The Preparation of Ce^{3+}doped Y-SiAlON for LED Phosphor.

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Abstract

We have investigated luminescence properties of Ln-SiAlON materials doped with Ce^{3+}. Low-energy 4f ↔5d transitions were observed as compared to the luminescence of this ion doped in oxidic host-lattices.[1] Ce-doped Y-α-SiAlON show bright long wavelength luminescence with high absorption for 305 and 455nm excitation. In our experiment, the sintering temperature of this material(1400 ℃) was lower than that of normal sintering temperature (1700 ℃). However, Single phase of SiAlON was not composed. we observed the YAG phase.

1. Introduction

Nitrogen containing crystal lattices such as $Y_5(SiO_4)_3N$ (apatite-type), $Y_4Si_2O_7N_2$ (cuspidine-type structure), $Y_2Si_3O_3N_4$ (melite-type structure) were significantly different from those in oxide environments. In this composition a variable amount of yttrium was replaced by cerium to act as an activator cation.

In $Y_{1.98}Ce_{0.02}Si_{3-x}Al_xO_{3+x}N_{4-x}$,the lager Ce^{3+} ion (1.143 Å vs. 1.019 Å for Y^{3+}) occupies the largest Y^{3+} site, which is preferentially coordinated with smaller O^{2-} ions instead of with the larger N^{3-} ions, as compared to the average Y^{3+} site.[2]

The coordination of cerium with nitrogen lowers the energy of the 5d band thus shifting the 5d→4f emission to longer wavelengths. Since these compounds absorb radiation in the visible part of the spectrum, they are considered to be interesting for LED (Light Emitting Diodes). Rare-earth ions are known to give efficient luminescence and e.g., rare-earth-doped phosphors are applied in fluorescent lamps or in cathode ray tube.[3]

In this report, this phosphor was developed for covering the 450-470nm excitation spectral range. In addition, for the Ce^{3+}-doped materials we also observed that the Stokes shift decreases for Y-Si-O-N lattices with a higher nitrogen concentration. This is ascribed to the increasing rigidity of the host-lattice as a result of a more extended silicon tetrahedral network in this sequence. [4]

Astwood and Prutton have reported that sintering temperature shows a significant dependence on crucible materials.[5] Thus, we attempted several ways of enhancing the performance of SiAlON phosphors. Alumina crucibles are commonly used in crystal growth. Using the various crucibles could be one of the most efficient approaches for this purpose. Especially, alumina, graphite and platinum crucibles has been examined.

2. Experiment

The materials used in the present investigation with the general formula: $Ln_{15-x}Si_{14.7}O_{54.1}N_{7.4}:Ce_x$ have been prepared by the solid-state reaction.

The following starting materials were used (purity > 99.9%): CeO_2, Y_2O_3, Al_2O_3, SiO_2 and Si_3N_4.

The raw materials were weighed out stoichiometrically. Next, they were suspended in iso-propanol, and mixed on a roller-bench for 24h. Although added as Ce_2O_3, cerium is assumed to be fully converted to the trivalent state in the glasses as a result of reaction with the added Si_3N_4:

$$12CeO_2 + Si_3N_4 \rightarrow 6CeO_2 + 3SiO_2 + 2N_2\uparrow.$$

This mechanism is well established for Si_3N_4-CeO_2 reaction system and is in accordance with thermodynamic calculations for Ce-Si-Al-O-N glass. The change of the overall composition due to this reaction is accounted for by adapting the Si_3N_4/SiO_2

The powder mixtures were wet mixed in a ball mill, dried and uniaxially pressed into pellets of ca 2g. The pellets were fired in an induction furnace at temperatures of approximately 1400~1500℃. Also, using the various crucibles could be one of the most efficient approaches for this purpose. Especially, alumina, graphite and platinum crucibles has been examined. Excitation and emission spectra were measured using a Perkin-Elmer LS-50B spectrofluorometer equipped with a Xe flashlamp. The spectra were corrected for lamp characteristics, detector characteristics and system transmission.

3. Results

X-Ray diffraction (XRD) patterns of the powders synthesized in nitrogen atmosphere with various crucible materials are shown in Fig. 1. All these samples were sintered at 1400℃ for 3hr. According to the XRD patterns, single phase of SiAlON was not composed. It seems that our sintering temperature is too low or present as a solid solution. As a result the YAG phase increased with low-temperature heat treatment, implying that the transformation from SiAlON to YAG occurred. It was concluded that the YAG phases stabilized as temperature go down. On the other hand, with increase of temperature, the phase of YAG decreased. Then, we observed the YAG phase in our powder.

Five types of crucible were used for this sequence of experiments. They are: (a) Alumina; (b) Platinum; (c) graphite; (d) graphite foil on a alumina; (e) graphite foil on platinum crucible.

Fig. 2 shows that there is a broad excitation band extending from about 400 to the UV part of the spectrum which are observed around 455nm. This absorption leads to efficient luminescence for LED phosphors, as can be seen from the excitation spectrum. Generally, sintering temperature and reaction time are two important factors that affect the crystallization and luminescence intensity. Also, in order to investigate effect of the crucible, we use the various crucible.

Fig.3 (a) and (b) shows the results of the emission measurements for several crucible materials. When alumina crucible was used, the emission intensity higher than in the case of the other crucibles.

Y-SiAlON:Ce phosphor having a broadband spectrum from blue through red. When the new phosphor with broadband spectrum is used for white LEDs, the color rendering index of the white LED is improved drastically.

4. conclusion

The emission of Ce-doped Ln-Si-Al-O-N glasses can be varied over a large spectral interval (450~630nm). The occupancy of these sites is governed by a competition between Ce and the other lanthanides depending on their relative sizes.

In this study, single phase of SiAlON was not composed. YAG phases were stabilized as sintering temperature go down. Therefore, Transformation from SiAlON to YAG was occurred Because sintering temperature was too low and Y-SiAlON presents as a solid solution.

Reference

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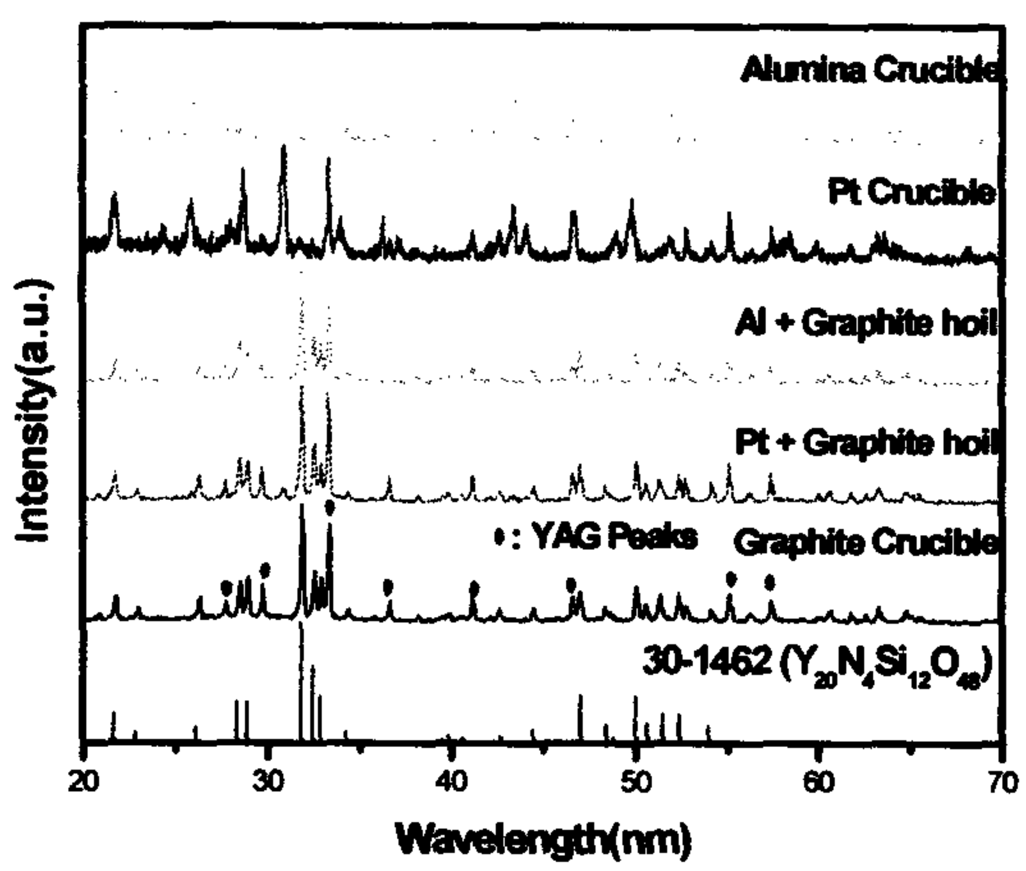

Fig. 1. XRD patterns of Y-SiAlON:Ce phosphors with various crucibles.

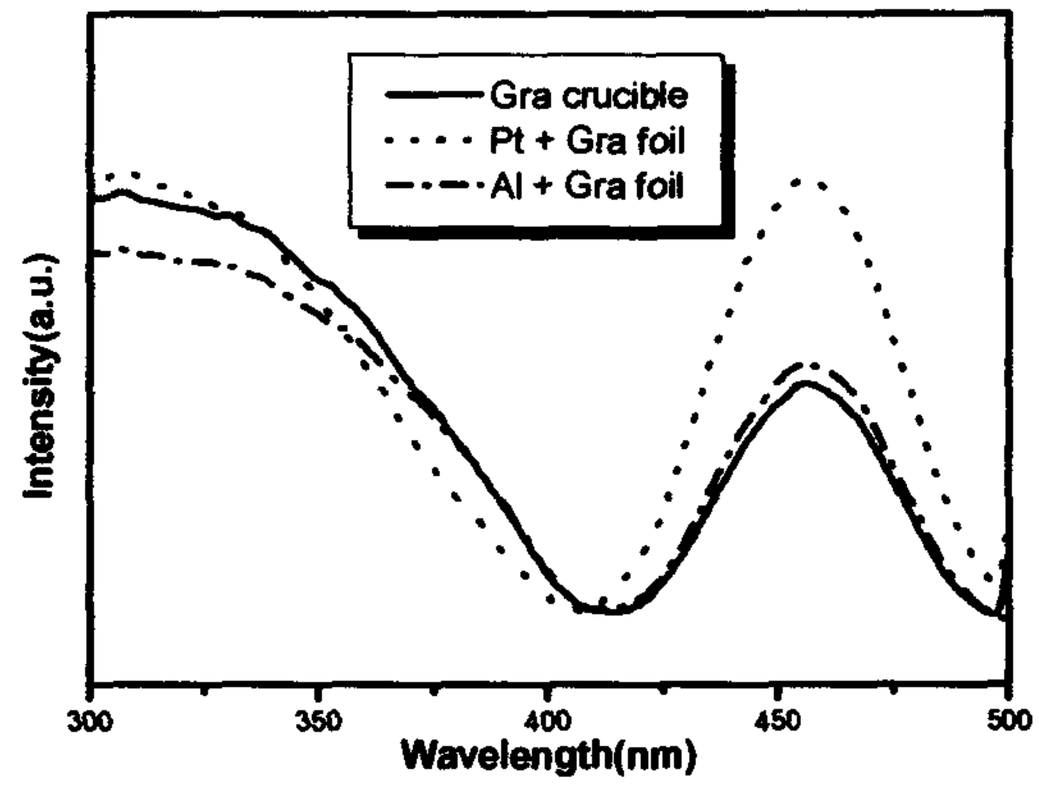

Fig. 2. Excitation spectrum of of Y-SiAlON:Ce phosphors in various crucible materials.

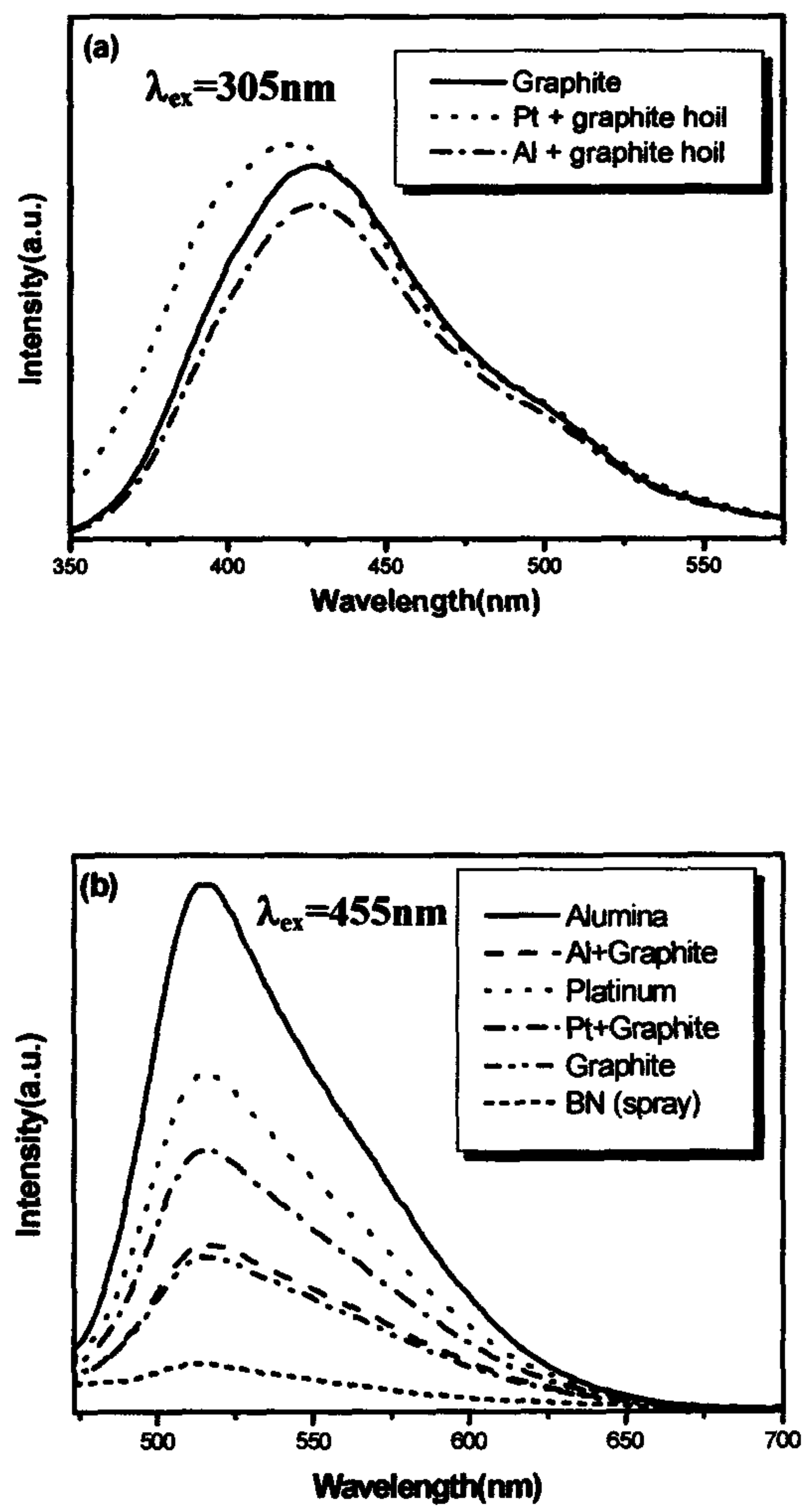

Fig. 3 (a) and (b). Emission spectrum of Y-SiAlON:Ce phosphors in various crucible materials.