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Synthesis of $SrTiO_3$:Pr,Al by ultrasonic spray pyrolysis

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Abstract

$SrTiO_3$:Pr,Al as an oxide compound phosphor shows potential application for a field emission display (FED). $SrTiO_3$:Pr, Al phosphor was prepared directly by a continuous droplet to particle preparation using an ultrasonic spray pyrolysis. We have studied the processing mechanism of continuous droplet to particle. Powder surface and morphology were investigated as a function of reaction temperature and precursor solution. The powder surface was improved by adding H_2O_2 because of controlling the decomposition rate. After post-heat treatment for short residence time, the cathodoluminescent measurement was carried out (operational pressure 10^{-6} Torr) using an electron beam excitation at 100 μA/cm^2 and the 800 voltage, and we obtained a sharp peak at 615 nm. Our results obtained in this work suggest that $SrTiO_3$:Pr,Al phosphors can be used as red phosphors in full-color FED. © 2002 Published by Elsevier Science Ltd and Techna S.r.l.

Keywords: A. Powders: gas phase reaction; C. Optical properties; Spray pyrolysis; $SrTiO_3$:PrAl, red phosphor; H_2O_2 effect

1. Introduction

Field emission display (FED) has been the most important flat panel display [1]. The future of FED technology depends heavily on the development of low-voltage cathodoluminescent phosphor [2]. Recently, FED phosphors have been actively investigated due to the importance of phosphor in the development of full-color FED [3].

Strontium titanate, $SrTiO_3$, is a well-known perovskite material and its optical bandgap is 3.3 eV [4]. Also, $SrTiO_3$ is chemically and compositionally very stable [5,6]. Because of these attractive advantages of $SrTiO_3$, it is considered as a good candidate for host material in low-voltage electron-excitation displays, such as FED and VFD (vacuum fluorescence display) [7].

For phosphor applications, one of the key issues concerns the powder morphology and particle size. Therefore, we applied the spray pyrolysis for producing spherical particles.

Ultrasonic spray pyrolysis can directly produce very homogeneous powder by a continuous decomposition from the droplets into the particles. Compared to other synthesis techniques, spray pyrolysis has the following advantages; (1) simple and continuous operation, (2) spherical shape of the particles, (3) high purity, (4) uniform particle size distribution, (5) controllable size from micrometer to submicrometer and (6) excellent control of chemical uniformity and stoichiometry in a mixed oxide system. In spite of these advantages, ultrasonic spray pyrolysis has a critical disadvantage, which is hollow structure or fractured particles. In this work, $SrTiO_3$ phosphor doped with Pr^{+3} and Al^{+3}, one of the red phosphor materials was prepared by the spray pyrolysis using the ultrasonic spray generator. We have studied H_2O_2 effect on the powder surface roughness and investigated the characteristics of particles such as cathodoluminescent, morphology, and crystallinity.

2. Experiment

In order to prepare precursor solutions, appropriate weights of raw materials were dissolved in water and nitric acid of 3 M concentration. H_2O_2 was added in some cases and then morphology and crystalline structure change of the resultant powders were observed. The raw materials were $Sr(NO_3)_2$(3 N), $Al(NO_3)_3 \cdot 9H_2O$ (4 N), $Pr(NO_3)_3 \cdot 2.7H_2O$ (4 N) from High Purity Chemi-

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cals Laboratory Co. Ltd., Japan; and $TiO(NO_3)_2 \cdot \chi\ H_2O$ solution was prepared with starting $TiCl_4$ solution. First, the $TiCl_4$ solution was diluted with water of a temperature below 10 °C and this solution was dropped into NH_4OH keeping the temperature at 15 °C. At higher temperature (>15 °C), $Ti(OH)_2Cl_2$ condensed into $Ti(OH)_4$ white cluster precipitation due to hydrolysis reaction. Then the precipitated $Ti(OH)_4$ was washed with water 7 times. This cake was dissolved in nitric acid of 13 M concentration. The resultant solution corresponded to $TiO(NO_3)_2 \cdot \chi\ H_2O$. In order to obtain decomposition, temperature differential thermal and thermogravimetric analysis were done at temperatures up to 1300 °C with a heating rate of 10 °C/min in air.

The concentration of solution ranged from 0.05 to 0.25 M. The amounts of Pr^{+3} and Al^{+3} added to the $SrTiO_3$ host material were 0.2 and 17 mol%, respectively. The generated droplets, which were carried by oxygen gas, flew into the tubular flow furnace, as shown in Fig. 1. The precursor solution was atomized at the frequency of 1.67 MHz using an ultrasonic nebulizer. Two tubular hot zones were used in order to control the process and to increase the residence time. The purpose of the first hot zone was mainly the evaporation of solvent while the second hot zone allowed for the synthesis reaction. The temperature of the first one was fixed at 200 °C and that of the second one varied from 600 to 1100 °C.

The measuring technique of surface tension in this work was a capillary tube ascending method at room temperature.

In order to obtain the luminescent property, the as-prepared powders were calcined at 1200 °C. The collected powders were ground in a mortar for approximately 5 min, and then characterized using the X-ray diffraction technique with Cu K_α radiation (Ni filter). Referring to JCPDS card file, the XRD patterns confirm that the powders have perovskite structure. Also we studied morphology by using the scanning electron microscopy. The cathodoluminescent (CL) property of the calcined powders were measured using an electron beam excitation at 100 μA/cm^2 and 800 voltage.

3. Results and discussion

We are interested in the process conditions leading to volume precipitation within the droplet and the subsequent conversion to a dense particle. The respective stages from the droplet to particle are following. The first stage of spray pyrolysis is evaporation of the solvent from the droplet surface in the first furnace. In first stage the solvent is vaporized from the droplet surface with the change of the droplet temperature and the solutes is diffuses the center of the droplet. The concentration of the

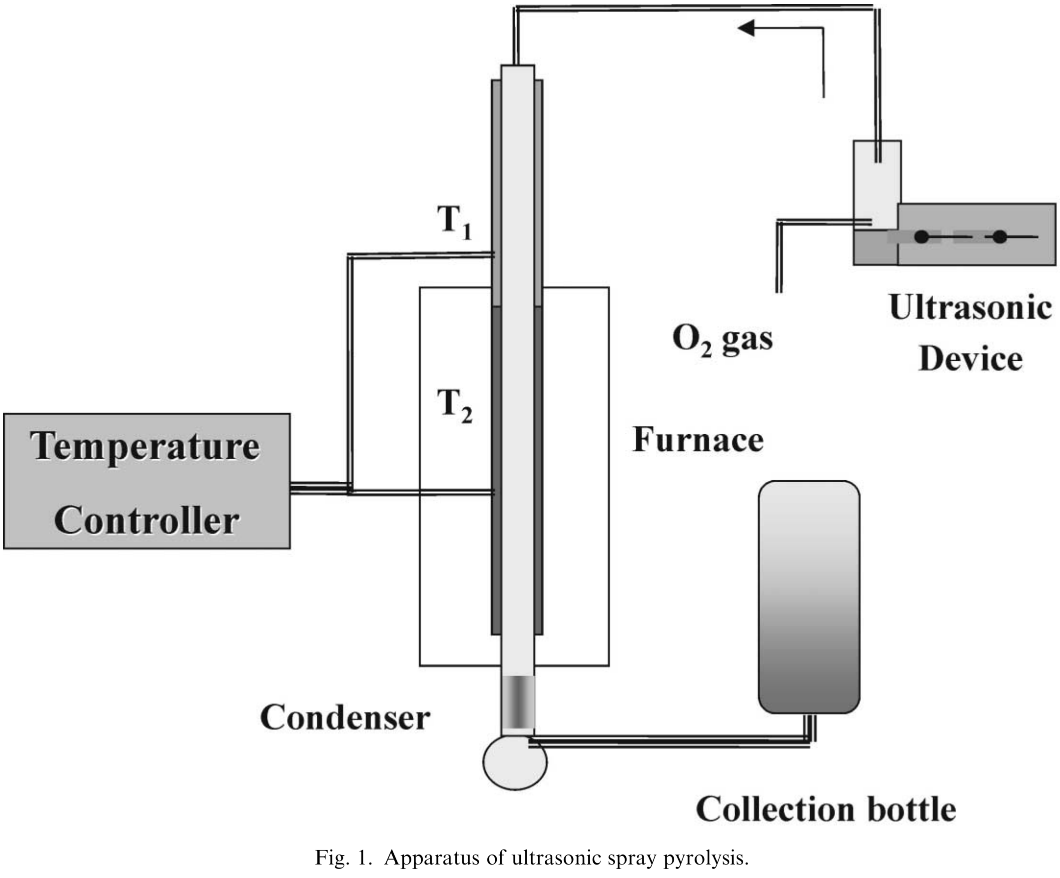

Fig. 1. Apparatus of ultrasonic spray pyrolysis.

solute in the droplet is not uniform throughout the evaporation period because the solvent is vaporized from the droplet surface at a faster rate than that of solute diffusion. Thus, the droplet surface of the solute concentration is higher than at its center. Salt crust, which is formed during the evaporation, prevents gas from being released and the solute evaporating.

During the second stage the solute starts to precipitate. There are two ways of precipitation. (1) If the solute concentration at the center of the drop is greater than or equal to the equilibrium saturation concentration of the solute at the droplet temperature, then nuclei on the surface catalyze precipitation throughout the droplet, i.e. volume precipitation. (2) If the solute concentration at the center of the droplet is lower than the equilibrium precipitation saturation of the solute at the droplet temperature, then precipitation occurs only in that part of the droplet where the concentration is higher than the equilibrium saturation, i.e. surface precipitation.

In the last step, nano-porous particles were obtained in the case of volume precipitation. One particle comprises the fine nanocrystallites, which should densify readily if it is exposed to appropriately high reactor temperature [8].

The effect of variation of synthesis temperature on the morphology was studied in terms of the reaction temperature while keeping the first hot zone at 200 °C. At first the crystalline phase of the $SrTiO_3$:Pr,Al was observed if the second hot zone temperature ranged between 600 and 1100 °C. The XRD patterns of the powders, which were produced at different reaction temperatures, are shown in Fig. 2. Since $SrTiO_3$: Pr,Al contains a few quantities of dopant, we compared $SrTiO_3$:Pr,Al with $SrTiO_3$ from JCPDS card. As a result, the creation of the perovskite $SrTiO_3$ phase occurs at 600 C. From this point of view, this method can form $SrTiO_3$ at low temperature in comparison with the conventional solid state method.

Fig. 3 shows scanning electron micrographs of ultrasonically derived powders, which were calcined at 600, 900 and 1100 °C. We kept the evaporating temperature as 200 °C. Other experimental conditions are consistent with a precursor of concentration; carrier gas type, and carrier gas flow rate (0.1 m, 444 cc/min, and O_2, respectively). These figures show that the powders consist of spherical particles with a rough surface. When the reaction temperature is relatively low (600 °C), the powder experiences a process of successive precipitation and forms the rough surface. Conversely, the powder surface, which is derived at a higher temperature and is passed through simultaneous precipitation, is smooth and dense, but it still needs some improvement to the particle surface. This phenomenon would seem to be due to the different rate of heat transfer. At high reaction temperature, heat transfer into the center of the droplet is faster than that at low reaction temperature.

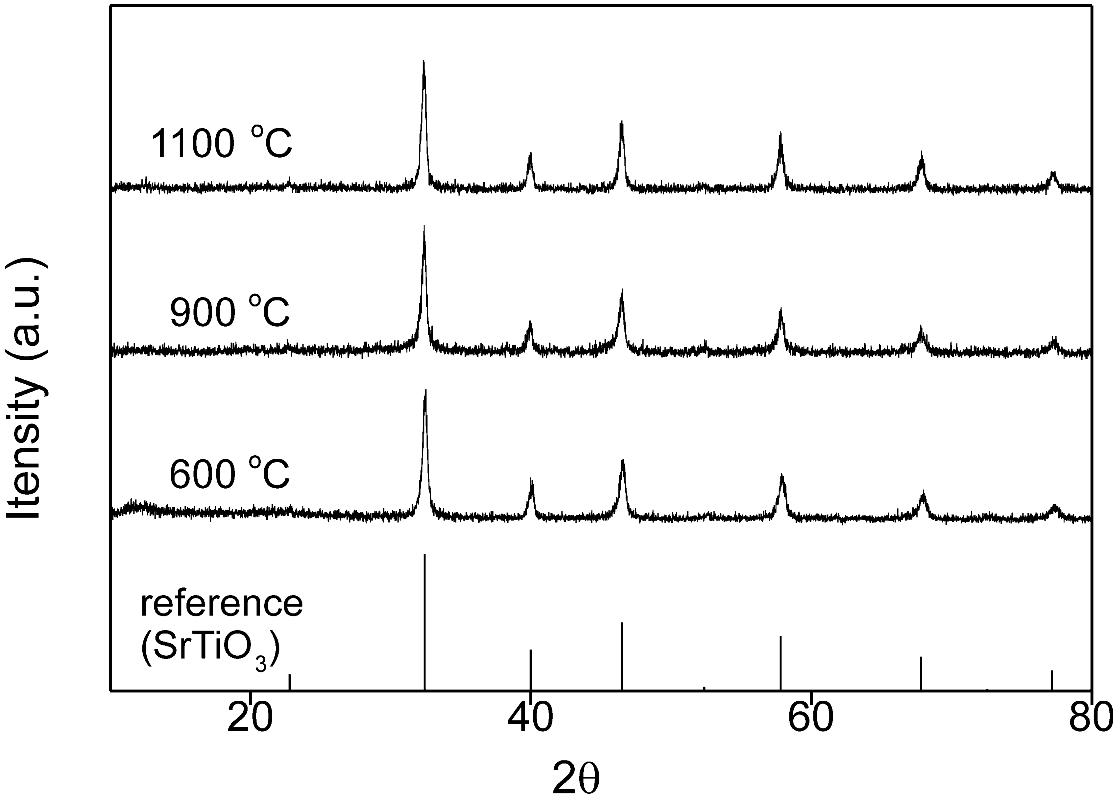

Fig. 2. XRD patterns of $SrTiO_3$:Pr,Al powders prepared at different reaction temperatures.

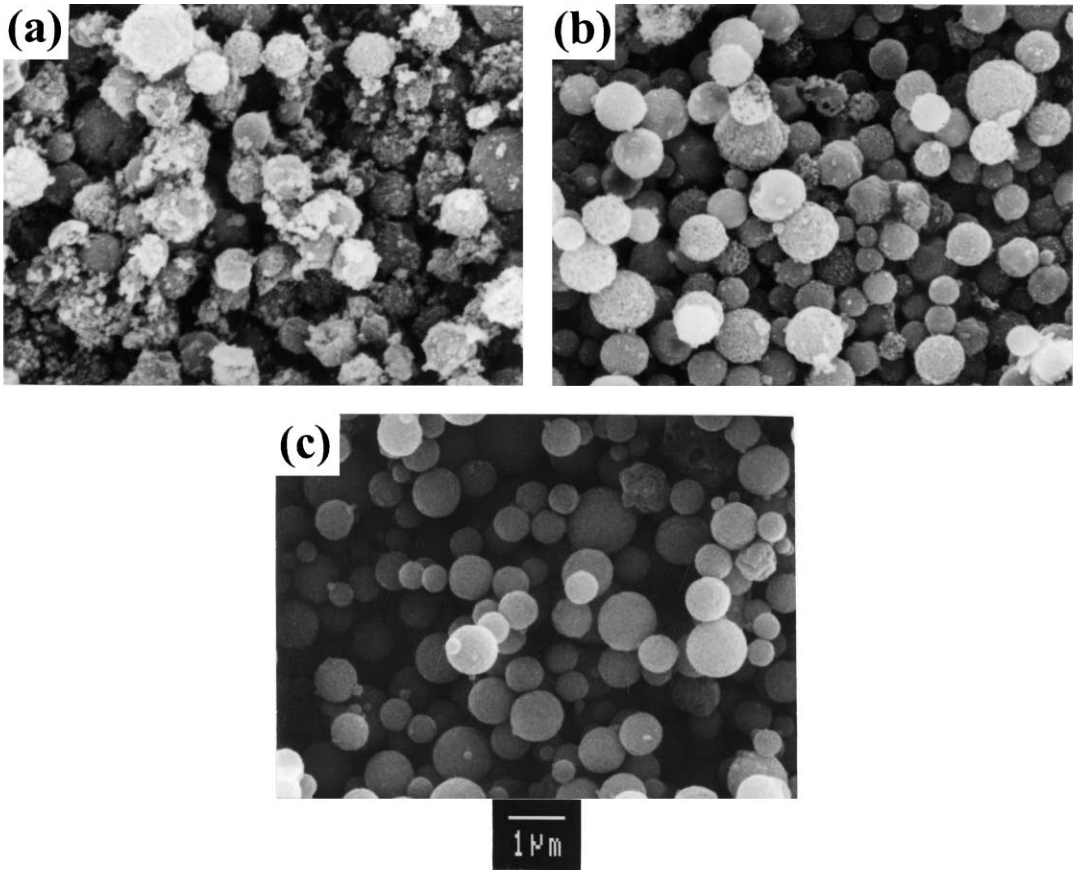

Fig. 3. SEM photographs of $SrTiO_3$:Pr,Al powders prepared at different reaction temperature (concentration = 0.1 m). (a) 600 °C, (b) 900 °C (c) 1100 °C.

Therefore, this fast heat transfer can accelerate the formation of smooth and dense particles.

However, as can be seen in the Fig. 3, some particles still show a rough shape. This is because the metal salts have low melting temperatures; $Sr(NO_3)\cdot 4H_2O$ is 100 °C, $Al(NO_3)\cdot 4H_2O$ is 73.5 °C [9], $Pr(NO_3)_3\cdot 6H_2O$ is 56 °C (according to the manufactural High Purity Chemicals Laboratory Co. Ltd.), $TiO(NO_3)\cdot xH_2O$ is 153 °C from TG-DTA. If the metal salts melt before the solvent is completely removed, the molten salts will inhibit removal of the entrapped solvent. This is one reason why powders, derived from metal nitrates, often consist of porous or irregular particles [8].

If the formation mechanism of particles is identical when they are prepared by various concentrations of precursor solution, particle size should depend on the solution concentration only. Therefore, we investigated the effect of concentration on the particle size. SEM photographs of $SrTiO_3$:Pr,Al powders, prepared by various concentrations of the solution, are shown in Fig. 4. The experimental conditions are as follows; the concentrations were 0.05, 0.1 and 0.25 M. The evaporation temperature was 200 °C and the reaction temperature was 900 °C. Flow rate was 300 cc/min, carrier gas was O_2 gas. There are some larger particles indicating a coalescence of the initial droplets.

We can see that the mean diameter decreases as the concentration decreases. Mean diameter (D_{droplet}) of the droplets generated by ultrasonic resonator can be calculated using the Lang's equation [10]. The surface tension by using the capillary tube ascending method and the density of the solution were measured at 25 °C. They ranged from 55.1 to 87.9 dyne/cm and from 1.04 to 1.14 g/cm^3, respectively.

From these data, the calculated value of D_{droplet} was about 2.8 μm. Assuming that one droplet transforms into one dense spherical particle inside the reaction furnace, the final volume mean diameter of the fine particles, D_{cal} can be calculated by the following formula [11].

$$D_{\mathrm{cal}} = \left(M_{\mathrm{powder}}\ C_{\mathrm{sol}}/M_{\mathrm{sol}}\ \rho_{\mathrm{th}}\right)^{1/3}\ D_{\mathrm{droplet}}$$

where M_{powder} is the molecular weight of final particle, C_{sol} is the concentration of solution range from 0.088 to 0.25 M, M_{sol} is the molecular weight of solute, and ρ_{th} is theoretical density of $SrTiO_3$ (about 5.12 g/cm^3). The

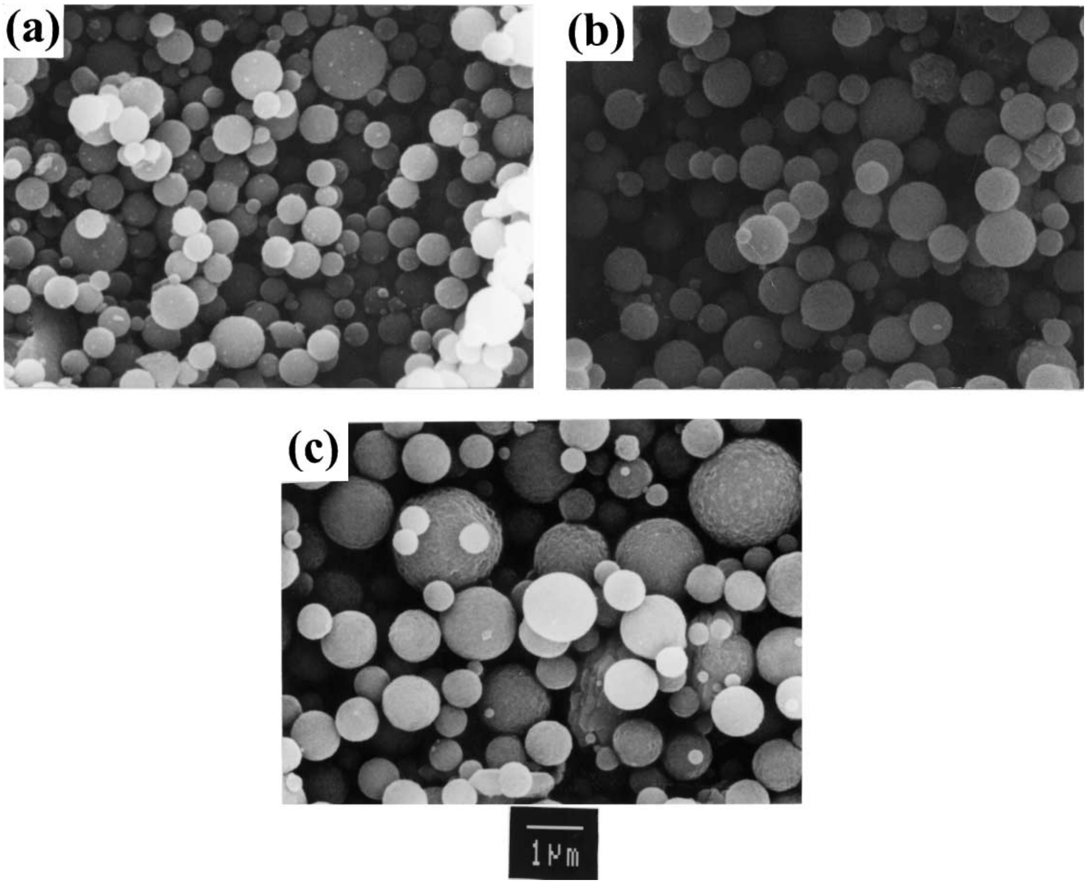

Fig. 4. SEM photographs of $SrTiO_3$:Pr,Al powders prepared at different concentration (reaction temperature = 900 °C). (a) 0.05 M, (b) 0.1 M, (c) 0.25 M.

particle size variation with respect to the concentration of precursor is listed in the Table 1. As can be seen in Table 1, there is an increasing tendency with respect to the precursor concentration.

The mean particle size from the experiment (D_{exp}) was compared with the calculation. It turned out that the D_{exp} is larger than D_{cal} (about 1.5–2.5 times). It seems that this is due to the spherical particle prepared in this study being a hollow sphere, which resulted from none-quilibrium drying of the droplet [11], while the calculation assumes solid spheres. The particle size derived by the pyrolysis method was found to be approximately proportional to the concentration of the metal nitrates in solution. Therefore, we can conclude that the particle size depends on the solution concentration.

As mentioned above, the major disadvantage of spray pyrolysis is to produce the potential for hollow or/and fractured structure of particles. After annealing at high temperature, particles are broken. To remove the defect, 10 wt.% of H_2O_2 was added to the total solution weight and the concentration of precursor solutions was 0.25 M.

As shown in the Fig. 5, $SrTiO_3$:Pr,Al powder, which is prepared by using the metal nitrate solution had some shell fragments. But the $SrTiO_3$:Pr,Al powder prepared by the metal nitrate solution with added H_2O_2, did not show the shell fragments. The possible reasons for the change of powder morphology and crystallinity were proposed by Cho et al. [12]. Our explanations on the experiments are the following.

Table 1
Particle size by calculation

Concentration (molality)	Density (g/cm^3)	$D_{droplet}$ (μm)	D_{cal} (μm)
0.25	1.14	2.8	0.61
0.1	1.05	2.7	0.44
0.125 (H_2O_2)	1.08	2.8	0.46
0.888 (H_2O_2)	1.04	2.9	0.37

First, H_2O_2 may change the physical properties of the surface crust layer. Especially, the permeability of crust can be increased by H_2O_2. When metal salt droplets pass the high temperature zone in spray pyrolysis, solvents start to evaporate from the surface and a surface crust is formed on the entire surface before the droplet is completely dried. As a result, an internal pressure is developed due to the evaporation and decomposition gas from the inner part of the droplet. The salts can be easily broken when it has low permeability or it is gen-

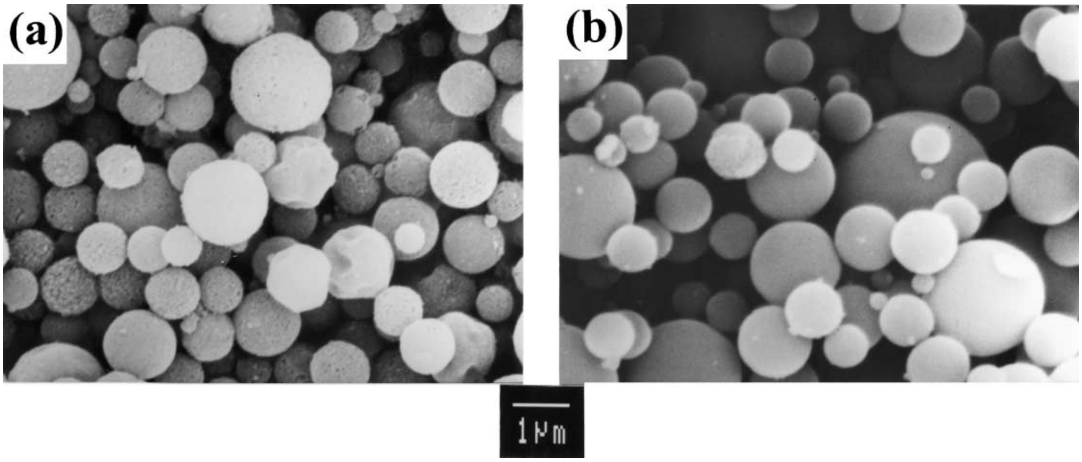

Fig. 5. SEM photographs of $SrTiO_3$:Pr,Al powders prepared at different solvent (concentration = 0.25 M, evaporation temp.:reaction temp. = 200 °C:600 °C). (a) $H_2O + HNO_3$, (b) (a) + H_2O_2.

erated by rapid decomposition reaction. Therefore, the pressure usually breaks the crust into fragments. On the contrary, as-prepared particle surface from metal nitrate solution with added H_2O_2 is smoother, probably because of its higher permeability.

Second, H_2O_2 could delay the formation of surface crust. H_2O_2 is a strong oxidizer and usually increases the solubility of cations in the solution [13]. It had been also reported that its complex ion is thermostable in an acidic solution under pH < 2 [14]. It has been well known that aqueous solution of Ti^{+4} and its complexes develop an intense orange color with H_2O_2. The color was due to the formation of stable peroxo complexes such as $[Ti(O_2)OH\ aq]^+$, $[Ti(H_2O_2)]^{+4}$ and so on. Formation of this complex ion was very effective in retarding polymerization of Ti^{+4} ions in the solution [14]. Therefore, solvent evaporating and salt crusting retard; and the time for solvent evaporating and gas releasing gets longer. We suppose that these are the reasons for a smoother surface with the H_2O_2 precursor and we find out the shape is unchanged even after post-heat treatment. However, particles with post-heat treatment tend to agglomerate slightly.

The powders prepared by spray pyrolysis did not show a luminescent property because of short residence time of particles inside the tubular flow hot reactor [15].

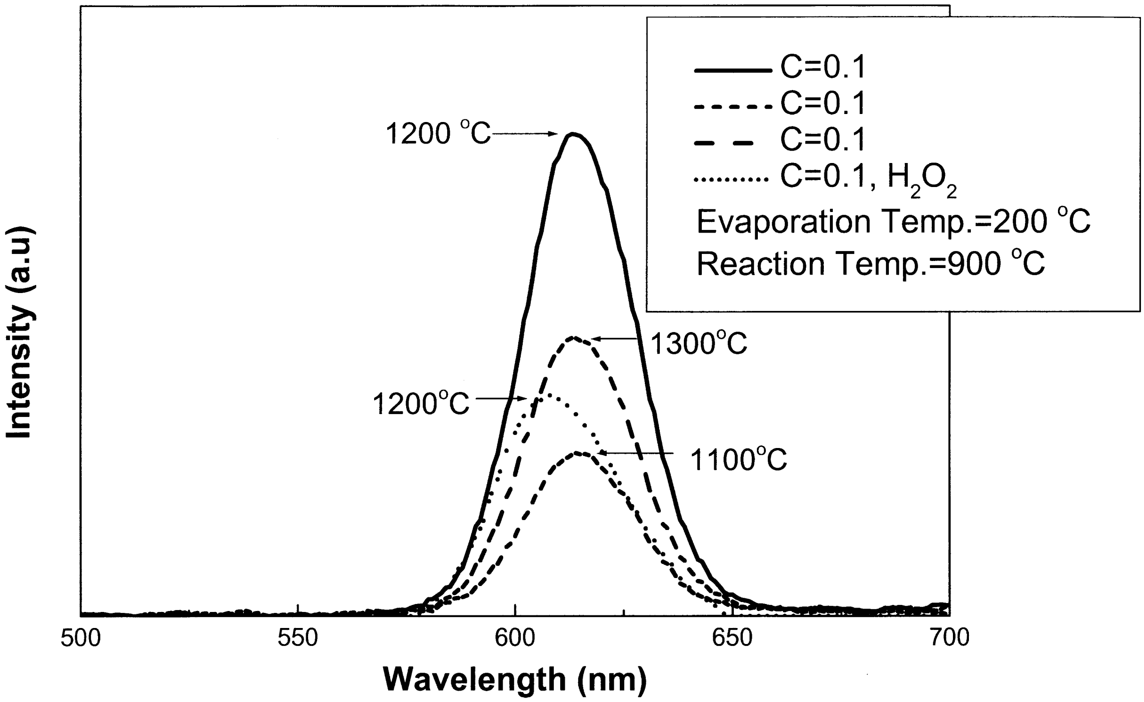

Fig. 6. Cathodoluminescent spectra of $SrTiO_3$:Pr,Al powders prepared at different annealing temperatures.

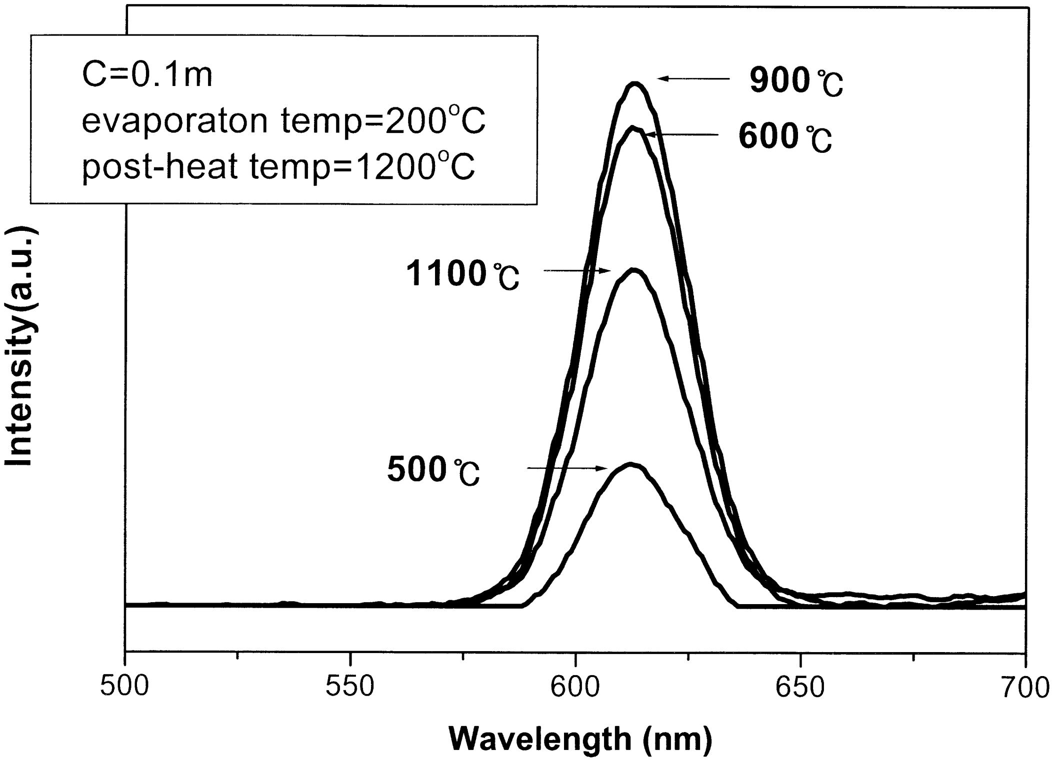

Fig. 7. Cathodoluminescent spectra of $SrTiO_3$:Pr,Al powders prepared at various reaction temperatures.

The activation of Pr^{+3} and Al^{+3} dopant does not completely occur [14]. High temperature is required for improving crystallization and activation of the substituent in the lattice. The optimum temperature for the maximum brightness of $SrTiO_3$: Pr,Al is 1200 °C. Fig. 6 shows CL property of red phosphor $SrTiO_3$: Pr,Al prepared at various annealing temperatures. The emission spectra of particles had sharp peaks at 615 nm which is due to the transition of $^1D_2 \rightarrow {}^3H_4$. Generally, the particles prepared by spray pyrolysis have hollow morphology, and the sphericity of the particles is broken after annealing at high temperature because of low thermal stability of the hollow particle [16]. Therefore, dense particles are required for maintaining shape to obtain high luminance property. As a result, as-prepared particles with high reaction temperature have higher intensity of CL property. Although the particle surface is improved by H_2O_2, we could not obtain highest brightness of the CL property.

In Fig. 7, the CL intensity of particles annealed at 1200 °C, increases as reaction temperature increases. However, reaction temperature is too high to activate the activator and sensitizer during annealing. The brightness of the phosphor is strongly affected by the crystallinity of the particles and morphology. Despite the same short residence time, high reaction temperature could offer the thermal stability after annealing.

In conventional phosphor materials, the activator absorbs the exciting radiation. However, $SrTiO_3$:Pr, Al red phosphor is more complicated. In this phosphor the activator, which emits the red color, is Pr^{+3}, but the exciting radiation is not efficiently absorbed by it. Therefore, it is necessary for another ion (Al^{+3}) to absorb the radiation efficiently. The Al^{+3} ion absorbs the exciting radiation and the absorbed energy is transferred to the Pr ion and then the Pr^{+3} ion emits the radiation. It seems that the energy transfers in the $SrTiO_3$:Pr, Al phosphor are due to the activator (Pr^{+3}) and the sensitizer (Al^{+3}).

4. Conclusion

$SrTiO_3$;Pr,Al red phosphor of particle shape was directly prepared by ultrasonic spray pyrolysis. The prepared $SrTiO_3$:Pr,Al powder showed fine size, sphericity and non-aggregation characteristics. The effect of the temperature on crystalline phase and morphology of as-prepared particles were investigated and a morphological change was shown in the $SrTiO_3$:Pr,Al. At higher reaction temperature, we observed that particle has the smooth surface and it seems solid particle by hardly showing broken particle after annealing. As increasing precursor concentration, the $SrTiO_3$; Pr,Al size was increased. This study also indicated that changing of the precursor concentrations did not affect the luminescent property of the particles. Adding H_2O_2 to precursor might change the physical properties of the surface crust layer and delay the formation of surface crust. For luminescent property, post-heat treatment was required because of short residence time (32–12 s) and the optimum temperature was 1200 °C. The CL property exhibits a red luminescence due to the radiative decay of the $^1D_2$ states ($^1D_2 \rightarrow {}^3H_4$). In this study, we showed $SrTiO_3$;Pr,Al is a potential red phosphor which can be applied in full-color FED.

Acknowledgements

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