

of Al₂O₃ and SiO₂, after firing, shows that Al₂O₃, SiO₂, and a trace of mullite (3Al₂O₃·2SiO₂) are present. Activation of these three compounds by Eu²⁺ results in materials whose emission is much weaker than fired mixtures of Al₂O₃ and SiO₂. Even phosphors containing limited solid solutions of Al₂O₃ in SiO₂ and SiO₂ in Al₂O₃ result in weak emission. An examination of the optical properties of all of these phosphors shows them to be different from the mixed "Al₂O₃·SiO₂:Eu" phosphors. The only conclusion that can be reached is that both Al₂O₃ and SiO₂ are necessary for phosphor formation but the specific host is not known. Subsequent to this work, Wachtel (5) also worked on this system. He believes that the Eu²⁺ is located at the interface between mullite and a second phase which may be Al₂O₃ or SiO₂.

The band emission of these phosphors is due to the presence of Eu²⁺ since Eu³⁺ causes line emission (6). Further evidence for the presence of Eu²⁺ is the need for firing in a reducing atmosphere, the body color in the case of EuAlO₃ and EuAl₂Si₂O₈ and the lack of luminescence or line emission when fired in O₂.

Normally Eu²⁺ emission is blue. However, in EuAl₂Si₂O₈ and in EuAlO₃, the Eu²⁺ emission is green-yellow and green, respectively. Note, however, Fig. 9, that both of these phosphors peak at the same wavelength. Their visual color difference is due to the wider emission band of the SrAl₂Si₂O₈ phosphor. The difference in emission color, blue vs. green, is most likely due to a different lattice environment of the Eu²⁺ ion.

There are other Eu²⁺ activated phosphors that have green emissions, for example, some of the alkaline earth silicates (7), Na₂B₄O₇ (8), and Al₂O₃-AlN (9). In fact, it appears that almost any emission color can be obtained with divalent Eu. For example, Jaffe and Banks have obtained yellow, orange, and red band emissions with the alkaline earth sulfides (6).

The interesting thing about the EuAl₂Si₂O₈ phosphor is that even with such high Eu concentrations,

the phosphor is very efficient, Table II. At these concentrations, one would expect concentration quenching to occur, resulting in relatively low efficiency. The EuAlO₃:Eu²⁺ phosphor is interesting in that Eu is present in both the +2 and +3 oxidation states. Examination of Fig. 3B shows that the excitation spectra of Eu³⁺ AlO₃:Eu²⁺ and EuAl₂Si₂O₈ are somewhat similar. The main peak at 350 mμ is most likely due to a 4f⁷ to 4f⁶ 5d¹ transition of the Eu²⁺.

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REFERENCES

1. J. F. Hammann, *Z. Angew. Phys.*, **10**, 187 (1958).
2. P. M. Jaffe, U. S. Pat. No. 3,359,211, Dec. 19, 1967.
3. P. M. Jaffe, U. S. Pat. No. 3,359,210, Dec. 19, 1967.
4. E. M. Levin, C. R. Robbins, and H. F. McMurdie, "Phase Diagrams for Ceramists," Fig. 294, Am. Ceramic Soc., Columbus, Ohio (1964).
5. A. Wachtel, *This Journal*, **116**, 61 (1969).
6. P. M. Jaffe and E. Banks, *ibid.*, **102**, 518 (1955).
7. H. McKeag and A. Ranby, *ibid.*, **97**, 415 (1950).
8. H. Gobrecht and R. Tomaschek, *Ann. Phys.*, **28**, 673 (1937).
9. I. Adams, T. R. Au Coin, and G. A. Wolff, *This Journal*, **109**, 1050 (1962).

LiYO₂:Eu as a Red Phosphor

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ABSTRACT

LiYO₂ can be activated by Eu(III) to give an efficient red emitting phosphor under cathode-ray and under 2537Å excitation. This phosphor has optical properties which indicate its possible use as the red component in color television screens. Unfortunately, during tube fabrication, the phosphor decomposes to Y₂O₃:Eu. The main cause of this deterioration has been found to be hydrocarbons which are present during tube manufacture.

The search for new and efficient red cathodoluminescent phosphors over the past several years has resulted in a number of interesting host materials activated with rare earth elements. Among these hosts are compounds having the general formula LiMO₂ where M is a rare earth element. Hoppe (1), Vorres (2), Bertaut and Gondrand (3) have described the preparation of the pure undoped hosts while Blasse (4) and Brixner (5) have described the luminescent properties of some of the Eu activated compounds.

We have investigated LiYO₂:Eu for possible use in color television screens. Cathodo and photoluminescent properties of this phosphor as well as some problems involving its use in CR tubes are presented here.

Experimental Procedure

Phosphor preparation.—The preparation of the host has been most completely described by Bertaut and

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Gondrand. They fired a mixture of the rare earth oxide with an excess of Li₂CO₃ for two days at 900°C in an alumina crucible in air.

We prepared the compound LiYO₂, without prior knowledge of the papers listed, by firing a mixture of Li₂CO₃ and Y₂(C₂O₄)₃ at 1000°C for 2 hr in an oxygen atmosphere. We found that the materials attacked platinum and that recrystallized alumina crucibles should be used. Following a procedure which was similar to that of Bertaut and Gondrand, we fired samples in an excess of Li₂CO₃ in order to force the reaction to completion. X-ray diffraction patterns for these samples were much stronger and better resolved than for similar samples without excess Li₂CO₃.

Bertaut and Gondrand state that firing above 900°C results in a room temperature metastable tetragonal structure which, after some time, changes to the monoclinic form, while firing at 900°C or below results in the stable monoclinic form. We fired our charges at

temperatures up to 1200°C for 2 hr and obtained only the monoclinic form. This difference might be due to Bertaut and Gondrand's long firing time and/or may also be due to the incorporation of europium in our samples. We have found that the europium doped monoclinic form results in a bright red phosphor while Eu doped samples which were fired at temperatures high enough and for times long enough to form the tetragonal structure were not luminescent.

In our procedure, firing time is critical. If the materials are fired for periods much longer than 2 hr we obtain mixtures of $\text{LiYO}_2\text{:Eu}$ and $\text{Y}_2\text{O}_3\text{:Eu}$ as evidenced by the presence of $\text{Y}_2\text{O}_3\text{:Eu}$ lines in the emission spectra.¹

Our phosphors were prepared by ball milling a water slurry of the freshly coprecipitated oxalates of yttrium and europium with about a 1.2 fold excess of Li_2CO_3 . This was dried and fired for 1 hr at 1000°C in oxygen. After cooling, the sample was ground finely in a mortar and refired an additional hour. The resultant phosphors have a white body color and are efficiently excited by both 2537Å uv rays and cathode rays. The determined density of the phosphor is 4.29 ± 0.032 g/cc. The maximum solubility in water was 0.06% by weight. The pH of this material was determined to be 12.2. After several washings with boiling water to remove the excess Li_2CO_3 , the pH was about 9. After about 1 hr, however, the pH rose to 10 indicating either that some hydrolysis of the sample occurred or that all the Li_2CO_3 was not removed.

Preparations using freshly coprecipitated hydroxides of europium and yttrium mixed with Li_2CO_3 result in even better yield of the phosphor than those obtained using the oxalates. The phosphors resulting from the two methods have the same spectral properties, but the hydroxide method results in a purer and a brighter product.

Measurements.—Emission spectra were obtained with a Jarrell-Ash 1/4 meter grating monochromator equipped with a wavelength drive and a photomultiplier whose output was recorded on a B&L VOM 7 recorder. The spectra were corrected for spectral sensitivity of the photomultiplier and instrument transmission. For the photoluminescent emission, the exciting source was a 2537Å Mineralight while excitation spectra were taken under a 150w d-c Xenon lamp. All spectra are given relative to a 0.2% fluorescein solution which has constant quantum efficiency over the range of 250-500 nm (6). Diffuse reflection spectra were obtained by attaching a Beckman diffuse reflectance unit to the output of the Jarrell-Ash monochromator. The reflected light was detected by a Hitachi 913B photomultiplier and its output recorded on the B&L recorder. The reflection spectra were taken relative to MgCO_3 . Absorption spectra are reported using the relationship: % absorption = $(100 - \% \text{ reflectance})$.

The cathodoluminescent data were taken using a demountable cathode-ray tube.

Discussion of Experimental Results

Figure 1 shows the brightness of LiYO_2 as a function of europium concentration for both 2537Å and cathode-ray excitation relative to a commercial batch of $\text{YVO}_4\text{:Eu}$. The optimum europium concentration occurs in the vicinity of 4-5 a/o (atom per cent) for both modes of excitation although the actual intensities are quite different. This curve represents a larger number of points than is indicated and agrees with the data reported by Brixner (5). However, our data, not shown here, indicate that a small dip occurs at about 5½ to 6 a/o europium. Our original hypothesis was that this dip represented differences in preparation and purity of our samples and so the curve is drawn smoothly through this region ignoring this dip.

¹ The emission spectrum of a sample was much more indicative of the presence of $\text{Y}_2\text{O}_3\text{:Eu}$ than x-ray analysis. The latter technique cannot detect less than 3-5 w/o $\text{Y}_2\text{O}_3\text{:Eu}$. The former method could detect less than 1%.

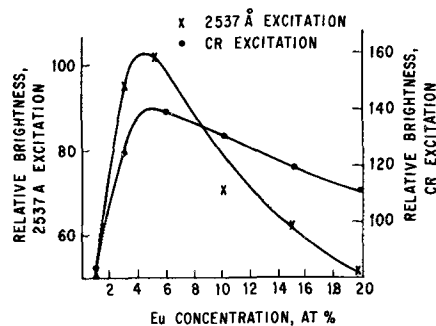


Fig. 1. Emission intensity of $\text{LiYO}_2\text{:Eu}$ relative to $\text{YVO}_4\text{:Eu}$ under cathode-ray excitation and 2537Å excitation.

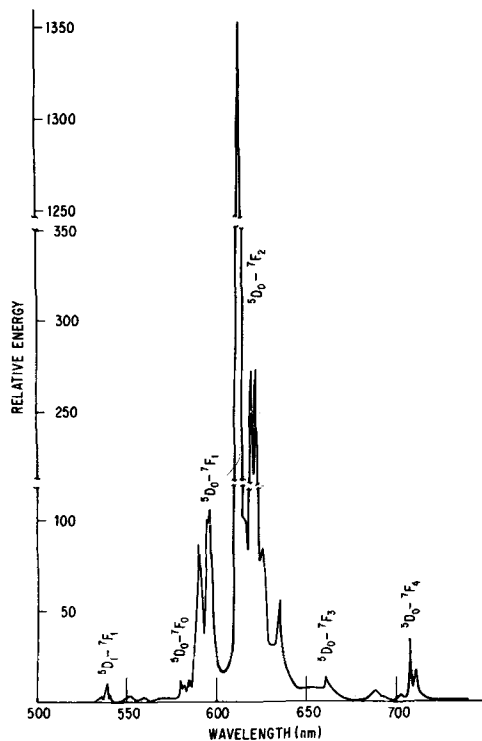


Fig. 2. Expanded scale emission spectrum of $\text{LiYO}_2\text{:Eu}$ under 2537Å excitation. The same spectrum is obtained with cathode-ray excitation.

More recent work indicates that this dip may be real, but if so, we do not know the reason for it.

The emission spectrum of $\text{LiYO}_2\text{:3 a/o Eu}$ is shown in Fig. 2 for uv excitation. The same spectrum is obtained with cathode-ray excitation. It consists primarily of a very strong line at 613 nm and a weaker doublet at 620 and 622 nm.

The transitions shown in Fig. 2 are derived from El'Yashevich (7). According to Blasse, the splitting of these lines should be such that two lines appear for each of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ and the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions. It seems that the 613 and 620 nm lines may represent the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition except that the 620 nm line is further split into two lines. Blasse reports that LiYO_2 has a distorted unit cell (4). This may be the cause of the additional splitting. Evidence for the 620 nm lines being due to additional splitting of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition and not to an impurity is found by measurement of its persistence. The persistence of the 5920, 6118, 6132, 6200, and 6217 nm lines is the same as that of the 620 lines indicating that all these lines originate from the same $^5\text{D}_0$ level, Fig. 3.

Under both uv and cr excitation, $\text{LiYO}_2\text{:Eu}$ shows a slight color shift as a function of the europium concentration as shown in Fig. 4. This is an enlarged view of the lower right side of the chromaticity diagram. Also shown, for comparison, are the color shifts for

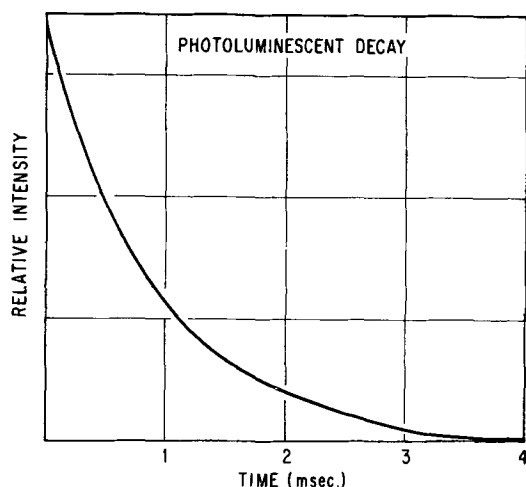


Fig. 3. Relative decay of the 5919, 6118, 6132, 6200, and 6217Å lines from LiYO₂:Eu for 2537Å excitation. Identical curves are obtained with europium concentrations of 2 and 10 a/o.

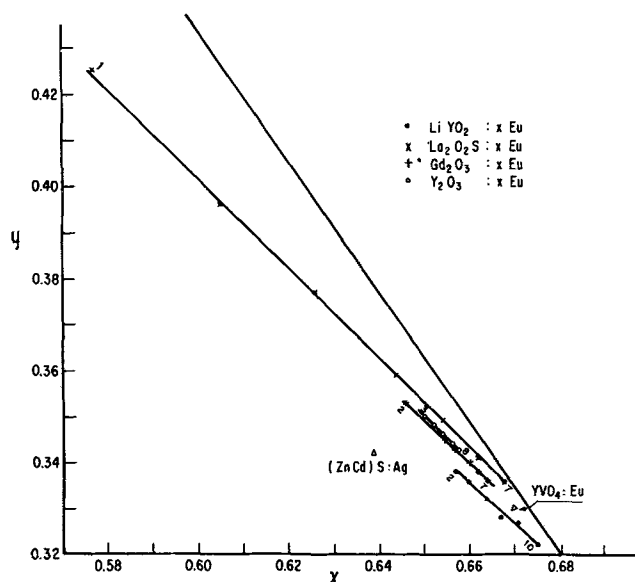


Fig. 4. Color coordinates of several recent and commercial cathodoluminescent phosphors. This figure is a greatly expanded portion of the lower right corner of the C.I.E. chromaticity diagram.

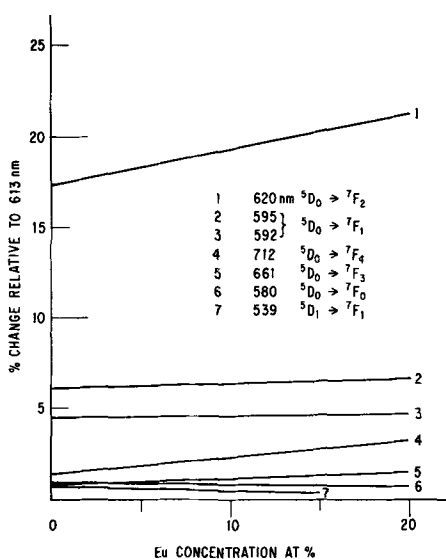


Fig. 5. Ultraviolet excited emission intensities of selected lines from LiYO₂ as a function of europium concentration compared to the emission intensity of the 613 nm line. This diagram shows the emission lines which are responsible for the color change as a function of the europium concentration.

La₂O₂S:Eu, Y₂O₃:Eu and Gd₂O₃:Eu and the color coordinates for YVO₄:5 a/o Eu and P22 (ZnCd)S:Ag. Figure 5 shows a least-squares plot of the per cent intensities of selected spectral emission lines from LiYO₂: 5 a/o Eu relative to the 613 nm line. From Fig. 5 it can be seen that the color shift is due to a combination of a decrease in the ⁵D₁ → ⁷F_{1,2} and ⁵D₀ → ⁷F₀ emissions and an increase in the ⁵D₀ → ⁷F_{3,4} emissions as well as in the doublet at 620 and 622 nm (hereafter called the 620 nm lines).

Figure 6 shows the absorption and excitation spectra of LiYO₂ containing 0, 2, and 10 a/o Eu, respectively. The undoped sample exhibits no excitation spectrum. Its absorption spectrum has no structure, but shows a weak band below 240 nm. The absorption and excitation spectra of the Eu containing samples show a strong band lying below 280 nm plus fine structure above 280 nm. The fine structure is due to direct excitation or absorption in the Eu centers (f → f transitions). The band below 280 nm is most likely due to a charge transfer process (8). Blasse (4) reports similar data.

Figure 7 compares the phosphorescent decay of LiYO₂:4 a/o with a YVO₄:5 a/o Eu production phosphor under cathode-ray excitation at ambient temperature. Both phosphors show an exponential decay. The LiYO₂:Eu has a decay time of 1.08 msec which is twice that observed for YVO₄:Eu, but still well within the limits necessary for use in color television.

Figure 8 shows the brightness of LiYO₂:Eu as a function of electron beam current density under an

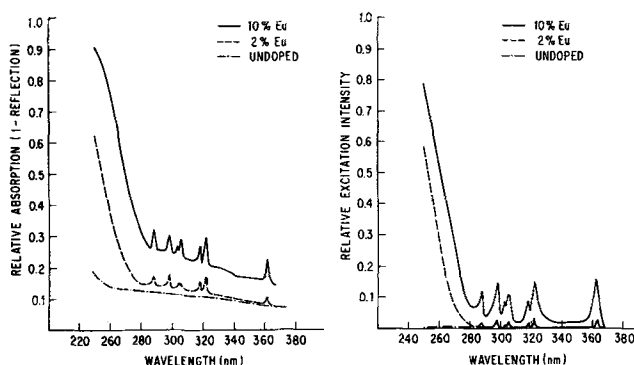


Fig. 6. Absorption (left) and excitation (right) spectra of pure undoped LiYO₂ and of europium doped LiYO₂.

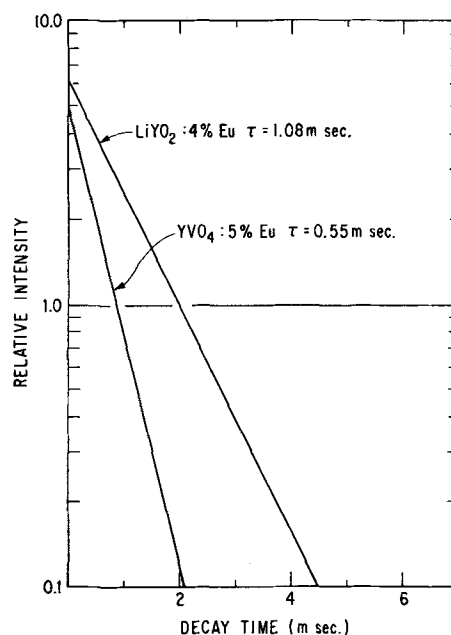


Fig. 7. Plot of decay time (msec) vs. log intensity of LiYO₂:Eu compared to YVO₄:Eu. The time constant of the LiYO₂:Eu is about twice that of YVO₄:Eu.

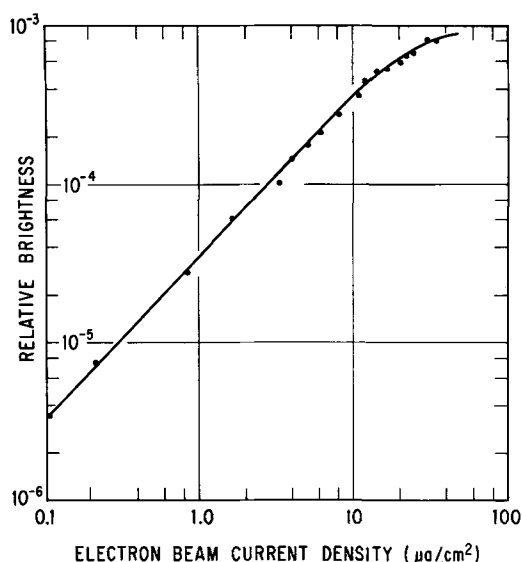


Fig. 8. Relative brightness of $\text{LiYO}_2:\text{Eu}$ phosphor as a function of electron beam current density for a constant accelerating potential of 20 kv. Linear portion indicates usable range of current densities. Saturation of the phosphor is indicated by the deviation from linearity.

accelerating potential of 20 kv. Below $10 \mu\text{a}/\text{cm}^2$ the curve is linear; above this value the phosphors start to saturate. This saturation occurs above the normal operating current density of $0.8 \mu\text{a}/\text{cm}^2$. Since we were able to reproduce this curve on the same sample we conclude that the phosphor is stable under cathode-ray bombardment.

In Table I we list some of the luminescent properties of $\text{LiYO}_2:\text{Eu}$ which are important for evaluating the phosphor for possible use in color television tubes. The relative luminosity compares the brightness of $\text{LiYO}_2:\text{Eu}$ and $\text{YVO}_4:\text{Eu}$ assuming 100% for $\text{YVO}_4:\text{Eu}$. The luminosity factors were calculated from the cathode-ray spectra of both phosphors. The fact that the luminosity factors are the same implies that the emission spectra are quite similar. This is also apparent from the color coordinates listed in Table I and the data in Fig. 4. The last column of Table I, relative luminous conversion efficiency, also indicates that the $\text{LiYO}_2:\text{Eu}$ is about 1.5 times brighter than the commercial $\text{YVO}_4:\text{Eu}$ phosphor.

Experimental Tube Production

All of the data so far presented indicate that $\text{LiYO}_2:\text{Eu}$ should be a successful color television phosphor. However, our attempts to produce a monochrome tube were very disappointing. The resultant tube was low in brightness and showed the emission spectrum of $\text{Y}_2\text{O}_3:\text{Eu}$ indicating that the $\text{LiYO}_2:\text{Eu}$ decomposed during the tube fabrication process.

Table II lists some of the steps in tube fabrication processes which could cause decomposition of the phosphor. Table III shows the actual observations that we made under simulated conditions.

Examination of Table III shows that heating of the phosphor in the presence of hydrocarbons, i.e., pump oil, polyvinyl alcohol, polymethylmethacrylate, but not benzene, resulted in complete degradation to low brightness $\text{Y}_2\text{O}_3:\text{Eu}$.

Conclusions

The phosphor $\text{LiYO}_2:\text{Eu}$ is a very efficient one which could be used as the red component in cathode-ray tubes, but is not compatible with present tube fabrication processes. Coating the phosphor with silicate could help to stabilize the phosphor in production methods.

Table I. Cathodoluminescent data for $\text{LiYO}_2:\text{Eu}$ and $\text{YVO}_4:\text{Eu}$

Phosphor	Relative luminosity	C.I.E. color coordinates x	y	Luminosity factor	Luminous efficiency lumens/rad. watt	Relative luminous conversion efficiency
$\text{LiYO}_2:4 \text{ a/o Eu}$	155	0.664	0.332	0.493	335	1.54
$\text{YVO}_4:6 \text{ a/o Eu}$	100	0.661	0.336	0.493	335	1.00

Table II. Steps in CR tube manufacture in which LiYO_2 could decompose

- Vacuum heat-treatment;
- Water washing;
- Air or vacuum heating in contact with metallic Al;
- Vacuum heating in the presence of organic materials such as polyvinyl alcohol or polymethylmethacrylate;
- Air heating in the presence of the above organics.

Note: All heating done at $400^\circ\text{--}500^\circ\text{C}$.

Table III. Effects of various tube fabrication procedures on the $\text{LiYO}_2:\text{Eu}$ phosphor

Treatment	Observation
Heat in vacuum	no change
Heat in $\text{O}_2, \text{N}_2, \text{air}, \text{H}_2$	no change
Wash with water	slight change over long time
heat in vacuum in	
a. presence of carbon	no change
b. vacuum pump oil	degradation
c. contact with aluminum foil	degradation of portion in contact with the aluminum
d. presence of polyvinyl alcohol	degradation
e. presence of polymethylmethacrylate	degradation
f. presence of benzene	no change

Our attempts to do this did not appear to help. Perhaps a dusting process would help, but there still remains the problem of decomposition after deposition of the aluminum film. Because the phosphor is unstable in the presence of the organic materials currently used, a new process of applying it to a screen and a means to prevent its contact with aluminum would have to be developed. In view of these difficulties and the difficulties which new processes would generate, it is concluded that $\text{LiYO}_2:\text{Eu}$ has no immediate application to color television tubes.

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REFERENCES

- R. Hoppe, *Angew. Chem.*, **71**, 457 (1959); *Z. anorg. u. allgem. Chem.*, **339**, 130 (1965).
- K. Vorres, Proceedings, Third Conf. Rare Earth Research (1963).
- F. Bertaut and M. Gondrand, *Compt. rend.*, **255**, 1135 (1962).
- G. Blasse and A. Bril, *J. Chem. Phys.*, **45**, 3327 (1966).
- L. Brixner, *This Journal*, **114**, 252 (1967).
- J. F. Hamman, *Z. Angew. Phys.*, **10**, 187 (1958).
- M. A. El'Yashevich, "Spectra of the Rare Earths," AEC-TL-4403C Chemistry, 1953.
- G. Blasse and A. Bril, *This Journal*, **115**, 1067 (1968).