

Influence of HMDS additive on the properties of YAG:Ce nanophosphor

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요 약

YAG:Ce 형광체 제조에 있어서 공침(co-precipitation) 후 n-butanol 공비증류(azeotropic distillation)시 HMDS(hexadimethyldisilazane)를 첨가하였을 때, 형광체가 광학특성에 미치는 영향에 관하여 연구하였다. 물과 유기용제에 의한 공비증류 시 유기용제의 분자량이 크면 표면의 수소결합이 유기용제로 치환됨으로서 표면장력을 감소시켜 분체의 원형화(conglobation)와 응집(agglomerate)을 감소시키므로 유기용제로 n-butanol보다 분자량이 큰 HMDS를 첨가하였다. N-butanol 만을 사용한 형광체가 HMDS를 첨가한 것 보다 응집(agglomerate)되는 현상이 감소하였으며 우수한 광학적 특성을 나타내었다.

Key Words : Powder, HMDS, Heterogeneous, Azeotropic Distillation, Luminescence.

ABSTRACT

Influence of hexamethyldisilazane(HMDS) in post processing technique by using n-butanol azeotropic distillation on the luminescence properties of YAG:Ce nanophosphor were studied. The organic solvent(n-butanol) azeotropic distillation which prevent powders from conglobation since lager molecules decrease the surface tension and more complete replace the residual water in the precipitate. HMDS that had larger molecules than that of n-butanol was added in azeotropic distillation. The phosphor synthesized from n-butanol azeotropic distillation exhibited lower agglomerate and better photoluminescence properties than that from HMDS added heterogeneous azeotropic distillation..

1 . Introduction

White light source was able to produce by mixing tree primary light such as red, green and blue light or two complement ones. Recently, blue light emitting diodes(LEDs) based on Gallium Nitride(GaN) were developed and trivalent cerium activated yttrium aluminum

garnet(YAG:Ce) phosphor has been reported to be suitable for converting blue LED light into a broad band yellow light[1]. This yellow light complements the blue light to produce white light.

Co-precipitation was relatively low temperature and low cost technique to obtain ultrafine YAG powder than the other processes

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such as solid state reaction, sol-gel method and combustion method. However, co-precipitation process suffers from the production of hard agglomerates[2] which mitigates luminescence properties[3].

Low surface tension and hydrogen bonding caused by replacing water with an organic solvent decrease the agglomeration, since water has very high surface tension and is bond by strong hydrogen bonds[4]. Surface treatment by organic polymer surfactant reduce the agglomeration[5]. Heterogeneous azeotropic distillation(HAD) technique that is reported free of hard agglomeration is adopted to synthesize YAG:Ce nanophosphor[6-9]. Especially, n-butanol HAD processing with co-precipitation is reported on excellent photoluminescence results[10]

In this work, HMDS as organic solvent, that had larger molecules than that of n-butanol was chosen in azeotropic distillation, and mixed into n-butanol or applied after n-butanol treatment since HMDS is immiscible with water.

II. Sample preparation

1. Synthesis of YAG:Ce

Rare earth oxide Y_2O_3 , $Ce(NO_3)_3 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$. Y_2O_3 were the base materials for YAG:Ce nanophosphor. The multi-cation solution will prepared according to stoichiometric proportion of $Y_{2.95}Ce_{0.05}Al_5O_{12}$ with 0.1% molar weight.

7.877gm of $Al(NO_3)_3 \cdot 9H_2O$, 4.745gm of $Y(NO_3)_3 \cdot 6H_2O$ and 0.082gm of $Ce(NO_3)_3 \cdot 6H_2O$ dissolved into distilled water separately. All these three solutions mixed in one beaker to make multi-cation solution. The precipitant solution was made by dissolving 20gm of

NH_4HCO_3 into distilled water.

The multi-cation solution dropped into the precipitant solution under magnetic stirring for 15min. at room temperature. Reverse strike technique was adopted to keep the pH concentration constant(7.96-7.84) during precipitation[2]. Mixed solution was stirred another 45min, aged for 8 Hr at 50oC, filtered and washed with distilled water until the filter cake become neutral to PH paper(Ph=7).

Filtered cake was divided three parts. The two parts of them were dissolved into the n-butanol and one of them was the reference sample (HAD), and then the second one was dissolved into the HMDS (POST). The third one was dissolved into the mixed solution with n-butanol and HMDS (MIX). Then all of them were dried 30min. at 95oC. HAD sample was refluxed at 117oC which is the melting point of n-butanol. POST and MIX samples were done at 129oC which is that of HMDS for 1Hr respectively then cooling and dried at 120oC over 12Hr.

Each sample was calcined at different temperature 1000oC or 1250oC with the nitrogen gas ambient.

2. Sample characterization

The products were characterized by powder X-ray Diffraction(XRD) collected on a Rigaku model DMAX-2500 diffractometer. Scanning Electron Microscopy(SEM) images were taken on a SEC, Mini-SEM. The photoluminescence properties of all the phosphors were measured by Integrating Sphere System at room temperature.

III. Results and Discussions

1. Structure

YAG powders synthesized by co-precipitation were found to be amorphous below 800°C and crystallize as YAG at 900°C, and YAG was only the phase above the 1000°C[2,11].

The samples calcined at 1250°C were investigated under powder XRD. The results were shown in Fig. 1. All the samples were crystallized the garnet structure(YAG) and hard to find the intermediate phases like perovskite(YAP) and monoclinic(YAM) which deteriorate the photoluminescence properties. From XRD analysis, the structure of nanophosphor of POST sample was affected by processes involved in HMDS.

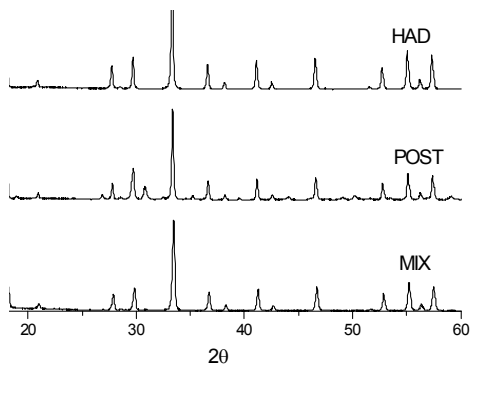
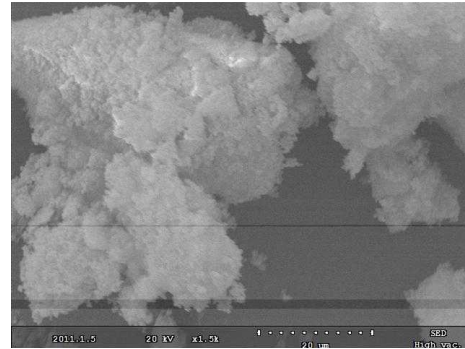


Fig. 1 XRD patterns of HAD, POST and MIX samples calcined at 1250°C

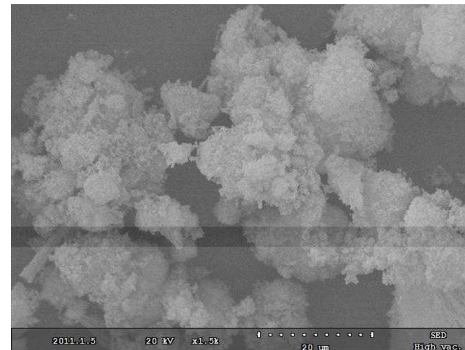
2. Morphology

A series of SEM images were made to characterize and compare the microstructure of YAG phosphors prepared by different processes. The particles of HAD precursor were better dispersive than that of others. In contrast HAD

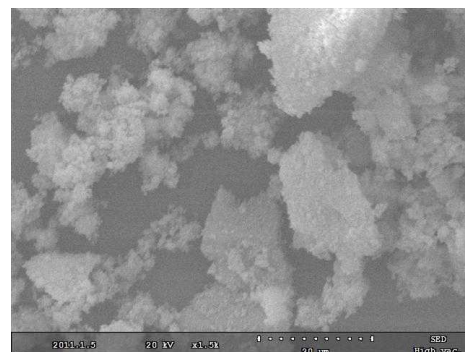
case, particles of MIX and POST precursors presented compact agglomeration. Hard agglomerate deteriorates the luminescence properties. Fig. 2 shows the SEM images of the (a)HAD, (b)MIX and (c)POST precursors.



(a)



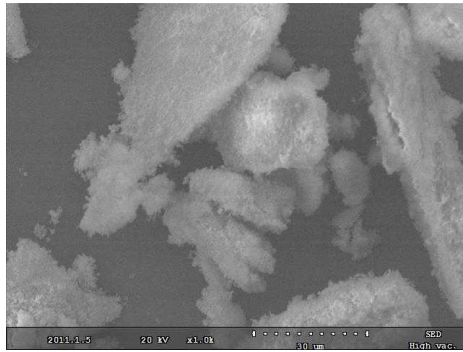
(b)



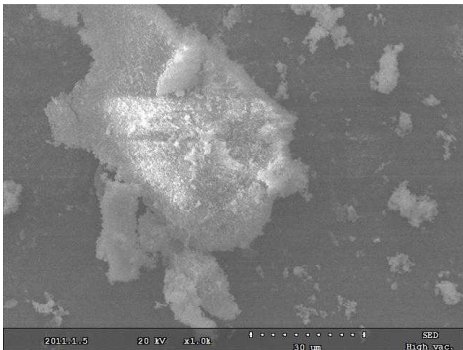
(c)

Fig. 2 SEM images of (a) HAD, (b) POST and (c) MIX precursors.

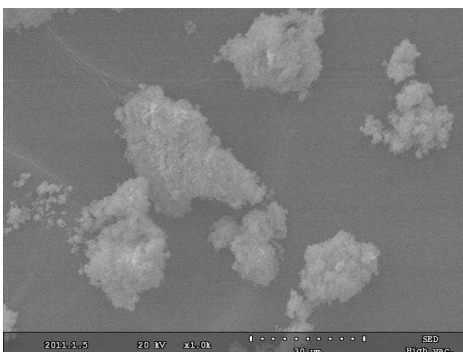
After calcination at 1250°C, particles merged and grew. Fig. 3 shows the SEM images of the (a)HAD, (b)MIX and (c)POST samples calcined at 1250°C. Particle sizes of MIX sample were smaller than that of others.



(a)



(b)



(c)

Fig. 3 shows the SEM images of the (a)HAD, (b)MIX and (c)POST samples calcined at 1250°C.

3. Photoluminescence properties of YAG:Ce

In YAG:Ce crystal, absorption bands were located between 200 and 500nm since Ce occupies the site of the strong crystal field of O²⁻ and the energy state of 5d is split by the crystal field [12,13]. And the most intense excitation band is located between 400–500nm [10] in contrast absorption spectrum. Re-emission spectrum band located 500–700nm is yellow.

Fig. 4 shows that luminescence characteristics of HAD samples calcined at 1000°C and 1250°C as a function of wavelength. Relative intensity was a ratio of the peak intensity re-emitted (580nm) to that penetrated (450nm). There are two apparent peaks in spectrum. The emitted light by source was divided three components which were the absorbed and re-emitted light by phosphor and the penetrated one through phosphor. The measured 450nm peak was the penetrated light through phosphor. The broad spectrum near 580nm was re-emitted light from phosphor.

In HAD sample, re-emitted intensity increased as calcined temperature increased since the particle size and density of nanophosphor were in proportion to luminescence properties. The intensity of MIX and POST samples also increased as calcined temperature increased however increments of intensities were not much as that of HAD samples. The agglomeration caused by poor sinterability [2] obstructed the crystallization and densification of particles.

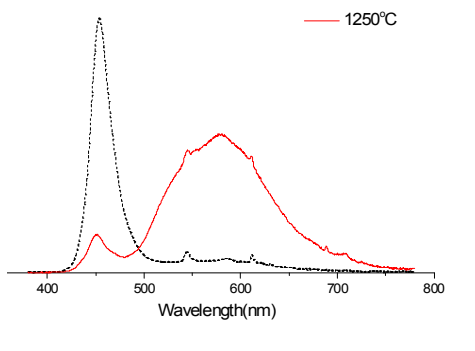


Fig. 4 Luminescence spectrums of HAD samples calcined at 1000°C and 1250°C as a function of wavelength.

Fig. 5 shows the luminescence characteristics of phosphor with different treatment. Different processing treatments did not affect the spectrum location of excitation and absorption bands. The center wavelength of emission bands was 580nm and the full width half maximum(FWHM) was 120nm which were slightly different 520nm, 78nm respectively from the that of K. Zhang, et al[10]. Longer wavelength and wider FWHM represented small energy band gap and broad energy band respectively which may be caused by the contamination or significant quantity of side elements of raw materials.

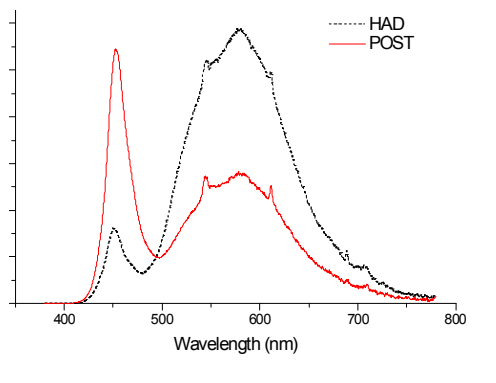


Fig. 5. Luminescence spectrums of HAD and POST samples calcined at 1250°C.

Fig. 6 shows the relative photoluminescence intensities of different process techniques, which were the peak intensity ratio of yellow light to blue one. The HAD sample showed the best results among them.

The MIX and POST samples were mitigated the relative luminescence intensity by agglomeration caused by additive. The increase of particle size and agglomeration in n-butanol heterogeneous azeotropic distillation were enhanced by HMDS additive.

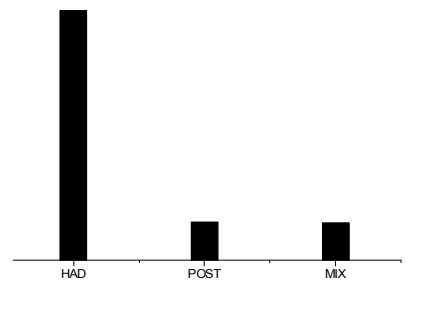


Fig. 6. Luminescence ratio of HAD, POST and MIX samples calcined at 1250°C.

IV. Conclusions

Effects of HMDS additive in n-butanol heterogeneous distillation during synthesis of YAG:Ce nanophosphor were investigated.

The additive affected a little deviation of crystallographic structure. However, additive obstructed the particle size increment and the agglomeration diminishment resulted in the decrease of photoluminescence intensities.

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