Luminescence properties of $\text{M}_2\text{Si}_5\text{N}_8:\text{Ce}^{3+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) mixed nitrides prepared by metal hydrides as starting materials

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Abstract. Mixed metal nitrides, $\text{M}_2\text{Si}_5\text{N}_8:\text{Ce}^{3+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$), were synthesized from $\text{M}_2\text{yCe}_x\text{Si}_5$ or an appropriate mixture of $\text{MSiH}_x$, $\text{Si}_3\text{N}_4$ and $\text{CeF}_3$, by a direct nitriding process in $\text{N}_2$ gas: $2 \text{MSiH}_x + \text{Si}_3\text{N}_4 + \text{CeF}_3 \rightarrow \text{M}_2\text{Si}_5\text{N}_8:\text{Ce}^{3+}$. Also, charge-compensated materials, $\text{M}_2\text{Al}_z\text{Si}_5-z\text{N}_8:\text{Ce}^{3+}$, were prepared (from an appropriate mixture of $\text{MSiH}_x$, $\text{MAlSiH}_x$, $\text{Si}_3\text{N}_4$ and $\text{CeF}_3$) and the luminescence properties were characterized. The resultant phosphors showed green emission suitable for LED illumination by optimizing the mixing ratio of metal elements.

1. Introduction

White LEDs have come to attract attention, because they are environment-friendly in several points, such as the durability, thrifty power consumption, non-use of mercury and so on. Green emission phosphors are very important for white LEDs as a light source, e.g., backlights and general solid illuminations, which need a high color rendering index since human eyes are more sensitive to green color than any other color. Conventional green phosphors such as oxides [1-4] and sulfides [5-7], however, have low thermal quenching temperature. Then sulfides are especially weak for moisture. Therefore, nitride phosphors have come to attract attention because of the wide emission spectra, the chemical stabilities and the high thermal quenching temperature due to their excellent thermal stability. The photoluminescence properties of the rare-earth ions result from lowering the gravity center of the 5d levels and decreasing the Stokes shift, because metal-nitrogen bonding has a high covalency and large crystal-field splitting effect on the luminescent centers (e.g., $\text{Eu}^{2+}$, $\text{Ce}^{3+}$) caused by the surrounding $\text{N}^-$ ions [8-18]. In synthesis of phosphors, direct nitridation is easier to operate and is effective to save productions cost than the conventional solid state reaction method. That’s because, almost metal nitrides, such as $\text{Ca}_3\text{N}_2$, $\text{EuN}$, $\text{CeN}$ and so on, which are used in conventional solid state reaction method are chemically unstable and expensive [19]. Lately, we found that $\text{Ca}_3\text{Si}_5\text{N}_8:\text{Eu}^{2+}$ red phosphors prepared from $\text{CaH}_2$ have stronger luminescence intensity than synthesized from $\text{Ca}_3\text{N}_2$ powder [20]. In this research, alloy hydride powders were adopted as reactive intermediates. The synthesis conditions were optimized and the photoluminescence properties were characterized.
2. Experimental

The following alloys, MSi, MAlSi and M$_2$yCe$_z$Al$_{5-z}$Si$_{5-z}$ (M is an alkaline earth metal: Ca, Sr or Ba) were prepared from M, Ce, Al and Si metals by arc melting in argon atmosphere. Alloy hydrides were derived from their respective alloys by heating under high pressure (3.0 MPa) of H$_2$ at 723 K. Subsequently, alloy or alloy hydride powders were well mixed with Si$_3$N$_4$ and CeF$_3$ as Ce$^{3+}$ ion source (the ratio was shown in Table 1) in the agate mortar and put into BN crucible. These raw material powders were adjusted to become stoichiometric amount. Total amount of Al and Si was adjusted to be 5. Then the mixtures were reacted with N$_2$ to synthesize M$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$ phosphors in a radio-frequency furnace filled with N$_2$ (0.15 MPa) using a ZrB$_2$ heater. The raw materials were heated in two stages: 1223 K for 3 h followed by 1723 K for 5 h. Finally, the phosphors were obtained after washing by 1N-HCl aqueous solution. The concentrations of activator Ce$^{3+}$ ion were adjusted to 2 at% of M in all samples. The properties were evaluated by XRD, spectrophotofluorometer, NO analyzer and SEM/EDX.

| Table 1. Mixing ratio for M$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$ synthesized from MSi, MAlSi, Si$_3$N$_4$ and CeF$_3$. |
|---------------------------------------------------------------|
| Al amount (z value) | MSi (M$i$SiH$_x$) | MAlSi (MAl$i$SiH$_y$) | Si$_3$N$_4$ | CeF$_3$ |
| z = 0 | 2 | 0 | 1 | 0.04 |
| z = 0.5 | 1.5 | 0.5 | 0.83 | 0.04 |
| z = 1 | 1 | 1 | 0.66 | 0.04 |
| z = 2 | 0 | 2 | 0.33 | 0.04 |

3. Results and discussion

A series of XRD profiles of obtained Ba$_{2-y}$Ce$_y$Al$_{5-z}$Si$_{5-z}$ (z = 0 to 2) and Ba$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$ (z = 0.5, 2) phosphors are shown in Figure 1. With an increasing amount of Al, the BaAlSi ratio to BaSi$_2$ increased. Additionally, the amount of AlN impurity also increased.

Figure 2 shows the typical excitation and emission spectra of Ba$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$ and commercially used YAG:Ce$^{3+}$ yellow phosphor for comparison. The Ce concentrations of synthesized phosphors were 2 at% of Ba. The emission spectra of these phosphors show an intense broad emission band ranging from 450 to 650 nm with a peak around 510 nm. The emission properties of the phosphors synthesized from M$_2$yCe$_z$Al$_{5-z}$Si$_{5-z}$ (M = Sr, Ba) were low. Also in the case of hydride powders, the emission properties were low. This is because of the low crystallinity of the synthesized phosphors due to the difficulty of direct nitridation. So, the inadequate nitridation was caused by the imbalance of the electro charge balance from Ce$^{3+}$ ion.

Figure 3 (a) - (c) represent the typical excitation and emission spectra of Sr$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$ prepared from an appropriate mixture of MSi, MAlSi, Si$_3$N$_4$, CeF$_3$ and commercially used Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$, YAG:Ce$^{3+}$, yellow phosphor for comparison. In the case of Ca$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$, emission intensities decreased and peak top positions shifted to the longer wavelength side with increasing Al amount. On the other hand, emission properties of Sr$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$ and Ba$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$ have a different tendency from Ca$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$. The PL properties were improved by adding Al. To add Al, Si was replaced by Al and expansion of the lattice was caused. The highest emission intensities were observed when the Al amount was 0.5. This was because of the difference in crystal structures: Ca$_2$Si$_5$N$_8$ is monoclinic, whereas Sr$_2$Si$_5$N$_8$ and Ba$_2$Si$_5$N$_8$ are orthorhombic [21, 22]. The structures of Sr$_2$Si$_5$N$_8$ and Ba$_2$Si$_5$N$_8$ had larger airspaces than that of Ca$_2$Si$_5$N$_8$, so there is little distortion of the lattice by Al addition. Figure 3 (d) shows the PL properties of Sr$_2$Al$_{5-z}$Si$_{5-z}$N$_8$:Ce$^{3+}$ (z = 0, 0.5) composed from MSiH$_x$, MAl$i$SiH$_y$, Si$_3$N$_4$ and CeF$_3$. The Ce concentrations were also 2 at% of Sr. The highest emission intensity (74% / YAG:Ce$^{3+}$) was observed when the Al amount was 0.5.
These improvements of properties are because the size of powder particles became smaller by hydrogenation so that the reactivity of powders could increase. The SEM images of Sr-Al-Si alloy and Sr-Al-Si hydride powder are shown in Figure 4. Clearly, the sizes of alloys were decreased by hydridation.

From nitrogen and oxygen analysis, to adding Al caused an increase in the oxygen content of the phosphors. In addition, by increasing the Al amount, the nitrogen number changed from 8 to 7. These anion contents were lower than the stoichiometric amount. Therefore, a lattice defect existed and this also affected the photoluminescence properties.

4. Conclusions

$\text{M}_2\text{Si}_5\text{N}_8;\text{Ce}^{3+}$ (M = Ca, Sr, Ba) phosphors were synthesized from $\text{M}_{2-y}\text{Ce}_y\text{Al}_z\text{Si}_{5-z}$ or an appropriate mixture of $\text{MSiH}_x$, $\text{Si}_x\text{N}_4$ and $\text{CeF}_3$ by direct nitridation method. These phosphors can be effectively excited by violet-blue light around 400-430 nm and emit green light ranging from 450 to 650 nm with a peak around 489-528 nm. The properties of phosphor prepared from appropriate mixture of MSi, MAiSi, Si$_x$N$_4$ and CeF$_3$ were superior to that from $\text{M}_{2-y}\text{Ce}_y\text{Al}_z\text{Si}_{5-z}$ alloy. The activator, Ce$^{3+}$, condition was optimized by controlling the aluminum amount. The highest emission intensity was observed when the sample was prepared from alloy with Al = 0.5, except for $\text{Ca}_2\text{Al}_z\text{Si}_{5-z}\text{N}_8;\text{Ce}^{3+}$. In the $\text{Ca}_2\text{Al}_z\text{Si}_{5-z}\text{N}_8;\text{Ce}^{3+}$ case, the sample with Al = 0 had strong emission intensity. Then the phosphor...
synthesized from alloy hydride indicated strong emission intensity in \( \text{Sr}_2(\text{Al, Si})_5\text{N}_8: \text{Ce}^{3+} \) with \( \text{Al} = 0, 0.5 \). From the result of photoluminescence properties, it is demonstrated that the alloy hydride powders can promote homogeneous nitridation.

**Figure 3.** Photoluminescence spectra of (a) \( \text{Ca}_2\text{Al}_z\text{Si}_{5-z}\text{N}_8: \text{Ce}^{3+} \) from \( \text{CaSi, CaAlSi, Si}_3\text{N}_4 \) and \( \text{CeF}_3 \), (b) \( \text{Sr}_2\text{Al}_z\text{Si}_{5-z}\text{N}_8: \text{Ce}^{3+} \) from \( \text{SrSi, SrAlSi, Si}_3\text{N}_4 \) and \( \text{CeF}_3 \), (c) \( \text{Ba}_2\text{Al}_z\text{Si}_{5-z}\text{N}_8: \text{Ce}^{3+} \) from \( \text{BaSi, BaAlSi, Si}_3\text{N}_4 \) and \( \text{CeF}_3 \), and (d) \( \text{Sr}_2\text{Al}_z\text{Si}_{5-z}\text{N}_8: \text{Ce}^{3+} \) from \( \text{SrSiH}_x, \text{SrAlSiH}_x, \text{Si}_3\text{N}_4 \) and \( \text{CeF}_3 \) from \( \text{SrSiH}_x, \text{SrAlSiH}_x, \text{Si}_3\text{N}_4 \) and \( \text{CeF}_3 \) from \( \text{SrSiH}_x, \text{SrAlSiH}_x, \text{Si}_3\text{N}_4 \) and \( \text{CeF}_3 \) for comparison. The excitation and monitoring wavelengths was 400-430 and 489-528 nm for obtained phosphors and 460 and 545 nm for \( \text{YAG:Ce}^{3+} \), respectively.

**Figure 4.** SEM images of (a) \( \text{SrSi} \), (b) \( \text{SrSiH}_x \), (c) \( \text{SrAlSi} \) and (d) \( \text{SrAlSiH}_x \).
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