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Luminescent characteristics and morphology of $Eu^{3+}:YVO_4$ phosphor powders prepared by HCR and flux techniques

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The emission intensities of $Eu^{3+}:YVO_4$ red phosphors depend significantly on the morphology and Y–V–O stoichiometry of powder particles. The low-temperature hydrolyzed colloid reaction (HCR) technique with different firing regimes in air and crystallization from lithium metavanadate ($LiVO_3$) flux with subsequent grinding have been investigated. Powders reacted at the quasi-congruent (49.3 mol% V_2O_5–50.7 mol% Y_2O_3) composition and fired at temperatures up to 1200 °C exhibited higher emission intensities than the powders weighed at the stoichiometric (50 mol% V_2O_5–50 mol% Y_2O_3) ratio. After higher temperature (1400, 1600 °C) treatments the stoichiometric composition produces better luminescent properties approaching that of the highly optimized industrial powder standard (Sylvania 2391). Only limited emission was obtained for the crystalline powder prepared from $LiVO_3$ flux due to the influence of mechanical grinding. Powder morphology and crystal structure were investigated by high-resolution transmission electron microscopy (TEM). The small particles produced at low temperature are surprisingly well crystallized with well resolved lattice images. The small particles contain internal surfaces as well as large external surfaces which contribute to the degradation of phosphor properties.

Eu^{3+} activated yttrium orthovanadate ($Eu^{3+}:YVO_4$) red phosphor is commonly used in the lighting industry as a color corrector for high-pressure mercury vapor lamps. In order to obtain color phosphors for high-resolution flat panel displays, powders with small particle size (*ca.* 1 µm) are preferred. The newly discovered hydrolyzed colloid reaction (HCR) technique has been successfully adopted for the preparation of $Eu^{3+}:YVO_4$.[1,2] The method allows the reaction of Y_2O_3, Eu_2O_3 and V_2O_5 oxides in water at room temperature and atmospheric pressure. It is known from the Y_2O_3–V_2O_5 phase diagram that a solid solution region for YVO_4 occurs because of point defects.[3] Consequently YVO_4 has a (quasi-) congruent maximum melting point around 50.7 mol% Y_2O_3–49.3 mol% V_2O_5 concentrations which differs from the ideal stoichiometric (50 mol% Y_2O_3–50 mol% V_2O_5) composition.[4,5] Previous studies have indicated that different color effects were observed in the region of stoichiometric and congruent compositions during annealing procedures.[4] In addition, a local peak in the photoluminescence spectra was also found at about 49.3 mol% V_2O_5 congruent composition.[6] The purpose of this work is to investigate the influence of Y–V stoichiometry and morphology on the luminescence characteristics of $Eu^{3+}:YVO_4$ powders which were prepared by different routes, taking particular account of particle size and particle crystallinity.

Experimental

High-purity vanadium pentoxide (99.995% V_2O_5, Puratronic), yttrium oxide (99.99% Y_2O_3, REaction) chemicals from Johnson Matthey–Alfa, and europium oxide (99.99% Eu_2O_3) obtained from Research Chemicals (Phoenix, AR) were weighed in amounts to yield $Eu_{0.0467}Y_{0.9533}VO_4$ in stoichiometric [50 mol% ($Eu_2O_3+Y_2O_3$)+50 mol% V_2O_5] and $Eu_{0.0467}Y_{0.9533}V_{0.9723}O_4$ powder in congruent [50.7 mol% ($Eu_2O_3+Y_2O_3$)+49.3 mol% V_2O_5] compositions. These mixtures were reacted by the hydrolyzed colloid reaction (HCR) technique in deionized water at room temperature and atmospheric pressure as is described elsewhere[1,2] and by slow cooling crystallization from $LiVO_3$ flux at high temperature.

In the latter case, the $LiVO_3$ flux (high-temperature solvent medium) was prepared by reacting 30.31 g of V_2O_5 (see above described specifications) and 12.31 g of Li_2CO_3 (J. T. Baker, Reagent-grade) powders under a slow heating up to 900 °C for 6 h, 1 h homogenization and 1 h cooling program. Subsequently 5 mass% $Eu_{0.0467}Y_{0.9533}VO_4$ powder with stoichiometric composition was added to the $LiVO_3$ flux. The complex mixture was heated to 1200 °C in 3 h, held at 1200 °C for 8 h, cooled to 900 °C at 30 h and brought to room temperature in 3 h (see more details in ref. 7). The abundance of small transparent needle-shaped crystals were recovered in hot water. After grinding these needle crystals in an agate mortar, the cracked crystalline powder was further ground for 24 h in a ball mill (see ref. 1 and 2) filled with ethanol. This phosphor powder was dried and subsequently analyzed using a Hitachi F-4010 fluorescence spectrophotometer.

The powders reacted by the HCR technique in both stoichiometric and congruent compositions were fired under different conditions to check the changes in morphology and luminescence characteristics. These powder samples were fired in air at 300 °C for 1 h, 300 °C for 10 h, 600 °C for 1 h, 600 °C for 6 h, 800 °C for 2 h, 1000 °C for 4 h, 1200 °C for 8 h, 1400 °C for 12 h and at 1600 °C for 16 h, respectively. After firing the pellets were ground into a powder in an agate mortar. The luminescence characteristics of these powders and the industrial standard powder (Sylvania 2391) of $Eu^{3+}:YVO_4$ were measured and compared to each other by conducting experiments in the above mentioned Hitachi spectrophotometer.

Samples of stoichiometric $Eu^{3+}:YVO_4$ powders were ultrasonically dispersed in butan-2-ol and a droplet of the supernatant was subsequently applied onto a carbon grid. The specimens were examined in a JEOL 2000 EX II transmission electron microscope (TEM) fitted with a high-resolution pole piece that allows for observations at a lattice resolution of 1.4 Å, at an accelerating voltage of 200 keV.

Influence of stoichiometry

The HCR process at low (< 100 °C) temperature produced a white powder of $Eu^{3+}:YVO_4$ in both congruent and stoichiometric compositions. The reaction produced a single phase as reported in our previous work.[2] However the powder was very porous consisting of very small (*ca.* 100 nm) crystalline particles with loose structure. Fig. 1 shows high-resolution TEM pictures of simple HCR treated powder of stoichiometric composition. It can be seen that the approximately 100 nm particles [Fig. 1(*a*)] are created from very small needle like crystals [Fig. 1(*b*)]. Fig. 1(*b*) shows that the average thickness of these needles is *ca.* 2.5 nm and they adapt the same orientation as the whole particle. This structure produced only a very limited emission intensity as seen in Table 1. The luminescence structure of this phosphor (Fig. 2) shows the characteristic formed dipole bands of Eu^{3+} at 619 nm. The Eu^{3+} band intensity of these powders increases with increasing firing temperature for both congruent and stoichiometric compositions (Table 1 and Fig. 3).

Both compositions have a low luminescence intensity until the firing temperature reaches 600 °C. The intensity rises almost linearly with temperature up to 1200 °C. The intensity of luminescense in the congruent composition is *ca.* 10–20% higher than that of the stoichiometric composition. From 1200 °C upwards, the intensity of the congruent composition levels off to about 30% of the intensity of the reference phosphor. The intensity of the stoichiometric composition continues to increase until at 1600 °C the intensity is very close to that of the reference phosphor.

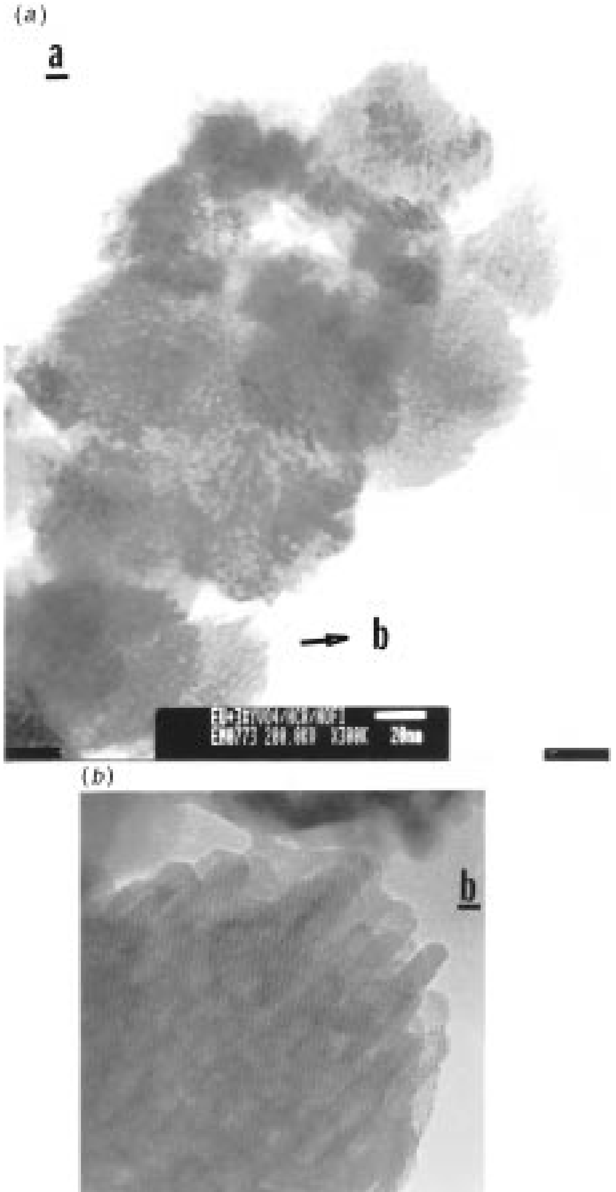

Fig. 1 TEM micrograph of $Eu^{3+}:YVO_4$ powder reacted by the HCR technique in stoichiometric composition (*a*) and its magnified section (*b*) no firing procedure

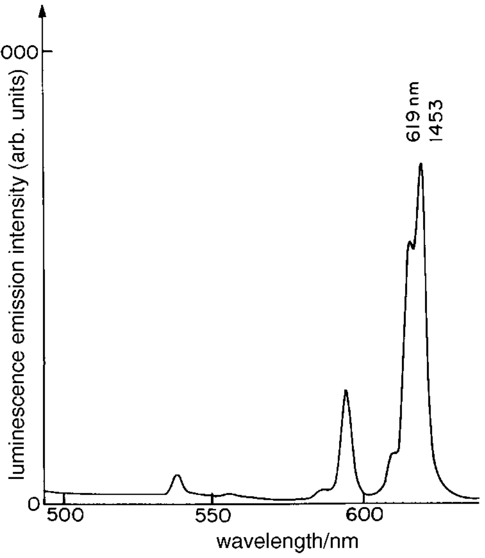

Fig. 2 Typical luminescence spectra of $Eu^{3+}:YVO_4$ red phosphor reacted by the HCR technique in congruent (49.3 mol% V_2O_5–50.7 mol% Y_2O_3) composition after firing at 800 °C for 2 h

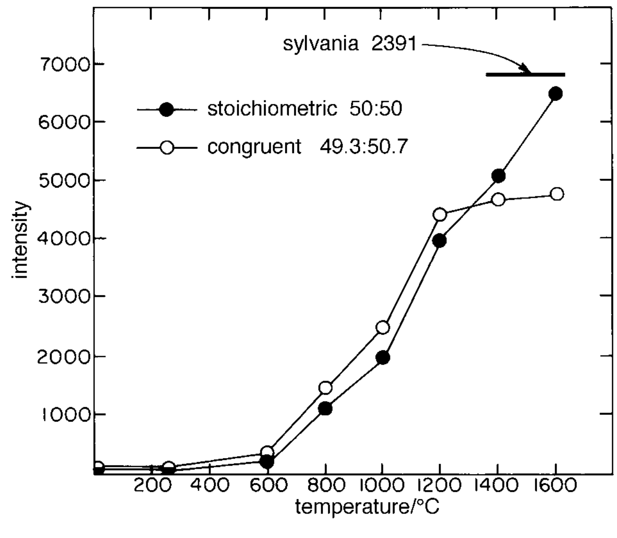

Fig. 3 Intensity of 619 nm emission band as a function of firing temperature for two YVO_4 compositions. Intensity is given in terms of the raw count rate of the spectroflurometer.

On the other hand specific color centers are also formed due to annealing processes. Fig. 4 demonstrates the dependence of this color on the firing conditions in both stoichiometric (50 mol% V_2O_5) and congruent (49.3 mol% V_2O_5) specimens.

At very low intensity of firing (300 °C for 1 h) the initial white powder obtained by the HCR process turned light yellow with visible brownish pigments (Fig. 4). These relatively large precipitates dissolve and disappear under more intensive firings. No significant changes in the pellet densities were observed until firing at 1000 °C for 4 h. In the case of congruent (49.3 mol% V_2O_5) samples less contraction with white coloration was observed at 1000 °C after firing for 4 h. Strong brown coloration with substantial densification appeared in the stoichiometric (50 mol% V_2O_5) pellet. The stoichiometric composition, after firing of HCR powder at 1200 °C for 8 h (Fig. 4), became greenish–gray and after 1400 °C, 12 h treatment, bluish–gray pellets were formed. At very intensive firing

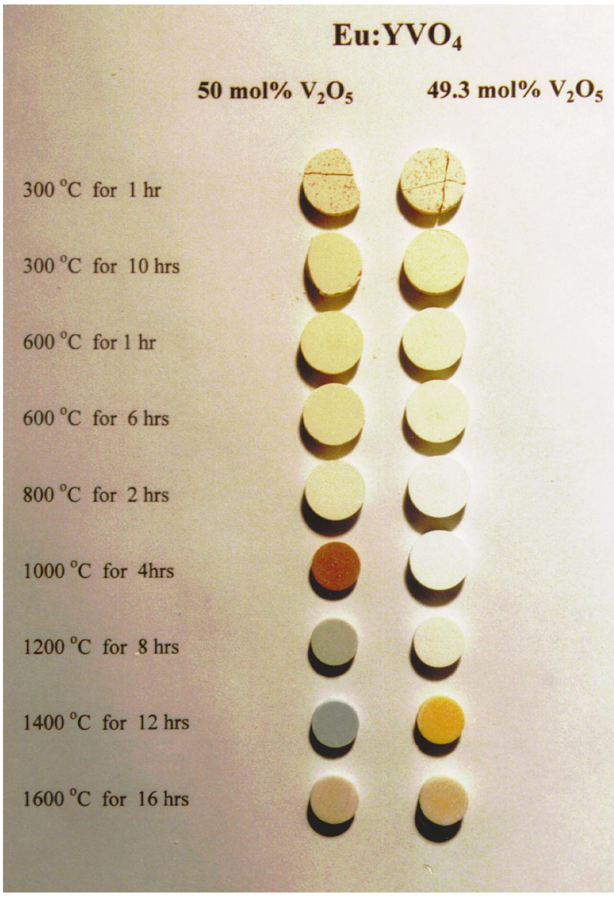

Fig. 4 Different coloration effects in $Eu^{3+}:YVO_4$ pellets weighed in stoichiometric (50 mol% V_2O_5) and congruent (49.3 mol% V_2O_5) compositions after various firing processes

(1600 °C for 16 h) both congruent and stoichiometric compositions displayed a whitish–yellow color.

It is highly probable that these coloration effects are directly related to the special precipitation effects generated at the border of limited solubility of the YVO_4 homogeneity region. (In more exact terminology, the congruent yttrium orthovanadate can be described as $YVO_{4-x}^{\bullet}$ where x is the derivation from ideal oxygen stoichiometry and $^{\bullet}$ indicates the deviations of Y–V stoichiometry.) The influence of the Eu_2O_3 dopant on the coloration should be limited since the color transitions were also observed in undoped YVO_4 powders.[8] Fig. 5 shows a possible schematic homogeneity region of the $YVO_{4-x}^{\bullet}$ phase. Although exact borders of homogeneity regions are, as yet, not known both low- and high-temperature precipitates and dissolutions are available. At low-temperature (300–600 °C) firings of the stoichiometric composition, a limited amount of excess vanadium precipitates were formed at points 3 and 4 of the P2 line in Fig. 5. At higher temperatures (>1000 °C) the right hand side of the congruent composition in the Y_2O_3–V_2O_5 solid-solution system, as for the stoichiometric composition, has an excess of V_2O_5 which will be partially melted along the S2 line in Fig. 5 causing a significant coloration and contraction in pellet size. Little or no comparable effects were observed in the quasi-congruent (49.3 mol% V_2O_5) composition.

Since the HCR powders exhibit limited crystallinity (Fig. 1), during firing they can relatively easily form precipitates by crystal growth in the solid phase. It is expected that the stoichiometric (or almost stoichiometric) yttrium orthovanadate crystals doped with Eu^{3+} should contain less precipitate owing to their well crystallized idealistic structure. However the needle like stoichiometric $Eu^{3+}:YVO_4$ crystals are too large and with an undesirable shape for phosphor applications. In order to decrease the average particle size mechanical grinding in a ball mill was performed. A TEM image (Fig. 6) shows that the average particle size was reduced to *ca.* 0.5 µm (500 nm) after 24 h milling. Unfortunately the dislocations and strains in the particles are so drastically increased that the luminescent excitation and emission intensities were significantly reduced to 1463 and 1666 arb. units (see Table 1).

This is a remarkable fact that serves to demonstrate that the influence of undesired defects generated by ball milling is stronger than the effect of improved Y–V–O stoichiometry[9] achieved by growth from $LiVO_3$ flux.

Our best powder, the HCR stoichiometric composition fired at 1600 °C for 16 h (Fig. 7) has an emission intensity (6537) very close to the intensity of highly optimized Sylvania

Table 1 Luminescent characteristics of $Eu^{3+}:YVO_4$ red phosphors reacted by both the hydrolyzed reaction (HCR) technique after firing in air and by a slow cooling technique in $LiVO_3$ flux

		sample										
												Sylvania
	firing temp./°C		300	300	600	600	800	1000	1200	1400	1600	2391
phosphor	firing time/h		1	10	1	6	2	4	8	12	16	standard
stoichiometric (HCR)	$\lambda_{exc}{}^{b}$/nm	321	321	321	321	318.6	320.2	325.2	328.6	332	332.8	330.4
	I^{c}					219.6	1049	1754	3521	4394	5592	6135
	%					3.6	17	29	57	72	91	100
	$\lambda_{em}{}^{d}$/nm	618.6	618.6	618.6	618.9	619	619	619	619	619	619	619
	I^{e}	45.7	29.19	47.66	178.8	207	1126	2021	4044	5102	6537	6881
	%	0.7	0.4	0.7	2.6	3.0	16	29	59	74	95	100
congruent (HCR)	λ_{exc}/nm	321	321	321	321	321.4	322.4	323.6	326.8	328.2	328.4	
	I					345.6	1346	2468	3770	4084	4163	
	%					5.6	22	40	61	66	68	
	λ_{em}/nm	618.6	618.6	618.6	618.6	618.8	618.8	618.8	619	619	619	
	I	45.6	41.84	62.39	299.4	363.3	1453	2939	4427	4713	4808	
	%	0.7	0.6	0.9	4.4	5.3	21	43	64	69	70	
stoichiometric^{f} ($LiVO_3$ flux)	λ_{exc}/nm											321.8
	I											1463
	%											24
	λ_{em}/nm											619.0
	I											1666
	%											24

[a] The congruent sample was fired at 1675 °C for 8 h in addition to firing at 1600 °C for 16 h. [b] Excitation wavelength. [c] Excitation peak intensity (arb. units). [d] Emission wavelength. [e] Emission peak intensity (arb. units). [f] Needle crystals after grinding in a ball mill for 24 h without firing.

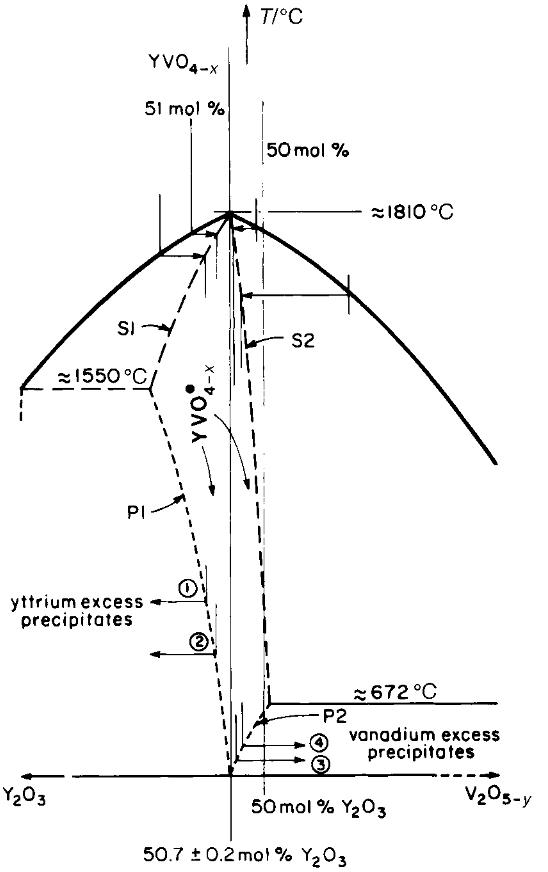

Fig. 5 Schematic homogeneity region of yttrium orthovanadate in the yttrium oxide and slightly oxygen deficient vanadium oxide (V_2O_{5-y}) phase system

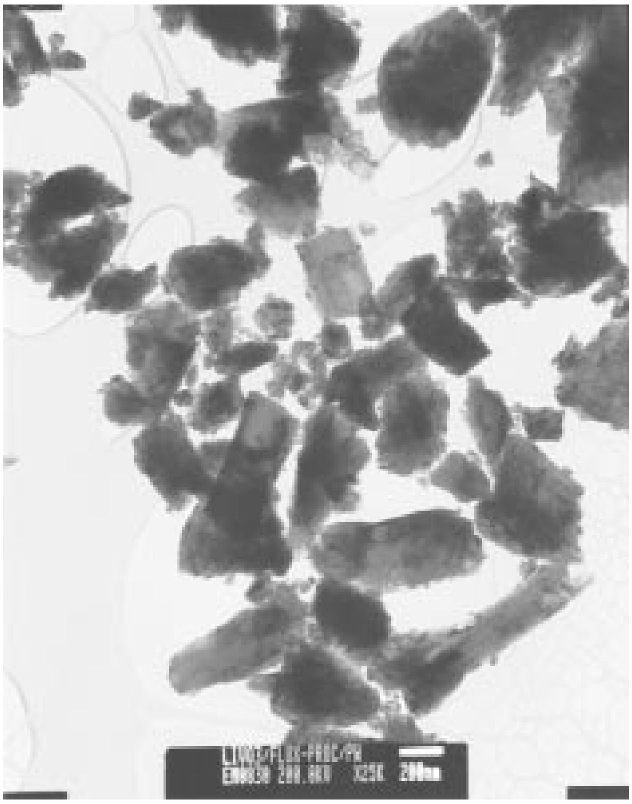

Fig. 6 TEM micrograph of $Eu^{3+}:YVO_4$ powder crystallized in $LiVO_3$ flux after grinding in ball mill

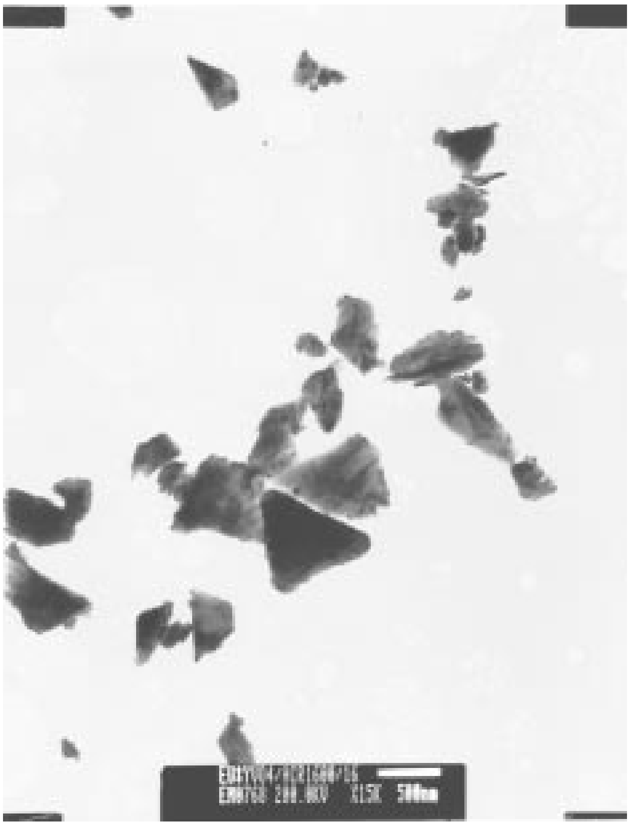

Fig. 7 TEM micrograph of stoichiometric $Eu^{3+}:YVO_4$ powder reacted by the HCR technique after firing at 1600 °C for 16 hours. This powder has very high emission peak (6537 arb. units) at 619 nm compared to Sylvania 2391 standard (6881 arb. units).

industrial standard powder (6881) at 619 nm. Fig. 7 shows that a *ca.* 0.5 μm (500 nm) average particle size powder was formed by our treatment. These findings indicate that the irregular particles probably have a vanadium oxide deficiency as a consequence of the extended firing process.

Crystallinity of small phosphor particles

It is well known that small particles (<1 μm) generally have poor luminescence efficiencies. The poor brightness is often ascribed, without any supporting evidence, to 'poor crystallinity' or to the presence of 'dead layers' on the particle surfaces. The sequence of heat treatments of an initially extremely fine-grained precursor provides an opportunity for a high-resolution TEM investigation of the crystallinity of individual particles. Such data should help decide between 'poor crystallinity' and 'dead layers' as a structural mechanism for the poor luminescence efficiency.

The loose crystalline structure seen in Fig. 1 is significantly changed by the different firing processes. The crystal particles grow in the solid phase to produce better crystallinity in many different spontaneous orientations. Fig. 8 shows the modified morphology of $Eu^{3+}:YVO_4$ particles after firing at 800 °C for 2 h. At (*b*) and (*c*) in Fig. 8(*a*) well oriented atomic structures can be recognized as shown in Fig. 8(*b*) and (*c*) which shows high magnification images of different crystallographic orientations in the different particles.

The 800 °C particles with only moderate luminescence are well crystallized and the grains are beginning to show smooth facetial surfaces; the internal crystallinity is also very good, as indicated by the well developed lattice images. The rise in Eu^{3+} emission intensity seen in Fig. 3 appears to be due to the impurity quality of the grain surface rather than the grain interiors. The high temperature required to obtain optimum luminescences are required to remove hydroxy groups, anneal

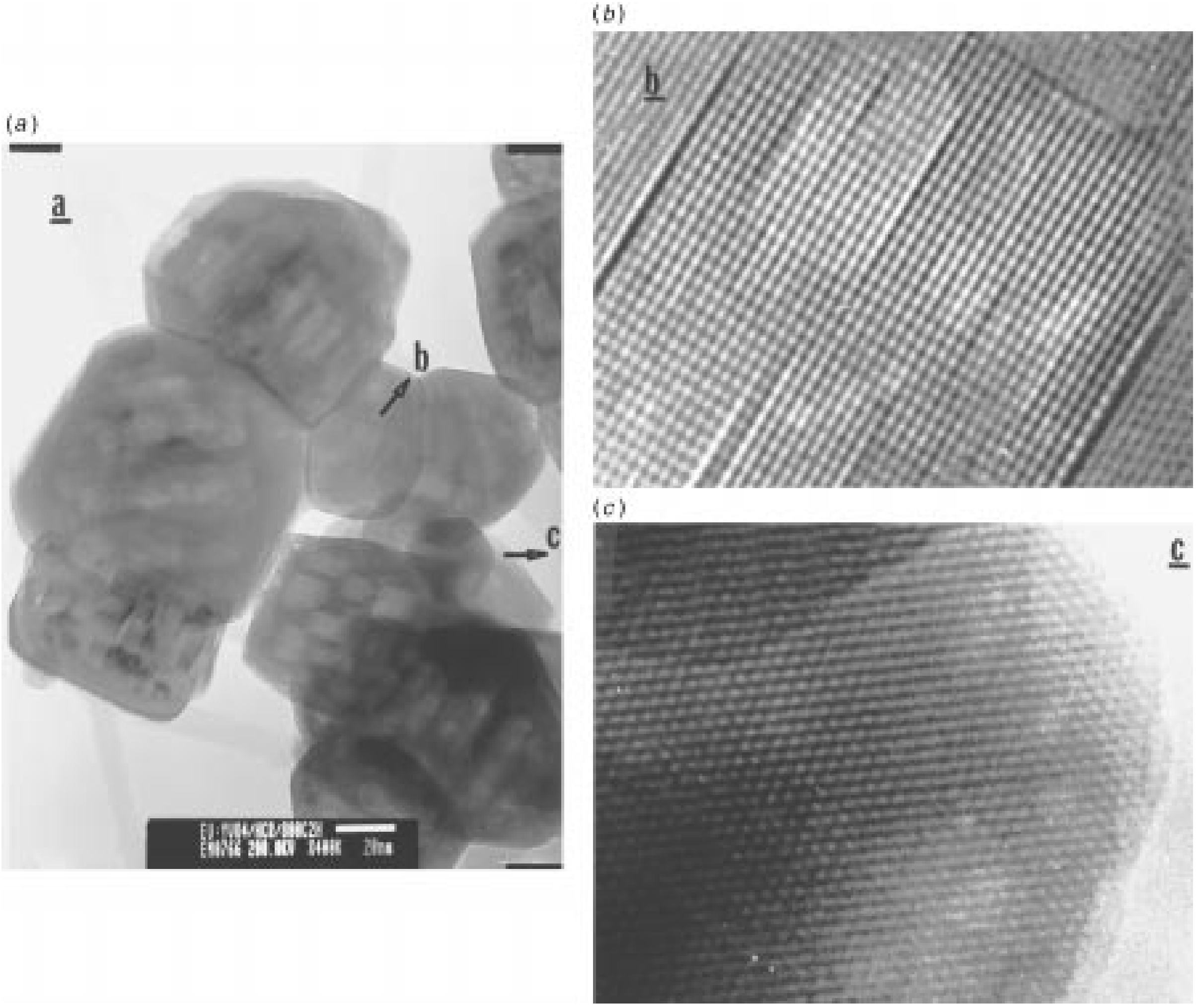

Fig. 8 TEM micrograph of crystalline $Eu^{3+}:YVO_4$ powder reacted by the HCR technique after firing at 800 °C for 2 h (*a*) with its magnified sections in (*b*) and (*c*) of Fig. 5 in different orientations. Different atomic arrangements can be seen in the magnified pictures.

dangling bonds, and anneal out defect structures from the surfaces. The temperatures at which the luminescence efficiency begins to increase (600–800 °C) also corresponds to typical decomposition temperatures of metal hydroxides and oxyhydroxides in accord with previous observations of potential lamp phoshor manufacturers.[10]

Conclusions

The $Eu^{3+}:YVO_4$ red phosphor powders reacted by the hydrolyzed colloid reaction (HCR) technique and fired by various annealing programs in air show different morphological and luminescent characteristics. At lower temperature annealing, the congruent composition shows better characteristics while at higher temperature firing, the stoichiometric compositions offer the better emission and excitation peak intensities. Very high intensities can be achieved by extended firing of $Eu^{3+}:YVO_4$ powder obtained from the hydrolyzed colloid reaction (HCR) technique. $Eu^{3+}:YVO_4$ needle crystals prepared from $LiVO_3$ flux, in spite of their better Eu–Y–V–O stoichiometry, can only produce a limited emission as a consequence of mechanical grinding required for particle size reduction. TEM studies show that even the low-temperature particles have good internal crystallization.

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References

1 S. Erdei, *J. Mater. Sci.*, 1995, **30**, 4950.
2 S. Erdei, F. W. Ainger, D. Ravichandran, W. B. White and L. E. Cross, *Mater. Lett.*, 1997, **30**, 389.
3 S. Erdei and F. W. Ainger, *J. Cryst. Growth*, 1997, **174**, 293.
4 S. Erdei and F. W. Ainger, *J. Cryst. Growth*, 1993, **128**, 1025.
5 S. Erdei, M. Klimkiewicz, F. W. Ainger, B. Keszei, J. Vandlik and A. Süveges, *Mater. Lett.*, 1995, **24**, 301.
6 T. Katsumata, H. Takashima, T. Michino and Y. Nobe, *Mater. Res. Bull.*, 1994, **29**, 1247.
7 S. Erdei, *J. Cryst. Growth*, 1993, **134**, 1.
8 S. Erdei, unpublished work.
9 S. Erdei, B. M. Jin, F. W. Ainger, A. S. Bhalla, B. Keszei, J. Vandlik and A. Süveges, *J. Appl. Phys.*, 1996, **79**, 2834.
10 A. Dutta, E. A.Dale and L. V. Dullea, Method of reducing the degradation of the red phosphor Y_2O_3:Eu in water base lamp suspensions, *USPat.* 5 126 166, 1992.

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