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Low-Temperature Flux Synthesis, Crystal Structure and Ce-Doped Luminescence of the First Lutetium Diphosphate $NH_4LuP_2O_7$

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The first lutetium diphosphate $NH_4LuP_2O_7$ has been prepared by a two-step, low-temperature self-flux synthesis in the presence of the F^- anion, functioning as a mineralizer, which played a significant role in the synthetic process. The crystal structure has been characterized by single-crystal X-ray diffraction. The title compound crystallizes in a monoclinic system of the space group $P2_1/c$ (No. 14), a = 7.651(2) Å, b = 10.789(2) Å, c = 8.577(2) Å, β = 105.75(3)°, V = 681.4(2) Å^3, Z = 4. The three-dimensional framework of $NH_4LuP_2O_7$, composed of $Lu_2P_4O_{14}$ building units formed by vertex-linking LuO_6 and P_2O_7 goups, is isostructural with compounds of the type $KAlP_2O_7$ in the ternary diphosphate($A^IM^{III}P_2O_7$) system. X-ray-excited luminescence measurements of Ce-activated samples show insteresting scintillation properties with a short decay time of 16 ns at room temperature.

Introduction

Recently, investigation of the synthesis and characterization of wide-bandgap rare-earth (RE) phosphate materials has gained much more attention, for their potential applications in diverse areas such as X- and gamma-radiation detectors, lighting, display phosphors, light-emitting diodes, scintillators, and solid state lasers, and because they are highly transparent, easily shaped, and cost-effective.[1–4] In contrast to the well-known ternary rare-earth phosphates, the diphosphates, which should have had potentially attractive applications on the basis of their analogous structure with the phosphates, are still to be explored, except for the compounds already reported, partly because it is difficult to synthesize them in the crystalline and pure phase requested for considerable applications. $MLaP_2O_7$ (M = Li, Na, K),[5] $NaCeP_2O_7{\cdot}4.5H_2O$,[6] and $NaGdP_2O_7{\cdot}4.5H_2O$,[7] obtained from reaction in solution, have been reported, but only some complex X-ray powder diffraction patterns have been given without further indexing for the lattice parameters, and no single-crystal X-ray structural determinations have been reported to support the lattice parameters until now. In addition, the function of the pH value is rather subtle in the solution method. Jansen et al.[8] prepared $CsYbP_2O_7$ by rigorous solid-state reaction (under argon at 1173 K) and characterized the crystal structure without further investigation. Most often it is not so easy to obtain the pure phase and carry out further purification by high-temperature solid reactions, as reported in the preparations of $NaGdP_2O_7$,[7] AYP_2O_7 (A = Na,[9] K,[10] Cs[11]), and $NaEuP_2O_7$[12] in the presence of an auxiliary solvent.

The above compounds have been mostly prepared by reaction in solution and by the high-temperature flux method. In addition, other relevant characterization data and optical properties of this type of compounds have been seldom reported. Along this line of research, we present here the novel two-step, low-temperature self-flux synthesis, crystal structure, and Ce-activated luminescence of $NH_4LuP_2O_7$.

Results and Discussion

F^--Optimized Procedure

The preparation procedure is outlined in reaction (1) and reaction (2). As shown in reaction (1), sodium lutetium tetrafluoride, $NaLuF_4$, was obtained under mild water-free flux of abundant H_3BO_3, with a low melting point of 458 K, instead of the traditional synthetic method for this type of compounds.[13] Excess H_3BO_3 and a stoichiometric quantity of NaF were essential in the first reaction.

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$$Lu_2O_3 + 8\ NaF + 2\ H_3BO_3 \xrightarrow{523\ K} 2\ NaLuF_4 + 2\ Na_3BO_3 + 3\ H_2O\uparrow \quad (1)$$

$$NaLuF_4 + 3\ NH_4H_2PO_4 + 2\ NaF \xrightarrow{553\ K} NH_4LuP_2O_7 + Na_3PO_4 + 2\ NH_3\uparrow + HF\uparrow + H_2O\uparrow \quad (2)$$

In reaction (2), the mixture of prepared $NaLuF_4$, excess $NH_4H_2PO_4$, and the correct quantity of NaF was heated in a Teflon-lined stainless steel autoclave at 553 K. Here the excess $NH_4H_2PO_4$ (melting point: 453 K) was used as the self-flux, and the quantity of NaF played a very important role. Lots of $LuPO_4$ powder and a few crystals of $NH_4LuP_2O_7$ were produced in the absence of NaF. The yield of $NH_4LuP_2O_7$ increased by adding NaF, and the pure phase of the target compound could only be obtained when the molar ratio of F/Lu was larger than two. This observation indicates that reaction (2) tends to yield $NH_4LuP_2O_7$ instead of $LuPO_4$ in the presence of a large quantity of F^-.

Related investigations were carried out for systems with RE (RE = Y, La, Nd, Gd, Er, Yb) instead of Lu. $NH_4YP_2O_7$ and $NH_4YbP_2O_7$ were obtained with the same structure type, while $REPO_4$ was produced in systems containing La, Nd, and Gd. The Er system yielded a mixture of $ErPO_4$ and $NaErF_4$. Obviously, the size of the ion plays a very important role in the synthetic procedure.

Crystal Structures of $NH_4LuP_2O_7$

The many structural investigations devoted to the A^I-$M^{III}P_2O_7$-type diphosphates in the past two decades have shown the existence of eight structural types.

The compounds of type I exhibit the $KAlP_2O_7$[14] structure, whereas those of type II are isotypic with $NaFeP_2O_7$.[15] The lithium-containing compounds constitute the third family and adopt the $LiFeP_2O_7$ structure.[16] The fourth type is only represented by α-$NaTiP_2O_7$.[17] A fifth type occurs for the $NaYP_2O_7$ structure,[9] and KYP_2O_7 belongs to structural type VI.[10] The structural investigation of $NaEuP_2O_7$[12] and $NaGaP_2O_7$[7] reveals new structural arrangements of type VII and type VIII, respectively.

The crystal structure of the title compound $NH_4LuP_2O_7$ was determined by single-crystal X-ray diffraction. It is isotypic with type I compounds and possesses a three-dimensional framework consisting of $Lu_2P_4O_{14}$ building units as shown in Figure 1. The NH_4^+ cations occupy the one-dimensional six-membered ring tunnels (about 3.83 × 3.83 Å, evaluated from the O···O distances) and participate in moderate hydrogen bonding with the framework oxygen atoms (N–H···O hydrogen bonds with distances of 2.884–3.344 Å). The tunnels running along [001] result from the stacking of rings formed by the edges of three LuO_6 octahedra and four PO_4 tetrahedra. Adjacent layers are generated by the *c*-glide plane, and these layers form a three-dimensional network with tunnels running along the *c*-axis.

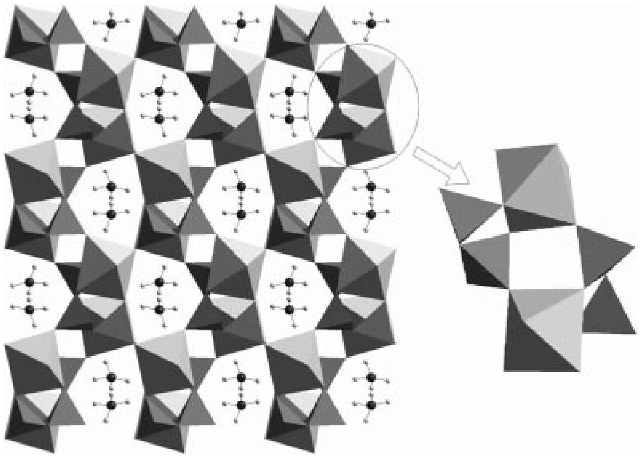
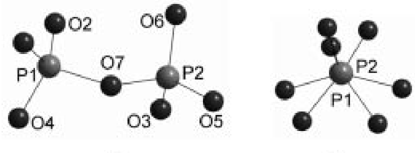


Figure 1. (a) 3D polyview structure along the [001] direction (b) $Lu_2P_4O_{14}$ structural building unit in the crystal structure of $NH_4LuP_2O_7$ (LuO_6, light-gray octahedra; PO_4, dark-gray tetrahedra; N atoms black spheres; H atoms, light gray spheres).

Lu atoms have a hexagonal close-packed arrangement. Each LuO_6 group is connected, through Lu–O–P bonds, to five P_2O_7 groups: two corners of the LuO_6 octahedron are linked to one P_2O_7 group, and the other four corners are connected with four distinct P_2O_7 groups. The LuO_6 octahedra are also distorted [the bond valence sum (BVS) of Lu is 3.19], as shown by the Lu–O distances ranging from 2.143(12) to 2.223(11) Å and O–Lu–O bond angles ranging from 82.8(4) to 178.9(5)°. The P_2O_7 group presents a staggered configuration with one long P–O bond and three much shorter P–O bonds (Figure 2), which is very common in the $A^IM^{III}P_2O_7$ family except for the semi-staggered configuration in several compounds ($NaInP_2O_7$,[18] $NH_4VP_2O_7$,[19] and $NaYP_2O_7$[9]) and the eclipsed configuration in type II, III, VI, VII, and VIII compounds. The P–$O_{terminal}$ bonds (average: 1.511 Å) are shorter than the P–$O_{bridging}$ bonds (average: 1.597 Å), and the P–O–P bond angle is 128.9(8)°, which falls into the generally observed range of 122–141° for ternary diphosphate compounds. The O–P–O angles show distortion from the ideal tetrahedral geometry [105.1(6) to 113.9(8)°], and the BVSs of the two P atoms are 4.93 and 4.90. The calculated BVSs are very close to the chemical valences; this confirms the reliability of the determined structure.[20,21]



(a) (b)

Figure 2. Configuration of P_2O_7 in $NH_4LuP_2O_7$ viewed (a) in plane (b) along the P–P direction.

Luminescence Properties

The Ce-doped crystals were grown under the same conditions by adding CeF_3 in reaction (1). X-ray-excited luminescence (XEL) measurements showed that $NH_4LuP_2O_7$ activated with 0.5 at.-% Ce^{3+} exhibited the strongest band emission when the concentration of Ce^{3+} was in the range 0.1–3 at.-% (stoichiometric amounts of lutetium oxide). The XEL spectrum of $NH_4LuP_2O_7$:Ce^{3+} (0.5 at.-%) shows a band emission with a maximum at 375 nm (Figure 3), which can be explained by transitions occurring between the lowest level of the excited 5d (2D) sate and the ground $^2F_{5/2}$ and $^2F_{7/2}$ levels of 4f(^{2}F) in the Ce^{3+} ion. Compared with the reported Ce^{3+}-activated spectrum of lutetium phosphate,[22] the emission band in Figure 3 is less well-resolved because of increased overlap. A Gaussian fit reveals that the emission band consists of two sub-bands centered at about 364 and 395 nm. An energy discrepancy of about 2156 cm^{-1}, which is a typical value for the spin-orbit-split ground level of the Ce^{3+} ion ($^2F_{5/2}$ and $^2F_{7/2}$), confirms the Ce^{3+} d-f origin of this emission.

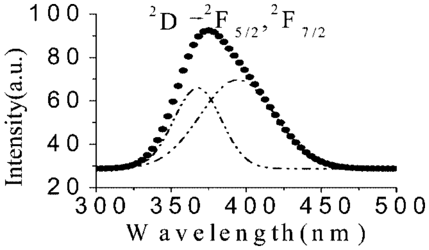


Figure 3. The X-ray-excited luminescence spectra of 0.5 at.-% Ce-activated $NH_4LuP_2O_7$ measured at room temperature.

The scintillation pulse shape for the 0.5 at.-% Ce-activated sample is shown in Figure 4, which exhibits a decay time of about 16 ns. The large contribution and very short decay time of this compound produces an excellent zero-time (initial) scintillation amplitude. This is very advantageous, since for the majority of (and especially for timing) applications, it is the zero-time scintillation amplitude that is the most important factor.[23]

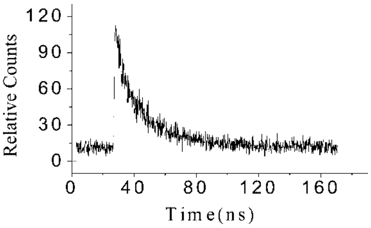


Figure 4. Scintillation decay curve of 0.5 at.-% Ce-activated $NH_4LuP_2O_7$ measured after pulsed X-ray excitation.

The luminescence properties of Ce^{3+} in different phosphate hosts are interesting because of their influence on the crystal field.[24] $LuPO_4$:Ce^{3+} (0.1 at.-%)[25] has the strongest band emission (360 nm) with a decay time of 24 ns, while $K_3Lu(PO_4)_2$:Ce^{3+} (0.5 at.-%)[22,26] and $Rb_3Lu(PO_4)_2$:Ce^{3+} (1 at.-%)[26] show strong band emissions (410 nm) with decay times of 37 and 34 ns respectively.

Conclusions

The first lutetium diphosphate $NH_4LuP_2O_7$ was synthesized under novel two-step, mild reaction conditions. The F^- optimized synthetic procedure is very significant. The open-framework crystal structure is isotypic with $KAlP_2O_7$ type compounds. The P_2O_7 group is staggered. The Ce-doped sample shows interesting luminescence and scintillation properties with a very fast decay time of 16 ns. Ternary diphosphates of other representative rare-earth systems are being investigated by this new method of synthesis for their analogous properties, and further researche will be carried out on the relation between activator concentration and activator type and luminescence and scintillation properties.

Experimental Section

Materials and Measurements: All chemicals were obtained from commercial sources and used as received. The products were examined by powder X-ray diffraction (Rigaku D/max 2550 V diffractometer, Cu-K_α) in order to confirm their phase identity and purity. Single-crystal X-ray diffraction data were collected with a Nonius Kappa CCD with graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). The XEL and decay time measurements were carried out at room temperature with a FluoMain X-ray-excited luminescence spectrometer and a pulsed X-ray-excited decay measuring equipment designed at Tongji University. IR spectra were recorded with a Nicolet-NEXUS spectrophotometer using KBr discs. Elemental analysis was performed with an EPMA-8705H_2 (Lu, P) and a PE-2004II (N) apparatus.

Reaction (1): Lu_2O_3 (1.592 g), H_3BO_3 (1.855 g), and NaF (0.67 g) were mixed in the molar ratio 2:15:8. The mixture was sealed in a 40-mL Teflon-lined stainless steel autoclave after grinding fully and heated under autogenous pressure at 523 K for 120 h. It was cooled to 443 K at a rate of 1 K h^{-1} and then left to cool to room temperature. The product was washed with hot deionized water for purification (2.081 g, 95% based on Lu_2O_3). X-ray powder diffraction indicated that $NaLuF_4$ was obtained (J.C.P.D.S No. 27–726).

Reaction (2): $NaLuF_4$ (2.08 g), $NH_4H_2PO_4$ (3.68 g), and NaF (0.67 g) were mixed in the molar ratio 1:4:2 and heated in a Teflon-lined stainless steel autoclave at 553 K for 120 h. It was cooled to 453 K at a rate of 1 K h^{-1} and then left to cool to room temperature. The product was washed with hot deionized water for purification, and colorless, octahedral bipyramidal crystals of $NH_4LuP_2O_7$ were obtained (2.120 g, 76% based on $NaLuF_4$). $NH_4LuP_2O_7$(366.949): calcd. N 3.81, P 16.88, Lu 47.68; found N 3.48, P 17.46, Lu 48.26. IR(KBr): υ_3(N–H) (3286 cm^{-1}), υ_1(N–H) (3035 cm^{-1}), 2υ_4(N–H) (2850 cm^{-1}), υ_4(N–H) (1434 cm^{-1}), υ_s(PO_3) (1203 cm^{-1}, 1110 cm^{-1}), υ_{as}(POP) (941 cm^{-1}), υ_s(POP) (748 cm^{-1}), δ(PO_2 terminal bending) (624, 574, 470, 420 cm^{-1}).

X-ray Crystallographic Study: Monoclinic, space group $P2_1/c$ (No. 14), a = 7.6507(15) Å, b = 10.789(2) Å, c = 8.577(2) Å, β = 105.75(3)°, V = 681.4(2) Å^3, Z = 4, D = 3.577 g cm^{-3}, crystal dimensions [mm], $0.07 \times 0.03 \times 0.02$; μ = 14.951 cm^{-1}, F(000) = 672, T = 293(2) K; 1588 unique reflections (R_{int} = 0.0874) and 101 parameters were used for the full-matrix, least-squares refinement of F^2 using the direct method in the program package SHELXL-97/2,[27] R_1 = 0.0690 [$I > 2\sigma(I)$], R_1 = 0.0842 (all data); wR_2 = 0.1211 [$I > 2\sigma(I)$], wR_2 = 0.1271 (all data). Further details of the crystal-structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the CSD-391320 (crysdata@FIZ-Karlsruhe.de).

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