SOLID STATE RADIOLUMINESCENT SOURCES: MIXED ORGANIC/INORGANIC HYBRIDS

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DISCLAIMER

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ABSTRACT

This concept brings a condensed source of tritium into close proximity with an inorganic phosphor. That source may thus become the equivalent of many atmospheres of tritium gas pressure. If both phosphor and tritium source material are optically clear, then a lamp's brightness may be made to scale with optical path length. Proof of principle of this concept has been demonstrated and will be described. A theoretical treatment is presented for the results here and for results from aerogel experiments.

INTRODUCTION

The attainable brightness of conventional tritium lamps is limited by several factors [1]. Among them is the modest 1-3 atmosphere pressure of tritium gas which is practical to enclose within the typical glass envelope design. In addition the ruggedness of the device is limited by the possibility of breakage of the envelope, after which virtually all tritium escapes (and glow ceases). Both factors above could be alleviated by employing a solidified tritium source directly bound to the particles of a solid-state phosphor. The solidified tritium source could represent the equivalent of many atmospheres of tritium gas. Both source and phosphor being solid, the material would continue to perform even in the event of container rupture. If the phosphor were comprised of optically transparent crystallites, light production could be collected from a large optical path length: light output would scale with thickness of the matrix. If the refractive index of the tritium source material were similar to that of the phosphor material, minimization of internal reflectance losses could be minimized and overall light output would be further increased. Figure 1 displays the concept of this solid-state phosphor/source "hybrid" design [2].

In an effort to explore the utility of this design, experiments have been performed with two phosphor types, $ZnS:Cu,Al$ and $Y_3(Al,Ga)_5O_{12}:Tb$. Each of these have been mixed with a condensed tritium source in the form of tritiated p-di(phenylethynyl)benzene, the utility of which has been previously noted [3].

EXPERIMENTS AND RESULTS

Phosphor type GR-500 (ZnS:Cu,Al) was obtained from USR Optonix Inc., Hackettstown, NJ. This material is a powder of high refractive index (ca. 2.2) and high opacity to visible light, similar to that used in the tritium lamp industry to coat the inside of glass envelopes. Phosphor type 1271 [$Y_3(Al,Ga)_5O_{12}$:Tb] (YAG) was obtained from the Chemical Division of GTE Sylvania, Towanda, PA. This is a white (clear microcrystalline) powder used for special CRT displays; its refractive index is ca. 1.8. The p-di(phenylethynyl)benzene (DEB) employed was ball-milled with a Pd (5 wt%) on activated carbon catalyst in an overall proportion of 75 wt% DEB / 25 wt% catalyst.

DEB/catalyst powder, 0.2349g (in two batches of 0.101g and 0.134g), was taken into an evacuable ampoule and outgassed for 30 min at < 50 millitorr pressure. Tritium gas (as 60.4 mole% T, 0.6 mole% H+D, 39.0 mole% He-3) was expanded into the 155.5 cm^3 ampoule at 493.5 torr pressure and 21.7°C. This gas represented a 0.5 % stoichiometric excess of hydrogens with respect to the available ethynyl groups of DEB (4 H_2 react per molecule). It is important that pure hydrogen not be allowed to react with the powder, as overly vigorous reaction occurs, accompanied by loss of some absorption capability [3]. Hydrogenation (tritiation) of the powder was allowed to proceed for 40 hours to 80% completion, as monitored by pressure measurements, although reaction was 76% complete in 22 hours. Residual tritiated gasses were then evacuated from the ampoule and replaced with one atmosphere of helium.

Of the reacted DEB powder above, the smaller original batch was removed from the ampoule and slurried in 0.4 cm^3 of ethylbenzene (in which hydrogenated p-DEB is ca. 20 wt% soluble) for 5 min. Slurry was transferred to the barrel of a syringe with attached filter disc, and filtrate was forced into a fresh vial. The filter syringe (and retained catalyst) was then washed with an additional 0.1 cm^3 of solvent. The colorless solution of DEB-t_8, containing 50 Ci of tritium, was then successively diluted and transferred to four 0.50 g batches of phosphor powder. Onto three batches of ZnS:Cu,Al powder were added dropwise (from ca. 0.15 cm^3 of ethylbenzene solvent each) 20 Ci, 15 Ci , and 7.5 Ci of DEB-t_8 (samples ZnS#1, ZnS#2, ZnS#3, respectively). Onto one batch of YAG powder was likewise added 7.5 Ci of DEB-t_8.

Solvent containing 20 Ci of DEB-t_8 was initially added to the ZnS#1 sample powder, while the powder was disposed in a 3-4 mm thick pile on a 2" x 2" silvered glass slide. A brightness level of 0.97 ft-Lambert was observed, even though the solvent had not yet evaporated. The luminance was measured using a Minolta LS-110 photopically-corrected instrument. Shortly thereafter the sample was mixed and pressed into a ca. 0.5 mm-thick film, of about 1" diameter, between the silvered glass and a transparent 2" x 2" glass coverslip. Brightness of the film then registered a uniform 0.43 ft-Lambert while still a wet 1" diameter, and 0.36 ft-Lambert at a wet 1.25" dia. Addition of solution holding 15 Ci to the ZnS#2 sample was marred by excess solvent (ca. 0.2 cm^3 total), which ultimately caused the film to run beyond the confines of the flat square glass slides. Nevertheless, a brightness of 0.19 ft-Lambert was observed while this sample was still at about a 1.5" diameter wet spot on the slide. Finally, addition of solutions containing 7.5 Ci each to the ZnS#3 and YAG samples was performed. Spots were essentially confined to 1.25" dia., and registered 0.11 and 0.04 ft-Lambert while fresh.

Solvent was allowed to evaporate from sample preparations overnight. Light outputs were then measured at 0.32, 0.04-0.06, 0.08-0.24, 0.04-0.11 ft-Lambert for the samples in the order as given above. The range of luminance values given for the last three samples reflects the non-uniform light output observed from the materials. In all three cases enhanced brightness was noted at the periphery of the dry films. Presumably the DEB-t_8 is most concentrated in those zones, suggesting that as the solvent dried it carried with it the DEB-t_8 toward the exterior of the film. This indicates a rather poor affinity between the phosphors and the tritiated DEB.

On the second day of the experiment, the material of sample ZnS#2 was removed from its glass slide, placed into a glass vial, and thoroughly mixed (this was a free-flowing powder). Light output as a function of thickness of this sample was measured and is shown in Figure 2. It may be noted that the output approximates a linear function of thickness below 1 mm, but above 1 mm diminishing returns of the output with thickness are observed. This scaling presumably results from the substantial opacity of the powder to its own emitted light, as observed elsewhere [4]. The scaling also appears to account for the observations on the ZnS#1 sample of about 0.4 ft-Lambert brightness for a ca. 0.5 mm thick film and 1.0 ft-Lambert brightness for a 3-4 mm thick film.

Brightness of the films was monitored over the ensuing 40 days. In Figure 3 are plotted the results. Light output decreased with a half-life of 10-20 days. By the 21st day, darkened rings of material became apparent extending beyond the phosphor spots on the glass slides. This material was probably DEB-t_8 which had undergone radiation-induced darkening. On day 39 DEB-t_8 was extracted from the ZnS#2 sample (which had remained and been measured in the small vial). Ethylbenzene, 1 cm^3 total, was added in two stages to the sample, with the supernatant successively decanted following slurrying. About 9 Ci of the original 15 Ci was removed, judging by the decrease in luminance from the sample. The ease with which DEB-t_8 was extracted from the ZnS#2 sample is further indication that little affinity exists between the DEB and the phosphor. Consistent with the conclusion of radiation darkening, the extracted DEB-t_8 solution was observed to be yellow in color (versus the original colorless solution). The extracted DEB-t_8 could nevertheless be used successfully to spot onto fresh phosphor. From addition of 0.9 Ci of aged DEB-t_8 solution to a 2 mm dia. x 3 mm deep well of ZnS:Cu,Al phosphor (ca. 19 mg in an aluminum block), luminance of 0.61 ft-Lambert was observed. This spot, and others prepared at the same time, lost brightness with a half-life similar to that noted above.

DISCUSSION

The addition of DEB-t_8 to ZnS#1 resulted in a film composite retaining 82 Ci/cm^3 and producing a glow of about 1.0 ft-Lambert initially. This may be compared to the data in reference [4] for ZnS:Cu,Al powder surrounded by T_2 gas at 1 atm pressure (1.2 Ci/cm^3 given the 50% theoretical density of the loose powder): 0.08 ft-Lambert was observed. For a 68-fold increase in total tritium density for the DEB-t_8 loading, only a 12-fold increase in brightness was observed versus the T_2 loading. This lack of efficiency will now be investigated further via a model which is described below.

It has been shown previously [5] that the fractional absorption of tritium beta energy within a spherical volume of tritiated material increases with the density of that material (in g/cm^3) and radius a of the sphere (in cm) according to the following function:

$$G = 1 - 3/(2\alpha) + (3/\alpha^3)[1 - (\alpha+1)\exp(-\alpha)] , \qquad (eqn. 1)$$

where $\alpha = 2\mu$ aR, μ is the mass absorption coefficient 9600 cm^2/g for nitrogen gas, and R is the ratio of electrons per unit mass in the material versus that for nitrogen (since loss of tritium beta energy occurs primarily through collisions with electrons in the material [6]). A useful plot of G versus α is given on p.18 of reference [5]. The fraction F of tritium beta energy which escapes the mass of tritiated material to excite phosphor is then

$$F = 1 - G . \qquad (eqn. 2)$$

For tritium gas filling the voids between loose-packed 5 μm dia ZnS particles, and assuming 5 μm dia (more or less) spherical voids, one obtains $\alpha=0.0008$ and F=1.0. This implies very low self-absorption of beta-power by tritium in bulk phosphor/tritium gas lamps, as has been noted [4]. For the ZnS#1 sample above, 23 mg of DEB-t_8 was dispersed in 0.5 g phosphor. If the DEB-t_8 were evenly dispersed throughout the ZnS, one can show that the effective radius of that DEB between phosphor particles would vary from 0.34 μm (uniform coating of the phosphor surfaces of area ca. 0.3 m^2/g) to about 1.5 μm (globules between all phosphor particles). The factor α then varies between 0.60 and 2.6, for which the energy utilization factor F is 0.82 and 0.46, respectively. The 68-fold increase in tritium density in going from ZnS with 1 atm tritium gas to sample ZnS#1 should thus have been met with a 56-fold (for uniform coating) to 31-fold (for small globules) increase in brightness, assuming light propagation in the samples to be unperturbed by the presence of DEB-t_8. The modest 12-fold brightness increase observed suggests formation of larger masses of DEB-t_8 precipitate, of an average 5 μm in diameter (using the model above). Self-agglomeration of the DEB-t_8 molecule within the phosphor matrix is therefore detrimental to the brightness of the sample; efficient thin coatings of the phosphor by DEB-t_8 would have been preferred.

In the three ZnS "hybrid" experiments performed in this paper, light output appeared to scale about linearly with tritium loading. The efficiency of beta utilization F thus appears constant. This may indicate that the precipitation of DEB occurred to about the same agglomerate size in each of the samples, and that there were simply more such agglomerates to produce beta power and hence more light in the higher loadings.

The lower luminance from the YAG sample versus ZnS#3 presumably represents the lower energy conversion efficiency of the phosphor itself [7]. Although it was not attempted, it is expected that increasing the thickness of a YAG "hybrid" would produce greater luminance returns with powder depth than did the ZnS samples, because of the optically transparent nature of the YAG crystallites. Sustantially greater output from thick YAG samples could result.

Radiation darkening of the DEB-t$_8$ used in this work is not unreasonable. Dosage to a 5 μm sphere is easy to calculate from the energy deposition fraction G=82%. Since the material contains 24 g of tritium per 302 g molecular weight, dose D will be:

$$D = 24 \text{ g} \times 9619 \text{ Ci/g} \times 3.7E10 \text{ dis/secCi} \times 5700 \text{ eV/dis} \times 1.6E\text{-}12 \text{ erg/eV}$$
$$\times \text{ rad/100 erg/g} \times .82 \times 2.6E6 \text{ sec/mo} / 302 \text{ g} = 6 \text{ Grad/mo} .$$

This is a large dose even for an organic material with substantial phenylation [8]. Darkening is expected to be a function of the increase in unsaturation (i.e., H$_2$ loss) [9]. Radiation-induced H$_2$ production from a material similar to DEB-t$_8$, polystyrene, is about 100 times less than that for polyethylene [10]. Since yellowing of polyethylene under T$_2$ gas becomes apparent at a dose around 0.1 Grad [9], a similar effect at about 100 times that dose is expected for the DEB-t$_8$. This is consistent with the present observation. Inhibiting agglomeration of the DEB-t$_8$ within the samples would lower the dose by a decrease in the factor G (eqn. 1).

The model noted in equations 1 and 2 above may be extended to aerogel/phosphor samples which have been investigated to date [11]. Restricting ourselves to aerogels with ZnS density 0.5 or 0.75 g/cm^3, the pertinent data and results from several experiments are given in Table 1. Since the phosphor particle spacing is a constant across all the samples (except perhaps one - see below), while tritium loading and mass of non-ZnS in the matrices was varied, luminance output L is considered to be directly proportional to tritium density [T] and the fraction of beta power utilized:

$$L = K \cdot F \cdot [T] , \qquad\qquad (eqn. 3)$$

where the constant K accounts for phosphor energy conversion efficiency, phosphor loading density within the aerogel, volumetric light scattering effects within the aerogel, and unit conversions. Table 1 includes calculations of L for four experiments, as compared to the observed results. Two predictions for logical extension experiments are also given. It may be seen that, although the model accounts for the observed data consistently within three of the four experiments, the DEB experiment is anomalous. Electron micrographs of DEB-loaded aerogels have in fact shown considerable disruption of the matrix. Self-agglomeration of the DEB, with accompanying low effiency F, is again the apparent result.

Table 1 does predict a high light level of 10.4 ft-Lambert from an aerogel with an overpressure of 100 atm of tritium gas. Although this is not practical for safety lighting applications, this output could be put to use in the producton of an electrical power supply as noted in another paper in this conference [12]. Similar calculations for loose ZnS phosphor powder under 100 atm of tritium gas predict an 9.8 ft-Lambert luminance (α=0.078, F=0.98).

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Table 1. Comparison of luminance observations from aerogel experiments (0.5 or 0.75 g(ZnS)/cm^3 in 0.15 g/cm^3 aerogel) with calculations based on model described in text, together with predictions for two logical extensions.

Source of tritium		[T] (Ci/cm^3)	R(g/cm^3 of non-ZnS)	F [a]	Luminance (ft-L) L [b]	
					obs.	calc.
1) T$_2$ gas	1 atm	1.9	0.150	0.30	0.13	0.11
2) "	100 atm	190	0.163	0.28		10.4 [c]
3) OT	hydroxyl exchange	18	0.150	0.30	0.85	1.05
4) "	maximum	43	0.150	0.30		2.13 [d]
5) T$_2$O	1.0 monolayer	87	0.183	0.26	4.6	4.4 [e]
6) DEB-t$_8$		148	0.348	0.14	1.2	4.0

[a] Determination of F uses a=16.3μm for effective spherical radius of material between phosphor particles. This has been made consistent with a Monte-Carlo calculation which has estimated F=0.3 for tritium as exchange OT in these aerogel/phosphor matrices (line 3, personal communication, R. J. Walko, Sandia National Laboratory). This is also consistent with electron microscopic observations.

[b] L calc. uses K=0.195 (from eqn. 3) derived as best fit to lines 1) and 3) data.

[c] Prediction.

[d] Prediction based on 9 x 10^{20} OH/cm^3 for optimized aerogel.

[e] Tritium density value has been fit to produce this calculated result. Monolayer coverage is based on 600 m^2/g aerogel surface areas and 9.6 Å^2 per T$_2$O molecule.
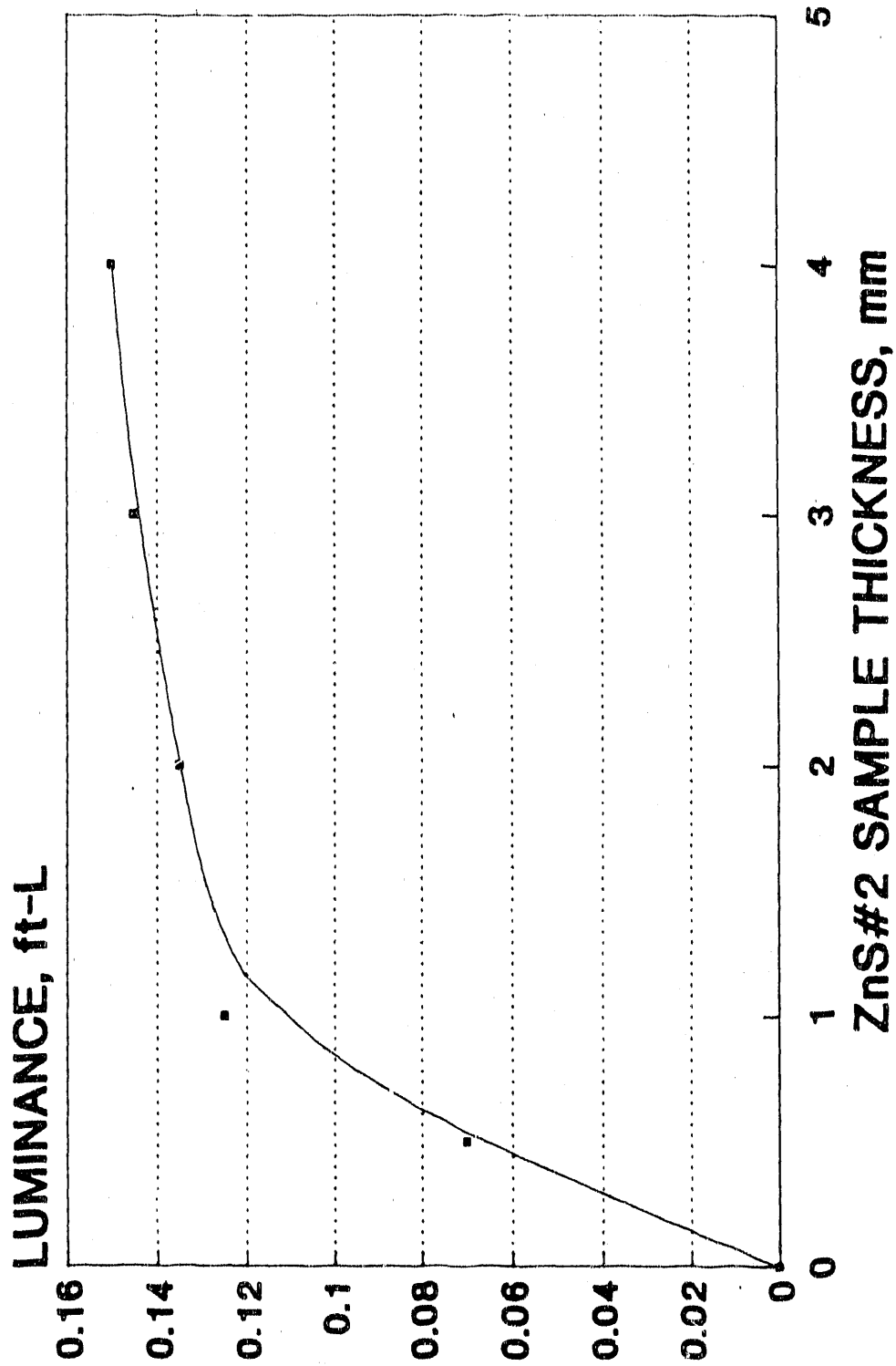
FIGURE 1. THE HYBRID CONCEPT:
INORGANIC PHOSPHOR / ORGANIC TRITIUM

PHOSPHOR

T SOURCE
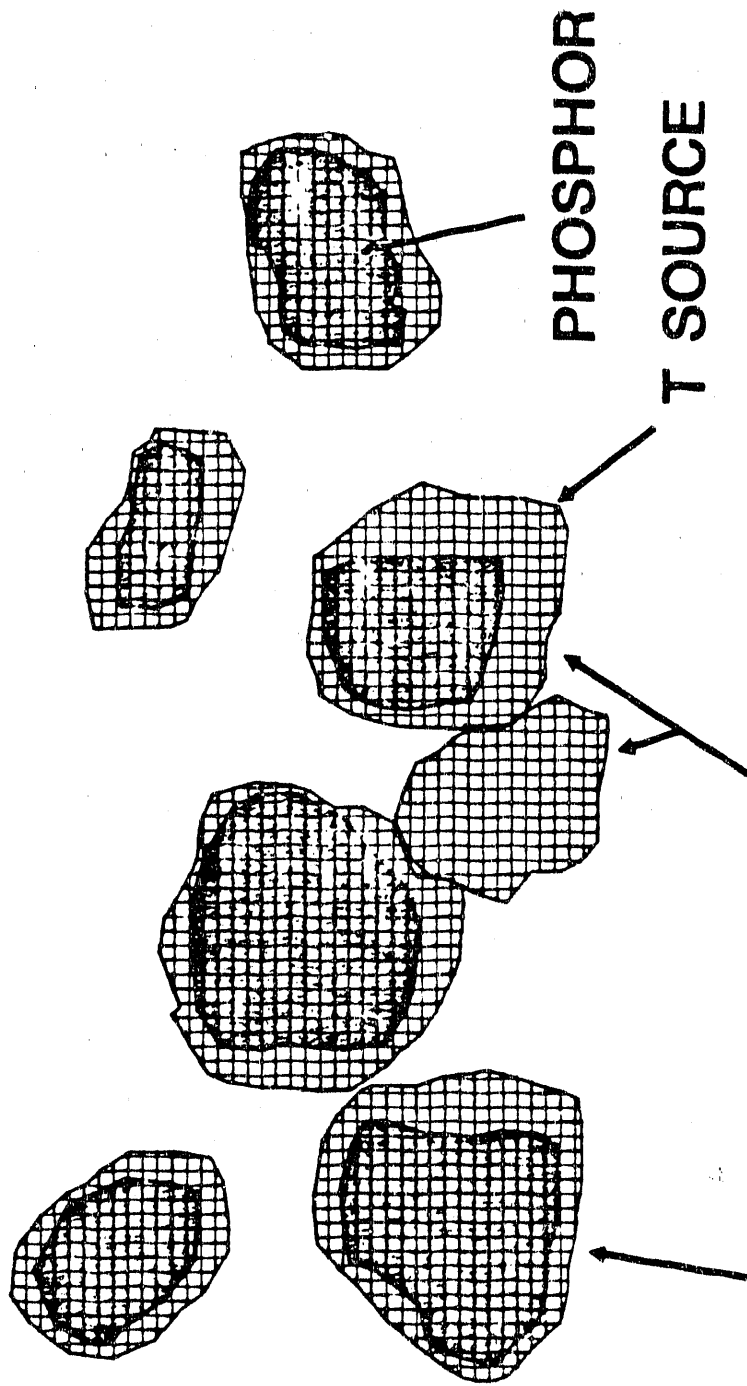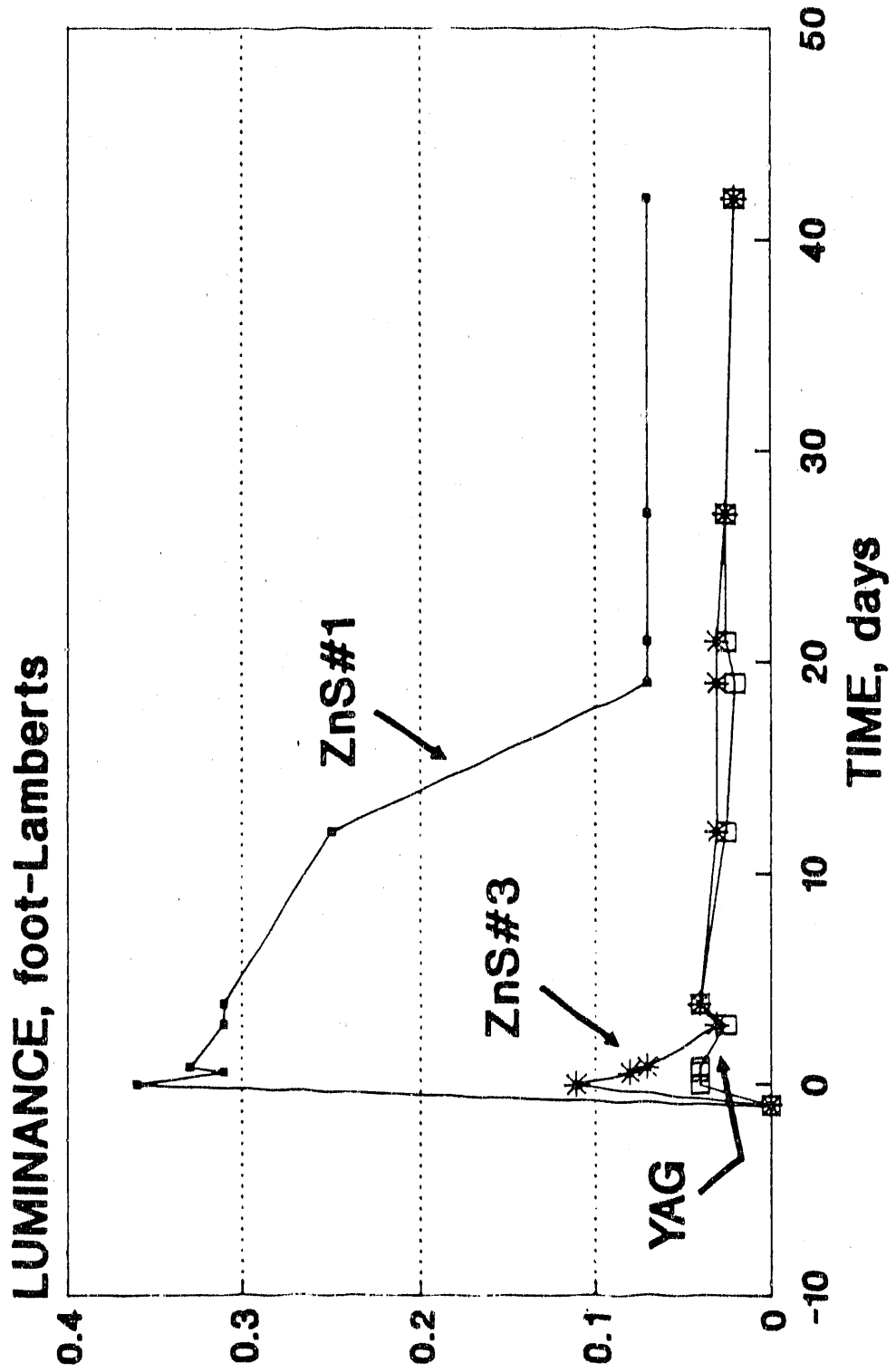
THICK FILMS OR AGGLOMERATES
MAY RAD-DAMAGE

THIN FILMS ARE PREFERRED

FIGURE 2. LIGHT OUTPUT vs. THICKNESS FOR SAMPLE ZnS#2

FIGURE 3. LUMINANCE vs. TIME FOR ZnS#1, ZnS#3, and YAG SAMPLES

END

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