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Crystal structures in NaBa$_{1-x}$Ca$_x$PO$_4$ system changed depending on the Ca substitution. Three kind of crystal structure were observed at $x = 0$, $1/3$ and $0.5$. New crystal structures were formed rather than formation of solid solutions between NaBaPO$_4$ and NaCaPO$_4$. Eu-doped samples exhibited emission maximum between 435 nm and 460 nm, depending on the amount of Ca.
Crystal Structures and Luminescence Properties of Eu\textsuperscript{2+}-activated new NaBa\textsubscript{0.5}Ca\textsubscript{0.5}PO\textsubscript{4} and Na\textsubscript{3}Ba\textsubscript{2}Ca(PO\textsubscript{4})\textsubscript{3}

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NaBa\textsubscript{0.5}Ca\textsubscript{0.5}PO\textsubscript{4}:Eu\textsuperscript{2+} were synthesized by polymerizable complex method. New phases were observed at \(x = 1/3\) and 0.5, which were identified by single-crystal XRD analysis as Na\textsubscript{3}Ba\textsubscript{2}Ca(PO\textsubscript{4})\textsubscript{3} and Na\textsubscript{2}Ba\textsubscript{0.5}Ca\textsubscript{0.5}PO\textsubscript{4} with trigonal system. Though both phases pretend to be the solid solutions between NaBaPO\textsubscript{4} and NaCaPO\textsubscript{4}, they have different coordination environments and PO\textsubscript{4} orderings. 1 mol% Eu\textsuperscript{2+}-activated NaBaPO\textsubscript{4}, Na\textsubscript{2}Ba\textsubscript{2}Ca(PO\textsubscript{4})\textsubscript{3}, and Na\textsubscript{2}Ba\textsubscript{0.5}Ca\textsubscript{0.5}PO\textsubscript{4} exhibited emission maximum at 435 nm, 458 nm, and 460 nm, respectively. The shift of the emission maximum might be due to a change in the Eu-O bond length.

Experimental Section

Synthesis of NaBa\textsubscript{0.5}Ca\textsubscript{0.5}PO\textsubscript{4}:Eu\textsuperscript{2+}

Eu\textsuperscript{2+}-doped NaBa\textsubscript{0.5}Ca\textsubscript{0.5}PO\textsubscript{4} phosphors were synthesized via the PC method with polyethylene glycol-conjugated phosphate ester (PEG-P)\textsuperscript{7} as a P source. PEG-P was synthesized from reactions among polyethylene glycol 300, phosphorus pentoxide, and polyphosphoric acid under a N\textsubscript{2} atmosphere at 353 K. Details of the PEG-P preparation procedure are described elsewhere.\textsuperscript{7} Na\textsubscript{2}CO\textsubscript{3} (99%, Kanto Chemical), BaCO\textsubscript{3} (99%, Kanto Chemical), CaCO\textsubscript{3} (99.99%, Kanto Chemical), and Eu(NO\textsubscript{3})\textsubscript{3} (prepared by the dissolution of Eu\textsubscript{2}O\textsubscript{3} (99.9 %,
Furuuchi Chemical) in HNO₃ were dissolved in an aqueous solution of citric acid (CA) at a molar ratio of Na : Ba : Ca : Eu : P : CA = 1 : (1-x-y) : x : y : 1 : 12. In the present research, y was fixed to 0.01, that is, the 1 mol% Eu-doped samples were synthesized. To assist chelation, the mixture was heated at 353 K for 2 h, after which PEG-P and propylene glycol (PG) were added into the solution at a molar ratio of 1 : 8. The temperature was subsequently increased to 423 K to initiate gel formation by polyesterification.⁵ After gel formation, the reaction mixture was heated at 1123 K in air to remove organic residues, and then reduced at 1273 K under a flow of Ar containing 4% H₂ for 3 h. For crystal structure analysis, single crystals were prepared using the flux growth method. Samples without Eu dopant (x = 0 and 0.5) were mixed with NaCl as a flux at a weight ratio of 1:2 using an agate mortar and pestle. The mixture was formed into pellets, sealed under vacuum in a quartz ampoule, heated at 1273 K for 5 h, and then slowly cooled to 1073 K at a rate of 100 K h⁻¹. After subsequent cooling to room temperature, the single crystals were washed with distilled water. Colorless crystals with dimensions of 0.093 mm × 0.073 mm × 0.048 mm (x = 0.5) and 0.106 mm × 0.101 mm × 0.037 mm (x = 1/3) were used for single crystal X-ray diffraction (XRD) analysis.

**Measurements and characterization**

The crystal phases of the samples were identified by powder XRD (Bruker AXS; D2 Phaser) using a Cu Kα source (λ = 1.5418 Å) scanning 2θ from 10° to 70°. Rietveld analysis was conducted using the TOPAS software supplied by Bruker Co. Ltd. The emission and excitation spectra were collected at room temperature using a fluorescence spectrophotometer (Hitachi; F-4500) scanning the wavelength range of 200 nm to 600 nm. A quartz sample chamber was filled with phosphor powder and mounted to the goniometer of a single-crystal X-ray spectrometer (Rigaku; R.AXIS RAPID.II). X-ray diffraction patterns for single crystals were analyzed using the SHELXL.97⁷ program, and structure parameters were refined by numerical least-squares procedures. Crystal structures of new phases in NaBa₃Ca₇PO₄ were solved using the SHELXL.97 program,¹³ and structure parameters were refined by numerical least-squares procedures. Crystal structures of the crystals are provided as supplementary information. The single crystal analysis revealed that phase 1 was a trigonal system (P31c) with a composition of Na₃Ba₃Ca₇PO₁₆, abbreviated as NBC321, and phase 2 was synthesized in NaBa₃Ca₇PO₄.

**Synthesis of NaBa₃ₓCa₇PO₄ solid solutions**

Fig. 1 shows the XRD patterns of NaBa₃ₓCa₇PO₄:0.01Eu²⁺ with x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 reduced at 1273 K for 3 h in Ar/4% H₂ atmosphere, and a simulated pattern of NaBaPO₄ from the Inorganic Crystal Structure Database (ICSD #73704). The XRD pattern of the sample without Ca (x = 0) was in good agreement with that of trigonal (P-3m1) NaBaPO₄. The diffraction pattern of samples with x = 0.1 and 0.2 contained several additional peaks at 18.77°, 24.31°, 29.89°, and 32.80° as compared with NaBaPO₄. These additional peaks were not assigned to any known substances, but instead indicated the formation of a new crystal phase, denoted here as phase 1. The intensity of the peaks from phase 1 increased with increase of Ca substitution until x = 0.3, decreased at x = 0.4, and finally, the peaks disappeared at x = 0.5. Another unknown phase, denoted here as phase 2, was also observed. Phase 2 appeared from x = 0.3, and the corresponding peak intensity increased with increasing Ca content.

**Crystal structures of new phases in NaBa₃ₓCa₇PO₄**

The single crystal data are compared with that of NaBaPO₄ (ICSD #73704) in Table 1 (Crystallographic Information Frameworks (CIFs) of the crystals are provided as supplementary material). The single crystal analysis revealed that phase 1 was a trigonal system (P31c) with a composition of Na₃Ba₃Ca₇PO₄, abbreviated as NBC321, and phase 2 was synthesized in NaBa₃Ca₇PO₄.

**Result and discussion**

Fig. 1 XRD patterns of NaBa₃ₓCa₇PO₄:0.01Eu²⁺ solid solutions for x = 0 ~ 0.5 reduced at 1273 K for 3 h in Ar/4% H₂ atmosphere, and a simulated pattern of NaBaPO₄ (ICSD #73704); unknown phase 1 (▼) and phase 2 (●).
also a trigonal system (P-3m1, the same as NaBaPO₄) with a composition of NaBa₀ₓCaₓPO₄ (abbreviated as NBCP). The lattice constants of NBC321 were a = 5.4515(2) Å and c = 23.1283(8) Å, and those of NBCP were a = 5.4474(4) Å and c = 7.3624(5) Å. The cell volume (V) decreased from 198.37 Å³ (NaBaPO₄) to 189.20(2) Å³ (NBCP).

**Table 1** Comparison of single crystal data of NaₓBa₂Ca(PO₄)ₓ, NaBa₀ₓCaₓPO₄, and crystal data of NaBaPO₄ (ICSD #73704).

<table>
<thead>
<tr>
<th>Formula</th>
<th>NaBaPO₄</th>
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<th>NaBa₀ₓCaₓPO₄</th>
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<td>Abbr.</td>
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<td>NBCP</td>
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<td>Trigonal</td>
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<tr>
<td>c (Å)</td>
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<td>23.1283(8)</td>
<td>7.3624(5)</td>
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<td>V(Å³)</td>
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<td>595.24(6)</td>
<td>189.20(2)</td>
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<tr>
<td>R indices (all data)</td>
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<td>R₁ = 0.0388</td>
<td>R₁ = 0.0168</td>
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<td>wR₂ = 0.0744</td>
<td>wR₂ = 0.0408</td>
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</table>

**Fig. 2** Crystal structures of the (a,d) NaBaPO₄ₙ, (b,e) NaₓBa₂Ca(PO₄)ₓ, and (c,f) NBCP visualized using VESTA crystal drawing software.¹⁴

**Fig. 2** shows the crystal structures of (a) NaBaPO₄, (b) NBC321, and (c) NBCP. Atomic arrangements in the three crystals are similar. Both NaBaPO₄ and NBCP are isotropic structures of glaserite and were determined to have the same space group. However, the coordination numbers (CN) for each cation in NaBaPO₄ and NBCP were different. NaBaPO₄ and NBCP have three metal cation sites with coordination numbers 6, 10, and 12. In NaBaPO₄, Na⁺ and Ba²⁺ exist at the CN 10 site with half occupancy. The remaining Na⁺ and Ba²⁺ occupy the CN 6 and 12 sites, respectively. In NBCP, Ca²⁺, Na⁺, and Ba²⁺ occupy the CN sites 6, 10 and 12, respectively. The two compounds have the same crystal structure but different their coordination environments, therefore, NBCP is a new phase. The c axis of NBC321 is approximately three times larger than those of NaBaPO₄ and NBCP. In NBC321, PO₄ units are tilted with respect to the c axis, while those in NaBaPO₄ and NBCP are aligned with the axis. In addition, regularity of PO₄ unit direction in the NBC321 is different from others, though a series of NaBaₓCaₓPO₄ pretend to be the solid solutions. In NaBaPO₄ and NBCP, Ba and Na/Ca alternate along the c axis, whereas in NBC321, a set of two Ba and Ca/Na propagates along the c axis. In a series of NaBaₓCaₓPO₄, one of faces at PO₄ units faces to ab plane constructing by Na/Ca sites. In other words, the ab plane exists in between PO₄ faces. The ionic radius of Ba²⁺ is the largest of the three cations, which means that the space between Na⁺/Ca⁺ on ab plane is free in comparison with that between Ba²⁺. As a result, PO₄ faces can exist on the side of the ab plane of Ca⁺/Na⁺. Therefore, the difference of arrangement of cations along c-axis leads to development of new phase NaₓBa₂Ca(PO₄)ₓ. One Na site in NBC321 was analysed as a split, which could be due to the

**Fig. 3** Rietveld refinement of NaBaₓCaₓPO₄ powder diffraction for (a) x = 1/3 and (b) x = 0.5 (solid curve: calculated, ‘×’: observed and ‘|’: Bragg peaks for (a) NaₓBa₂Ca(PO₄)ₓ and (b) NaBa₀ₓCaₓPO₄.)
space, created by oppositely ordered PO₄ units. Rietveld refinement of the powder diffraction data for x = 1/3 and 0.5 was conducted using the single crystal data as a model structure as shown in Fig. 3. The differences between the calculated and observed patterns are shown at the bottom of each figure. To confirm whether a single phase of NBC321 can be obtained, the sample with x = 1/3 was synthesized. Rietveld refinement using the powder pattern for x = 1/3 revealed that the single phase NBC321 was successfully synthesized. The final reliability factors, R_p, R_wp and χ² were 6.40 %, 8.58 % and 1.42, respectively. It was also confirmed that NBC321 and its solid solutions were formed with Ca substitution at x = 0.1 - 0.4, and the single phase Na₃Ba₂Ca(PO₄)₃ could be obtained at x = 1/3. The single crystal data of NBCP matched the powder diffraction for x = 0.5. Reliability factors, R_p, R_wp and χ² were 5.21 %, 7.30 %, and 1.46, respectively, indicating that the powder sample for x = 0.5 was a single phase of NBCP without any impurities or secondary phases. Samples with x > 0.5 were also synthesized by 0.1 for x. The samples with x = 1.0 consisted of NaCaPO₄ without any other phases. At 0.6 ≤ x ≤ 0.9, mixtures of solid solutions of NBCP and NaCaPO₄ were formed. No other new phase was obtained at x > 0.5 in the present study.

Photoluminescence properties of Eu²⁺-activated NaBaPO₄, NBC321, and NBCP

Fig. 4 shows the normalized excitation and emission spectra of 1 mol% Eu²⁺-activated (a) NaBaPO₄, NBC321, and (c) NBCP excited at 330 nm. In the absence of Eu, the present samples exhibit practically no emission. Therefore, the observed excitation and emission peaks are attributed to f-d transition in Eu²⁺. NaBaPO₄:Eu²⁺ exhibited a maximum emission center at 435 nm, which agrees with a previous report. Ca substitution causes a redshift of the emission center. NBC321:0.01Eu²⁺ and NBCP:0.01Eu²⁺ showed emission maxima at 458 nm and 460 nm, respectively. Emission lifetime (τ) plots and fitting curves for each sample are shown in Fig. 5. All curves were primarily fitted to a single exponential function. However, to carry out precise fitting, average values calculated using double exponential function were considered in the present study. The results for 1 mol% Eu-doped samples indicated τ = 598 ns for NaBaPO₄, 461 ns for NBC321 and 546 ns for NBCP. The value for 1 mol% Eu²⁺-doped NaBaPO₄ is in good agreement with the one (570 ns) reported previously, and the others are in the range of the values reported in Eu²⁺-doped ABPO₄. The τ values for NBC321 and NBCP were smaller than that of the known NaBaPO₄ phosphor, however, no clear correlation between τ and the content of Ca in the samples was found.

Eu²⁺ ion is thought to substitute preferentially for Ba²⁺ site considering the ionic radius (Ba²⁺ = 1.61 Å at CN 12) and valence at the Ca²⁺ site. The averages of Ba–O bond lengths in NBC321 and NBCP were found to be 2.938 Å and 2.915 Å, which were shorter than that in NaBaPO₄ (3.016 Å). The relationship between bond lengths remains the same after Eu substitution, a shorter Ba-O bond length would increase the crystal field splitting of the Eu 5d orbitals, and as a result, the emission center would be shifted to lower energy with Ca substitution. The internal quantum efficiencies of Eu²⁺-activated NaBaPO₄, NBC321, and NBCP excited at 330 nm were 84 %, 7 %, and 51 %, respectively, with the corresponding absorption rates of 76 %, 50 %, and 72 %. One of the reasons for the rather small quantum efficiency in NBC321 system might be concentration quenching in Eu²⁺ ions residing at adjacent Ba sites. It is expected that the photoluminescence properties of new phases can be enhanced by optimization of the synthesis conditions. The excitation spectra covered a range from UV to near UV region, and the phosphors could be excited efficiently under 330 nm. Thus the NBC321 and NBCP may be considered as candidate phosphors for W-LEDs.
the luminescence properties such as emission intensity are improved.

Conclusions

The two new phases, Na\textsubscript{1}Ba\textsubscript{2}Ca\textsubscript{3}PO\textsubscript{4}\textsubscript{3} and NaBa\textsubscript{0.5}Ca\textsubscript{0.5}PO\textsubscript{4}, were found during the synthesis of NaBa\textsubscript{1.5}Ca\textsubscript{1.5}PO\textsubscript{4} solid solutions by the PC method employing PEG-P. The crystal structures of the new phases were determined to be described as trigonal systems (P\textsubscript{3}\textsubscript{1}c for NBC321 and P\textsubscript{3}\textsubscript{m}1 for NBCP) by the single crystal XRD analysis. Regularity of PO\textsubscript{4} unit arrangement is different among NaBa\textsubscript{1.5}Ca\textsubscript{0.5}PO\textsubscript{4} due to different arrangements of cations. Eu\textsuperscript{2+}-activated samples exhibited blue emission under UV or near UV irradiations. The Ba−O bond length was shortened by Ca ion substitution, and as a result, the wavelength giving the maximum emission in the Eu\textsuperscript{2+} activated samples was red-shifted from 435 nm (for x = 0) to 458 nm (for x = 1/3) and 460 nm (for x = 0.5) under excitation at 330 nm.

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Notes and references