Phase Development and Luminescence in Chromium-Doped Yttrium Aluminum Garnet (YAG:Cr) Phosphors

Karin M. Kinsman[†] and Joanna McKittrick[*]

Department of Applied Mechanics and Engineering Sciences, and
Materials Science Program, University of California—San Diego, La Jolla, California 92093-0411

Esther Sluzky and Kenneth Hesse[*]

Hughes Aircraft Company, Carlsbad, California 92008

The phase development and luminescence of chromium-doped yttrium aluminum garnet ($Y_3Al_5O_{12}$:Cr or YAG:Cr) phosphors, prepared by both a chemical precipitation technique and a solid-state reaction, were studied. The YAG structure formed at a much lower temperature and by a different phase development sequence when the chemical method was employed. The light output of the chemically synthesized powders, measured by laser excitation, was discovered to increase with increasing heat treatment temperature and was found to be brightest when the YAG:Cr phosphor had excess aluminum.

I. Introduction

PHOSPHORS are materials that emit light when bombarded with an energy source such as photons or an electron beam. These luminescent materials are used in such applications as fluorescent lamps, cathode-ray tubes, and electron microscope screens. They are composed of a host lattice which is doped with a small amount of impurity ions which activate the luminescence. YAG phosphors such as YAG:Tb are employed in cathode ray applications because they are thermally stable and resist saturation at high current excitation.[1] The most important properties of cathode-ray tube phosphors are the brightness they exhibit when excited by an electron beam, their spectral energy distribution, and their decay time.[2] Typically, YAG phosphors are synthesized by a solid-state reaction between the component oxides, which requires long heat treatments at high temperatures. This, coupled with the extensive ball milling to break up sintered particles, leads to the possibility of contamination by unwanted phases or impurities that "kill" the luminescent properties. It was the goal of this research to produce YAG phosphors that exhibit good luminescent properties, without the high-temperature heat treatments and long processing times currently required.

The Y_2O_3–Al_2O_3 system has three intermediate compounds which have compositions of $Y_3Al_5O_{12}$, $YAlO_3$, and $Y_4Al_2O_9$. The phase diagram for the Y_2O_3–Al_2O_3 system is shown in Fig. 1.[3] $Y_3Al_5O_{12}$, called YAG because of its garnet structure,[4] is the desired phase for phosphors in the Y_2O_3–Al_2O_3 system.[5] $Y_4Al_2O_9$ exists in the monoclinic form and is given the name YAM.[3,5] There are three polymorphs that have been identified in $YAlO_3$. It is usually observed as orthorhombic with a

distorted perovskite structure (YAP),[5–7] but several researchers have reported a hexagonal modification obtained by coprecipitation from yttrium and aluminum alkoxides and nitrate evaporation methods.[8,9] In addition, a cubic garnet structure produced by an alkoxide precipitation method[10] has also been observed. The hexagonal structure has also been detected in manganese(III) trioxides containing heavy lanthanides or yttrium (ABO_3; A = La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Dy^{3+}, Y^{3+}, or Tb^{3+}, B = Mn^{3+}) when synthesized by evaporation of a nitrate solution.[11]

YAG belongs to the cubic space group $O_h^{10}(Ia3d)$ and contains eight formula units per unit cell.[4,12] The crystal can be described by the formula $C_3A_2D_3O_{12}$, where the Y ions sit in dodecahedral C sites and the Al ions occupy both tetrahedral D sites and trigonally distorted octahedral A sites.[4,13,14] When Cr^{3+} is incorporated into the YAG structure, it substitutes for Al in the octahedral sites.[4,15] Cr^{3+} prefers octahedral sites in all compounds due to crystal-chemistry considerations.[15–17]

Yttrium aluminates have been synthesized by various chemical methods such as the sol-gel process,[18] coprecipitation of hydroxides,[8,9,19–21] thermal decomposition of hydrated nitrates,[22] a glycothermal method,[23] and hydrothermal synthesis.[24] The results concerning the sequence of phase development, the phases that exist, and the temperatures at which the processes occur are conflicting. Gowda[18] formed pure YAG at 810°C from an amorphous gel prepared by mixing aluminum tri-*sec*-butoxide and yttrium acetate at 80–85°C. In another study when
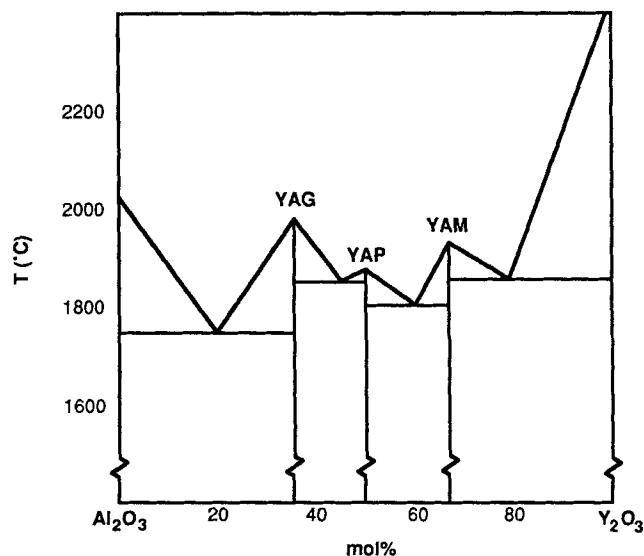
Fig. 1. Y_2O_3–Al_2O_3 phase diagram.[3]

hydroxides were precipitated from nitrate solutions, it was again discovered that pure YAG started to crystallize at 800°C.[20] However, other researchers,[8,9] using alkoxide precipitation and evaporation techniques, discovered that the amorphous powders began to form a hexagonal YAP phase at approximately 800°C and transformed to pure YAG at about 1050°C.

The chemical method chosen for this research was the coprecipitation of hydroxides from a nitrate solution. Results on the phase development of YAG:Cr phosphors synthesized by a solid-state reaction and by coprecipitation from nitrates will be presented. The effect that stoichiometry, chromium concentration, and heat treatment temperature have on the phosphors' light output will also be discussed.

II. Experimental Procedure

The YAG:Cr powders were prepared by combining $0.5M$ solutions of 99.999% pure aluminum nitrate (Alpha Products, Ward Hill, MA) and 99.99% pure yttrium nitrate (Alpha Products) with a $0.1M$ solution of chromium nitrate (Fisher Scientific, Tustin, CA) in the desired ratio. The mixture was stirred with a magnetic stirrer at room temperature for approximately 1 h before being added to a room-temperature bath of aqueous ammonia under vigorous stirring. As the nitrates were being added to the ammonia bath, the pH was continuously monitored and adjusted to 9–10 by adding ammonia. After all of the nitrates were added to the ammonia bath, the resulting cloudy solution was stirred for 1–3 h to ensure that the solution had fully reacted. The precipitates were rinsed several times with isopropyl alcohol in a centrifuge and then either filtered in a buchner funnel or heated in a rotating evaporator (Buchi RE121 Rotavapor, Brinkman Instruments, Westbury, NY) to remove the excess isopropyl alcohol. The gelatinous precipitates were dried overnight at 120°C, crushed with a mortar and pestle, and subsequently heat-treated at various temperatures up to 1600°C. In addition, a batch of YAG:Cr phosphors was synthesized by a solid-state reaction. Oxides of aluminum (99.998% pure, 1.7 μm) and yttrium (99.99% pure, <10 μm) were mixed in the desired molar ratio and then bathed in a hydrous CrO_3 solution. The powders were dried and heat-treated at various temperatures up to 1600°C. These powders were prepared in order to compare the phase development of the two techniques.

Powders with varying Y:Al molar ratios and chromium contents were prepared to observe how changes in stoichiometry and chromium concentration affected the phosphors' luminescent properties. The Y:Al molar ratios studied were 2.7:5, 2.87:5, 3:5, 3.25:5, and 4.3:5, where the 3:5 ratio is the stoichiometric yttrium aluminum garnet phase. Chromium

concentrations of 0.25, 0.4, 0.5, 0.65, and 0.8 mol% in a powder with a Y:Al molar ratio of 3:5 were studied.

The crystallization behavior of the powders was analyzed by differential thermal analysis (Perkin-Elmer, Model 1800) conducted with a heating rate of 10°C/min in flowing air. The phase development of the powders incurred during various heat treatments was examined by X-ray diffraction (GE Diano powder diffractometer). Laser spectroscopy (He-Cd laser 442 nm, CCD detector) was employed to determine the relative light output and spectral energy distribution of the phosphors. No chemical analysis of the as-synthesized powders was performed.

III. Results and Discussion

Figure 2 shows the XRD patterns for the solid-state reacted powders after heat-treating at 950°, 1100°, 1300°, and 1600°C. At 950°C the reaction between Y_2O_3 and Al_2O_3 began and two small peaks of YAM were detected along with peaks corresponding to Al_2O_3 and Y_2O_3. The YAM peaks increased in intensity after the powder was heat-treated at 1100°C. At 1300°C, all of the phases of the Y_2O_3–Al_2O_3 system were detected in the powder. YAG was the dominant phase after a 1600°C heat treatment, but several peaks of YAP and Al_2O_3 were still present. The presence of α-Al_2O_3 was not detected by XRD at 1600°C; however, its existence was indicated by laser spectroscopy, as will be shown later in the paper.

These XRD results were in good agreement with those of other researchers, who found that the reaction sequence, regardless of Y_2O_3:Al_2O_3 molar ratio, proceeds by a series of reactions shown in the following reactions:[25,26]

$$Y_2O_3 + Al_2O_3 \longrightarrow YAM \qquad (900-1100°C) \qquad (1)$$

$$YAM + Al_2O_3 \longrightarrow 4YAP \qquad (1100-1250°C) \qquad (2)$$

$$3YAP + Al_2O_3 \longrightarrow YAG \qquad (1400-1600°C) \qquad (3)$$

The temperatures in parentheses indicate within what range the reactions begin. The reaction between Y_2O_3 and Al_2O_3 occurs by the diffusion of Al into Y_2O_3. The first phase to develop during a heat treatment, regardless of the stoichiometry, is the yttrium-rich YAM phase. This reaction starts at about 950°C, and as it progresses, the Al continues to react with the Y_2O_3 but also diffuses into YAM to form YAP, starting at a temperature of about 1100°C. Finally, the Al_2O_3 reacts with YAP at approximately 1250°C to produce YAG. It has been demonstrated that as the concentration of Al_2O_3 in the powder mixture was increased, the reaction rate also increased; the highest reaction rate occurred for YAG with a Y:Al ratio of 3:5 and the lowest reaction rate occurred for YAM with a Y:Al ratio of 2:1.[25-27]
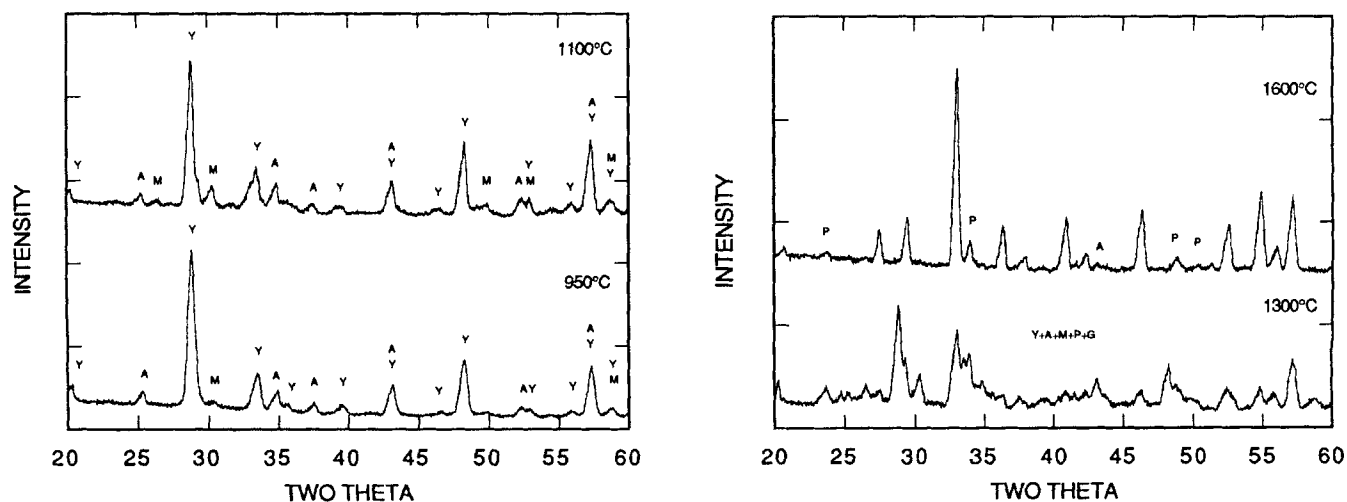

Fig. 2. X-ray diffraction pattern of solid-state-reacted powders with a Y:Al ratio of 3:5 heat-treated at 950°, 1100°, 1300°, and 1600°C. A = α-Al_2O_3, Y = Y_2O_3, M = YAM ($Y_4Al_2O_9$), P = YAP ($YAlO_3$), G = YAG ($Y_3Al_5O_{12}$).

The reaction can also be accelerated if the particle size of the starting powders is reduced.[25]

The reaction to form pure YAG from an initial Y_2O_3:Al_2O_3 ratio of 3:5 progresses more easily than the reactions to form pure YAM from a 2:1 ratio or pure YAP from a 1:1 ratio because during YAG formation there is excess Al_2O_3 present in the material until equilibrium is reached. Although the YAG reaction is faster, the kinetics are still relatively slow; in some cases, unreacted Al_2O_3 and YAP remain in the YAG sample after the heat treatment due to insufficient temperatures and times.[28,29] Some studies have shown that unreacted Al_2O_3 and YAP remain in the YAG unless the sample is heated at 1600°C for 20 h or heated to 1700°C.[25,26]

The phase development of the chemically synthesized powders, shown in Fig. 3, was much different from the phase development in the solid-state-reacted powders. The coprecipitated powders with a Y:Al molar ratio of 3:5 were found to be amorphous by XRD until about 850°C. At 900°C, hexagonal YAP was present along with small peaks of YAG. At 950°C, the hexagonal YAP peaks persisted, but with loss of intensity as more YAG peaks appeared. At 1000°C and above, YAG was the only phase detected. The crystallization of hexagonal YAP from amorphous precursors was first reported by Bertaut and Mareschal[9] from alkoxide precursors and later by Yamaguchi *et al.*[8] from nitrate evaporation. The *d*-spacings for the hexagonal YAP phase from this work are compared to these previous findings in Table I. These results differ from earlier findings in which direct crystallization of YAG was obtained from aqueous precipitation of nitrate precursors.[20]

The DTA trace of the coprecipitated powders, as shown in Fig. 4, revealed two exothermic peaks. The peak occurring at 938°C is due to the crystallization of hexagonal YAP, as confirmed by XRD. The exotherm at 1020°C corresponds to YAP reacting with a polymorph of Al_2O_3 to form YAG by reaction (3). The Al_2O_3 polymorph most likely present at the 1020°C exotherm is θ-Al_2O_3 which transforms to α-Al_2O_3 at $\geq$1200°C.[30-32]

The emission spectra of the phosphors were measured under ambient conditions to determine the effect of stoichiometry, chromium concentration, and heat treatment temperature on the relative light output. The phases present in the samples could also be determined by comparing their spectra to well-documented spectra of YAG:Cr,[33-35] YAP:Cr,[33] and Al_2O_3:Cr.[36] The emission spectra for YAG:Cr and YAP:Cr are shown in Fig. 5 and that of Al_2O_3:Cr is shown in Fig. 6.

The emission spectrum of the solid-state synthesized phosphors, heat-treated to 1600°C for 2 h, is shown in Fig. 7. The results show the characteristic spectrum for YAG:Cr as well as the characteristic peaks of Al_2O_3:Cr and YAP:Cr, thus confirming the residual α-Al_2O_3 and YAP in the powder. The emission spectra of the coprecipitated phosphors with a Y:Al ratio of 3:5 are shown in Fig. 8 for various heat treatments. The intensities of the peaks increase with increasing heat treatment temperature, but at all temperatures the spectra correspond to that of YAG:Cr. It has been suggested that the crystallinity of YAG phosphors influences their luminescent behavior: In order to obtain good luminescent properties, the phosphors must be pure YAG with no additional phases and must be well crystallized.[1,28] In the chemical synthesis technique, the pure YAG phase is present at 1000°C, but the lattice may be slightly distorted until the higher heat treatment temperatures. Therefore, the electronic environment around the Cr^{3+} ion may be changing.

Another explanation of the change in luminescence with heat treatment temperature is that the chromium did not coprecipitate with the yttrium and aluminum hydroxides and the light output is changing as the chromium diffuses into the YAG lattice at higher temperatures. If the increase in light output is a thermally activated process of diffusion of Cr^{3+}, the light output may be expressed as

$$\frac{I}{I_0} = \exp\left(\frac{-Q}{kT}\right)$$

where I/I_0 is the normalized light intensity and Q is the activation energy for Cr^{3+} diffusion. Figure 9 is a plot of the natural log of the light output versus inverse temperature for several

Table I. Comparison of *d*-Spacings Observed in Hexagonal YAlO₃

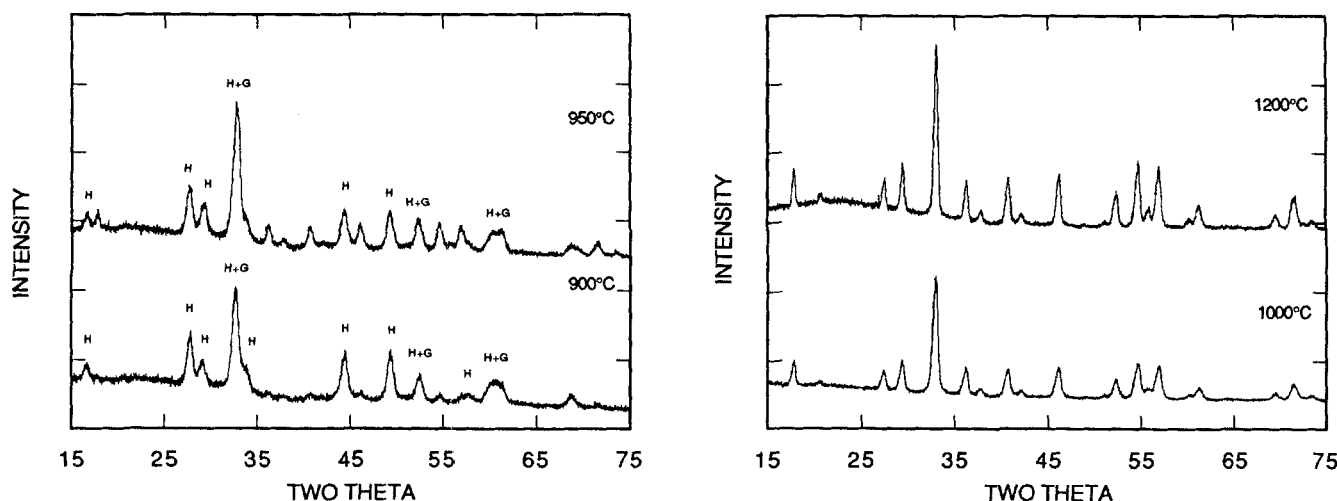|	*d*-spacing (nm)	
Ref. 8	Ref. 9	Present study
0.526	0.524	0.530
0.318	0.317	0.318
0.305	0.304	0.305
0.2720	0.2716	0.2724
0.2616	0.2620	0.2635
0.2020	0.2024	0.2026
0.1839	0.1838	0.1836

Fig. 3. X-ray diffraction pattern of chemically synthesized phosphors with Y:Al ratio of 3:5 heat-treated at 900°, 950°, 1000°, 1100°, and 1200°C. G = YAG ($Y_3Al_5O_{12}$), H = hexagonal YAG. Unmarked peaks are all YAG.
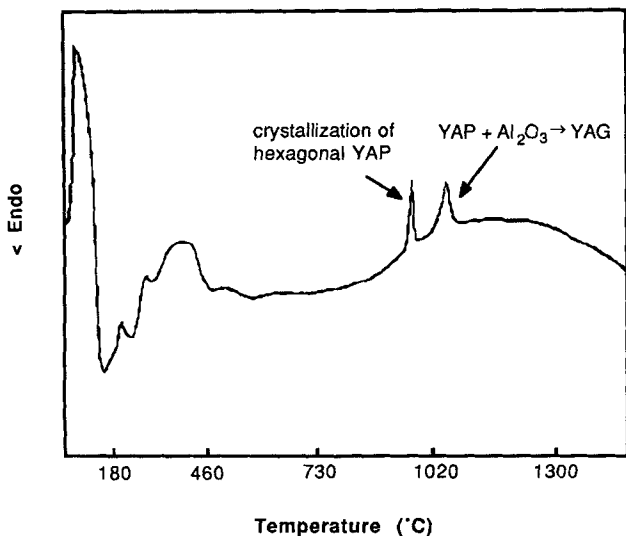
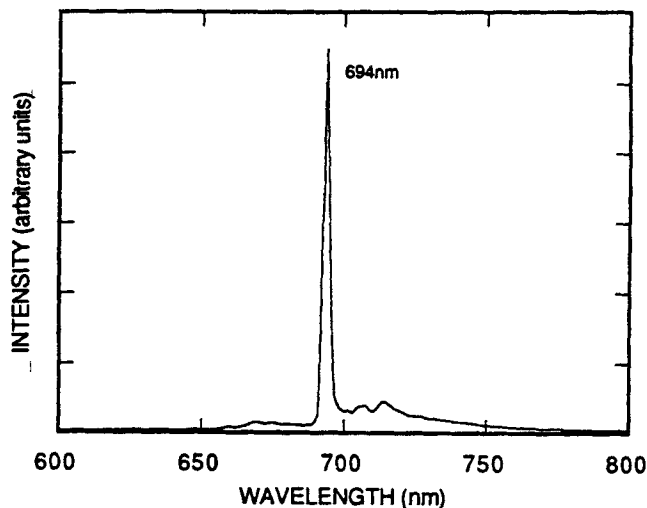**Fig. 4.** DTA trace of a chemically synthesized powder with a Y:Al ratio of 3:5.

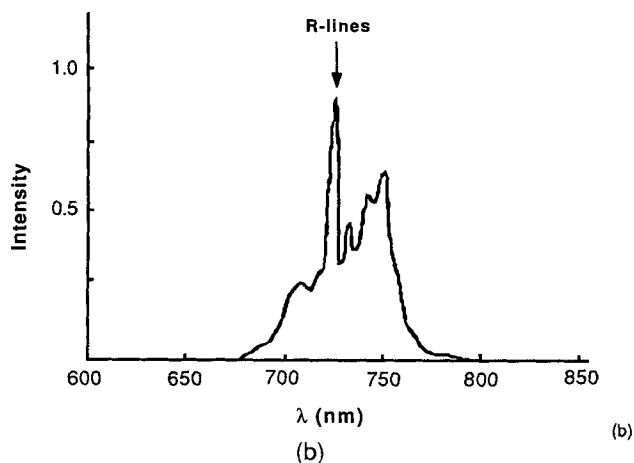

Fig. 6. Emission spectra of Al_2O_3:Cr.
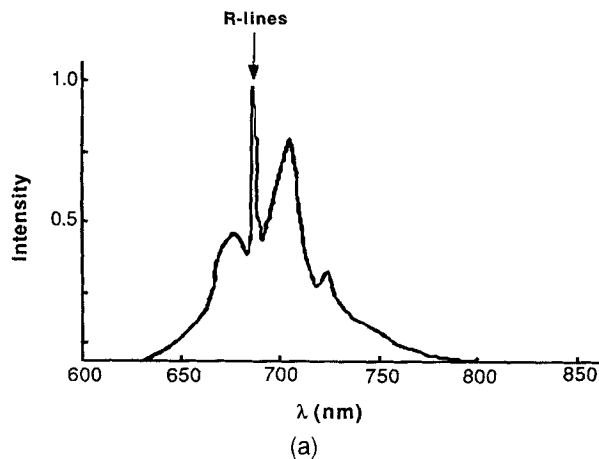
Fig. 5. Emission spectra of (a) YAG:Cr and (b) YAP:Cr.[33]

Fig. 7. Emission spectra of conventionally synthesized phosphors heat-treated at 1600°C. Characteristic lines of YAG:Cr, Al_2O_3:Cr, and YAP:Cr are marked. Unmarked peaks are vibronic sidebands associated with the peaks.

different powder batches, all with Y:Al ratios of 3:5. The normalized light intensity is the integrated intensity over λ = 600–800 nm from the laser emission data. An activation energy was calculated for each of the powders and the average was found to be 19.0 ± 5 kJ/mol. This activation energy is too low
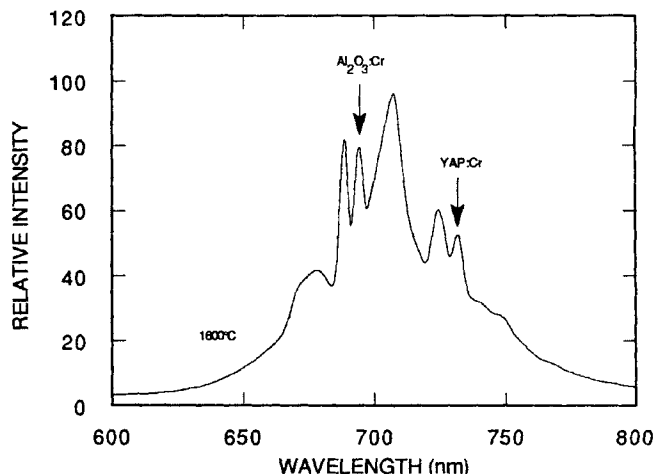
for a diffusion mechanism. Although no data were found for Cr^{3+} diffusion in YAG, typical activation energies for diffusion in other oxides such as diffusion of Al^{3+} in Al_2O_3 and Y^{3+} in Y_2O_3 are 475 and 285 kJ/mol, respectively.[37]

The emission spectra of the phosphors having Y:Al ratios of 3.25:5 and 4.3:5 are shown in Fig. 10. Again, it is seen that the intensity of the emission increases with increasing heat treatment temperature. When the yttrium concentration is increased, the spectra develop peaks associated with YAP:Cr and the total light output or integrated intensity at each temperature becomes reduced. The emission spectra of the phosphors with Y:Al molar ratios of 2.7:5 and 2.9:5 are shown in Fig. 11. At heat treatment temperatures of 1400° and 1600°C the spectra for both molar ratios show the characteristic Al_2O_3:Cr peak along with the YAG:Cr spectrum. At 1200°C, however, the spectra only indicate YAG:Cr. The Al_2O_3:Cr peak is not observed because, at 1200°C, the nonluminescent θ-Al_2O_3:Cr phase has not yet transformed to α-Al_2O_3:Cr.
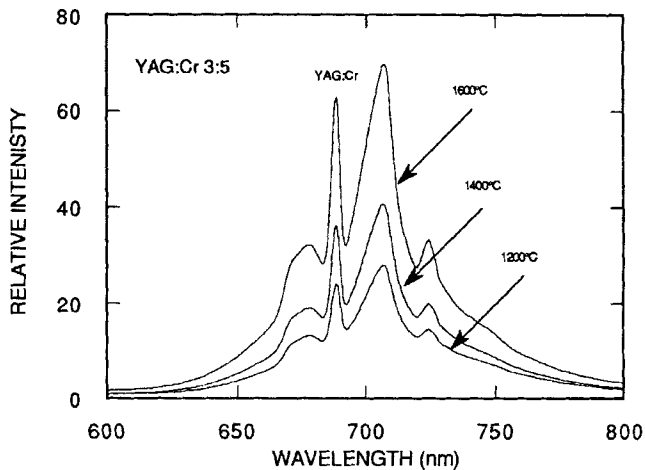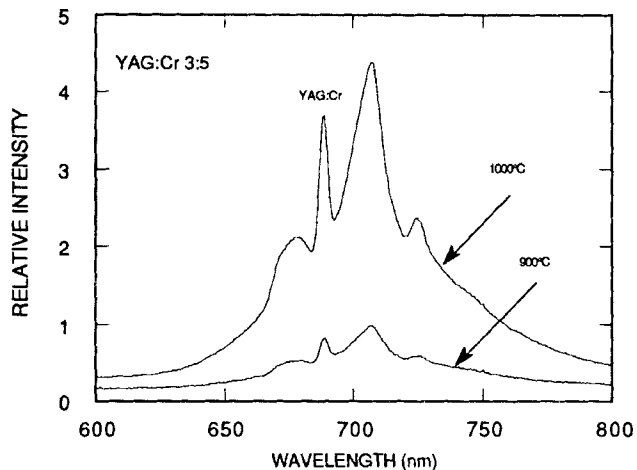
Fig. 8. Laser emission spectra of chemically synthesized phosphors with a Y:Al ratio of 3:5 heat-treated at various temperatures.
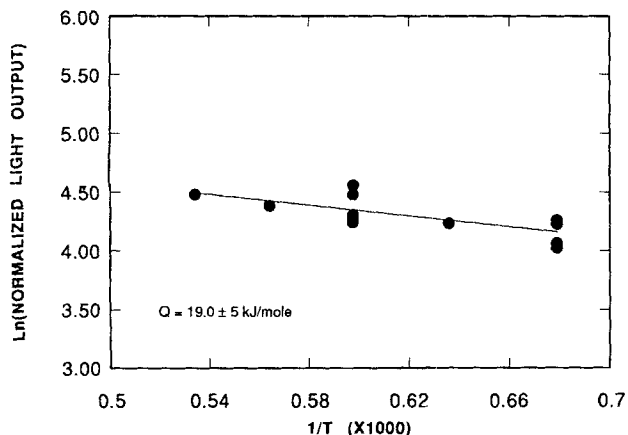

Fig. 9. Normalized light output as a function of $1/T$ for several different batches of YAG:Cr powders.

The results of the chromium concentration studies are shown in Fig. 12. The phosphors were activated by a laser and the light output with respect to a standard is plotted versus the chromium mol%. The maximum light output was found to occur at 0.65 mol% chromium. In phosphors, there is always an optimum

activator concentration but it is difficult to predict or calculate; it is usually experimentally obtained. As the activator concentration increases in the host lattice, the luminescence increases up to a certain point as more activators are available for excitation, and then will decay because of several factors. There may be resonant (i.e., direct ion exchange coupling or virtual phonon exchange) or nonresonant (i.e., coupled multipole oscillators) processes.[2] For the YAG:Cr phosphors, it is unclear which mechanisms operate during the luminescence process. Figure 12 also shows that when a slight excess of Al_2O_3 was present, the light output increased dramatically. These results could not be compared with the solid-state-reacted powders as they were never found to be completely reacted and always contained an excess of Al_2O_3.

IV. Conclusions

It was shown that the phase development in chemically synthesized powders differs from that of powders produced by a solid-state reaction. The phase development in the coprecipitated powders follows a hexagonal YAP → cubic YAG phase sequence, where the powder has fully transformed to YAG at 1000°C. The solid-state-reacted powders follow a path by which Al_2O_3 reacts with Y_2O_3 to form YAM as the first phase. The orthorhombic form of YAP is then developed, which transforms to cubic YAG at 1600°C. However, unless heated for
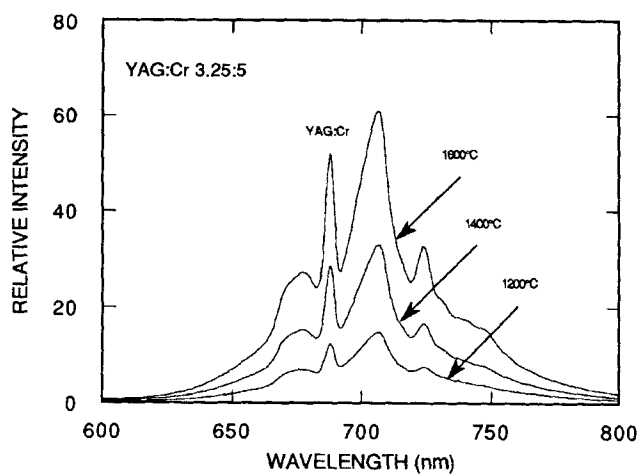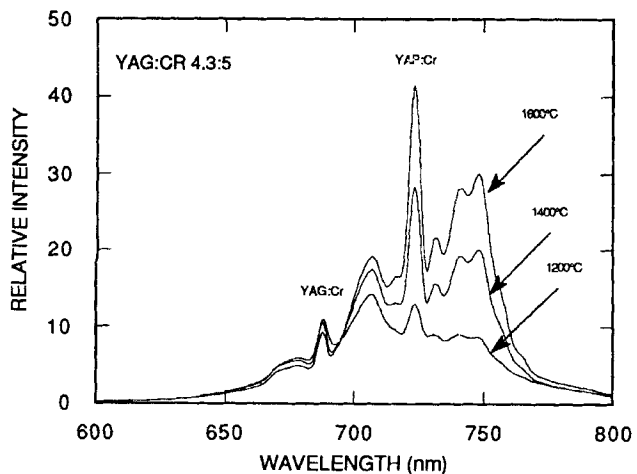

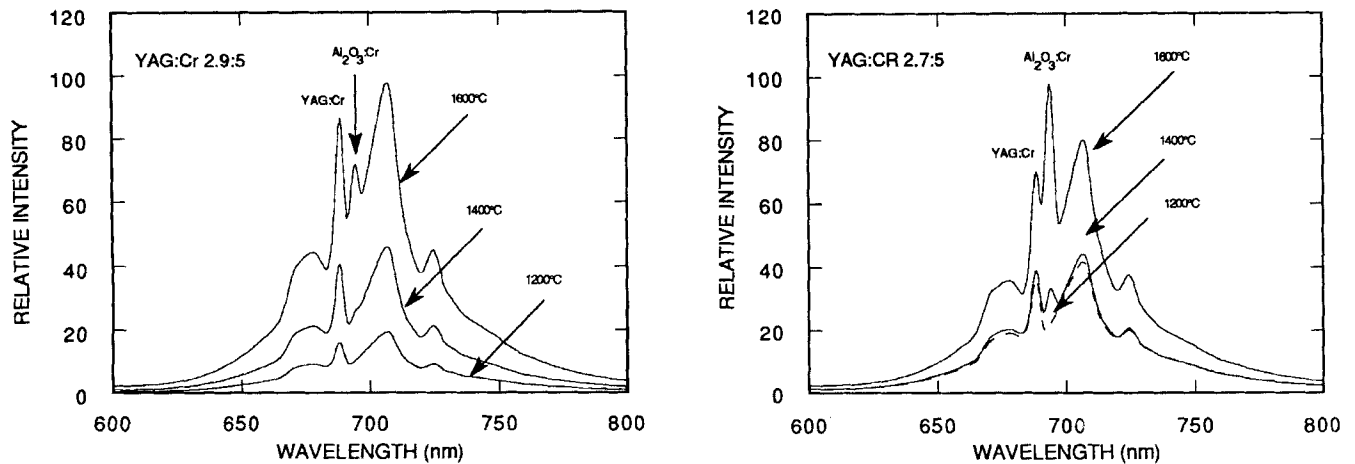Fig. 10. Laser emission spectra of phosphors containing excess yttrium.

Fig. 11.   Laser emission spectra of phosphors containing excess aluminum.
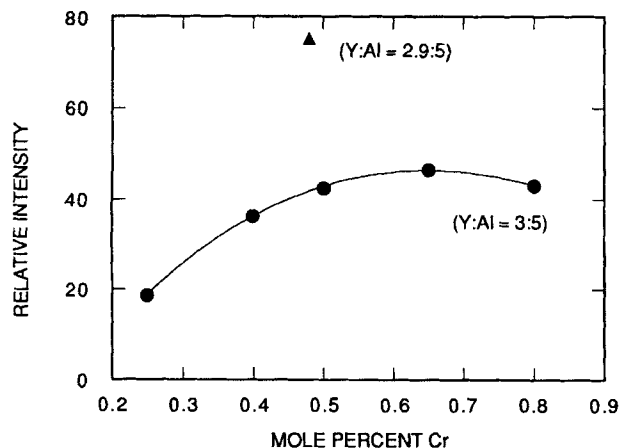

Fig. 12.   Relative light output vs chromium concentration in phosphors with Y:Al ratio 3:5.

very long times or at a higher temperature, the solid-state-reacted powders are contaminated with unreacted Al_2O_3 and YAP. The increase of light output at increasing annealing temperatures appears not to be from the diffusion of Cr^{3+} into the octahedral sites in the YAG lattice.

The laser spectroscopy results showed that if excess yttrium in the form of the YAP phase is present in the powder, the light output of the phosphors is reduced. However, when there is a slight excess of aluminum, the light output is increased. All of the powders showed an increase in light output with increasing heat treatment temperature. In the stoichiometric YAG ratio, the optimum chromium concentration was found to be 0.65 mol% when the powders were excited by a laser operating at 440 nm.

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