

New Compounds with Eulytine Structure: Crystal Chemistry and Luminescence

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Some new compounds with eulytine structure are reported. Their composition is: $\text{Me}_3\text{Ln}(\text{PO}_4)_3$, where $\text{Me}=\text{Sr}$ or Ba and $\text{Ln}=\text{La}$, Nd , Gd , Y , Lu , Sc , In , Bi ; $\text{Ca}_3\text{Bi}(\text{PO}_4)_3$; $\text{Me}_4(\text{PO}_4)_2\text{SO}_4$, where $\text{Me}=\text{Ba}$ or Sr and $\text{Me}_{3-x}\text{Ln}_{1+x}(\text{PO}_4)_{3-x}(\text{SiO}_4)_x$, where $0 < x < 1$. The Ce^{3+} ion shows efficient ultraviolet emission in the eulytine phosphates, the Sb^{3+} ion shows an efficient near-white emission in these host lattices.

I. Introduction

The crystal structure of the mineral $\text{Bi}_4\text{Si}_3\text{O}_{12}$ (eulytine) was solved many years ago by Menzer (1) and later on refined by Segal et al. (2). The structure is cubic; the Si^{4+} ions are tetrahedrally coordinated by oxygen, whereas Bi^{3+} occupies a distorted octahedron of oxygen ions (three close neighbours at 2.15 Å and three more at 2.62 Å). A number of Pb^{2+} and Bi^{3+} compounds are isomorphous with eulytine (3).

Shinn (4) seems to be the first to have reported compounds with eulytine structure that do not contain cations with outer s^2 electron configuration, viz., $\text{Sr}_7\text{Sn}(\text{PO}_4)_6$ and $\text{Sr}_7\text{Zr}(\text{PO}_4)_6$ and the analogous barium compounds. This paper presents results that were obtained in an attempt to introduce trivalent lanthanide ions in the eulytine structure. New compounds of the type $\text{Me}_3\text{Ln}(\text{PO}_4)_3$ and $\text{Me}_4(\text{PO}_4)_2\text{SO}_4$ ($\text{Me}=\text{Sr}$ or Ba , $\text{Ln}=\text{trivalent lanthanide}$) were found. Their crystal chemistry and applicability as phosphor host lattices are discussed.

2. Experimental Part

Samples were prepared by usual ceramic methods. Firing temperatures varied from 950-1150°C. Phosphates $\text{Me}_3\text{Ln}(\text{PO}_4)_3$ were prepared from MeHPO_4 and Ln_2O_3 , mixed phosphate-sulphates $\text{Me}_4(\text{PO}_4)_2\text{SO}_4$ from MeHPO_4 , MeCO_3 and $(\text{NH}_4)_2\text{SO}_4$. The starting material for silicon was very fine-grained SiO_2 . X-ray powder diagrams were obtained using a Philips diffractometer ($\text{CuK}\alpha$

radiation). The optical properties were measured as described previously (5).

3. Results and Discussion

3.1. Compounds $\text{Me}_3\text{Ln}(\text{PO}_4)_3$

Compositions $\text{Me}_3\text{Ln}(\text{PO}_4)_3$ were found to be isomorphous with eulytine if $\text{Me}=\text{Sr}$ or Ba and $\text{Ln}=\text{La}$, Nd , Gd , Bi , Y , La , Sc , or In (see Table I).

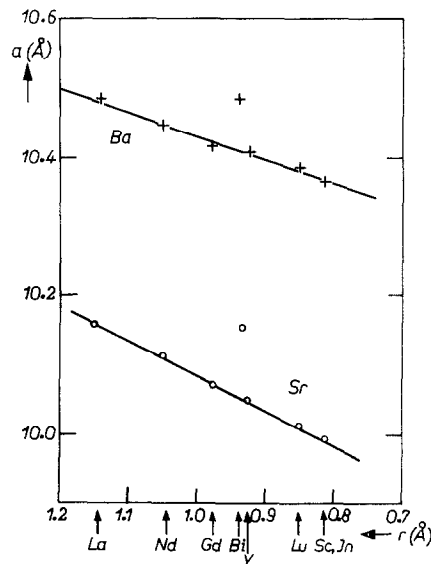


FIG. 1. Lattice parameter a of compounds $\text{Me}_3\text{Ln}(\text{PO}_4)_3$ with eulytine structure versus Ahrens radius of Ln^{3+} ion. Crosses are for $\text{Me}=\text{Ba}$, circles for $\text{Me}=\text{Sr}$.

TABLE I
LATTICE PARAMETERS (Å) OF COMPOUNDS WITH EULYTINE STRUCTURE

Ba ₃ La(PO ₄) ₃	10.48	Sr ₃ La(PO ₄) ₃	10.13	Ba ₄ (PO ₄) ₂ SO ₄	10.61
Ba ₃ Nd(PO ₄) ₃	10.44	Sr ₃ Nd(PO ₄) ₃	10.09	Sr ₄ (PO ₄) ₂ SO ₄	10.18
Ba ₃ Gd(PO ₄) ₃	10.41	Sr ₃ Gd(PO ₄) ₃	10.05	Ba _{2.5} Gd _{1.5} (PO ₄) _{2.5} (SiO ₄) _{0.5}	10.40
Ba ₃ Y(PO ₄) ₃	10.40	Sr ₃ Y(PO ₄) ₃	10.03	Ba ₂ Gd ₂ (PO ₄) ₂ SiO ₄	10.40
Ba ₃ Lu(PO ₄) ₃	10.38	Sr ₃ Lu(PO ₄) ₃	10.00	Ba ₂ Y ₂ (PO ₄) ₂ SiO ₄	10.38
Ba ₃ Sc(PO ₄) ₃	10.36	Sr ₃ Sc(PO ₄) ₃	9.98	Ca ₃ Bi(PO ₄) ₃	9.92
Ba ₃ In(PO ₄) ₃	10.36	Sr ₃ In(PO ₄) ₃	9.98		
Ba ₃ Bi(PO ₄) ₃	10.48	Sr ₃ Bi(PO ₄) ₃	10.15		

It seems reasonable to assume that this is also the case for the other lanthanide ions. The lattice parameter varies linearly with the Ahrens radius of the Ln³⁺ ion (Fig. 1). Only the Bi³⁺ ion does not fit into this scheme. The data in Table I and Fig. 1 seem to indicate that in the present compounds Bi³⁺ is of the same size as La³⁺. This was also observed by Wolfe and Newnham (6) in a study on lanthanide-substituted bismuth titanate (Bi_{4-x}Ln_xTi₃O₁₂) and may be related to the very asymmetric coordination of Bi³⁺ in eulytine as well as in the titanate. This asymmetry is probably due to the s² configuration of the Bi³⁺ ion and will, therefore, be less pronounced for the lanthanide ions (7, 8).

That such a distortion seems to stabilize the eulytine structure may be concluded from the fact that compositions Ca₃Ln(PO₄)₃ do not show eulytine structure except for Ca₃Bi(PO₄)₃ (Table I). For all other Ln ions we found two phases in the X-ray powder diagram, viz., whitlockite [β -Ca₃(PO₄)₂] and the lanthanide phosphate (monazite, zircon, or CrVO₄ structure). Using Pb²⁺ instead of the alkaline earth ions yielded very complicated X-ray diagrams which were not investigated further. Only Pb₃Bi(PO₄)₃ has eulytine structure as reported by Durif (3).

The corresponding vanadates do not have eulytine structure. The compositions Me₃La(VO₄)₃ (Me=Ba, Sr, Ca) are isomorphous with α -Sr₃(PO₄)₂ as reported by Le Flem and Olazcuaga (9). We found the same for Bi. For Gd, Y, and Lu, however, the X-ray diagrams show a mixture of an α -Sr₃(PO₄)₂ phase and a zircon phase, whereas for In the results were too complicated for interpretation.

In view of the complete miscibility in a system like Me₃(VO₄)₂-Me₃La(VO₄)₃ (9), we investigated superficially the systems Sr₃(PO₄)₂-Sr₃Y(PO₄)₃ and Sr₃(PO₄)₂-Sr₃La(PO₄)₃ where the end members have α -Sr₃(PO₄)₂ and eulytine structure, respectively. Samples were cooled slowly after firing at

1150°C. It was found that about 10% of the strontium in Sr₃(PO₄)₂ may be replaced by yttrium (according to 3 Sr²⁺ → 2 Y³⁺ + vacancy). For higher yttrium concentrations the eulytine phase appears. The solid solution series on the Sr₃(PO₄)₂-rich side of the system shows β -Sr₃(PO₄)₂ structure [also known as modified Sr₃(PO₄)₂]. In the system Sr₃(PO₄)₂-Sr₃La(PO₄)₃ about 15% of the strontium ions in Sr₃(PO₄)₂ can be replaced by lanthanum. The structure remains that of α -Sr₃(PO₄)₂. For higher lanthanum concentrations the eulytine phase appears.

The compounds Me₃Ln(PO₄)₃ described above offer a possibility to introduce lanthanide ions in the eulytine structure. The lanthanide concentration may be lowered by replacing the phosphate group by sulphate (and Ln by Me) or increased by replacing the phosphate group by silicate (and Me by Ln). These experiments are described in the next two sections.

3.2. Compounds Me₄(PO₄)₂SO₄

The compounds Ba₄(PO₄)₂SO₄ and Sr₄(PO₄)₂SO₄ have eulytine structure (Table I). The calcium analogue, however, could not be obtained. The X-ray diagram contains the reflections of β -Ca₃(PO₄)₂ and CaSO₄. The corresponding vanadium compounds could not be obtained either.

3.3. Compositions Me_{3-x}Ln_{1+x}(PO₄)_{3-x}(SiO₄)_x

The lanthanide concentration in the eulytine structure can be increased by preparing compositions Me_{3-x}Ln_{1+x}(PO₄)_{3-x}(SiO₄)_x. This was performed for a small number of combinations of Me and Ln only. The limiting composition of these solid solutions with eulytine structure corresponds to roughly $x = 1$ (see Table I).

If Ln=Bi, however, a solid solution with eulytine structure is expected for the complete series, because the end members [e.g., Ba₃Bi(PO₄)₃ and Bi₄(SiO₄)₃]

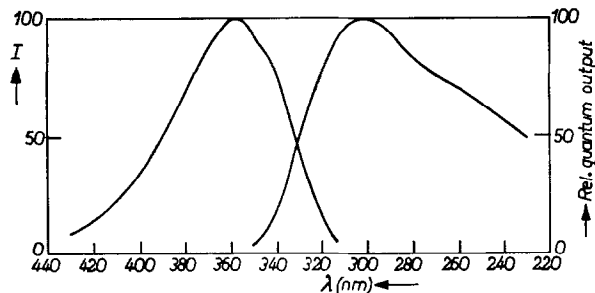


FIG. 2. Spectral energy distribution (left) and excitation spectrum (right) of the emission of $\text{Sr}_3\text{Y}(\text{PO}_4)_3\text{-Ce}$. I gives the radiant power per constant wavelength interval in arbitrary units.

both have eulytine structure and their lattice parameters do not differ much (10.48 and 10.30 Å, respectively). Surprisingly enough we observed a very broad miscibility gap in this system. The limiting composition of the phosphate-rich side of the system is at low values of x (in contradiction to the corresponding case with Gd or Y).

3.4. Luminescence Studies

The chemical composition of the compounds described above recalls the compositions of the host lattice of a number of well-known, efficient phosphors, such as $\text{Sr}_3(\text{PO}_4)_2$, YPO_4 , BaSO_4 . For this reason, we introduced a number of well-known luminescence centres into a selected group of the compounds with eulytine structure.

For many of the activators we observed emission at room temperature with moderate to low efficiencies under ultraviolet excitation. In some cases, the unactivated host lattices also show a weak blue emission, as reported previously for YPO_4 and LaPO_4 by Wanmaker et al. (10). Substitution of V for P in the eulytine phosphates results in materials with weak blue emission. Eu^{3+} and Tb^{3+} give a weak red and green emission, respectively. Practically no emission was observed for Bi^{3+} , Pb^{2+} , and Sn^{2+} ,

whereas Tl^+ gives a blue, Cu^+ a green and Ti^{4+} a green-white emission. The Eu^{2+} ion in the phosphate-sulphate gives a blue-white emission of medium efficiency.

The Ce^{3+} ion gives efficient emission under ultraviolet excitation. In Fig. 2 the excitation spectrum and spectral energy distribution of the emission of $\text{Sr}_3\text{Y}(\text{PO}_4)_3\text{-Ce}$ are given. The emission band peaks at about 360 nm. Its half-width value is 60 nm. For Ce^{3+} in YPO_4 these values are 355 and 30 nm (11), for Ce^{3+} in $\text{Sr}_3(\text{PO}_4)_2$ 325 and 40 nm (12). The broadness of the Ce^{3+} emission band in the eulytine structure may be due to a disorder between the Sr^{2+} and Y^{3+} ions which occupy the Bi^{3+} sites of the eulytine structure of $\text{Sr}_3\text{Y}(\text{PO}_4)_3$. Due to this disorder, the crystal field at the Ce^{3+} ion varies from ion to ion, resulting in a somewhat different position of the emission peak maximum for the different Ce^{3+} ions. We found that all activators in the present host lattices show relatively broad line or band emission. We observed quantum efficiencies for the Ce^{3+} emission of $\text{Sr}_3\text{Y}(\text{PO}_4)_3\text{-Ce}$ amounting to 40% for 254-nm excitation and 50% for 300-nm excitation (maximum excitation band). The radiant efficiency for cathode-ray excitation (20 kV) was found to be 0.5%. By varying the preparation conditions, higher values can probably be obtained. For Ce^{3+} in $\text{Ba}_3\text{La}(\text{PO}_4)_3$, similar results were found.

The Sb^{3+} ion too shows efficient luminescence in the eulytine phosphates. The emission colour is near-white. Figure 3 shows the excitation and emission spectra of the emission of $\text{Sr}_3\text{Y}(\text{PO}_4)_3\text{-Sb}$. The half-width value is considerably larger than observed usually for Sb-activated phosphates [see e.g. (13)]. We observed a quantum efficiency of the Sb^{3+} emission 35% for 254-nm excitation and 40% for excitation into the excitation band maximum. The efficiency for cathode-ray excitation is very low. The luminescence properties of Sb^{3+} in these compounds do not vary strongly with the choice of the large cations of the host lattice. The composition $\text{Sr}_3\text{La}(\text{PO}_4)_3\text{-Sb}$, however, did not luminesce.

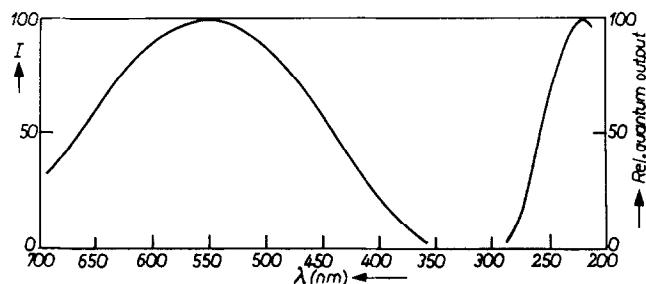


FIG. 3. Spectral energy distribution (left) and excitation spectrum (right) of the emission of $\text{Sr}_3\text{Y}(\text{PO}_4)_3\text{-Sb}$.

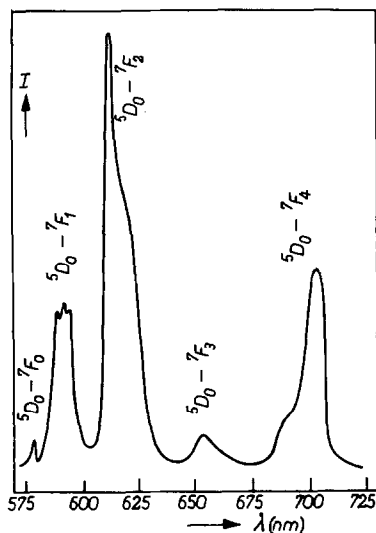


FIG. 4. Spectral energy distribution of the emission of $\text{Sr}_3\text{Y}(\text{PO}_4)_3\text{-Eu}^{3+}$. The assignment of the transitions is indicated.

The phenomenon of broad emission bands or lines in the present compounds is most dramatically shown by the Eu^{3+} ion (see Fig. 4). The emission lines of Eu^{3+} are usually less than 10 Å broad. In $\text{Sr}_3\text{Y}(\text{PO}_4)_3$, however, the half-width values are an order of magnitude larger. This is a strong indication that the Sr^{2+} and Y^{3+} ions are not long-range ordered (14).

A number of well-known examples of energy transfer were also observed in the compounds with

eulytine structure, e.g., from Ce^{3+} to Tb^{3+} or Mn^{2+} . The latter ion shows a red emission.

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