# Coactivation of α-$Sr(PO_3)_2$ and $SrM(P_2O_7)$ (M = Zn, Sr) with $Eu^{2+}$ and $Mn^{2+}$

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The phosphates α-$Sr(PO_3)_2$, $SrZn(P_2O_7)$, and α-$Sr_2(P_2O_7)$ were doped and codoped with $Eu^{2+}$ and $Mn^{2+}$, structurally characterized, and analyzed by fluorescence spectroscopy. α-$Sr(PO_3)_2$ was found to enable the energy transfer between $Eu^{2+}$ and $Mn^{2+}$, leading to a new phosphor emitting at 404 and 625 nm and giving white light under excitation at 323 nm. In $SrZn(P_2O_7)$ and α-$Sr_2(P_2O_7)$, the codoping was also successful but the luminescence intensity of the red emission was found to be less intense. Moreover, the crystal structure of $SrZn(P_2O_7)$ has been determined based on single-crystal data ($P2_1/n$, $Z = 4$, $a =$ 531.43(2) pm, $b =$ 820.80(3) pm, $c =$ 1272.50(6) pm, $\beta =$ 90.192(4)°, R1 = 0.035, and wR2 = 0.070).

## 1. Introduction

White-light light-emitting diodes (LEDs) are of interest in terms of energy efficiency and practical advantages compared to conventional bulbs of 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] Another approach is the use of ultraviolet (UV) LEDs fitted with three phosphors emitting blue, red, and green.[1] In the latter two approaches, at least two phosphors are needed to convert the UV/blue light into the desired visible light, and therefore it should be advantageous to find phosphors that are able to absorb UV/blue light and simultaneously emit at least two colors. For this purpose, e.g., compounds codoped with $Eu^{2+}$ and $Mn^{2+}$ like $CaAl_2Si_2O_8$ or $Ba_3MgSi_2O_8$ have been investigated recently.[3,4] $Eu^{2+}$ has been proven to be an efficient absorber and emitter, while transitions within $Mn^{2+}$ are forbidden according to parity and spin-selection rules. However, $Eu^{2+}$ has also proven to be an efficient sensitizer for $Mn^{2+}$.[5]

Both ions are capable of substitution for $Sr^{2+}$ in inorganic materials, and during earlier investigations, the crystal structure of α-$Sr(PO_3)_2$ has been elucidated.[6] Its crystal structure is chiral and therefore allows for mixing of different parity states within the optically active ions like $Eu^{2+}$ or $Mn^{2+}$, which may lead to high transition probabilities.

Because $Mn^{2+}$ and $Eu^{2+}$ are of quite different size (67 and 117 pm, respectively),[7] it might be more efficient to provide different sites for the two optically active ions, and because of their size, charge and optical neutrality Sr−Zn compounds (ionic radii: 116 pm for $Sr^{2+}$ and 75 pm for $Zn^{2+}$)[7] could act as suitable host structures, in which the $Mn^{2+}$ ions prefer the Zn sites and the $Eu^{2+}$ ions prefer the Sr sites.

In this contribution, we report about our investigations on singly and doubly doped strontium phosphate α-$Sr(PO_3)_2$ compared with equivalently doped diphosphates α-$Sr_2(P_2O_7)$ and $SrZn(P_2O_7)$. Additionally, we present the crystal structure determination of $SrZn(P_2O_7)$ based on single-crystal data.

## 2. Experimental Section

The pure as well as the doped phosphates were synthesized using a tube furnace starting from ammonium hydrogen phosphate, strontium carbonate, zinc oxide, europium oxide, and manganese nitrate. Typical synthesis procedures for the codoped phases are as follows.

**Synthesis of a Typical Sample of α-$Sr(PO_3)_2$:Eu,Mn.** A mixture of 88.6 mg (0.600 mmol) of strontium carbonate (Alfa Aesar, 97.5%), 2.1 mg (0.006 mmol, doping concn 2.0%) of europium oxide $Eu_2O_3$ (Kristallhandel Kelpin, 99.9%), 5.0 mg (0.026 mmol, doping concn 4.4%) of manganese nitrate $Mn(NO_3)_2 \cdot 4H_2O$ (Merck, 98.5%), and 174.5 mg (1.32 mmol) of ammonium dihydrogenphosphate (ABCR, 98%) was transferred into an alumina boat. The latter was then heated under a hydrogen/nitrogen (10/90) flow (2 L $h^{-1}$) to 1120 K at a rate of 60 K $h^{-1}$ and maintained at this temperature for 4 h. After cooling to room temperature at a rate of 180 K $h^{-1}$, α-$Sr(PO_3)_2$:Eu,Mn was obtained quantitatively as a crystalline, colorless, and nonhygroscopic powder.

**Synthesis of a Typical Sample of $SrM(P_2O_7)$:Eu,Mn (M = Sr, Zn).** A mixture of 44.3 mg [0.300 mmol; for $Sr_2(P_2O_7)$, 0.6 mmol] of strontium carbonate (Alfa Aesar, 97.5%), 24.3 mg [0.300 mmol; only for $SrZn(P_2O_7)$] of zinc oxide, 1.0 mg (0.003 mmol, doping concn 1.9%) of europium oxide $Eu_2O_3$ (Kristallhandel Kelpin, 99.9%), 2.5 mg (0.013 mmol, doping concn 4.3%) of

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**Table 1. Crystallographic Data of $SrZn(P_2O_7)$ (ESDs in Parentheses)**

| Crystal Data | |
|---|---|
| $SrZn(P_2O_7)$ | $F(000) = 616$ |
| $M = 394.17$ g mol$^{-1}$ | $\rho_{X\text{-ray}} = 3.91$ g cm$^{-3}$ |
| monoclinic | Mo Kα radiation |
| space group $P2_1/n$ (No. 14) | $\lambda = 71.073$ pm |
| $a = 531.43(2)$ pm | $\mu = 14.5$ mm$^{-1}$ |
| $b = 820.80(3)$ pm, $\beta = 90.192(4)°$ | $T = 293(2)$ K |
| $c = 1272.50(6)$ pm | crystal shape: block |
| $V = 555.1(1) \times 10^6$ pm$^3$ | $0.10 \times 0.11 \times 0.12$ mm$^3$ |
| $Z = 4$ | colorless |
| **Data Collection** | |
| absorption correction: multiscan [8] | Bruker AXS CCD (APEX-II) |
| $T_{min} = 0.159$; $T_{max} = 0.374$ | $h = -6 \rightarrow 6$ |
| $R_{int} = 0.1312$ | $k = -10 \rightarrow 10$ |
| $2\theta_{max} = 55.0°$ | $l = -16 \rightarrow 16$ |
| | 12 722 measured reflections |
| | 1274 independent reflections |
| | 929 observed reflections $[F_o^2 \geq 2\,\sigma(F_o^2)]$ |
| **Refinement** | |
| refinement on $F^2$ | $\chi = 0.0039(6)$ |
| R1 = 0.0350, wR2 = 0.0701, GOF = 1.018 | $w^{-1} = \sigma^2F_o^2 + (0.0153P)^2 + 0.90P$; $P = (F_o^2 + 2F_c^2)/3$ |
| 101 parameters | min residual electron density: −0.85 e Å$^{-3}$ |
| | max residual electron density: 1.06 e Å$^{-3}$ |

manganese nitrate $Mn(NO_3)_2 \cdot 4H_2O$ (Merck, 98.5%), and 83.2 mg (0.630 mmol) of 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$^{-1}$) to 1070 K at a rate of 60 K h$^{-1}$. After 18 h, the mixture was cooled to room temperature at a rate of 180 K h$^{-1}$. Finally, $SrM(P_2O_7)$:Eu,Mn was obtained quantitatively as a crystalline, colorless, and nonhygroscopic 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 and confirmed the respective M/P (M = Sr, Zn) ratios.

**Crystal Structure Analysis of $SrZn(P_2O_7)$.** X-ray diffraction data were collected on a Bruker AXS CCD diffractometer fitted with an APEX-II detector and corrected for absorption.[8] The diffraction pattern was indexed on the basis of a primitive monoclinic unit cell. The crystal structure of $SrZn(P_2O_7)$ was solved by direct methods using *SHELXTL*[9] and refined with anisotropic displacement parameters for all atoms. Details of the data collection and the structure refinement are listed in Table 1; atomic coordinates and displacement parameters of all atoms are given in Tables 2 and 3.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-418441 [$SrZn(P_2O_7)$], the names of the authors, and the 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.

**Table 2. Atomic Coordinates and Isotropic Displacement Parameters $U_{eq}$/Å$^2$ for $SrZn(P_2O_7)$ with ESDs in Parentheses[a]**

| atom | Wyckoff position | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|
| Sr | 4e | 0.21291(11) | 0.33897(6) | 0.22068(5) | 0.0084(2) |
| Zn | 4e | 0.82890(13) | −0.34924(8) | 0.10542(6) | 0.0082(2) |
| P1 | 4e | 0.7471(3) | 0.0344(2) | 0.16471(13) | 0.0075(4) |
| O1 | 4e | 0.7300(8) | 0.1128(5) | 0.0497(4) | 0.0083(9) |
| O11 | 4e | 0.0123(8) | 0.0593(5) | 0.2043(4) | 0.0095(9) |
| O12 | 4e | 0.6727(8) | −0.1424(5) | 0.1522(4) | 0.0100(9) |
| O13 | 4e | 0.5533(8) | 0.1187(5) | 0.2336(4) | 0.0075(9) |
| P2 | 4e | 0.6821(3) | 0.3011(2) | 0.01959(13) | 0.0067(4) |
| O21 | 4e | 0.8274(8) | 0.4022(5) | 0.1005(4) | 0.0086(9) |
| O22 | 4e | 0.7952(8) | 0.3163(5) | −0.0895(4) | 0.0069(9) |
| O23 | 4e | 0.3996(8) | 0.3331(5) | 0.0261(4) | 0.0092(9) |

[a] $U_{eq}$ is defined as one-third of the trace of the $U_{ij}$ tensor.

## 3. Crystal Structures of α-$Sr(PO_3)_2$ and $SrM(P_2O_7)$ with M = Sr, Zn

The crystal structure of α-$Sr(PO_3)_2$ has been determined recently[6] (space group $P2_1$). It consists of a diamondlike arrangement of Sr ions that hosts helical polyphosphate chains. Around the Sr ions, terminal O atoms of the polyphosphate chain form an 8-fold coordination polyhedron [Sr−O = 243.6(8)–303.4(12) pm]. Four of the eight O atoms form an almost planar tetragonal plane around the central $Sr^{2+}$, above and below of which the other four O atoms are positioned in a strongly compressed tetrahedral arrangement. The crystal structure of α-$Sr(PO_3)_2$ is chiral and therefore enables mixing of states of different parity, allowing for high transition probabilities in optical transitions.

According to our single-crystal data (Tables 1–3), the crystal structure of $SrZn(P_2O_7)$ is isotypic with that of $SrMg(P_2O_7)$[10] (space group $P2_1/n$) and consists of diphosphate anions with an antiperiplanar arrangement of the terminal $PO_3$ groups, as shown in Figure 1. In the voids of the resulting structure, the Sr and Zn atoms are situated. The Sr ions are 8-fold-coordinated [251.1(4)–276.5(4) pm; a ninth O atom is aloof by 328.5(4) pm], while the Zn atoms are 5-fold-coordinated in a distorted square-pyramidal environment [198.2(4)–215.7(5) pm], thus exhibiting the usual distances according to the ionic radii (Sr−O = 261 pm; Zn−O = 216 pm).[7] Both coordination environments are presented in Figure 2. For codoping purposes, it is desirable to keep the Sr−Zn distance as short as possible because the efficiency of the energy-transfer Eu−Mn decreases with their distance and should be best if $Eu^{2+}$ (on Sr sites) and $Mn^{2+}$ (on Zn sites) are located on adjacent sites. In $SrZn(P_2O_7)$, both sites are directly connected via a common O bridge. The bond lengths between the P and terminal O atoms, ranging from 151.0(5) to 153.0(5) pm, are shorter than the bond lengths between the P and bridging O atoms [160.1(5) and 161.2(4) pm]. They agree well with typical bond lengths inside phosphate chains in other condensed phosphates.[11,12]

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**Table 3. Anisotropic Displacement Parameters $U_{ij}$/Å$^2$ for the Atoms in SrZn($P_2O_7$) with ESDs in Parentheses[a]**

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Sr | 0.0076(3) | 0.0083(3) | 0.0095(4) | −0.0011(2) | −0.0012(2) | 0.0001(2) |
| Zn | 0.0075(4) | 0.0077(3) | 0.0092(4) | −0.0003(3) | −0.0017(3) | 0.0001(3) |
| P1 | 0.0082(8) | 0.0077(7) | 0.0065(9) | −0.0004(6) | 0.0002(7) | 0.0016(6) |
| O1 | 0.010(2) | 0.0030(18) | 0.012(3) | 0.0038(16) | −0.002(2) | 0.0018(16) |
| O11 | 0.007(2) | 0.010(2) | 0.012(3) | 0.0014(17) | −0.0016(19) | −0.0033(16) |
| O12 | 0.010(2) | 0.0058(18) | 0.014(3) | −0.0041(17) | −0.0006(19) | 0.0009(17) |
| O13 | 0.006(2) | 0.011(2) | 0.005(2) | −0.0035(16) | −0.0016(18) | 0.0020(16) |
| P2 | 0.0061(7) | 0.0069(7) | 0.0071(9) | 0.0009(6) | −0.0011(6) | −0.0009(6) |
| O21 | 0.008(2) | 0.0098(19) | 0.008(3) | 0.0006(16) | −0.0031(19) | −0.0014(17) |
| O22 | 0.005(2) | 0.011(2) | 0.005(2) | 0.0038(15) | 0.0013(17) | −0.0003(16) |
| O23 | 0.006(2) | 0.013(2) | 0.009(2) | 0.0018(18) | 0.0004(17) | −0.0003(18) |

[a] The anisotropic displacement factor exponent is of the form $\exp\{-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{13}hla^*c^*)\}$.

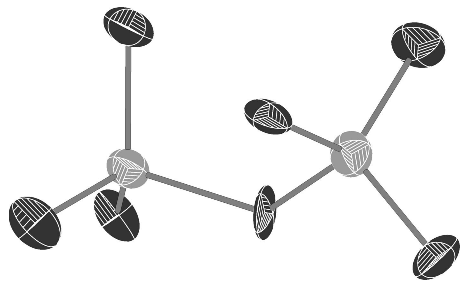

**Figure 1.** Diphosphate anion in SrZn($P_2O_7$). P atoms are drawn medium gray and O atoms black. The thermal ellipsoids are drawn at a 95% probability level.

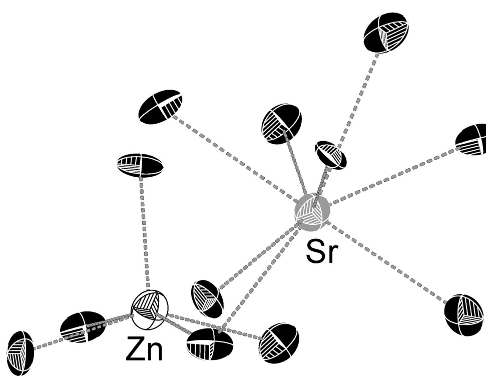


**Figure 2.** Coordination environments of Sr and Zn in SrZn($P_2O_7$). The site symmetry of both positions is 1.

α-$Sr_2(P_2O_7)$[13] (space group *Pnma*) crystallizes similarly to SrZn($P_2O_7$). However, the diphosphate anions show a syn-periplanar arrangement of the terminal $PO_3$ groups, leading to two very similar 9-fold-coordination environments [Sr−O = 239.0(2)–299.9(8) pm] around the Sr ions.

## 4. Fluorescence Spectroscopy

**Optical Properties of α-Sr($PO_3$)$_2$:Eu,Mn.** Under excitation at 323 nm, exclusively with Eu doped α-Sr($PO_3$)$_2$:Eu (2%) exhibits an intense broad emission band peaking at 404 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 3).

If doped with Mn only, a very weak emission $^4T_{1g}(G) \rightarrow {}^6A_{1g}$ around 625 nm is observed, which is excited around 420 and 440 nm [$^6A_{1g} \rightarrow {}^4A_{1g}(^4G)$ and $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$], which are typical values found for $Mn^{2+}$.[14] Therefore, it was promising to transfer the emission energy from $Eu^{2+}$ around 404 nm to $Mn^{2+}$ in a codoped sample. After codoping of α-Sr($PO_3$)$_2$ with $Eu^{2+}$ (2%) and $Mn^{2+}$ (4%), two emission bands at 404 and 625 nm, respectively, were observed (Figure 4). The optical impression of the emission is white as a result of the mixing of blue and red-orange.

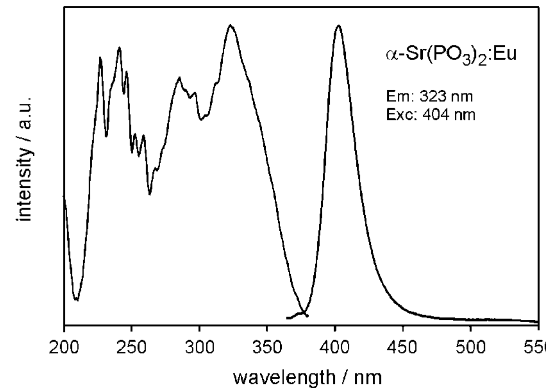


**Figure 3.** Fluorescence spectra of α-Sr($PO_3$)$_2$:Eu (2%) excited at 323 nm. The maximum of the excitation spectrum (left) was recorded at 404 nm.

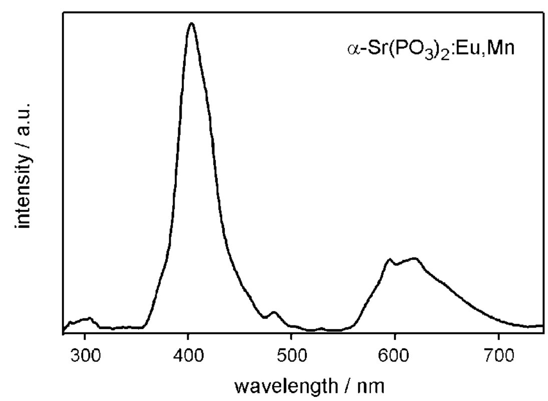


**Figure 4.** Emission spectrum of α-Sr($PO_3$)$_2$:Eu,Mn, codoped with $Eu^{2+}$ (2%) and $Mn^{2+}$ (4%) and excited at 323 nm.

**Optical Properties of SrM($P_2O_7$)$_2$:Eu,Mn with M = Sr, Zn.** Because of their different sizes, in SrZn($P_2O_7$):Eu,Mn the $Eu^{2+}$ ions are expected to be predominantly found on $Sr^{2+}$ sites and the $Mn^{2+}$ ions on $Zn^{2+}$ sites. The emission spectrum of SrZn($P_2O_7$):Eu (2%) shows an intense broad emission band peaking at 393 nm due to $Eu^{2+}$; the spectrum

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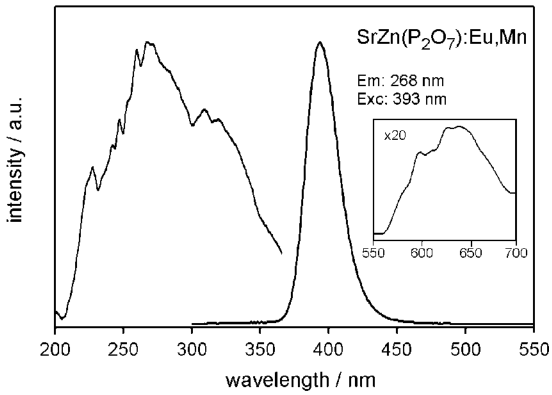


**Figure 5.** Fluorescence spectra of $SrZn(P_2O_7)$:Eu,Mn, codoped with $Eu^{2+}$ (2%) and $Mn^{2+}$ (4%) excited at 268 nm at the maximum of the excitation spectrum (left), which was recorded at 393 nm. The inset shows the emission caused by Mn enlarged by a factor of 20.

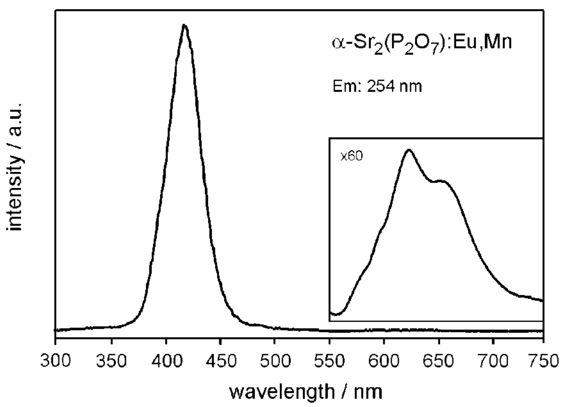


**Figure 6.** Emission spectrum of α-$Sr_2(P_2O_7)$:Eu,Mn, codoped with $Eu^{2+}$ (2%) and $Mn^{2+}$ (4%) excited at 254 nm (maximum of excitation spectrum). The inset shows the emission caused by Mn enlarged by a factor of 60.

gave no evidence for the presence of $Eu^{3+}$. $SrZn(P_2O_7)$:Mn (4%) exhibits an emission around 530 nm accompanied by a very weak emission $^4T_{1g}(^4G) \rightarrow {}^6A_{1g}$ around 640 nm with an excitation maximum at 396 nm due to a $^6A_{1g} \rightarrow {}^4A_{1g}(^4G)/{}^4E_g(^4G)$ transition. Because of the overlap of the excitation spectrum of $Mn^{2+}$ and the emission spectrum of $Eu^{2+}$, an energy-transfer Eu−Mn should be possible. If codoped with Mn and Eu, this phosphor shows two emission bands peaking at 393 and 640 nm, respectively (Figures 5 and 6). The formerly found emission below 600 nm was not detectable. We conclude, therefore, that the $Mn^{2+}$ ions located on the Sr sites emit at 640 nm while those positioned on the $Zn^{2+}$ site are responsible for the emission around 530 nm.

In α-$Sr_2(P_2O_7)$:Mn, almost no emission could be observed, but α-$Sr_2(P_2O_7)$:Mn,Eu exhibits two emission bands at 418 nm, which is the same emission observed in singly doped α-$Sr_2(P_2O_7)$:Eu,[15] and a rather weak band around 625 nm attributed to the $^4T_{1g}(^4G) \rightarrow {}^6A_{1g}$ in $Mn^{2+}$.

## 5. Discussion and Conclusions

We conclude from these facts that the energy transfer from $Eu^{2+}$ to $Mn^{2+}$ is only possible as long as both ions are located on Sr sites.

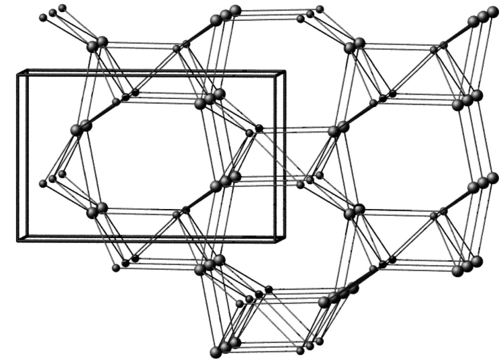

**Figure 7.** Arrangement of Sr and Zn in $SrZn(P_2O_7)$ (view approximately along [100]; Sr large spheres; Zn small spheres). The "bonds" connecting the atoms visualize the topology of the arrangement and do not represent bonds in a chemical sense.

Our first approach to explain the differing energy-transfer efficiencies was to look at the distances between adjacent cation sites because the size of these distances might play an important role in the energy-transfer process. In α-$Sr_2(P_2O_7)$, the closest Sr−Sr distances range between 3.9819(2) and 4.4810(3) Å;[13] in $SrZn(P_2O_7)$, the closest Sr−Zn distances lie between 3.5841(9) and 4.156(1) Å and the shortest Sr−Sr distance amounts to 4.1896(3) Å. In α-$Sr(PO_3)_2$, very homogeneously distributed Sr−Sr distances between 4.340(3) and 4.380(3) Å are found.[6] The shortest distances, i.e., Sr−Zn, have been determined in $SrZn(P_2O_7)$, but the visible $Mn^{2+}$ emission apparently originates from $Mn^{2+}$ doped on $Sr^{2+}$ sites. In this context, it is noteworthy that the statistical probability of finding $Eu^{2+}$ doped on a $Sr^{2+}$ position and $Mn^{2+}$ doped on a $Zn^{2+}$ position adjacent to each other is low. On average, the Sr−Sr distances are the shortest in $SrZn(P_2O_7)$ compared with α-$Sr_2(P_2O_7)$ and α-$Sr(PO_3)_2$ (4.19 vs 4.22 vs 4.36 Å). Therefore, the more intense relative intensity of the $Mn^{2+}$ emission of $SrZn(P_2O_7)$ compared with that of α-$Sr_2(P_2O_7)$ should be attributed to the shorter Sr−Sr distances. Unfortunately, this consideration does not deliver a satisfactory explanation as to why coactivated α-$Sr(PO_3)_2$ gives white light fluorescence and the others do not.

Another effect to be considered is the fact that "defects" in coactivated host structures show a tendency to form local pairs. In this context, "defects" mean the ions doped into the host matrix. This effect has been carefully investigated and described quantitatively several years ago in codoped single crystals of alkali-metal halides like potassium chloride.[16] Local pairing of $Eu^{2+}$ and $Mn^{2+}$ enhances the direct energy transfer from the first ion onto the latter. Murrieta et al. explained this pairing by minimization of the lattice energy due to local structural distortions. Consequently, the higher the symmetry of the packing of the $Sr^{2+}$ ions is, the more powerful this effect is.

The relative blue/red luminescence found for coactivated α-$Sr_2(P_2O_7)$ and $SrZn(P_2O_7)$ is by far worse than that found in α-$Sr(PO_3)_2$. In the latter a highly symmetric diamondlike substructure of the Sr ions has been found,[6] while in the first ones, the Sr−Sr and Sr−Zn arrangements have a very

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low symmetry, exhibiting channels (Figure 7) in which the diphosphate ions are positioned. If codoped with $Eu^{2+}$ and $Mn^{2+}$, the local structural distortions should be more effective in α-$Sr(PO_3)_2$. Accordingly, the "pairing of defects" concept explains our results best and delivers an excellent explanation for the white fluorescence observed.

Thus, codoped α-$Sr(PO_3)_2$:Eu,Mn emits white light during excitation with an UV wavelength of 323 nm, which is accessible by UV LEDs based on AlGaN.[17] Therefore, we think that this two-color phosphor might be useful for the development of white LEDs based on UV LEDs. Further investigations to shift the excitation as well as the emission wavelength to slightly longer wavelengths are being conducted and will be presented elsewhere.

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**Supporting Information Available:** X-ray crystallographic files (CIF) of $SrZn(P_2O_7)$, fluorescence spectra of α-$Sr(PO_3)_2$:Mn and $SrZn(P_2O_7)$:Mn, and a representation of the $Sr^{2+}$ arrangement in α-$Sr_2(P_2O_7)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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