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Crystal Structure, Vibrational Spectra and Activation of $BaCa(P_4O_{12})$ with Eu^{2+} Compared with β-$Sr(PO_3)_2$:Eu

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1. Introduction

White light LEDs are of interest in terms of energy efficiency and practical advantages compared to conventional bulbs and phosphorescent tubes. Such LEDs may be based on blue LEDs which are coated with a yellow [1] or a green and a red phosphor.[2,3] Due to technological reasons the colour point of blue LEDs varies from sample to sample. Therefore, another approach might solve this problem by using a UV-LED fitted with three phosphors emitting blue, red and green.[1] We recently reported about the host material α-$Sr(PO_3)_2$ which was then co-doped with Eu^{2+} and Mn^{2+} to give white light under UV excitation.[4,5] The emission of α-$Sr(PO_3)_2$:Eu peaks at 404 nm with a line width of 29 nm which is very small for a divalent europium emission.

To come as close to the sun light it is desirable to shift the europium emission slightly to longer wavelengths, i.e. a more bluish light, and to enlarge the line width of the emission. The emission wavelength of Eu^{2+} can be influenced by a stronger crystal-field splitting due to smaller coordination distances and enhancement of covalent interactions. In this contribution we report about our investigations on the europium doped strontium phosphate β-$Sr(PO_3)_2$ compared with the equivalently doped mixed barium calcium polyphosphate $BaCa(PO_3)_4$ to assess their suitability as phosphors for white LEDs. Additionally, we present the first crystal structure determination of $BaCa(PO_3)_4$ based on single-crystal data to clarify to which extent the cations are ordered in the crystal structure and to show similarities in the crystal structures of $BaCa(PO_3)_4$, β-$Sr(PO_3)_2$ and α-$Sr(PO_3)_2$. Then the differences in the emission spectra of europium doped into these three host lattices can be explained.

2. Experimental Section

The pure as well as the doped phosphates were synthesised starting from ammonium hydrogen phosphate, alkaline earth carbonate and europium oxide. Typical synthesis procedures for the doped phases are as follows:

Synthesis of a Typical Sample of β-$Sr(PO_3)_2$:Eu: A mixture of 147.7 mg (1.000 mmol) strontium carbonate (Alfa Aesar, 97.5%), 2.2 mg (0.0063 mmol, doping conc. 1.2%) europium oxide Eu_2O_3 (Kristallhandel Kelpin, 99.9%) and 462.0 mg (3.499 mmol) ammonium dihydrogenphosphate (ABCR, 98%) was transferred into an alumina boat. The latter was then heated under a hydrogen/nitrogen (10:90) flow (2 L/h) to 870 K with a rate of 90 $K\,h^{-1}$ and maintained at this temperature for 6 h. After cooling to room temperature with a rate of 180 $K\,h^{-1}$ β-$Sr(PO_3)_2$:Eu was obtained almost quantitatively as a crystalline, colourless and non-hygroscopic powder.

Phase-pure α-$Sr(PO_3)_2$:Eu can be obtained by heating an analogous mixture of starting materials to 1150 K.[5] For the synthesis an excess of hydrogenphosphate is necessary to avoid loss of P_4O_{10} and a subsequent formation of strontium diphosphate or other oligophosphates.

Synthesis of a Typical Sample of $BaCa(PO_3)_4$:Eu: A mixture of 49.3 mg (0.250 mmol) barium carbonate (Aldrich, 99.98%), 25.1 mg (0.251 mmol) calcium carbonate (Fisher Scientific, 97–100%), 0.4 mg (0.011 mmol, doping concd. 0.9%) europium oxide (Kristallhandel Kelpin, 99.9%) and 134.3 mg (1.017 mmol) ammonium dihydrogen phosphate (ABCR, 98%) was transferred into an alumina boat. The latter was then heated under a hydrogen/nitro-

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gen (10:90) flow (2 L/h) to 970 K with a rate of 90 K h^{-1}. After 48 h the mixture was cooled to room temperature with a rate of 90 K h^{-1}. Finally $BaCa(PO_3)_4$:Eu was obtained almost quantitatively as a crystalline, colourless and non-hygroscopic powder.

According to their powder diffraction patterns all samples presented herein were single-phase. The composition of obtained samples was checked by energy dispersive X-ray spectroscopy (EDX) and confirmed the respective M/P (M = Ba, Ca, Sr) ratios.

Crystal Structure Analysis of $BaCa(PO_3)_4$: X-ray diffraction data were collected on a Stoe IPDS 2 diffractometer using Mo-K_α radiation and corrected numerically for absorption.[6] The diffraction pattern was indexed on the basis of a primitive monoclinic unit cell. The crystal structure of $BaCa(PO_3)_4$ was solved by direct methods using SHELXTL[7] and refined with anisotropic displacement parameters for all atoms. Details of the data collection and the structure refinement are listed in Table 1. Table 2 gives a list with selected distances and angles of the structure model.

Table 1. Crystallographic data of $BaCa(PO_3)_4$ (esds in parentheses).

	$BaCa(PO_3)_4$
Ttemperature /K	293(2)
Molar weight /g mol^{-1}	493.30
Crystal system	monoclinic
Space group	$P2_1/n$
a /pm	723.00(11)
b /pm	917.05(19)
c /pm	1524.7(2)
β /°	90.995(12)
Cell volume /10^6 pm^3	1010.8(3)
Z	4
Calculated density ρ_x /g cm^{-3}	3.242
Crystal dimensions	$0.01 \times 0.02 \times 0.02$ mm^3
Crystal shape	block
μ /mm^{-1}	5.133
F(000)	928
Radiation	Mo-K_α radiation
Diffractometer	Stoe IPDS 2
Absorption correction	numerical[6]
Min./max. transmission	0.5763; 0.8434
Index range	–8/–10/–16–8/10/18
Theta range ($2\Theta_{max}$)	50.0
Refinement method	full-matrix least-squares on F^2
Reflections collected	6374
Data/restraints/parameters	1748/0/164
Observed reflections ($I>2\sigma$), R_{int}	995, 0.171
Extinction coefficient χ	0.0023(5)
R values (all data)	$R_1 = 0.050$; $wR_2 = 0.099$
Goodness of fit (GooF)	0.784
Largest diff. peak and hole /e Å^{-3}	–1.42/0.99

Table 2. Selected interatomic distances/pm and angles/° in $BaCa(PO_3)_4$ with esd values in parentheses.

Ba–O^{term}	265.1(9)–317.2(12) (9 distances)
Ca–O^{term}	230.8(9)–238.8(9) (6 distances)
P–O^{term}	146.3(10)–149.2(11)
P–O^{br}	156.8(10)–162.0(9)
O^{term}–P–O^{br}	104.0(5)–113.4(5)
O^{term}–P–O^{term}	114.2(5)–120.0(6)
O^{br}–P–O^{br}	99.6(6)–102.7(6)
P–O^{br}–P	133.1(7)–141.4(7)

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-420329 [$BaCa(PO_3)_4$], the names of the authors, and citation of this publication.

Fluorescence Spectroscopy: Fluorescence emission and excitation spectra were recorded on a Perkin–Elmer LS55 spectrometer scanning a range from 200 to 800 nm. The obtained data have been corrected for emission and excitation with respect to the Xe plasma excitation source.

3. The Crystal Structures of $BaCa(PO_3)_4$ and β-$Sr(PO_3)_2$

On a first view one might expect that the crystal structures of $BaCa(PO_3)_4$ and β-$Sr(PO_3)_2$ are homeotypic but according to our single-crystal data the crystal structure of $BaCa(PO_3)_4$,[8,9] [space group $P2_1/c$, a = 7.192(2) Å, b = 7.934(3) Å, c = 17.351(6) Å, β = 90.66(3)°] but isotypic with that of $BaCd(PO_3)_4$.[10] Both crystal structures comprise polyphosphate anions running as herringbone pattern like chains along a. In the voids of the resulting structure the barium and calcium atoms are situated (Figure 1).

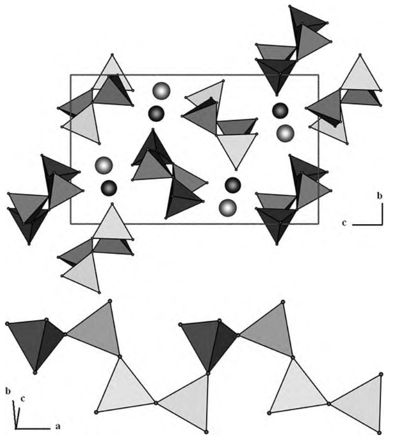

Figure 1. Representation of the crystal structure of $BaCa(PO_3)_4$ viewed along a (top) and a single chain (bottom); the PO_4 tetrahedra are drawn as closed polyhedra, the black and grey spheres represent calcium and barium atoms, respectively.

The calcium ions are sixfold coordinated (Ca–O 231–239 pm in a distorted prismatic environment, a seventh oxygen atom is aloof by 313 pm) while the barium atoms are ninefold coordinated (Ba–O 265–317 pm), thus exhibiting the expected distances according to the ionic radii (Ca–O 240, Ba–O: 287 pm).[11] Both coordination environments are presented in Figure 2. The bond lengths between phosphorus and terminal oxygen atoms ranging from 146 to 149 pm are shorter than the bond lengths between phosphorus and the bridging oxygen atoms (157 and 162 pm). They agree well with typical bond lengths inside phosphate chains in other condensed phosphates.[4,12,13]

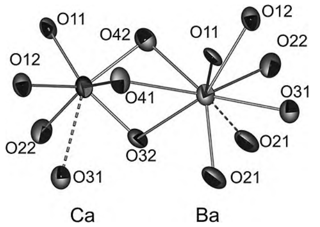

Figure 2. Coordination environments of Ca (dark grey) and Ba (light grey) with oxygen (medium grey) in $BaCa(PO_3)_4$; bonds with distances above 3 Å are dotted, the site symmetry of both positions is **1**, the thermal ellipsoids are drawn at a 75% probability level.

The barium and calcium atoms form a distorted diamond-like arrangement. In $BaCa(PO_3)_4$ this is more distorted than that found in α-$Sr(PO_3)_2$ [4] (Figure 3) since the Sr centered Sr_4 tetrahedra are rather regular compared with the Ba centered Ca_3Ba and Ca centered Ba_3Ca tetrahedra. Additionally, this can be seen from the respective angles inside these tetrahedra which vary between 106 and 115° in α-$Sr(PO_3)_2$ [4] and range from 92.3(1) to 136.7(1)° in $BaCa(PO_3)_4$. The distortion of an analogous arrangement in β-$Sr(PO_3)_2$ is even stronger and there is no crystallographic relationship between β-$Sr(PO_3)_2$ and $BaCa(PO_3)_4$. In the latter the tetrahedral voids are occupied by barium and calcium in a 3:1 ratio while in the β polymorph these are occupied by both crystallographically independent strontium sites in a 1:1 ratio.

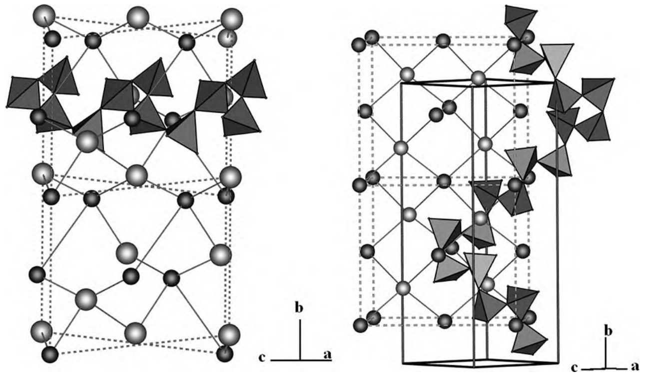

Figure 3. Virtual cells (dotted) of the diamond-like substructure of the cations in $BaCa(PO_3)_4$ (left, Ca dark grey, Ba light grey) and α-$Sr(PO_3)_2$ (right) interpenetrated by the respective PO_3^- anion (the "bonds" connecting the cations visualise the diamond-like network and do not represent bonds in a chemical sense, the PO_4 tetrahedra are shown as closed polyhedra).

In β-$Sr(PO_3)_2$ the Sr1 atoms are coordinated by eight oxygen atoms in a distorted quadratically antiprismatic arrangement in distances ranging from 250 to 280 pm, the Sr2 atoms are coordinated by eight oxygen atoms in seven distances ranging from 249–269 pm and an additional one 323 pm apart.[8] The surrounding of Sr2 can be described as bicapped trigonal prismatic. Thus the coordination environments of the cations in β-$Sr(PO_3)_2$ and $BaCa(PO_3)_4$ are very different. Moreover, the coordination distances in $BaCa(PO_3)_4$ differ in a larger range due to the differing ionic radii of Ba and Ca.

4. Fluorescence Spectroscopy

Optical Properties of β-$Sr(PO_3)_2$:Eu

Under excitation at 246 nm β-$Sr(PO_3)_2$:Eu (1%) exhibits an intense broad emission band peaking at 424 nm which is typical for parity allowed d–f transitions like in Eu^{2+}; the spectrum did not show any sharp 4f–4f transitions and thus delivered no evidence for Eu^{3+} present in our sample (Figure 4). The full width at half maximum is 41 nm or 2.3×10^3 cm^{-1}. The Stokes shift amounts to 17.1×10^3 cm^{-1}.

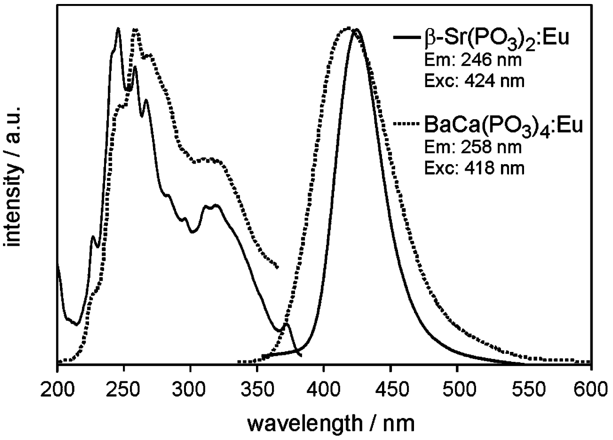

Figure 4. Fluorescence spectra of β-$Sr(PO_3)_2$:Eu(1%) (straight line) and $BaCa(PO_3)_4$:Eu(1%) (dotted line), the monitoring wavelengths of the excitation (Exc) and the excitation wavelengths of the emission spectra (Em) are given, respectively.

Optical Properties of $BaCa(PO_3)_4$:Eu

Under excitation at 259 nm $BaCa(PO_3)_4$:Eu (1%) exhibits an intense broad emission band peaking at 418 nm which is typical for parity allowed d–f transitions like in Eu^{2+}; the spectrum did not show any sharp 4f–4f transitions and thus delivered no evidence for Eu^{3+} present in our sample (Figure 4). The full width at half maximum is 67 nm or 3.9×10^3 cm^{-1}. The Stokes shift amounts to 14.7×10^3 cm^{-1}.

5. Vibrational Spectroscopy

Figure 5 shows the IR and Raman spectra of $BaCa(PO_3)_4$. The IR spectra of *catena*-polyphosphates are not significantly different from those of *catena*-oligophosphates.[14] The only characteristic bands should be found in the region between 800 and 650 cm^{-1}, where the number of bands should correspond to the periodicity of the phosphate chain. This holds for $BaCa(PO_3)_4$ as the periodicity of the polyphosphate chain is four and also four bands are found peaking at 682, 714, 746 and 776 cm^{-1}. In BaCa(PO$_3$)$_4$ the characteristic frequencies of *catena*-polyphosphate chains such as the ν_{as}(PO$_2$) are detected between 1200 and 1310 cm^{-1} with a maximum at 1244 cm^{-1}, the very intense ν_{as}(POP) at 916 cm^{-1} and ν(PO^{term}) ranging from 1010 up to 1100 cm^{-1}. Additionally, the Raman spectrum of BaCa(PO$_3$)$_4$ shows strong vibrations in the region around 1170 [ν_s(PO^{term})], and at 683 cm^{-1} [ν_s(POP)]. Thus the observed vibrational data are in good agreement with the expected values.

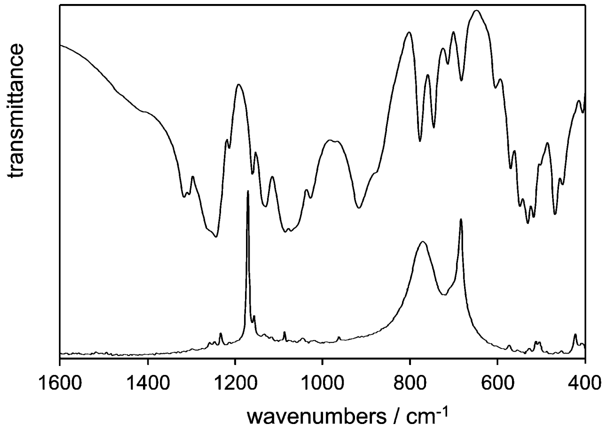

Figure 5. Vibrational spectra of BaCa(PO$_3$)$_4$.

6. Discussion and Conclusions

Doped β-Sr(PO$_3$)$_2$:Eu and BaCa(PO$_3$)$_4$:Eu emit blue light during excitation with an UV wavelength of 246 nm and 258 nm, respectively, but also around 330 nm which is accessible by UV LEDs based on AlGaN.[15] The line-width of BaCa(PO$_3$)$_4$:Eu is significantly larger (3.9×10^3 cm^{-1}) compared with that of β-Sr(PO$_3$)$_2$:Eu (2.3×10^3 cm^{-1}). The full width at half maximum in previously published α-Sr(PO$_3$)$_2$:Eu is 29 nm or 1.8×10^3 cm^{-1}. This was attributed to the very similar coordination environment of the Sr atoms.[5] The Stokes shift in α-Sr(PO$_3$)$_2$:Eu amounts to 15.7×10^3 cm^{-1}. In β-Sr(PO$_3$)$_2$:Eu the coordination spheres vary little more (quadratically antiprismatic surrounding with Sr–O distances from 249 to 280 pm and bicapped trigonal prismatic with distances from 249 to 324 pm)[8,9] than in its α-polymorph (Sr–O distances from 244 to 303 pm) where all cations are surrounded very similarly.[4] This is reflected in a slightly broader emission band for β-Sr(PO$_3$)$_2$:Eu. In BaCa(PO$_3$)$_4$:Eu the distances of the cations to oxygen vary in a very large range (Table 2) due to the presence of two different cations leading to a comparably broader emission band. The very different ion sizes of Ba and Ca led to a crystallographic ordering in the crystal structure. As expected, the sharp 4f–4f transitions in both excitation spectra which ride on the broad 4f–5d transitions are located at the same position for both phosphors since the 4f states are almost not affected by the crystal field in contrast to the broad 4f–5d excitation bands. These are significantly broader for BaCa(PO$_3$)$_4$:Eu.

Compared with α-Sr(PO$_3$)$_2$:Eu the emission wavelengths of β-Sr(PO$_3$)$_2$:Eu and BaCa(PO$_3$)$_4$:Eu are shifted to longer wavelengths thus giving a more bluish light than α-Sr(PO$_3$)$_2$:Eu. Moreover, the emission line width is larger than in α-Sr(PO$_3$)$_2$. This helps to adjust the emission of a white light source based on a LED closer to the sun light. Especially in the case of the mixed Ba–Ca compound the large range of coordination distances leads to a large line broadening of the emission band. Therefore we think that these phosphors will be useful for the development of white LEDs based on UV LEDs to act as blue broad band emitters with a stable blue colour point compared with the varying blue emission of blue InGaN LEDs. A further shift of the emission wavelength to longer wavelengths is still desirable.

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