vapor pressure of the components are also expected to be lower than the values for the pure

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substance shown in Table 1, in accordance with Raoult's law.

2. Complex Compounds

During the course of metal halide lamp development, it had been observed that there was considerable enhancement of the vapor pressure of, for example, CeI_3 and SmI_2 when these were added together with alkali iodide to the lamp. In the case of SmI_2 the enhancement factor was about 103. It became clear during our earlier work that the formation of stable vapor complexes played an important part in the enhanced vapor pressures of lanthanide iodides. Earlier reports in the literature showed the formation of stable complex compounds of some lanthanide chlorides with alkali chlorides.⁷⁾ More recently, it has become more noteworthy that vapor complex compounds play important roles in the chemical equilibria of mixed halide salt systems.⁹⁾

Our first direct evidence for the formation of stable vapor phase complexes between lanthanide iodides and alkali iodides was observed in the mass spectra of vapors of the iodide mixtures.^{8) 9)} Table 2 shows the mass spectra over the equimolar mixtures

Table 2 Mass spectra of vapors over $\text{CsI}\cdot\text{CeI}_3$, $1.2\text{CsI}\cdot\text{CeI}_3$, and $\text{CsI}\cdot\text{LaI}_3$ measured at 28 eV

	$\text{CsI}\cdot\text{CeI}_3(615^\circ\text{C})$	$1.2\text{CsI}\cdot\text{CeI}_3(740^\circ\text{C})$	$\text{CsI}\cdot\text{LaI}_3(668^\circ\text{C})$
LnI_3^+	16	12	18
LnI_2^+	100	100	100
LnI^+	52	48	65
Ln^+	88	122	98
CsI^+	75	74	106
Cs^+	1500	1550	1410
CsLnI_3^+	9	1.5	15
Cs_2I^+	<1	~4	—

$\text{CsI}\cdot\text{CeI}_3$ and $\text{CsI}\cdot\text{LaI}_3$, and over the mixture $1.2\text{CsI}\cdot\text{CeI}_3$. We also determined the temperature dependence of the mass spectra and plotted the data as the usual $\log i/T$ against $1/T$, where i is the ion intensity, T is the absolute temperature, and i/T is proportional to the partial pressure of the particular ion. The plotted data showed parallel temperature dependence for all of the ions, except Cs_2I^+ . This latter ion, which originates from Cs_2I_2 , was either below the detection limit or its intensity was too low to allow a good measure of its relative intensity. The CsLnI_3^+ ion in the mass spectra originates from the $\text{CsLnI}_4(\text{g})$ complex compound when its species is ionized by electron impact. The parallel temperature dependence of the ion relative intensities suggests that these ions originate from the same parent compound. Also, the absence, or very low partial pressure, of the cesium iodide dimer shows that the complex compound dominates the vapor phase. If there is significant vaporization of cesium iodide, its vaporization equilibrium would dictate a significant concentration of the dimer, Cs_2I_2 .⁸⁾ The complex compound is the domi-

nant species in the vapor, but as the CsI/CeI_3 ratio becomes greater than unity in the condensed phase, free CsI vaporization begins to contribute, and the $\text{Cs}_2\text{I}_2(\text{g})$ concentration will increase, as shown for the $1.2\text{CsI}\cdot\text{CeI}_3$ mixtures. On comparing our observations of the iodide mass spectra with that of $\text{CsCl}\cdot\text{NdCl}_3$, as reported by Gavryuchenkov and Novikov¹⁰⁾, it is clear that the lanthanide iodides have a greater tendency to form vapor complexes than do the chlorides. The latter system showed significant contribution of cesium chloride vaporization.

Fig. 1 Absorption spectra of the $\text{Nd}^{3+} {}^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition

Further evidence for the formation of $\text{CsCeI}_4(\text{g})$ and $\text{CsNdI}_4(\text{g})$ complexes was observed in the optical absorption spectra of the vapors over the iodide mixtures.¹¹⁾ In an optical cell containing equimolar quantities of solid NdI_3 and CsI heated to 900°C , the absorption spectrum of this vapor mixture was completely different from that of either CsI vapor or NdI_3 vapor alone and is illustrated in Fig. 1. The strongest maximum occurred at $\sim 602\text{ nm}$, while the strongest one for pure NdI_3 vapor was located at $\sim 612\text{ nm}$. This new absorption band originated from the $\text{Nd}^{3+} {}^4I_{9/2} \rightarrow {}^4G_{5/2}$ transition. In this combined absorption spectrum one observed very little pure NdI_3 vapor absorption ($<5\%$) thus showing that the vapor phase of the complex mixture consisted predominantly of the complex molecules. The neodymium species vaporization enhancement due to the formation of complex molecules in the NdI_3+CsI system was calculated to be a factor 3 at $\sim 900^\circ\text{C}$ and 6 at $\sim 800^\circ\text{C}$.

During the mass spectrometric and vaporization studies, we observed that the lanthanide iodides formed vapor complexes more readily with CsI than with NaI . For example, the mass spectrum of the vapors over the $\text{NaI}\cdot\text{CeI}_3$ mixture shows a signifi-

cant contribution from the vaporization of sodium iodide, as evidenced by the significant partial pressure of $\text{Na}_2\text{I}_2(\text{g})$. Also, there was a preferential vaporization of NaI from this mixture when it was heated in the Knudsen cell.

The mass spectra over the ScI_3 -alkali iodide systems also were investigated.¹²⁾ In this system it appeared that the NaI-ScI_3 combination has the strongest tendency to form the vapor complex. It was found that the complex, $\text{Na}_2\text{ScI}_5(\text{g})$, may make a significant contribution to the vapor phase composition over this binary iodide mixture. However, the $\text{NaScI}_4(\text{g})$ is the dominant species over this mixture.

As shown above, ScI_3 and the lanthanide triiodides readily formed the stable vapor complexes with alkali iodides in the temperature range of interest to HID lamps. On the other hand, our mass spectrometric and vapor pressure studies of the CsI-SmI_3 and NaI-SmI_3 systems in this temperature range showed only a weak tendency for the formation of $\text{CsSmI}_3(\text{g})$; the $\text{NaSmI}_3(\text{g})$ was not detected.⁹⁾ Nevertheless, spectroscopic measurements of lamps which contained SmI_3 , CeI_3 , CsI , and NaI had shown that there was approximately a 103 enhancement of the SmI_3 vaporization with this combination in the HID lamp.¹³⁾ This latter enhancement is attributed to the effect of high mercury pressure (see below).

3. Vapor Pressure Enhancement

It is of interest to determine the magnitude of vapor pressure enhancement and also to consider the thermodynamics of the halide mixture system.

The mass spectrometric⁹⁾ and optical absorption¹²⁾ measurements of most of these iodide systems showed the predominance of the $\text{MLnI}_4(\text{g})$ in the vapor, where M is the alkali metal and Ln is the lanthanide or scandium ion. Vapor pressure measurements were made on these systems by optical absorption, boiling point, and vapor transpiration techniques in the higher pressure region; the Knudsen cell technique was used in the low pressure region. In calculating the vapor pressure from the Knudsen cell and transpiration measurements, it was assumed that the $\text{MLnI}_4(\text{g})$ was the dominant species. The agreement between optical absorption, boiling point, and Knudsen cell measurements for CsI-CeI_3 was satisfactory. Fig. 2 shows the vapor pressures over NaI-ScI_3 , CsI-LaI_3 , and CsI-CeI_3 as compared to the vapor pressures of ScI_3 , LaI_3 , CeI_3 , CsI , and NaI . The vapor pressure data for the alkali iodide are those of Topor.¹⁴⁾ As it is seen, there is significant enhancement of the vapor pressures of the LnI_3 via vapor complex formation. In the case of the lanthanides the vapor pressure of the complex is at least 0.1 torr at lamp operating temperatures of ~ 1000 K, an enhancement of approximately fourfold for the lanthanide.

We have observed in the $\text{CsI-lanthanide triiodide}$ systems that the vapor pressure of the complex is

Fig. 2 Vapor pressures over: 1: NaI-ScI_3 , 2: ScI_3 , 3: CsI , 4: NaI , 5: CsI-LaI_3 , 6: CsI-CeI_3 , 7: CeI_3 , 8: LaI_3

intermediate between those of the CsI and LnI_3 , as shown in Fig. 2 for CsCeI_4 and CsLaI_4 . However, in the alkali iodide- ScI_3 systems, the vapor pressure of the complex is appreciably higher than that of both the ScI_3 and the alkali iodide.¹⁵⁾ In these systems there is enhancement of both the ScI_3 and the alkali iodides.

The mass spectrometric and vaporization studies of the SmI_3 -MI systems showed that there was no vapor pressure enhancement of the SmI_3 via complex formation. However, the arc measurements on experimental lamps which contained SmI_3 and alkali iodides showed that the samarium atom density was of the order of 10^{15} atoms/cm³.¹³⁾ This showed $\sim 10^3$ enhancement of the SmI_3 vapor pressure. It was observed in the optical absorption measurements of CsI-NdI_3 in a high-pressure mercury vapor atmosphere that there was an interaction between the complex and mercury, as shown by changes in the absorption spectra.¹¹⁾

It is of interest here to consider the reason for the predominance of the vapor complex over the mixed iodide system. For the system,

the enthalpy of formation of the $\text{MLnI}_4(\text{g})$ from the respective iodides is ~ -85 kcal/mole, -57 kcal/mole, and -67 kcal/mole, respectively for $\text{NaScI}_4(\text{g})$, $\text{CsNdI}_4(\text{g})$ and $\text{CsCeI}_4(\text{g})$.

For other $\text{MLnX}_4(\text{g})$ systems the enthalpy of formation is ~ -60 kcal/mole. In contrast, the dimerization energies for the MI and LnI_3 are ~ -50 kcal/mole. The formation of the $\text{MLnI}_4(\text{g})$ complex, therefore, results in a stabilization energy of at least 10 kcal/mole for the mixed iodide system.

It is important to consider another aspect of the stabilization of LnI_3 in mixed iodide systems. To date, all practical metal halide lamps use fused silica envelopes. It is well established that the LnI_3 react with silica at the temperatures of metal halide lamp operation, and that a silicate is formed as a reaction product on the arc tube wall. In the case of ScI_3 , this reaction may be represented by

The free energy change for reaction (2) at 1000 K is approximately 10 kcal, so that the equilibrium constant is $K \approx -148$. This constant is a relatively small negative value, and should the $\text{SiI}_4(\text{g})$ be removed from the system by dissociation at the hot electrode the reaction will tend to proceed to the right. However, a large part of the ScI_3 , as well as any other LnI_3 , in a lamp is present in the molten phase as the complex salt in solution with the alkali iodide, so that the chemical activity of the ScI_3 is much reduced. As a matter of fact, the formation of the complex NaScI_4 in the condensed phase also results in a stabilization energy of at least 10 kcal/mole over that of ScI_3 . Therefore, the reaction

is significantly less favorable than reaction (2). This is the reason for the improved compatibility of the LnI_3 with the silica envelope in metal halide lamps.

Fig. 3 High pressure vapor transport tube

We further investigated the effect of high-pressure mercury vapor on the vaporization, especially of SmI_2 , by utilizing a silica, high-pressure vapor transpiration apparatus, as shown in Fig. 3. Details of this experiment have been described.⁹⁾ The fused salt temperature T_1 , was at 650°C , T_2 was 485° , and $T_3 - T_2 \approx 5^\circ$. The tube contained saturated mercury vapor or xenon, and the pressure in the closed tube was ~ 8 atmospheres. The transported material was always collected in zone B and subsequently analyzed for alkali and lanthanide. The data in Table 3 show two significant aspects. The first is the enhancement of the vaporization of the samarium when it is present as a molten salt mixture with CsI and NaI . The second is the enhancement of the vaporization in high-pressure mercury, as com-

Table 3 Vapor transport of iodides in 8 atm of Hg and Xe in 240 hours. Molten salt temperature = 650°C

Molten Salt Composition	High Pressure Gas	Millimoles $\times 10^3$ Vaporized				Alkali/Ln
		Na	Cs	Sm	Ce	
SmI_2	Hg			0.014		
$2\text{SmI}_2 \cdot \text{CeI}$	Hg			0.0016		
$\text{SmI}_2 \cdot 2\text{NaI}$	Hg	1.45		0.075	0.0029	19
$\text{SmI}_2 \cdot 2\text{CsI}$	Hg		1.98	0.083		24
$\text{SmI}_2 \cdot 2\text{CsI}$	Xe		1.0	0.005		200
$\text{SmI}_2 \cdot \text{NaI} \cdot \text{CsI}$	Hg	0.84	0.65	0.065		23
$\text{CsI} \cdot \text{CeI}_3$	Hg		0.13	0.076		1.7
$\text{CsI} \cdot \text{CeI}_3$	Xe		0.25	0.056		4.5

pared to that in high-pressure xenon. In this latter aspect, the effect of the mercury on the $\text{CsI} \cdot \text{SmI}_2$ vaporization is appreciably greater than that on the $\text{CsI} \cdot \text{CeI}_3$. The greater enhancement of samarium vaporization is consistent with the observations in lamps which contain these iodides. The exact mechanism for the enhanced vaporization by high-pressure Hg is not known, but one might speculate that the mercury forms short lived complex species with the $\text{MI} \cdot \text{SmI}_2$ in the vapor, or that the high-pressure Hg may form clusters with the iodides.

4. Enhanced vaporization and lamp performance

The effect of enhanced vaporization by formation of a volatile complex is clearly shown by the lamp spectra in Fig. 4. The spectra of these two lamps were taken at identical lamp power and detector gain. The spectrum of lamp A, with a NaI/ScI_3 ratio of 2, shows significantly larger amounts of radiation from both Na and Sc, as compared to lamp B with NaI/ScI_3 ratio of 30. We have observed similar effects in experimental lamps filled with $\text{LiI} \cdot \text{ScI}_3$ mixtures,¹⁶⁾ where the ScI_3 vapor pressure enhancement is greater than in the $\text{NaI} \cdot \text{ScI}_3$ mixture.¹⁵⁾ It may be noted here that lamp arc measurements and calculations¹⁷⁾ are consistent with the enhanced vaporization by complex formation.

Fig. 5 shows the spectra of lamps filled with SmI_2 , CsI , and NaI , in addition to Hg and Ar. The latter is used as the starting gas. The lamp with only SmI_2 contained 150 mg Hg (~ 9 atm at the lamp temperature of ~ 5000 K), whereas the other two lamps contained 40 mg Hg (~ 3 atm). Note that the spectra for the lamp with SmI_2 , Fig. 5c, was recorded at a gain factor ten times greater than those in Figs. 5a and 5b. Aside from the mercury lines, the spectra are dominated by the samarium atomic radiation which is almost continuous. The cesium radiation is in the infrared, while Fig. 5B also shows the strong sodium radiation. Fig. 5 shows that the samarium radiation from the lamp with $\text{NaI} \cdot \text{SmI}_2$ is approximately tenfold greater than that from the lamp with SmI_2 . The samarium radiation from the lamp with $\text{CsI} \cdot \text{SmI}_2$ is increased by at least twofold over that of the $\text{NaI} \cdot \text{SmI}_2$ lamp. The lamp spectra therefore show that the apparent

Fig. 4 Spectra of NaI-ScI₃ lamps. A: 2NaI·ScI₃; B: 30NaI·ScI₃

Fig. 5 Lamp spectra. Gain factor of C is 10X those of A and B

samarium concentration is in the ratio of $\sim 20:10:1$ in the lamps with $\text{CsI}\cdot\text{SmI}_2$, $\text{NaI}\cdot\text{SmI}_2$, and SmI_2 , respectively. More detailed measurements taking into account the temperature profile and possible segregation would be necessary to determine the true samarium concentration.

In summary, it has been shown that the formation of vapor complex compounds plays an important role in the operation of metal-halide HID lamps. The vapor pressure enhancement which results from complex formation can result in higher lamp efficiency and better CRI. The vapor pressure enhancement factors can vary over a wide range, depending on the halide. The effect of the high mercury pressure also must be considered, as demonstrated in the case of SmI_2 .

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