HYDROTHERMAL SYNTHESIS OF NOVEL CERIUM(III) AND MANGANESE(II) ACTIVATED CALCIUM HYDROGENPHOSPHATE ANHYDRATE PHOSPHORS EMITTING BY BLACK LIGHT IRRADIATION

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Abstract: The present work was investigated about hydrothermal synthesis of Ce^{3+} and Mn^{2+} activated calcium hydrogenphosphate anhydrate ($\text{CaHPO}_4\cdot\text{Ce}^{3+},\text{Mn}^{2+}$) phosphors. $\text{CaHPO}_4\cdot\text{Ce}^{3+},\text{Mn}^{2+}$ was a novel unprecedented phosphor, which was synthesized by hydrothermal treatment of dipping amorphous calcium phosphate (ACP) in formic acid aqueous solution. The emission intensity of the $\text{CaHPO}_4\cdot\text{Ce}^{3+},\text{Mn}^{2+}$ phosphor was affected remarkably by synthetic conditions such as Ce/Ca and Mn/Ca atomic ratio, concentration of formic acid, temperature and aging time. The optimum conditions for the synthesis of $\text{CaHPO}_4\cdot\text{Ce}^{3+},\text{Mn}^{2+}$ phosphor were follows; Ce/Ca atomic ratio, 0.01; Mn/Ca atomic ratio, 0.02; concentration of formic acid, $1.0\text{ mol}\cdot\text{dm}^{-3}$; hydrothermal temperature, 170°C ; retention time, 0 h.

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INTRODUCTION

Black light is a lamp which emit near-UV (ultraviolet) of wavelengths at 300-400nm, and is widely used for traffic safety measures, illuminations in cities, indoor interiors, and so on. So a phosphor which is emitted by black light irradiation has attracted attention. On the other hand, calcium phosphate salt host as phosphor are known $\text{Sb}^{3+},\text{Mn}^{2+}$ activated apatite phosphor¹⁾, $\text{Ce}^{3+},\text{Mn}^{2+}$ activated apatite phosphor²⁾ with emitting by the UV of 254nm. And there are also known $\text{Ce}^{3+},\text{Mn}^{2+}$ activated tricalcium phosphate³⁾, which is emitting by the black light irradiation with around 360nm. Generally, a phosphor is prepared by sintering process with high temperature above 1000°C for several time⁴⁾. Because of this, there are no reports on the preparation of phosphor of unstable calcium hydrogenphosphate anhydrate (CaHPO_4 , DCPA) host, since it decomposed under the high temperature.

The authors have been conducting a series of studies on synthesis of amorphous calcium phosphate ($\text{Ca}_3(\text{PO}_4)_2\cdot n\text{H}_2\text{O}$, ACP) and its characteristics⁵⁾⁻²⁴⁾. The ACP as a precursor of calcium phosphate salts is useful as a starting material of functional materials. And, it is expected to decrease with the produced temperature of phosphor by using ACP as starting materials^{17),24)}.

DCPA is well known as a starting material of an apatite phosphor for general lamp phosphor, and it is easily obtained to dehydrate calcium hydrogenphosphate dihydrate ($\text{CaHPO}_4\cdot 2\text{H}_2\text{O}$, DCPD) by

heating in humid air process at $135^\circ\text{C}^{25)}$. On the other hand, the authors have already reported that ACP crystallized into DCPA by hydrothermal treatment in formic acid solution.

Therefore, it is suggested that preparation of a novel unprecedented phosphor is possible with DCPA host, by hydrothermal treatment of active ACP and $\text{Ce}^{3+},\text{Mn}^{2+}$ activation mixture in formic acid solution.

The present work was investigated about hydrothermal synthetic condition of novel cerium(III) and manganese(II) activated DCPA phosphor from active ACP, and its fluorescent property.

MATERIALS AND METHODS

MATERIALS

The ACP (Ca/P atomic ratio of 1.50) as a starting material was synthesized by mixing $0.17\text{ mol}\cdot\text{dm}^{-3}$ calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) solution with $0.10\text{ mol}\cdot\text{dm}^{-3}$ diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$) solution. The synthesized ACP gel was separated by filtering, it was washed with cold aqueous ammonia and acetone. After, the amorphous tricalcium phosphate anhydrate (amorphous- $\text{Ca}_3(\text{PO}_4)_2$, ATCP) as raw material of phosphor was obtained by dehydrating ACP at 300°C . Furthermore, all reagent were used with KANTO KAGAKU Co.,Ltd.

EXPERIMENTAL METHOD

Toyama T, Hashimoto M, Kojima T, Yasue T

A mixture ATCP, cerium(III) acetate monohydrate ($\text{Ce}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$) and manganese(II) acetate tetrahydrate ($\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) was adjusted to initial Ce/Ca, Mn/Ca atomic ratio of 0-0.08. The mixture was dipped in formic acid solution on liquid/solid weight ratio 48 in Teflon test tube. Concentration of formic acid solution was $0-2.0 \text{ mol} \cdot \text{dm}^{-3}$. After having been stirred for 5 minute with ultrasonic wave dispersion treatment, the suspension was heat at $120-200^\circ\text{C}$ for 0-3h in an autoclave. Finally, the phosphor was separated from suspension after the reaction and washed with pure water. The experiments were conducted in the autoclave of 120 cm^3 volume (TVS-N2 (SUS316), Taiatsu Co.,Ltd.) and packing rate was 50 vol%. This autoclave inside has performed Teflon coating processing and without stirring system.

The phosphor was characterized by means of X-ray powder diffractometry, observation of scanning electron microscopic (SEM-300, Topcon Co.,Ltd.) and chemical analysis. The fluorescent property was measurement of fluorescent spectrometer (RF-1500, Shimadzu Co., Ltd.). Also, the measurement of emission spectrum of phosphor was used by filter (UV35) which shut out excitation light at a wavelength below 350 nm.

Furthermore, the emission intensity of 100% was a value with 442 nm emission intensity of commercial calcium tungstate (Nakarai Tesque Co.,Ltd.) by the UV irradiated at 254 nm.

RESULTS AND DISCUSSION

PREPARATION CONDITION OF CERIUM(III) ACTIVATED DCPA PHOSPHOR

As a previously report, ACP crystallized into DCPA in formic acid under hydrothermal conditions²¹⁾. Figure 1 showed the X-ray diffraction pattern of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor with different Ce/Ca atomic ratio. In this study, ACP crystallized into DCPA single phase with Ce^{3+} addition until the atomic ratio of 0.01. However, cerium phosphate (CePO_4) was newly observed at the atomic ratio above 0.01, and the intensity of X-ray peak ($2\theta=28.7, 33.5^\circ$) of CePO_4 was increased with an increase in the Ce/Ca atomic ratio. Also, because of triclinic system, the lattice constant of DCPA was difficult to calculate. Thereupon, the examination was made from a changing of spacing whether the activator is incorporated or not. The spacing of (112) face of DCPA was increased with an increase in the Ce/Ca atomic ratio range from 0 to 0.01. Also, the ionic radius of Ce^{3+} (0.107 nm) is larger than that of Ca^{2+} (0.099 nm). The results indicate that additive Ce^{3+} was incorporated to Ca^{2+} with DCPA crystal structure.

Figure 2 showed the excitation and emission spectrum of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor. Under conditions of black light irradiation at 300-350 nm, the Ce^{3+} activated apatite or tricalcium phosphate phosphor were known as emitting in near-UV at

370-390 nm which is beyond the range of visible radiation^{1),2)}. The excitation spectrum was observed that $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor was irradiated at the near-UV of 370 nm. Also, the phosphor was emitted by black light irradiation at 320 nm. The emission peak wavelength of phosphor was 370 nm. This

Fig.1 X-ray diffraction pattern of phosphor with different Ce/Ca atomic ratio.

Temp.: 170°C , Retention time: 0 h, Concentration of formic acid: $1.0 \text{ mol} \cdot \text{dm}^{-3}$, Ce/Ca atomic ratio, (a): 0, (b): 0.01, (c): 0.02, (d): 0.04
○: CaHPO_4 , ▲: CePO_4

Fig. 2 Excitation and emission spectrum of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor.

Temp.: 170°C , Retention time: 0 h, Concentration of formic acid: $1.0 \text{ mol} \cdot \text{dm}^{-3}$, Ce/Ca atomic ratio: 0.01

Fig. 3 Effect of Ce/Ca atomic ratio on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor.

Temp.: 170°C , Retention time: 0 h, Concentration of formic acid: $1.0 \text{ mol} \cdot \text{dm}^{-3}$, Excitation wavelength: 320 nm, Measuring wavelength: 370 nm

emission spectrum was similar to the spectrum of other phosphors with emitting near-UV of 370 nm.

Figure 3 showed the effect of Ce/Ca atomic ratio on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor. The emission was not observed the phosphor without Ce^{3+} activated. However, the emission intensity was increased with an increase in the atomic ratio. Especially, the emission intensity of the phosphor with Ce/Ca atomic ratio of 0.01 was showed the maximum 90%. However, the emission intensity was rapidly decreased at Ce/Ca atomic ratio above 0.01. This reason is considered that CePO_4 which is impurity mixed into phosphor, and concentration quenching.

Figure 4 showed the effect of hydrothermal temperature on synthesis of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor. When temperature was lower at 120°C (a), low crystalline DCPA was observed. Also, as temperature was higher, crystalline of DCPA was improved(b), especially X-ray intensity of DCPA was the greatest at 170°C (c). However, as temperature was increased further temperature, hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp) observed.

Therefore, Figure 5 showed the effect of hydrothermal temperature on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor. When the X-ray intensity of DCPA was greatest at 170°C , the emission intensity was increased with an increase in the temperature. However, the intensity of phosphor was rapidly decreased, when HAp was appeared above 180°C .

Furthermore, Figure 6 showed scanning electron microscopic photographs of synthesized phosphor. The shape of synthesis phosphor was aggregation of small plate-like about $1 \mu\text{m}$ crystals at 120°C (a). The particle size was increased with an increase in the

Fig.4 X-ray diffraction pattern of phosphor in comparison to hydrothermal temperature.

Retention time: 0 h, Concentration of formic acid: $1.0 \text{ mol} \cdot \text{dm}^{-3}$, Ce/Ca atomic ratio: 0.01, Temp.($^\circ\text{C}$), (a): 120, (b): 150, (c): 170, (d): 200
○: CaHPO_4 , ■: HAp

Fig.5 Effect of hydrothermal temperature on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor.

Retention time: 0 h, Concentration of formic acid: $1.0 \text{ mol} \cdot \text{dm}^{-3}$, Ce/Ca atomic ratio: 0.01, Excitation wavelength: 320 nm, Measuring wavelength: 370 nm

temperature(b). When the emission intensity of phosphor was the greatest at 170°C (c), the shape was plate-like about $20\text{--}30 \mu\text{m}$ in length, $3 \mu\text{m}$ in thick. Also, the shape of this $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor was superior to high spreadability. But above 200°C (d), HAp was observed with needle-like crystal having $10\text{--}20 \mu\text{m}$ in size(d).

Fig.6 Scanning electron microscopic photograph of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor in comparison to hydrothermal temperature.

Retention time: 0 h, Concentration of formic acid: $1.0 \text{ mol} \cdot \text{dm}^{-3}$, Ce/Ca atomic ratio: 0.01, Temp.(°C), (a): 120, (b): 150, (c): 170, (d): 200

Fig.7 Effect of concentration of formic acid on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor.

Temp.: 170°C , Retention time: 0 h, Ce/Ca atomic ratio: 0.01, Excitation wavelength: 320 nm, Measuring wave-length: 370 nm.

Fig.8 Effect of hydrothermal time on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor.

Temp.: 170°C , Concentration of formic acid: $1.0 \text{ mol} \cdot \text{dm}^{-3}$, Ce/Ca atomic ratio: 0.01, Excitation wavelength: 320 nm, Measuring wavelength: 570 nm.

Figure 7 showed the effect of concentration of formic acid on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor. The emission of phosphor was little observed without adding formic acid. The emission intensity was increased with an increase in the concentration of formic acid. However, the intensity was gradually decreased at the concentration of formic acid above $1.0 \text{ mol} \cdot \text{dm}^{-3}$. The result was suggested

that the phosphor was dissolved into formic acid with high concentration having lower pH.

Figure 8 showed the effect of hydrothermal time on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor. In the course of this process, the emission intensity was showed the maximum of 90%. However, the emission intensity was decreased with an increase in the hydrothermal time. It was confirmed that the

Fig.9 Emission spectrum of $\text{CaHPO}_4:\text{Ce}^{3+}, \text{Mn}^{2+}$ phosphor.

Temp.: 170°C , Retention time: 0 h, Concentration of formic acid: $1.0 \text{ mol} \cdot \text{dm}^{-3}$, Ce/Ca atomic ratio: 0.01, Mn/Ca atomic ratio: 0.02, Excitation wavelength: 320 nm.

crystalline of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor which was synthesized at once was decreased, when the phosphor was dipped in formic acid solution with strong acid about pH 2 for a long time.

PREPARATION CONDITION OF CERIUM(III), MANGANESE(II) ACTIVATED DCPA PHOSPHOR

It is luminescence of $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor can not be confirmed by human eye, because the luminescence is UV region of 370 nm. However, Mn^{2+} was newly activated to $\text{CaHPO}_4:\text{Ce}^{3+}$ phosphor, energy transfer from Ce^{3+} to Mn^{2+} is induced, and it is expected that the orange-red emission would be observed.

Therefore, Figure 9 showed the emission spectrum of $\text{CaHPO}_4:\text{Ce}^{3+}, \text{Mn}^{2+}$ phosphor with the most suitable condition. It was observed that the phosphor was emitted the near-UV of Ce^{3+} at 370 nm and orange light of Mn^{2+} at 575 nm under conditions of black light irradiation at 320 nm. The phosphor of visible light emitting was able to produce by Ce^{3+} and Mn^{2+} activated with DCPA host.

Figure 10 showed the effect of Mn/Ca atomic ratio on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}, \text{Mn}^{2+}$ phosphor. The emission intensity of Ce^{3+} , which was observed at 370 nm, was decreased with an increase in Mn/Ca atomic ratio. According to this, it is confirmed that Ce^{3+} is working effectively as a sensitizer for Mn^{2+} . The intensity of Mn^{2+} , which was observed at 575 nm, was increased with an increase in the Mn/Ca atomic ratio. The intensity of phosphor with the Mn/Ca atomic ratio of 0.02 was showed the maximum of 12%. However, the intensity was decreased at the ratio above 0.02. The

Fig.10 Effect of Mn/Ca atomic ratio on the emission intensity of $\text{CaHPO}_4:\text{Ce}^{3+}, \text{Mn}^{2+}$ phosphor.

Temp.: 170°C , Retention time: 0 h, Concentration of formic acid: $1.0 \text{ mol} \cdot \text{dm}^{-3}$, Ce/Ca atomic ratio: 0.01, Excitation wavelength: 320 nm, Measuring wavelength: 370, 570 nm.

reason is considered that an increasing in the amount of incorporation of Mn^{2+} is caused a concentration quench.

The chemical formula of DCPA phosphor was quantified as $\text{Ca}_{0.949}\text{Ce}_{0.016}\text{Mn}_{0.027}\text{HPO}_4$ by chemical analysis.

SUMMARY

Generally, the synthesis of phosphor was produced on under conditions of the dry process with the high temperature above 1000°C . In this study, it was possible that activator of Ce^{3+} and Mn^{2+} was incorporation into DCPA host by using active ACP as starting material, in spite of wet process. Also, the activated DCPA was a new unprecedented phosphor. This phosphor was emitted the orange light at 570 nm by the near-UV irradiation at 320 nm. The shape of $\text{CaHPO}_4:\text{Ce}^{3+}, \text{Mn}^{2+}$ phosphor was plate-like, and it was superior to high sparedability.

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