Transport processes in metal halide gas discharge lamps*

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Abstract: An overview is given of transport reactions and corrosion phenomena in metal halide gas discharge lamps filled with a mixture of alkali halides with scandium or rare-earth iodides. The phenomena that are discussed are: (a) pressures of light-emitting species above the molten salt mixture, (b) interaction of the metal halides with the vessel wall, quartz glass as well as polycrystalline alumina, (c) transport processes along the vessel wall giving rise to wall corrosion, and (d) transport to and from the electrodes (i.e., electrode corrosion and wall blackening).

INTRODUCTION

In metal halide lamps light is generated in a high-pressure mercury discharge to which other light-emitting species are added to improve the spectrum of the lamp. In these lamps the gaps in the visible spectrum of a mercury discharge are filled up with radiation from other metals, which are evaporated as the name indicates, as their corresponding metal halides. Pure metals cannot be used as additive because most metals have a low-vapor pressure and/or attack the material in which the discharge is contained. When in a steady burning lamp the metal halide vapor enters the area of the discharge the molecules will dissociate, the resulting atoms and ions will be excited, and radiation can be emitted. Coming out of the discharge region, the particles will recombine again to metal halide compounds in the cooler part of the discharge vessel. This cyclic process results in lamps which are more efficient in generating visible light and which have better color rendering properties than mercury lamps. With respect to their contribution to the spectrum three kind of additives can be distinguished:

- Line radiators with one or a few dominant lines in the spectrum. Examples are: sodium (yellow-orange), thallium (green), and indium (blue). The combination of these three additives can produce white light.
- Multi-line radiators: the rare-earth metals and scandium belong to this category. Because of their many emission lines they better fill in the visible spectrum.
- Molecular radiators emit light in wide bands. This occurs mainly in the outer mantle of the arc when the temperature is high enough to excite the molecular states but not too high to cause dissociation. Due to vibrational and rotational effects, lines are broadened in such an extent that a quasi-continuous spectrum is generated. Examples are tin halides and rare-earth halides.

Metal halide gas discharge lamps are increasingly being used in all kinds of application areas such as accent lighting in shops, indoor and outdoor sports, studio, theater, and disco lighting, motor car head lights, and for projection purposes. When a warm white or a neutral white color (≈3000 K and 4000 K


color temperature resp.) is wanted, sodium iodide is combined with rare-earth iodides or scandium iodide or with tin, thallium, and indium halides. For a daylight white color (≈6000 K), used in sports, studio, theater, etc., rare-earth bromides are usually combined with cesium halides. In this contribution the focus will be on the mixtures based on sodium-scandium and on sodium-rare-earth because these are most commonly used in the lamp industry at the moment.

THE DISCHARGE VESSEL

In Fig. 1 a schematic drawing of an arc tube is shown. In this case the AC arc runs between the tips of two tungsten electrodes. Characteristic temperatures of this tip are between 2800 and 3300 K, so usually well below the melting point of tungsten. The temperature in the center of the arc is about 6000 K. The arc is contained in a vessel made out of quartz glass or, nowadays, also out of polycrystalline alumina (PCA). For quartz glass the temperature should not exceed 1300 K, but alumina has the advantage that it can withstand higher temperatures for long times. Quartz glass, being transparent, is most suited for optical applications where compactness of the light source is important. PCA is applied more for general lighting when good color quality is wanted. During steady-state burning, the mercury in the lamp is evaporated and its pressure can be between a few bars for long arc lamps or up to 50 bars for very short arc lamps. The strong temperature and corresponding density gradients in the gas cause a rather strong natural convective flow. In horizontal lamps, the flow is upward in the middle of the tube and downward along the vessel walls, as sketched in Fig 1. By this flow, energy is transported from the arc to the vessel wall, causing an asymmetric heating of the wall: the top of the arc tube in this example is 1250 K and the bottom 1100 K. At this so-called coldest spot, the excess of metal halide salt will condense, usually forming a molten salt pool. The convective flow also transports material in a fast way and can attribute to a good mixing in the gas phase.

The high temperatures and large temperature gradients, in combination with the presence of corrosive compounds such as metal halides, can lead to complex transport phenomena and corrosion processes. This makes it difficult to comply with requirements of a very long life-time of the lamp in combination with a good maintenance of light technical properties. As will be shown below, thermodynamic modeling can help in understanding what processes are going on in these high-temperature devices. This understanding can then help us design better lamps.
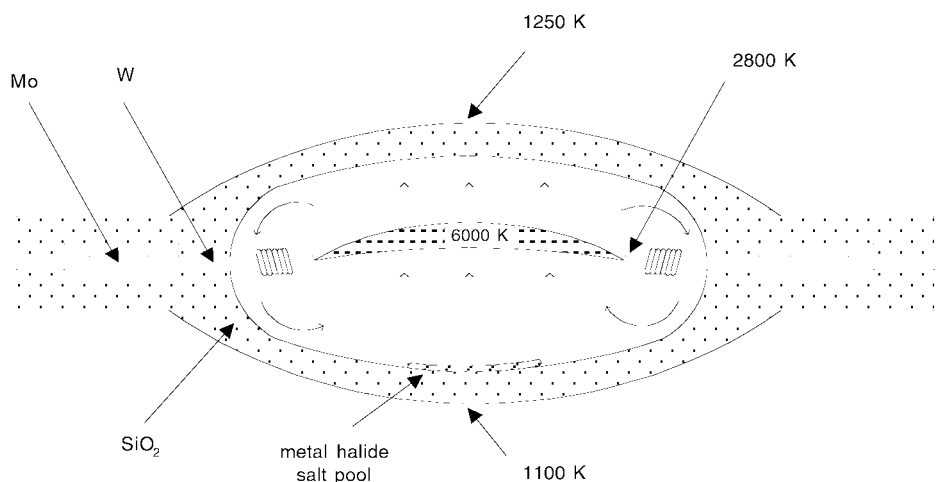
Fig. 1 Schematic drawing of a horizontal burning metal halide arc tube with temperature distribution under steady burning conditions.

The chemical modeling of these lamps is often complicated by the number of elements involved. For instance, in a simple sodium-scandium metal halide lamp 10 elements can be present: the filled elements Na, Sc, I, and Hg; electrode and wall material W, Si, and O; Th released by the electrodes (tungsten doped with ThO_2); and impurities containing H and C. During burning hydrogen is released by the quartz glass and the same holds for water that can have diffused into the glass during the forming of the bulb. Many of the metal halide salts are very hygroscopic, and so, despite the precautions taken to prevent this contamination, together with these metal halides some water will be introduced into the lamp. Hydrocarbons adsorbed on the vessel and electrode surface can be major carbon sources. Fortunately, thermodynamic databases and programs that can handle these complicated systems have been more and more improved during the last decades. The work described here has been done using the Thermo software from Philips Research Labs [1]. The data in this database have been obtained by careful evaluation of sources in literature, by performing own measurements, and via a close cooperation with the group of Hilpert at the Forschungszentrum Juelich [3–5] and with other research groups.

The model used here is based on the assumption of local chemical equilibrium. This is a useful approximation for gas-phase reactions at high temperatures. For heterogeneous reactions, such as the deposition of tungsten on the vessel wall, kinetic effects can be very important. Furthermore, in the area of the arc attachment on the electrode the temperature and density gradients are so high that this assumption most probably is invalidated. A second simplification is the assumption of "good mixing" or constant total element pressures in the whole lamp. However, demixing due to diffusional effects is well known, especially in vertical burning metal halide lamps [6,7]. It certainly affects the situation in the arc, but it will influence corrosion processes too, by causing concentration differences along the vessel wall and electrodes. All these effects have the result that the outcome of thermodynamic modeling must be interpreted with great care.

SITUATION AT THE COLDEST SPOT

It is common practice to dose an excess of those metal halides that have a relative low volability, such as sodium, scandium, and rare-earth halides. At the coldest spot in the lamp this excess of additives will condense and, in general, will form a liquid mixture. For the light technical properties of the lamp, but also for life-time determining processes, the composition of the gas phase in equilibrium with the molten salt mixture is important. It will depend on the temperature and the composition of the molten salt mixture. By convection and diffusion, the gas above the salt pool spreads through the whole inside of the lamp and will affect the light emission in the arc and participate in corrosion reactions on the vessel wall and electrodes. Schnedler [1] proposed the following procedure to describe the lamp chemistry: First, the real composition of the gas phase is calculated by determining the possible condensed phases that can exist at the coldest spot and by calculating the composition of the gas phase above these condensed phases. Then, this gas composition is used to calculate equilibrium situations at a higher temperature. This procedure is simple but very useful and will be followed here.

Gas composition above the metal halide salt mixture

The molten salt mixture formed by the excess of halides is certainly not an ideal solution. Complex formation in the salt between alkali and scandium or rare-earth halides gives rise to activity coefficients of these compounds which are in general smaller than one. This means that the mixing of these halides will have an adverse effect on their equilibrium vapor pressure: it will be lower than may be expected on the basis of their mole fraction. Fortunately, in the gas phase, complexes between alkali and scandium or rare-earth halides are formed, too. These so-called heterocomplexes play an important role in enhancing the total vapor pressure of the constituent elements [3]. An example of this is shown in Table 1.

The thermodynamic data were taken from the work of Hilpert and Niemann [4]. For the sodium-scandium mixture the sodium pressure is really enhanced: it is higher than for pure NaI. The hetero-

Table 1 Calculated total element pressures of Na, Dy, Sc, and Si and the pressure of the heterocomplex $NaMI_4$, where M = Dy or Sc, in hPa, at a cold spot temperature of 1100 K for the pure unmixed compounds and for mixtures with a molar ratio of 10 and 2. Additional assumptions: W and SiO_2 are present at the cold spot, the lamp volume is 1 cm^3, 10 bar of Hg and the 5 to 8 mg salt contains 45 ppm H_2O (by weight).

	Pure compounds	$NaI/ScI_3 = 10$	$NaI/DyI_3 = 10$	$NaI/DyI_3 = 2$
Σ Na (hPa)	7.0	10.9	5.8	4.4
Σ Dy (hPa)	1.5		0.16	2.7
Σ Sc (hPa)	142	5.1		
$NaMI_4$ (hPa)		5.0	0.15	2.4
Σ Si (hPa)	1.4 (DyI_3) 45 (ScI_3)	$3*10^{-2}$	$3*10^{-4}$	$7*10^{-2}$

complex $NaScI_4$ is very stable, and almost all scandium in the gas phase is originating from this compound. The calculated total Sc pressure above pure ScI_3 of 142 hPa is so high due to a strong contribution of the dimer $(ScI_3)_2$. For the mixture, the ScI_3 pressure is so low that the contribution of the dimer is negligible. The net effect of the mixing is thus a lowering of the scandium pressure. For the sodium-dysprosium mixture with the same molar ratio as the sodium-scandium mix, the Na pressure is lower than of pure NaI, and again the total Dy pressure is almost fully caused by $NaDyI_4$. Making the mixture more DyI_3 rich gives a lower Na pressure (less yellow-orange light) and a higher Dy pressure (more blue white), and so a color shift from warm white towards more neutral white. Again, the heterocomplex gives the main contribution to the total dysprosium pressure.

Reactions with the vessel wall

Because rare-earth oxides are very stable compounds, rare-earth halides have the tendency to react with oxidic wall materials such as SiO_2 (quartz glass) and Al_2O_3 (PCA: polycrystalline alumina) at elevated temperatures. Thermodynamic calculations predict the following reactions with SiO_2 [2]:

$$2\ REI_3 + SiO_2 \Leftrightarrow 2\ REOI + SiI_4 \tag{1}$$

or $$4\ REI_3 + 7\ SiO_2 \Leftrightarrow 2\ RE_2Si_2O_7 + 3\ SiI_4 \tag{2}$$

where RE stands for scandium, yttrium, and the rare-earth elements. Besides SiI_4, SiI_2 will be formed too. Furthermore, at the cold spot a reaction between W and the silicon iodides is predicted:

$$5\ W + 3\ SiI_4 + 6\ Hg \Leftrightarrow W_5Si_3 + 6\ HgI_2 \tag{3}$$

The compound W_5Si_3 has never been observed. A plausible explanation is that the silicon halides are transported to hotter parts of the tungsten electrodes and decompose there while silicon dissolves in tungsten [2] (see below).

The total silicon pressures shown in the last row of Table 1 were calculated assuming that enough W was present at the cold spot to form W_5Si_3. For pure ScI_3 the equilibrium total Si pressure Σ Si is high, wheras pure DyI_3 is clearly less aggressive towards quartz. A dramatic reduction of the Si pressure is obtained by mixing the scandium or rare-earth halides with alkali halides. Due to the complex formation in the salt the vapor pressure of the rare-earth halides is strongly reduced, leading to a much lower SiI_4 pressure. At the same time, the complex formation in the gas phase produces the total additive pressures that are necessary to get the desired light technical properties. The total silicon pressure depends on the choice of the metal halide: scandium being more aggressive than dysprosium, and on the dilution of the aggressive compound:

$$\Sigma\ Si\ (NaI/DyI_3 = 10) << \Sigma\ Si\ (NaI/DyI_3 = 2)\ [8]$$

Table 2 Calculated total element pressures for a $NaI/DyI_3 = 10$ mixture in hPa; cold spot temperature 1300 K for both Al_2O_3 and SiO_2. Other conditions are the same as used for the calculations of Table 1.

Wall material	Σ Na	Σ Dy	Σ Al	Σ Si
Al_2O_3	75	1.4	37	
SiO_2	75	1.4		2^*10^{-3}

The reaction product of reaction 1 REOI has never been observed by us, whereas, certainly in the case of scandium, the silicate (reaction 2) has been found [8]. In horizontal-burning, sodium-scandium lamps a white deposit consisting of $Sc_2Si_2O_7$ can be found on the hot spot in the middle of the upper side of the vessel. Due to the higher gas temperature there, the heterocomplex $NaScI_4$ is less stable than at the cold spot. Thus, at the hot spot the ScI_3 pressure is enhanced, and this causes the formation of scandium silicate.

In Table 2 a comparison is made between SiO_2 and Al_2O_3 as vessel wall material. In this case a cold spot of 1300 K was assumed as being more representative for ceramic arc tubes.

The difference in Al and Si pressure is striking. The dominant Al-containing gaseous species is AlI_3:

$$DyI_3 + Al_2O_3 \Leftrightarrow DyAlO_3 + AlI_3 \tag{4}$$

It is not certain which dysprosium aluminate is formed. There are no direct observations available. In contrast to silicon, aluminum does not form compounds with tungsten, at least not on the tungsten-rich side of the phase diagram. The solubility of aluminum in tungsten at high temperatures will be discussed below in the section "Transport to the electrodes".

CORROSION OF THE VESSEL WALL

Two types of corrosion processes can be distinguished:

- Corrosion via the gas phase, leading to blurring of the initially transparent quartz glass. In particular, this is adverse for lamps for optical applications. Whitening of the arc tube results then in a serious loss of lumens in the light beam.
- Corrosion under or close to the salt pool. For quartz glass this can lead to crystallization and to the growth of porous structures. For PCA, leaching of the vessel wall causing leakage of the arc tube is one of the major lamp failure mechanisms.

Gas-phase transport

During burning the initially smooth quartz glass surface is roughened by etching of the surface and by deposition of SiO_2 in crystalline but probably in amorphous form, too. Lamps with a rated life of more than 10 000 h will have relatively low vessel wall temperatures, and then the blurring of the glass will proceed very slowly. On the other hand, very high loaded lamps with maximum optical performance (i.e, for studio applications) can turn white within 500 h. These phenomena can be explained in terms of chemical transport of SiO_2 by silicon halides as transport agents [2]. Several reactions were proposed, based on estimated thermodynamic data for the compounds SiOI and $SiOI_2$:

$$SiO_2 + SiI_4 \Leftrightarrow 2\ SiOI_2 \tag{5a}$$

$$SiO_2 + SiI_4 \Leftrightarrow 2\ SiOI + 2\ I \tag{5b}$$

or $\quad SiO_2 + SiI_4 \Leftrightarrow 2\ SiO + 4\ I \tag{5c}$

Recently, the existence of the gaseous silicon oxyhalides has been proven and their thermodynamic data have been deduced [5]. Thermodynamic calculations show that in iodide systems, reactions 5a and 5c are important, while in bromide lamps the equivalent of reaction 5a is the dominant one.

The mechanism of the gas-phase transport is such that at places at the vessel wall with a relative high temperature the reactions 5 proceed to the right, whereas at lower temperatures the reactions proceed in the opposite direction. Via this mechanism, SiO_2 is transported through the gas phase from locations with a high temperature to places with a low temperature. In this chemical transport reaction SiI_4 is the transport agent bringing about the continuous transport of SiO_2 without itself being lost. In the case of the $NaI/DyI_3 = 2$ mixture the total Si pressure Σ Si above the salt pool is 7 Pa. If in that lamp the highest temperature of the wall is 1250 K then the total pressure of the SiO-containing compounds there is calculated to be 0.028 Pa, SiO and $SiOI_2$ being equally present. At the cold spot, 1100 K, SiO and $SiOI_2$ together have a pressure of $8*10^{-4}$ Pa.

Near the hot spot on the vessel wall mushroom-like growth features can be observed which have a crystalline appearance. A possible explanation is that these shapes are formed via a very localized gas-phase transport of SiO_2 from the glass surface to the crystalline structure. There is no temperature difference involved. The driving force is the free enthalpy difference between the glass and the crystalline state. This causes a pressure difference of $(SiO + SiOI_2) = 0.004$ Pa. Although a small value, due to the distances in the order of microns, it still may give rise to a reasonable pressure gradient.

In PCA arc tubes a similar transport could occur via:

$$Al_2O_3 + AlI_3 \Leftrightarrow 3\ AlOI \tag{6}$$

Based on estimated thermodynamic data of AlOI and the lamp conditions mentioned in Table 2, the calculated AlOI pressure at a hot spot temperature of 1450 K is 0.002 Pa. The existence of AlOI has however not yet been proven. This rather low value is in line with the observation that in PCA lamps, despite the higher temperatures, gas-phase transport of Al_2O_3 is not very strong.

Corrosion via the salt

As mentioned above, very close to or under the salt pool corrosion phenomena like crystallization of quartz glass, growth of porous structures and leaching of PCA can be observed. The mechanism of this is unclear. For quartz, a plausible driving force is the transition from the glass to the crystalline phase. Similar to the growth of the "mushrooms" via the gas phase, transport of SiO_2 via the molten salt could occur if either SiO_2 is (slightly) soluble in the salt, maybe in the form of $SiOI_n$, or if a compound like DyOI dissolves in the salt:

$$2DyI_3 + SiO_2(glass) \Leftrightarrow 2DyOI(dissolved) + SiI_4 \Leftrightarrow 2DyI_3 + SiO_2\ (cryst.) \tag{7}$$
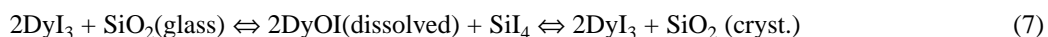
In literature it is reported that lanthanide oxyhalides are soluble in some alkali halides and in their trihalides [6]. For PCA, the driving force cannot be a structural change.

TRANSPORT TO THE ELECTRODES

So far, only the processes at or above the vessel wall have been considered. The temperatures there are moderate compared to the temperatures along the electrodes, the electrode tip having a temperature in the region of 3000 K. At those temperatures phenomena like the dissolution of other metals in tungsten may become important. The metals can be dosed on purpose in the form of metal halides or can be corrosion products like silicon or aluminum. Examples of the first cathegory are: Fe and Co dosed in sun tanning lamps to produce UV-A radiation, or Hf and Ta used to improve the visible spectrum. Of these additives an appreciable amount can disappear in the electrodes. This will cause a lowering of the melting point of tungsten and may in some cases lead to serious deformation of the electrodes.

According to the data of Miedema *et al.* [9], elements taking part in wall corrosion reactions, such as silicon in quartz glass lamps or aluminum in PCA lamps, can dissolve too. The silicon and aluminum halides formed at the vessel wall (reactions 1, 2, and 4) will be able to reach the hot parts of the electrodes via the convective flow. There they will decompose to their lower halides and to the pure elements in the gas phase. In the electrode tips in quartz lamps silicon contents up to about 500 ppm by weight have been found [2] after a few thousand hours of burning, in good agreement with calculated solubilities using an estimated heat of solution of silicon in tungsten [9]. Whereas the silicon disappears in the electrodes, the iodine remains in the gas phase. During lamp life the iodine pressure will therefore increase, and this will diminish the element pressure and thus the solubility of silicon; the process is self retarding. In PCA lamps a similar situation exists. Compared with quartz lamps the aluminum pressure is higher than the silicon pressure, but the estimated heat of solution of Al in W is lower and the aluminum halides are more stable than the silicon halides. This results in a calculated aluminum solubility which is about equal to the silicon solubility. Preliminary investigations do not indicate a high solubility of aluminum; this will be the subject of further investigations.

The situation gets more spectacular when excess scandium metal is dosed in the lamp as is sometimes the practice in sodium-scandium iodide lamps. The metal chip will react with the underlying wall material:

$$4 \, Sc + 3 \, SiO_2 \Rightarrow 2 \, Sc_2O_3 + 3 \, Si \tag{8}$$

and the silicon will be transported to nearest by electrode tip. This leads to high silicon concentrations in the tip, and so to melting phenomena and distortion of the electrode top. The effect on lamp behavior, however, is usually not adverse because it helps in releasing the emitter thorium which is contained inside the electrode material as ThO_2 dopant:

$$3 \, ThO_2 + 4 \, ScI_3 \Rightarrow 3 \, ThI_4 + 2 \, Sc_2O_3 \tag{9}$$

At high temperatures reaction 9 proceeds to the right. Depending on how much iodine is available in the lamp, thorium will form a macroscopic deposit on the electrode tip or a mono-layer [10,11]. In both cases, the work function will be reduced leading to a lower electrode top temperature and hence a smaller evaporation rate of tungsten evaporating from the electrode: less wall blackening (see next section below).

A second interesting phenomenon related to the use of an excess of scandium metal is the observation that scandium may change places with the thorium in the oxide particles present as dopant in the thoriated tungsten electrodes. Evidently, scandium is transported to the electrodes, penetrates into the interior, possibly via grain boundaries, and reacts there with ThO_2, releasing thorium metal.

TRANSPORT AWAY FROM THE ELECTRODE TIP

A very common problem with high-temperature light sources is the decrease in lumen output during lamp life due to blackening of the vessel wall. This so-called wall blackening is caused by tungsten transported from the hot electrode tips to the relatively cold arc tube wall. Here this problem will only be discussed briefly; more details can be found in [12,13].

The total tungsten pressure increases strongly with temperature. Hence, the tip of the electrode, where the arc attaches, can be considered as the source of tungsten. In metal iodide lamps the major contribution to the total tungsten pressure comes not from W but from the tungsten halides WI and WI_2. Therefore, the higher the iodine pressure in the lamp the higher the total tungsten pressure near the electrode tip. Via convective flow tungsten-containing gas will reach the vessel wall.

In lamps dosed with scandium or lanthanide iodide there will be no oxygen-containing species in the gas phase and so there will be no possibility to form WO_2I_2, a gaseous compound stable at the low temperatures prevailing at the vessel wall. The equilibrium pressure of the tungsten iodides is extremely low, so deposition of tungsten on the wall is inevitable. Fortunately, tungsten does not form a smooth

strongly light absorbing metal film, but precipitates in the form of crystalline particles and in between these particles the wall remains transparent to light. Therefore, the crystal density is an important factor for the amount of light coming out of the lamp. The rate of formation of crystals (i.e. the nucleation rate) strongly depends on the tungsten pressure in the gas (influence of the source) and on the temperature of the wall; a minor but still important effect is the presence of excess iodine in the form of HgI_2 [12]. The effect of wall blackening can be diminished by lowering the tungsten pressure in the gas (low tip temperature, low total iodine pressure) and by increasing the wall temperature. This last effect explains why PCA lamps tend to have a better lumen maintenance than quartz lamps in spite of their smaller internal wall surface: the same amount of tungsten is deposited on a smaller surface, but this effect is overruled by the lower crystal density.

CONCLUSIONS AND OUTLOOK

Metal halide discharge lamps are high-temperature devices in which, under influence of strong temperature gradients and convective flow and due to the nature of their filling, a number of complex transport phenomena and corrosion reactions occur.

Thermodynamic modeling assuming local chemical equilibrium and good mixing can help in understanding the chemistry inside these lamps and in improving them. In interpreting the results these approximations should always be kept in mind.

A prerequisite in thermodynamic modeling is the availability of reliable data regarding pure and mixed phases and of models describing complicated mixed phases. This remains a matter of constant concern.

A further improvement would be a more realistic description of transport effects such as convection and demixing, still in combination with local chemical equilibrium.

The understanding of the chemistry inside PCA lamps is lagging behind with respect to what is known for quartz glass lamps.

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