Synthesis of Novel Si-based Oxynitride Compounds for Eu2+-activated Phosphors

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論文内容要約

This thesis describes synthesis and investigation of luminescence properties of novel Eu^{2+}-activated Si-based oxynitride phosphors for white light emitting diode application. In Chapter 1, general introduction and research background will describe. From Chapter 2 to Chapter 4 describes experimental, results, and discussions. In Chapter 5, summary of each chapter will discuss.

Chapter 1: General introduction

White light emitting diodes (LEDs) have attracted considerable interest due to the advantages over the conventional incandescent and fluorescent lamps in energy efficiency, long lifetime, non-pollution and so on. However, the color temperature and the color rendering index (CRI) of the present white LEDs are not sufficient for the use at various places with many purposes. In this regard, the development of highly efficient phosphors for wLEDs is an important assignment for the researchers. Rare-earth doped nitride and oxynitride phosphors, especially, have been extensively researched in this field because of their remarkable properties such as high absorption and high conversion efficiency in near ultra violet (NUV) - blue region and excellent thermal stability.

Methods for development of new phosphors can be classified into three categories. The first category is tuning of known phosphors by element substitution to achieve excitation and/or emission properties desired for the purpose of the use. The second one is search for new phosphors by investigation of luminescence properties of known compounds doped with activators. The final one is synthesis of new compounds coupled with investigation of luminescence properties of those compounds with help of proper activators. Development of new phosphors by the second and last methods is very meaningful since the first method, fine tuning of luminescence properties, can be applied to those. In this thesis, the author reports development of new Eu^{2+}-activated oxynitride phosphors through the investigation of luminescence properties of $CaAl_{4-x}Si_xO_{7-x}N_x$ solid solutions and the synthesis of new compounds in Ca-Si-O-N and

Sr-Si-O-N systems at chapters 2, 3, and 4, respectively.

Chapter 2: Synthesis of a novel bluish-green emitting oxynitride $Ca_3Al_8Si_4O_{17}N_4$:Eu^{2+} phosphor in a $CaAl_{4-x}Si_xO_{7-x}N_x$ solid solution system

As mentioned in chapter 1, development of new oxynitride phosphors is an important research topic to enrich the phosphor library with various excitation and emission properties. Sun et al. have reported solid solutions between $CaAl_4O_7$ and $Ca_3Al_8Si_4O_{17}N_4$. Investigation of the luminescence properties of Eu^{2+}-activated these solid solutions is interesting for the development of new phosphors from two points of view, suitable sites for substitution of Eu^{2+} ions and containing of nitrogen. The solid solutions doped with Eu^{2+} ions were synthesized by a conventional solid state reaction method using either Si_3N_4 or AlN as a nitrogen source and an amorphous metal complex method with ammonia nitridation. The samples synthesized by these methods are represented as SSR-Si_3N_4, SSR-AlN, and AMC-NH_3, respectively.

Fig. 1 shows XRD patterns of $Ca_3Al_8Si_4O_{17}N_4$:Eu^{2+} synthesized by various methods. The AMC-NH_3 sample contained $Ca_2Al_2SiO_7$ and Al_2O_3 impurities, resulted in the low phase purity of $Ca_3Al_8Si_4O_{17}N_4$. The SSR-Si_3N_4 sample contained the target material as a main phase, however, impurities of $Ca_2Al_2SiO_7$ and Al_2O_3 still existed. In case of the SSR-AlN sample, almost the pure phase of target $Ca_3Al_8Si_4O_{17}N_4$ phase was obtained although the trace amount of AlN remained. This result indicates that AlN is a preferable nitrogen source rather than Si_3N_4 since the replacement of Al-O bonds in Al_2O_3 with Al-N bonds was a quite though reaction in comparison with the replacement of Si-O bonds in SiO_2 with Si-N bonds.

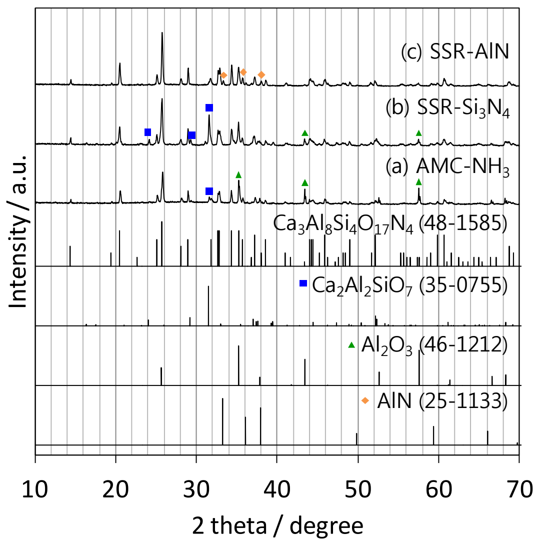

Fig. 1 XRD patterns of $Ca_3Al_8Si_4O_{17}N_4$:Eu^{2+} synthesized by various methods.

Fig. 2 shows excitation and emission spectra of $Ca_3Al_8Si_4O_{17}N_4$:Eu^{2+} synthesized by various methods. All of Eu^{2+}-activated $Ca_3Al_8Si_4O_{17}N_4$ exhibited bluish-green emission with a peak at 480 nm by excitation at 250–450 nm. The SSR-Si_3N_4 sample showed the lowest emission

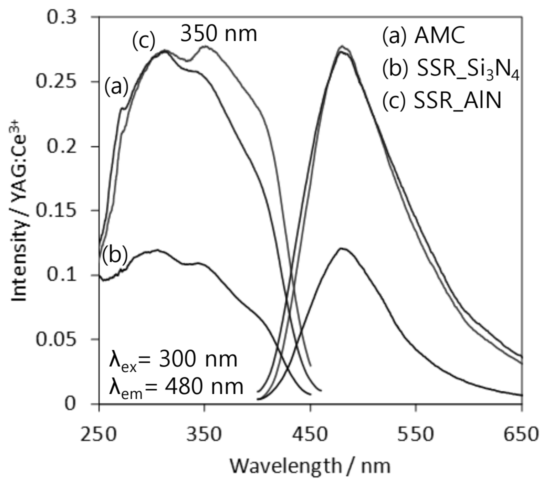

Fig. 2 Excitation and emission spectra of $Ca_3Al_8Si_4O_{17}N_4$:Eu^{2+} synthesized by various methods.

intensity among the samples because the present of impurity phases. The AMC-NH_3 sample exhibited the emission intensity comparable to the SSR-AlN sample despite of the lower phase purity. The homogeneous distribution of Eu^{2+} activators in the AMC-NH_3 sample would contribute to the relative strong intensity of luminescence.

As mentioned above, the $Ca_3Al_8Si_4O_{17}N_4$:Eu^{2+} phosphor has been developed as a novel bluish-green emitting phosphor excitable by NUV LEDs in the present study.

Chapter 3: Development of novel Eu^{2+}-activated phosphors in Ca-Si-O-N system by the synthesis of new compounds

The number of reports on phosphors in the Ca-Si-O-N system is quite few among oxynitride phosphors composed of alkaline earth metals and silicon. In this chapter, therefore, the author attempted development of novel phosphors in the CaO-SiO_2-Si_3N_4 system. From a CaO-SiO_2-Si_3N_4 phase diagram illustrated in Fig. 3, some compounds have been already reported as Eu^{2+}-activated phosphors. However, it is expected that new oxynitride compounds exist in this system.

In the present study, the author focused her interest on the grey-colored region in Fig. 3. Fourteen compounds with artificial compositions in this region were chosen. Synthesis of 14 samples was attempted by the AMC-NH_3 method. As results, the author found the presence of an unknown phase in the sample obtained by nitridation of an oxide precursor with a composition of Ca: Si = 1: 1. To investigate the unknown phase on compound more precisely, the sample with a composition of CaO: SiO_2: Si_3N_4 = 4: 2.5: 0.5 was synthesized by various methods including AMC-NH_3, SSR and a flux method using NH_4Cl as a flux reagent.

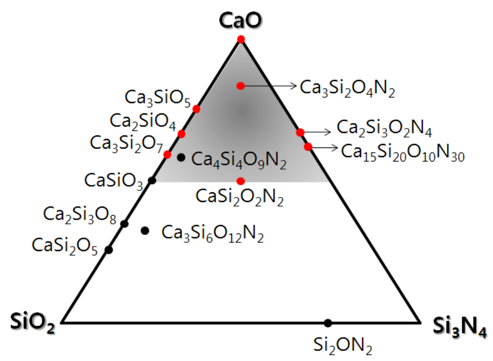

Fig. 3 Phase diagram of CaO-SiO_2-Si_3N_4 system.

From XRD patterns shown in Fig. 4, presence of three kinds of unknown phases was suggested. All samples were the mixture of three unknown phases although the ratio was different for each sample. The AMC-NH_3 sample exhibited emission at 559 nm with wide excitation range from 250 to 450 nm whereas the samples synthesized by

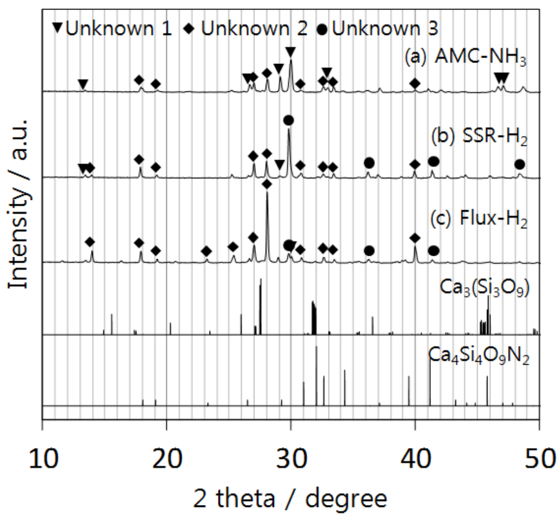

Fig. 4 XRD patterns of the samples synthesized from the mixture of CaO: SiO_2: Si_3N_4 = 4: 2.5: 0.5 by various methods.

the SSR and flux methods showed emission maxima at 515 nm and 496 nm, respectively, under the excitation at 250–420 nm. The observation of three kinds of emission also supports the presence of three new phosphors.

Thus, it has been found that three new compounds in the Ca-Si-O-N system were crystallized by different synthesis methods.

Chapter 4: Development of a novel Eu^{2+}-activated phosphor in a Sr-Si-O-N system by the synthesis of a new compound

As described in Chapter 3, the synthesis of new compounds in the Ca-Si-O-N system has been achieved. That result encouraged the author to synthesize new compounds in other systems. In Chapter 4, the author focused her interest on a Sr-Si-O-N system as a next candidate group. Synthesis of a number of compounds with various artificial compositions in the Sr-Si-O-N system was attempted as well as the Ca-Si-O-N system described in the previous chapter. Although most of the samples were obtained as the mixture of known phases such as $SrSiO_3$, Sr_2SiO_4 and $SrSi_2O_2N_2$, the formation of unknown phase was supported from the XRD analysis. Interestingly, the sample containing the unknown phase exhibited red emission even under the excitation by blue light. The results suggested the presence of a new red emitting phosphor in the Sr-Si-O-N system.

Chapter 5: Conclusions

In this thesis, the author has achieved the development of new Eu^{2+}-activated oxynitride phosphors through the investigation of luminescence properties with Eu^{2+}-activation and synthesis of new compounds. A novel $Ca_3Al_8Si_4O_{17}N_4{:}Eu^{2+}$ phosphor is a bluish green emitting phosphor with a broad excitation band ranging from 250 to 450 nm. In the CaO-SiO_2-Si_3N_4 system, the presence of three new phases is suggested from the present results. Three new phases activated with Eu^{2+} show emission maxima at 559, 496 and 515 nm, respectively. In the SrO-SiO_2-Si_3N_4 system, the new compound with Eu^{2+} activation exhibits red emission. All of the new phosphors developed in this work are capable of excitation by NUV or blue LEDs. These excitation properties are favored for application to the white LEDs. Moreover, the red emission achieved by the new phosphor in the Sr-Si-O-N is interesting nature of the new phosphors developed in this work since an efficient red-emitting phosphor is required to achieve artificial warm-white light by white LEDs.