Cathodoluminescent properties of Y_2O_2S:Eu phosphors synthesized by citric acid-gel method

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Abstract

Y_2O_2S:Eu phosphors with fine particle have been synthesized by citric acid-gel method. In this method, $Na_2S_2O_3$ was added to Y_2O_3:Eu precursor, then the mixture was fired at 1000℃ for 3h in S_2 atmosphere. When the Y_2O_3:Eu precursor was pre-annealed at 400~700℃ before the firing of the mixture, the fine particles with a diameter of around 1 μm were obtained after the firing. The phosphor pre-annealed at 400℃ showed a luminance and CIE color coordinates of 2350 cd/m^2 and (0.61, 0.37), respectively, at under excitation of 3 kV and 60μA/cm^2.

1. Introduction

Field emission displays (FEDs) are one of the future flat-panel display technologies [1,2]. At the low voltage excitation (lower than 5 kV), the phosphors which are used in CRTs can not show high luminance and efficiency in FEDs because of their high resistivity [3] and deterioration of the phosphor surface. Therefore,, phosphors must have low resistivity to suppress the charging-up, moreover, they must have stable surface for high-density electron beam irradiation io order to suppress deterioration.

Y_2O_3:Eu and Y_2O_2S:Eu are available as red emitting phosphors. A main emission of Y_2O_3:Eu phosphor is due to the transition of $^5D_0 \rightarrow {}^7F_2$ with a peak at about 611 nm, whose color purity is not good. Moreover, the band gap of Y_2O_3 is about 6 eV, which takes place charging-up on the surface of he Y_2O_3:Eu phosphor. Whereas the peak wavelength of Y_2O_2S:Eu is about 630 nm due to $^5D_0 \rightarrow {}^7F_3$ transition, whose color coordinates is very close that of red point in NTSC. Moreover, the band gap of Y_2O_2S is about 4 eV which is smaller than Y_2O_3, although the energy gap is too large for low voltage FEDs.

Therefore, in this investigation, the synthesis of Y_2O_2S:Eu phosphors by citric acid-gel method was tried and the morphology, structural and luminescent properties the synthesized phosphors will be reported.

2. Experimental

Figure 1 shows a flow chart of the synthesis of

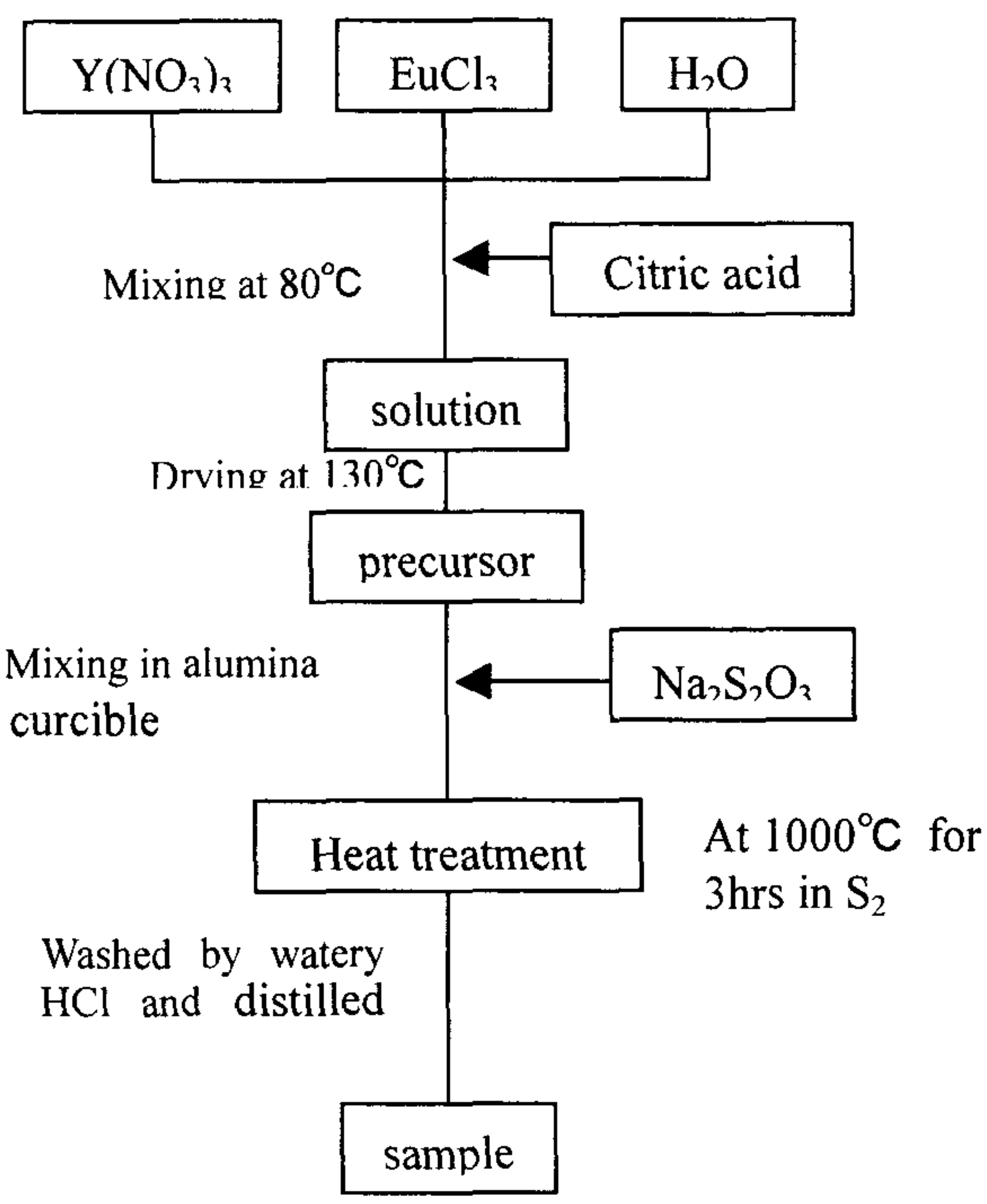

Fig.1 Flow chart of synthesis of phosphors by citric acid-gel method.

the Y_bO_2S:Eu phosphor by the citric acid-gel method. The citric acid is added to control reaction rate, as a result, the size of the syntheswized phosphor can be controlled. A pre-annealing of the precursor was also tried before the addition of $Na_2S_2O_3$ to the precursor. The pre-annealing was carried out at 400 to 700°C for 1 h in air. $Na_2S_2O_3$ was mixed with the precursor with or without the pre-annealing, then the mixture was fired at 1000°C for 3h in S_2 atmosphere. After the firing, the samples were washed in dilute HCl and distilled water in turn.

Structural properties and morphology of the phosphors were characterized by X-ray diffraction (XRD) measurement and SEM observation, respectively. The luminescent properties of the phosphors was characterized under excitation of electron beam of energy lower than 3 kV and 60 μA/cm^2.

3. Results and discussion

3.1 Synthesis of Y_2O_2S:Eu phosphors

Figure 2 shows XRD curves of (a) precursor, (b) 700°C-annealed precursor, (c) phosphor fired the mixture without pre-annealing, (d) phosphor fired the mixture with pre-annealing at 400°C and (e) 700°C. The sample annealed the precursor at 1000°C for 1h in air shows Y_2O_3 structure. It is seen from (c) to (e) that the samples fired the mixtures of the precursor and $Na_2S_2O_3$ in S_2 shows the formation of the Y_2O_2S without Y_2O_3 phase regardless of the pre-annealing.

Figure 3 shows CL spectra of the Y_2O_3:Eu and Y_2O_2S:Eu phosphors corresponding to (b) and (c), respectively, in Fig.2, where the phosphors were excited with 3 kV and 60 μA/cm^2. It is seen that each spectrum corresponds to emission spectrum of well known Y_2O_3:Eu and Y_2O_2S:Eu phosphors, respectively.

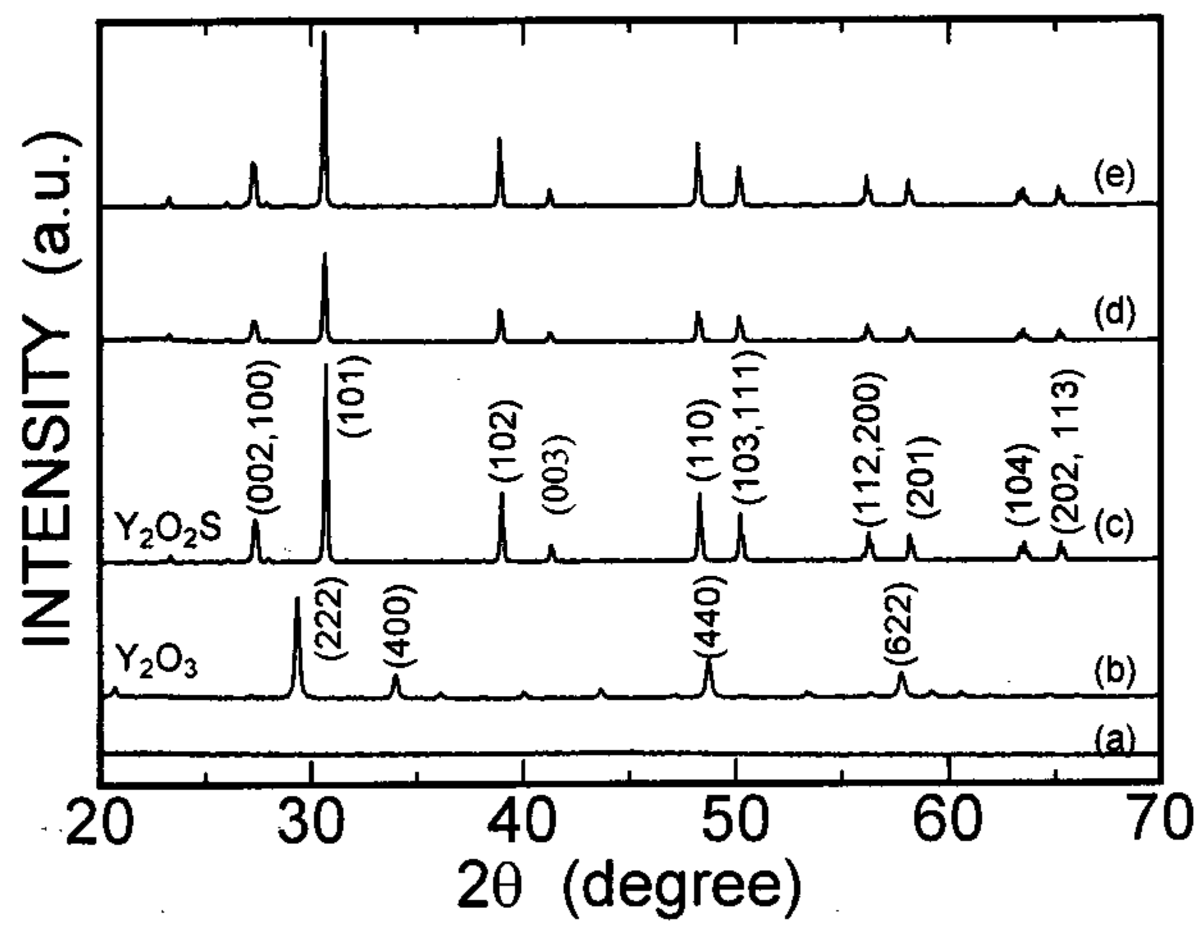

Fig.2 XRD curves of (a) precursor, b) annealed at 1000°C without $Na_2S_2O_3$, (c) non pre-annealed, (d) pre-annealed at 400°C and (e) pre-annealed at 700°C.

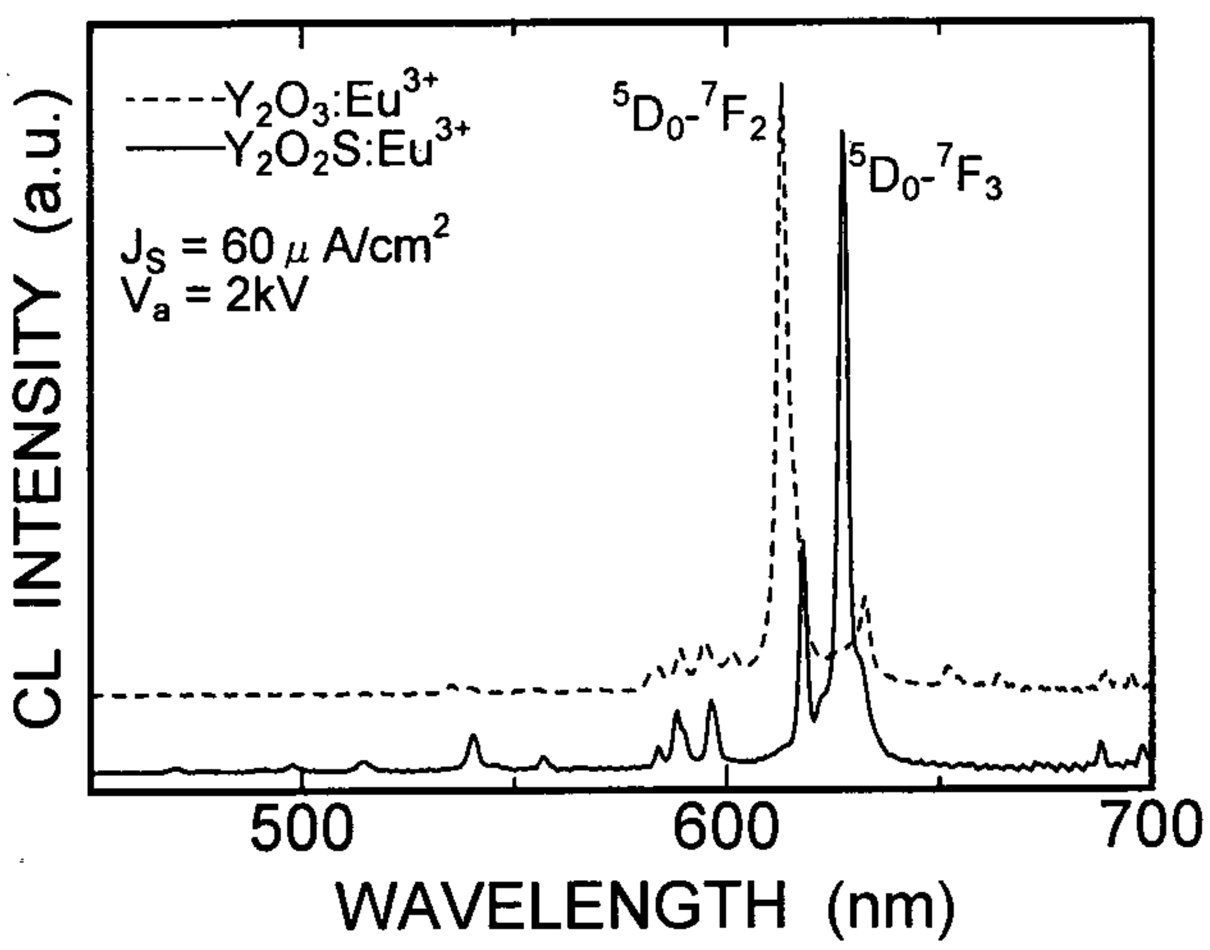

Fig.3 CL spectra of Y_2O_3:Eu and Y_2O_2S:Eu phopsphors

These results show that Y_2O_2S:Eu phosphor could be successfully synthesized by the citric acid-gel method.

3.2 Morphology of Y_2O_2S:Eu phosphor

Figure 4 shows SEM photographs of Y_2O_2S:Eu phosphors (a) without pre-annealing, (b) with pre-annealing at 400°C and (c) with pre-annealing at 700°C. It is seen from (a) that the phosphors with grain size around or smaller than 5 μm when no pre-annealing. On the other hand, it should be noticed that by the pre-annealing, the grain sizes of

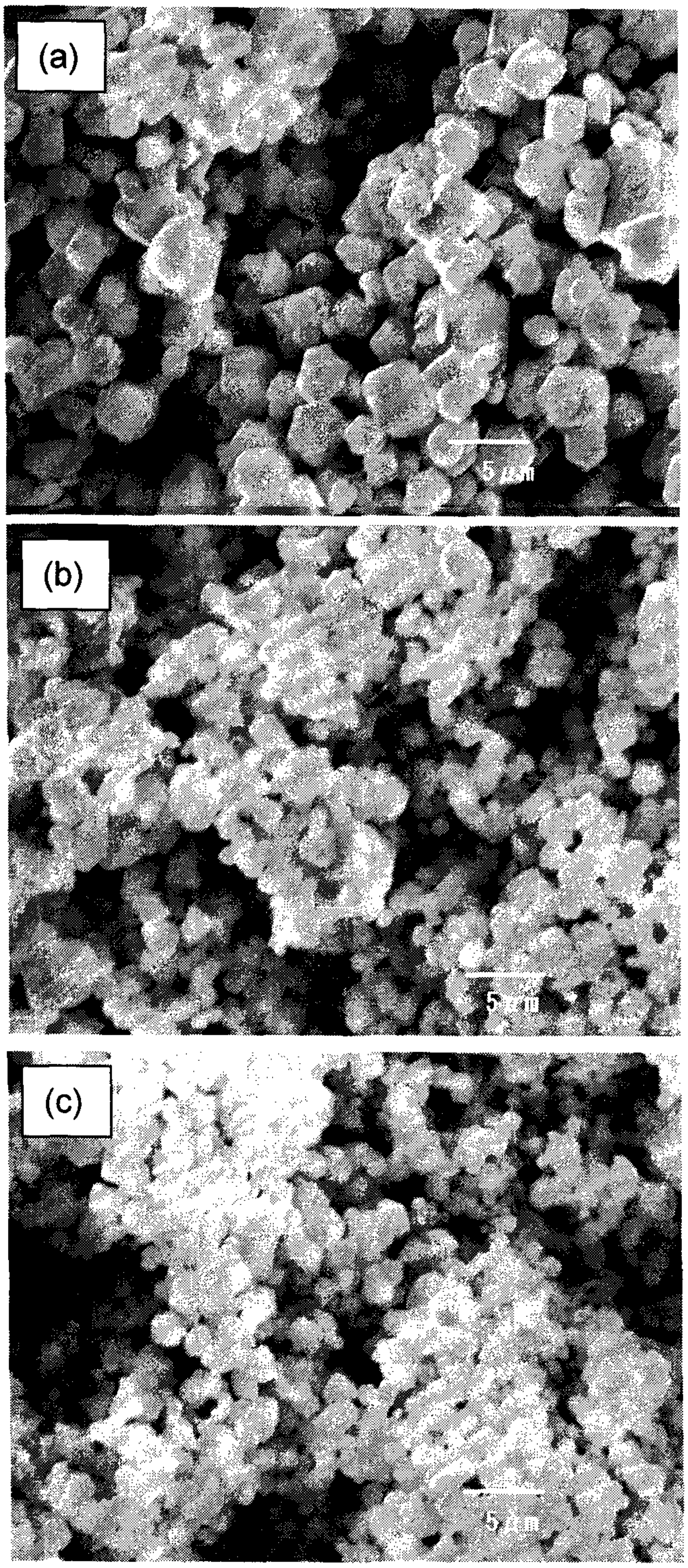

Fig.4 SEM photographs of Y_2O_2S:Eu phosphors (a) non pre-annealed, (b) pre-annealed at (b) 400°C and (c) 700°C.

the phosphor particles could be made small to around 1 μm or les and became uniform.

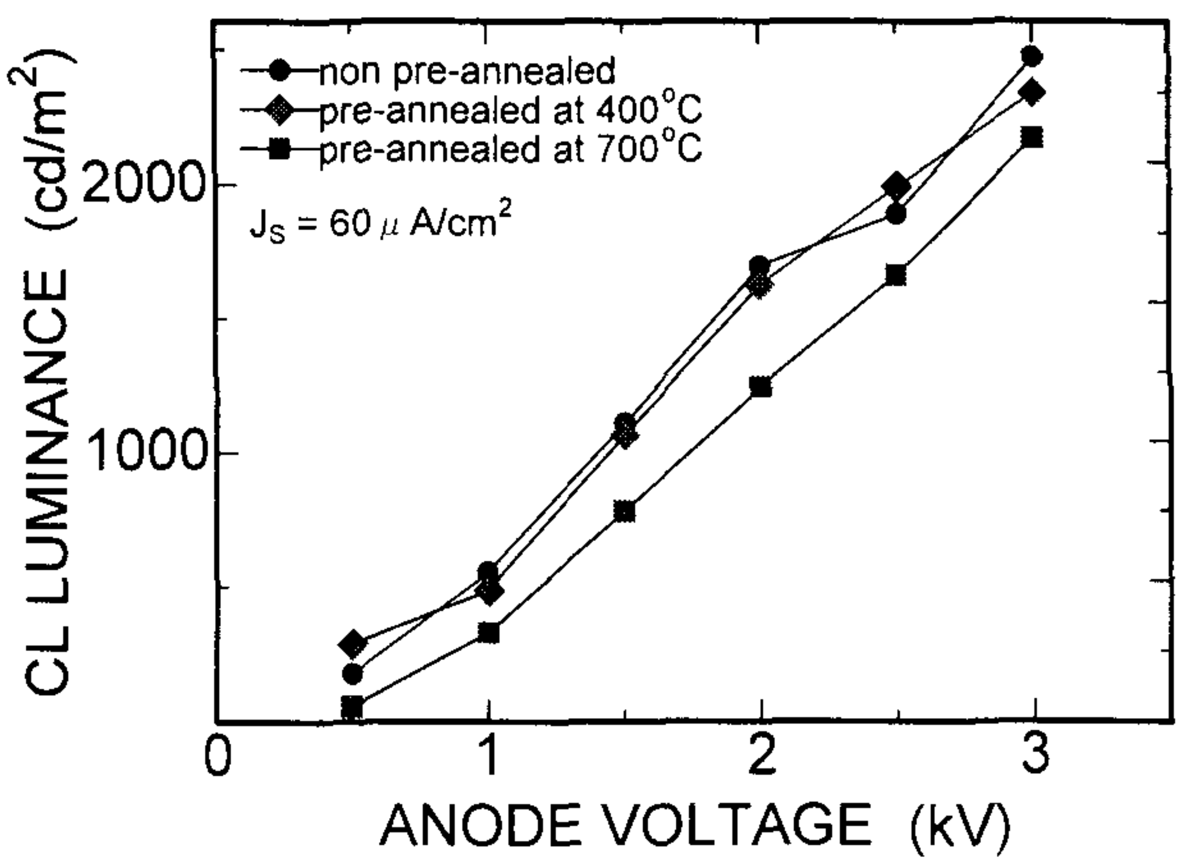

Fig.5 L-V characteristics of Y_2O_2S:Eu phosphors shown in Fig.4.

3.3 CL properties of Y_2O_2S:Eu phosphors

Figure 5 shows CL luminance vs. anode voltage characteristics of Y_2O_2S:Eu phosphors shown in Fig.4. It is seen that almost same characteristics are obtained for non pre-annealing and pre-annealing at 400°C, and the maximum luminance is about 2500 cd/m^2 under excitation at 3 kV, 60μA/cm^2. Whereas the luminance of the phosphor pre-annealed at 700°C is a little lower over whole anode voltage. The reason for this result might be due to the fine particle, however, the detail is not understood.

Figure 6 shows luminous efficiency vs. anode voltage characteristics of the phosphors shown in Fig.5. It is seen that the phosphors without the pre-annealing and with the pre-annealing at 400°C show luminous efficiency of about 4 lm/W

The luminance and luminous efficiency obtained in this investigation is expected as the phosphor material for FEDs.

4. Summary

Red emitting Y_2O_2S:Eu phosphors were synthesized by citric acid-gel method. It was confirmed from the measurements of XRD and CL spectra that nearly perfect Y_2O_2S:Eu phosphors could be synthesized by the method. Moreover, it was found that the fine particles with diameter of about 1 μm or less could be synthesized. The phosphors without the pre-annealing and with pre-annealing at 400°C showed a luminance and luminous efficiency of about 2500 cd/m^2 and 4 lm/W, respectively, under excitation at 3 kV and 60μA/cm^2. The phosphors with these properties are promising for low voltage FEDs

5. References

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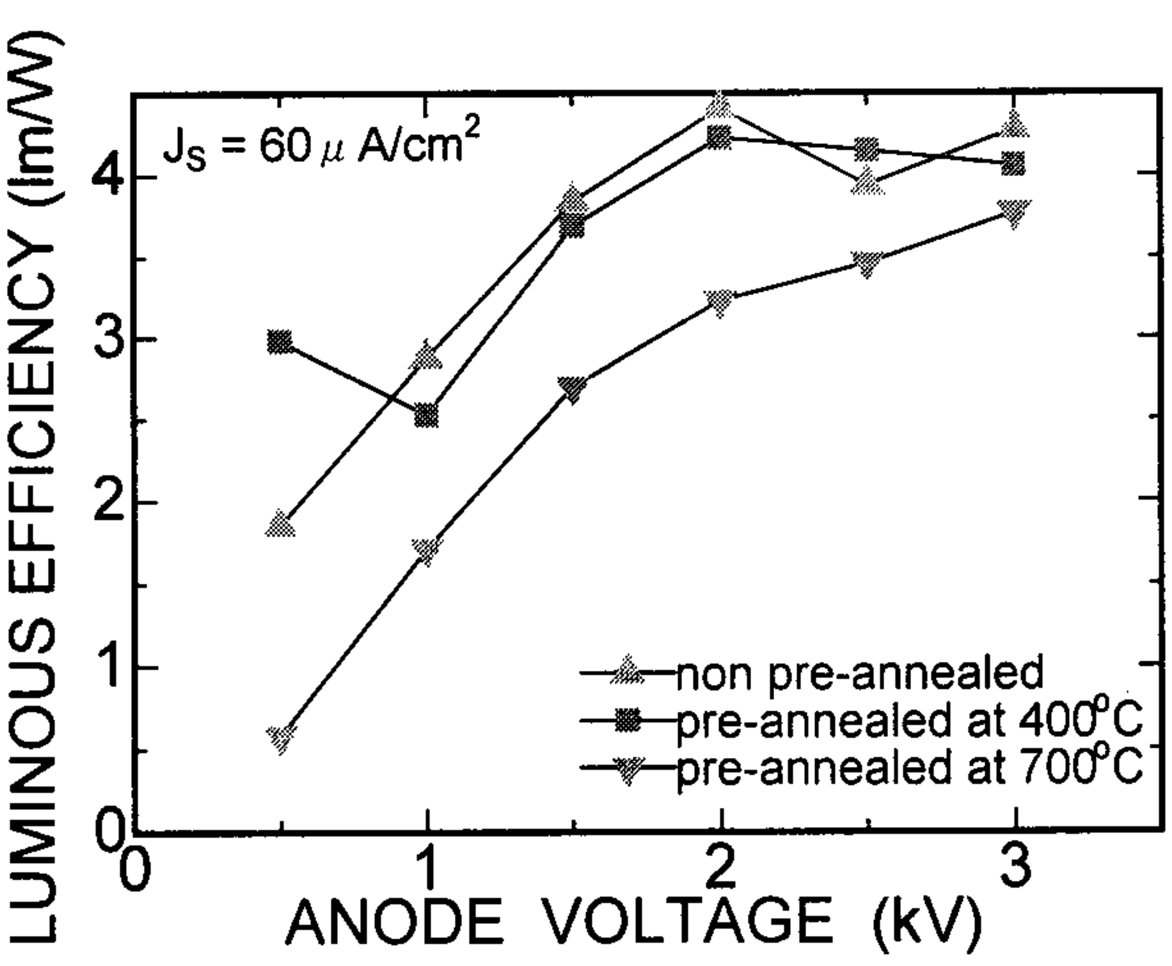

Fig.6 η-V characteristics of Y_2O_2S:Eu phosphors shown in Fig.4.