Available online at www.sciencedirect.com

SCIENCE DIRECT

Materials Chemistry and Physics 96 (2006) 511–516

MATERIALS CHEMISTRY AND PHYSICS

www.elsevier.com/locate/matchemphys

Eradication of oxygen contamination in production of ZnS:Ag:Cl blue phosphor powder

Lyuji Ozawa [a], Mika Makimura [b], Minoru Itoh [c,*]

[a] L.L. Technology, 8 Old Grange Road, Hopewell Junction, NY 12533, USA
[b] Industrial Research Institute of Nagano Prefecture, 1-18-1 Wakasato, Nagano 380-0928, Japan
[c] Department of Electrical and Electronic Engineering, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

Received 18 May 2005; received in revised form 21 July 2005; accepted 24 August 2005

Abstract

It has been pointed out that oxygen contamination of ZnS:Ag:Cl blue phosphor powder mainly comes from the air trapped in inevitably existing pores in heating mixture in crucible. Calculated amount of the trapped air is 2×10^{-3} mol per mole a-ZnS in crucible. It is found that addition of $AlCl_3$ (2×10^{-3} mole) eradicates the oxygen gas in heating mixture, by means of formation of Al_2O_3 solid. Segregating Na_2S_4 carries the fine Al_2O_3 particles to the place that Al_2O_3 converts to Al_2S_3 by the concentrated Na_2S_4. The segregation of Na_2S_4 requires a slow cooling from 950 to 850 °C. The segregation produces the large yellowish particles (>50 μm), which are confirmed as ZnO microcrystals surprisingly. Then, we have proposed a model of the growth of ZnO microcrystals in heated mixture which is a sulfur-rich atmosphere.

Keywords: Oxygen contamination; ZnS:Ag:Cl blue phosphor powder; Crystal growth

1. Introduction

ZnS:Ag:Cl is widely used as blue primary phosphor of cathodoluminescence (CL) display devices, such as cathode ray tube (CRT), vacuum fluorescent display (VFD), and field emission display (FED) [1,2]. Although the energy conversion efficiency of the commercial ZnS:Ag:Cl phosphors has been optimized by the producers [3], the phosphor producers still have difficulty in controlling a small variation in CL intensity and color of the produced ZnS:Ag:Cl phosphor by a contamination of oxygen [4]. For example, the color coordinate of CL (especially, the y-value = 0.062 in the x–y chromatic diagram) of commercially produced ZnS:Ag:Cl powder varies from lot to lot in the range of 0.062–0.067 [3]. CRT producers pay attention to the small variations in the receiving quality control. The contaminant oxygen forms a recombination center (a pair of Ag–O) in ZnS particles, which gives rise to an additional luminescence band on the long-wavelength side of the main blue band of Ag–Cl pair recombination centers [1]. It has been thought that the contamination source of oxygen is the air in the furnace and/or the air in an open space between charged blend-mixture and crucible. Accordingly, phosphor producers have tried to eradicate the oxygen contamination by the followings: (i) the air in a furnace is substituted by N_2 flowing gas and (ii) active charcoal powder is put on the blend-mixture in a crucible [5]. The unsatisfactory results are obtained in production.

We have extensively studied to figure out the contamination source of oxygen. It is found that the main source of oxygen is the air trapped in inevitably existing pores in the charged blend-mixture in a crucible [6]. Furthermore, when a small amount of $AlCl_3 \cdot 6H_2O$ (0.5 wt%) is added into the blend-mixture, the oxygen gas is eradicated from the heating mixture by formation of Al_2O_3 solid. With NaCl, yellowish particles with large sizes (>50 μm) are formed under a slow cooling from 950 to 850 °C. The formation of yellowish particles, which are confirmed as ZnO microcrystals, are to produce a reliable ZnS:Ag:Cl blue phosphor powder with a high reproducibility. The details are below.

2. Experiment

Table 1 shows the recipe of the raw materials studied, in which amorphous (a-) ZnS powder contains Ag (1×10^{-4} mole

---

* Corresponding author. Tel.: +81 26 269 5261; fax: +81 26 269 5220.
E-mail address: itohlab@shinshu-u.ac.jp (M. Itoh).

0254-0584/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2005.08.061

Table 1
Blend-mixture for ZnS blue phosphor production

Materials	Weight (g)	Percentage (wt%)	Mole ratio
a-ZnS (containing 10^{-4} Ag)	3400	100	1.0
NaCl	5.3	0.15	2.6×10^{-3}
$AlCl_3 \cdot 6H_2O$	17.2	0.5	2×10^{-3}
S	34.0	1.0	0.01

fraction) as an activator. We had examined the a-ZnS raw materials from Korean Zinc, US Radium, and Beijing Fine Chemical. The results did not change with the materials used. The small amount of $AlCl_3 \cdot 6H_2O$ and NaCl were added to 100 g of a-ZnS powder, which had been taken from 2000 g, and the powder was ground in a mortar. The ground powder returned to the original a-ZnS powder. The powder was blended in a V-shaped mill for 1 h, and charged in a 2-L quartz crucible with a density of 0.5 g cm^{-3}. The crucible was directly put in a heated furnace at 800 °C, and then heated up to 950 °C and kept there for 50 min. We took two cooling procedures from 950 °C to room temperature. One was that the crucible directly took out from the furnace at 950 °C, i.e., rapid cooling. The other was that the furnace temperature decreased to 850 °C with a rate of 1.3 °C min^{-1}, and then decreased to 400 °C with a rate of 3.5 °C min^{-1}. The temperature of the furnace at 400 °C was turned off to allow the crucible in the furnace to come to room temperature, i.e., slow cooling. The cooled product was transferred into a plastic container of 5 L, which contained deionized (DI) water. The DI water was stirred for suspension of phosphor particles after 1-h soaking. The suspension was poured on a 140-mesh sieve with open aperture of 100 μm. The particles left on the sieve were the samples for the study. The powder on the sieve was dried in a heated oven at 110 °C.

The dried particles (hereafter, residual particles) were adhered on the surface of a conductive tape on both sides. The residual particles were identified by X-ray diffraction analysis (Rigaku, RAD-IIA), and their shape was observed by a scanning electron microscope (SEM). The particle surface was investigated by a JEOL JXG-88R electron probe micro-analyzer (EPMA).

3. Results and discussion

3.1. Amount of oxygen in blend-mixture charged in crucible

As already mentioned in Section 1, the contaminant oxygen for ZnS:Ag:Cl phosphor comes from neither the air in a furnace nor the air in an open space between charged blend-mixture and crucible. Powdered mixture in crucible inevitably contains a large amount of air bubbles (pores), which are the contamination source of oxygen in ZnS phosphor production. The air bubbles have been overlooked in the ZnS phosphor study and production.

Amount of air bubbles in the charged mixture in the crucible is calculated as below. Since the density of cub-ZnS crystal is 4.1 g cm^{-3} [5], 88% (=1 − (0.5/4.1)) of the total volume of the softly charged mixture (0.5 g cm^{-3}) in crucible is occupied by air. In the densely charged mixture (1.0 g cm^{-3}), air occupies about 75%. Thus, the volume of air is less dependent on the charged density of the blend-mixture.

If the crucible of 2 L is fully filled with the softly charged mixture, the volume of air is calculated to be 1760 cm^3. Since the air is composed of N_2 (78%) and O_2 (21%), O_2 gas is 360 cm^3. The volume of 1-mole gas is 22.4×10^3 cm^3 at room temperature, so that the charged mixture in a 2-L crucible contains 0.02 mole O_2 gas $\{=360\,(22.4 \times 10^3)^{-1}\}$, corresponding to 2×10^{-3} mole per mole a-ZnS powder in the blend-mixture. Ten-mole a-ZnS powder charges in 2-L crucible.

3.2. Contamination source of oxygen in phosphor production

When a crucible is heated, the pores hold a positive pressure of air (and other gases) against an open space between the charged blend-mixture and the crucible. With the positive pressure, the air from the open space to the charged mixture is hard for diffusion into the charged mixture. It is also hard to get out the air from pores in the mixture to open space of the furnace in the heating process. The pores in the heating mixture hold the air with rising temperature throughout. Oxygen smoothly diffuses in heated ZnS crystal lattice, and once diffused oxygen does not diffuse out from ZnS lattice. Then it can be said that the contamination source of oxygen in ZnS:Ag:Cl phosphor production is air in the pores in the heating mixture. The active charcoal powder on the charged mixture in crucible and the infusion of N_2 gas into furnace do not work for the eradication of oxygen in the heating mixture.

3.3. Eradication of oxygen in heating mixture

The oxygen in pores must be eradicated from charged mixture before crystallization of ZnS particles by vaporized $ZnCl_2$ (732 °C) [4]. The gaseous oxygen in the pores in the heating mixture may be eradiated by means of a solid as a consequence of chemical reaction (oxidization) with metal compounds in the temperature range below 732 °C. For example, heated aluminum compounds smoothly react with gaseous oxygen at a low temperature to form Al_2O_3 solid. In the early stage of the heating process from room temperature, $AlCl_3$ reacts with oxygen at around 400 °C to form Al_2O_3 particles, of which the sizes are duplicated from $AlCl_3$ particles. Fortunately, Al_2O_3 particles are chemically stable even in sulfur-rich atmosphere, and are harmless to luminescence centers in ZnS:Ag:Cl phosphor particles. Following experiments were made by the addition of $AlCl_3$.

As described before, the amount of O_2 gas in the charged mixture in a 2-L crucible is 2×10^{-3} mole per mole a-ZnS powder. Since 1.5-mole O_2 is consumed to form 1-mole Al_2O_3, the amount of $AlCl_3$ for the conversion to Al_2O_3 is calculated as 1.3×10^{-3} mole per mole a-ZnS powder. We obtained 2×10^{-3} mole of $AlCl_3 \cdot 6H_2O$ as the optimal results (Table 1). The reproducibility of CL color is $y = 0.062 \pm 0.002$ with the high CL intensity (±1%), indicating that by the addition of $AlCl_3 \cdot 6H_2O$, the oxygen is effectively eradicated from the pores in heating mixture at the temperature below 732 °C.