

Improved luminescence properties of $\text{Na}_2\text{TiSiO}_5$ phosphor by the Ge^{4+} doping in the crystal lattice

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Rare earth free white emitting $\text{Na}_2\text{TiSi}_{1-x}\text{Ge}_x\text{O}_5$ phosphors were synthesized by a conventional solid-state reaction method, and the photoluminescence properties were characterized. The phosphors obtained in the present study showed broad bluish-white emission with a peak at 485 nm due to the charge transfer transition between O^{2-} and Ti^{4+} and the emission peak intensity was effectively enhanced by the Ge^{4+} doping in the $\text{Na}_2\text{TiSiO}_5$ crystal lattice. The emission peak intensity of $\text{Na}_2\text{TiSi}_{0.5}\text{Ge}_{0.5}\text{O}_5$ was 1.35 times higher than that of $\text{Na}_2\text{TiSiO}_5$ and the CIE chromaticity coordinate values for the phosphor were $x = 0.29$ and $y = 0.38$.

Keywords: White emission phosphor, Rare earth free, $\text{Na}_2\text{TiSiO}_5$

Introduction

Recent year, transition metal ions have been widely investigated as a luminescence ion an alternative to the rare earth ions [1-5], because rare earth elements are expensive compared with another metal and the price of rare earth ions go up every year. In particular, polyhedral oxides consisting of transition metal ions without electron in the outermost d orbital such as Ti^{4+} , V^{5+} , and W^{6+} have attracted considerable attention as activator in rare earth free phosphors and these transition metal ions doped phosphors can show good luminescence efficiency [6-12]. Among them, Ti^{4+} ions contained materials have extensively investigated and used in tunable solid-state laser materials [13], nonlinear optical materials [14], phosphors [15-18], and long-lasting phosphorescence materials [19], due to their optical properties and excellent chemical and thermal stability. Ti^{4+} ions contained materials are reported that these materials exhibit two different type luminescence under UV excitation such as blue emission corresponding to the charge transfer transition from 2p orbits of O^{2-} to 3d orbit of Ti^{4+} , i.e., $\text{O}^{2-}\text{-Ti}^{4+} \rightarrow \text{O}^-\text{-Ti}^{3+}$, and yellow emission due to the oxygen

defects in titanium octahedron [16, 17, 20]. In addition, the yellow emission in the Ti^{4+} contained materials is observed only at low temperature. According to the studies on luminescence properties of Ti^{4+} contained materials, however, some materials show the yellow- or white-emission at room temperature under UV excitation and these materials consist TiO_5 square pyramids in the crystal structure. It is well known that the luminescence corresponding to the charge transfer transition from 2p orbits of O^{2-} to 3d orbit of Ti^{4+} in the TiO_5 square pyramids has larger Stokes shift than that for the TiO_6 octahedra contain materials [9, 11, 21], and these materials show white-emission with high emission color purity.

Considering this, we have focused on $\text{Na}_2\text{TiSiO}_5$ as Ti^{4+} contained white emission phosphor, because the $\text{Na}_2\text{TiSiO}_5$ consist TiO_5 square pyramids in the crystal structure and TiO_5 pyramidal shared corners with the SiO_4 tetrahedral, which is separated by Na^+ ions in the direction to the c axis (Fig. 1) [11, 22]. In addition, $\text{Na}_2\text{TiSiO}_5$ has high chemical and thermal stability, which is advantageous for obtaining phosphor particles of high crystallinity. It is previously reported that $\text{Na}_2\text{TiSiO}_5$ exhibits the bluish-white emission at low temperature (4.2 k). In this study, in order to further enhance the emission efficiency of the $\text{Na}_2\text{TiSiO}_5$ phosphor, Si^{4+} ions in the $\text{Na}_2\text{TiSiO}_5$ crystal lattice were partially substituted with Ge^{4+} , because $\text{Na}_2\text{TiGeO}_5$ has similar crystal structure to that of $\text{Na}_2\text{TiSiO}_5$, which indicates that Ge^{4+} can be substituted in the $\text{Na}_2\text{TiSiO}_5$

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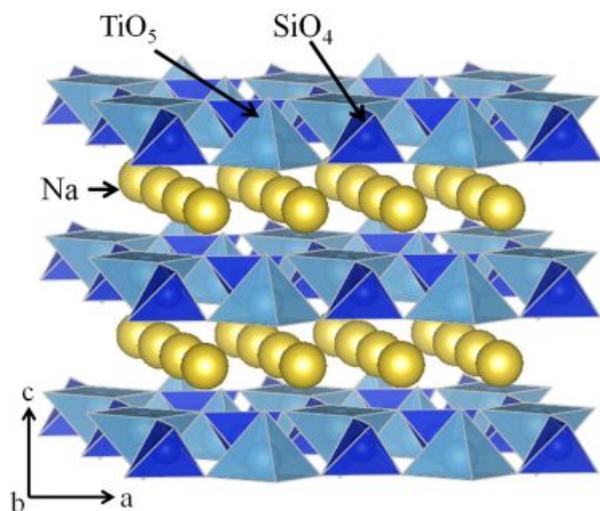


Fig. 1. Crystal structure of $\text{Na}_2\text{TiSiO}_5$.

lattice as solid solution form.

Experimental

Na_2CO_3 , TiO_2 , SiO_2 , and GeO_2 were mixed in a stoichiometric ratio using a mortar with acetone for obtaining a homogeneous chemical mixture, in which the Ge^{4+} content was varied from 0 to 100 mol%. The homogeneous mixture was pressed into pellets and heated at 870°C for 12 h in air, and then the samples were reground in a mortar.

The crystal structure of the samples was identified through powder X-ray diffraction (XRD; Mac Science Ltd. MX-Labo) analysis. The emission and excitation spectra were measured at room temperature with a spectrofluorometer (Jasco Corp. FP-6500/6600), where the emission spectrum was obtained for excitation at 254 nm and excitation spectrum was obtained for emission at 500 nm. The Commission International de l'Eclairage (CIE) chromaticity coordinate data for the samples were measured at room temperature with a luminescence colorimeter (Hamamatsu C7473-36 PMA-11).

Results and Discussion

X-ray powder diffraction (XRD) patterns of the $\text{Na}_2\text{TiSi}_{1-x}\text{Ge}_x\text{O}_5$ ($0 \leq x \leq 1.0$) phosphors are shown in Fig. 2. The standard XRD patterns of $\text{Na}_2\text{TiSiO}_5$ (#166623) and $\text{Na}_2\text{TiGeO}_5$ (#20129) from the inorganic crystal structure database (ICSD) are also shown in Fig. 2 as a reference. The XRD patterns of the samples with $x \leq 0.5$ were identical to a single phase of highly crystalline orthorhombic $\text{Na}_2\text{TiSiO}_5$ structure. On the other hand, the crystal structure of the samples transferred from $\text{Na}_2\text{TiSiO}_5$ to $\text{Na}_2\text{TiGeO}_5$ with increase in the Ge^{4+} content beyond $x = 0.5$ and these samples obtained in a single phase of $\text{Na}_2\text{TiGeO}_5$. However, there are no

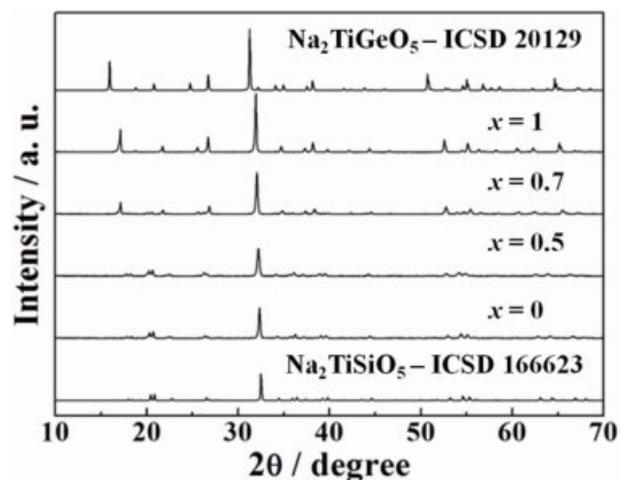


Fig. 2. XRD patterns of the $\text{Na}_2\text{TiSi}_{1-x}\text{Ge}_x\text{O}_5$ ($0 \leq x \leq 1.0$) phosphors.

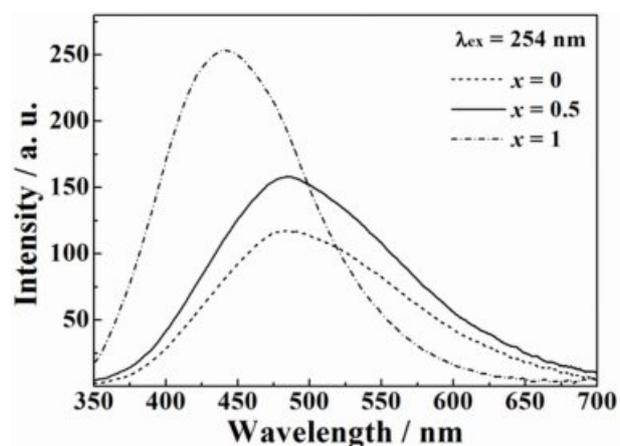


Fig. 3. Emission spectra of the $\text{Na}_2\text{TiSi}_{1-x}\text{Ge}_x\text{O}_5$ ($0 \leq x \leq 1.0$) phosphors under excitation at 254 nm.

diffraction peak corresponding to any impurities in all XRD patterns, which is attributed to the same crystal structure of both $\text{Na}_2\text{TiSiO}_5$ and $\text{Na}_2\text{TiGeO}_5$ [11, 22]. In addition, a peak shift to a lower diffraction angle was observed with increase in the Ge^{4+} content, because Si^{4+} (ionic radius: 0.026 nm for 4 coordination [23]) sites in the $\text{Na}_2\text{TiSiO}_5$ lattice is substituted with the larger Ge^{4+} (ionic radius: 0.026 nm for 4 coordination [23]) to form solid solutions.

Fig. 3 shows the emission spectra of the $\text{Na}_2\text{TiSi}_{1-x}\text{Ge}_x\text{O}_5$ ($0 \leq x \leq 1.0$) phosphors with excitation at 254 nm. The emission spectra of the samples with $x \leq 0.5$ exhibit a broad bluish-white emission band with a peak at 490 nm due to the charge transfer (CT) transition from 2p orbits of O^{2-} to 3d orbit of Ti^{4+} , i.e., $\text{O}^{2-}\text{-Ti}^{4+} \rightarrow \text{O}^-\text{-Ti}^{3+}$ in the isolated TiO_5 polyhedron in the $\text{Na}_2\text{TiSiO}_5$ lattices [16, 17, 20]. The emission intensity of $\text{Na}_2\text{TiSiO}_5$ was effectively enhanced by the Ge^{4+} doping into the crystal lattice, and the emission intensity of $\text{Na}_2\text{TiSi}_{0.5}\text{Ge}_{0.5}\text{O}_5$ was 1.35 times higher than that of $\text{Na}_2\text{TiSiO}_5$. In the

Table 1. Bond lengths between Ti^{4+} and O^{2-} in the isolated TiO_5 pyramid in $\text{Na}_2\text{TiSiO}_5$ and $\text{Na}_2\text{TiGeO}_5$.

	$\text{Na}_2\text{TiSiO}_5$	$\text{Na}_2\text{TiGeO}_5$
Ti – O1	0.1656 nm	0.1851 nm
Ti – O2	0.1976 nm	0.2020 nm

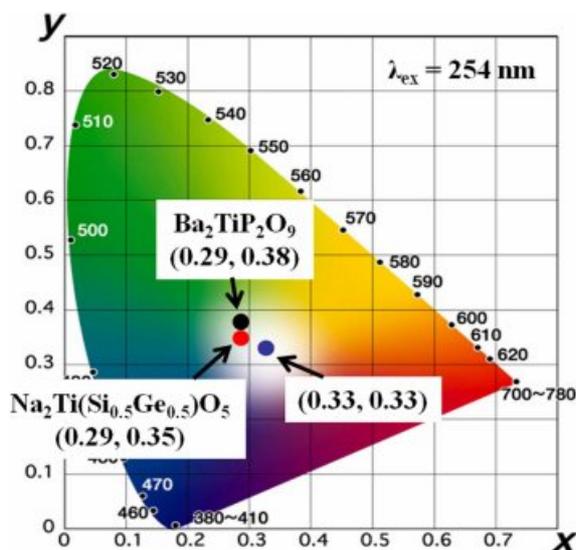


Fig. 4. CIE chromaticity diagram for the $\text{Na}_2\text{TiSi}_{0.5}\text{Ge}_{0.5}\text{O}_5$ and a conventional $\text{Ba}_2\text{TiP}_2\text{O}_9$ phosphors.

samples with $x > 0.5$, however, the emission band shifted to shorter wavelength (higher energy) side with increase in the Ge^{4+} content, which is considered to be due to the phase transition from $\text{Na}_2\text{TiSiO}_5$ to $\text{Na}_2\text{TiGeO}_5$. The emission peak wavelength corresponding to charge-transfer (CT) transition strongly depends on the excitation energy for the electron transfer between O^{2-} and Ti^{4+} in the crystal structure. Since the electronegativity of Ge^{4+} (2.01 [24]) is higher than that of Si^{4+} (1.90 [24]), the electronic attractive force between O^{2-} and Ti^{4+} in the $\text{Na}_2\text{TiGeO}_5$ is smaller than that in the $\text{Na}_2\text{TiSiO}_5$, which leads to shift the emission band to shorter wavelength (high energy) side due to increase the excitation energy for the electron transfer from O^{2-} to Ti^{4+} in the crystal structure. In addition, the $\text{Ti}^{4+}\text{-O}^{2-}$ bond length in the $\text{Na}_2\text{TiGeO}_5$ lattice is larger than that in $\text{Na}_2\text{TiSiO}_5$ lattice (Table 1), which also leads to shift the emission band to shorter wavelength side.

Fig. 4 presents the Commission International de l'Eclairage (CIE) chromaticity diagram for the $\text{Na}_2\text{TiSi}_{0.5}\text{Ge}_{0.5}\text{O}_5$ phosphor. Results for a conventional Ti^{4+} -contained white emitting $\text{Ba}_2\text{TiP}_2\text{O}_9$ phosphor is also included for comparison. The CIE chromaticity coordinate values of the $\text{Na}_2\text{TiSi}_{0.5}\text{Ge}_{0.5}\text{O}_5$ phosphor were $x = 0.29$ and $y = 0.35$ under excitation at 254 nm UV light, which is close to the standard white chromaticity ($x = 0.33$, $y = 0.33$) for the NTSC system. In addition, the x and y values of the $\text{Na}_2\text{TiSi}_{0.5}\text{Ge}_{0.5}\text{O}_5$

phosphor are more close to white light compared with a conventional Ti^{4+} contained $\text{Ba}_2\text{TiP}_2\text{O}_9$ phosphor ($x = 0.29$, $y = 0.38$).

Conclusion

Rare earth free white emitting $\text{Na}_2\text{TiSi}_{1-x}\text{Ge}_x\text{O}_5$ phosphors were in a single phase form synthesized by the conventional solid-state reaction method. These phosphors exhibited a broad bluish-white emission centered on 490 nm under excitation at 254 nm and the photoluminescence emission intensity was successfully enhanced by the Ge^{4+} doped into the Si^{4+} site in the $\text{Na}_2\text{TiSiO}_5$ lattice. The emission intensity of $\text{Na}_2\text{TiSi}_{0.5}\text{Ge}_{0.5}\text{O}_5$ was 1.35 times higher than that of $\text{Na}_2\text{TiSiO}_5$ and the CIE chromaticity coordinate values for the phosphor were $x = 0.29$ and $y = 0.35$ under excitation at 254 nm UV light.

Acknowledgements

This work was supported by a project from NEDO, New Energy and Industrial Technology Development Organization (Rare Metal Substitute Materials Development Project Development of Technology for Reducing Tb and Eu Usage in Phosphors for Fluorescent Lamp by High-speed Material Synthesis and Evaluation).

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