EDTA-assisted phase conversion synthesis of (Gd$_{0.95}$RE$_{0.05}$)PO$_4$ nanowires (RE = Eu, Tb) and investigation of photoluminescence

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ABSTRACT

Hexagonal (Gd$_{0.95}$RE$_{0.05}$)PO$_4$$

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1. Introduction

One-dimensional (1D) nanostructures such as nanowires, nanorods, and nanotubes are drawing broad research interest owing to their unique physicochemical properties and applications in nanoscale devices, and a variety of strategies have been developed for their synthesis, typically including template-directed growth, the use of supersaturation control to modify the growth habit of the seed, and the use of capping reagents to kinetically control the growth rates of different crystal facets [1–5]. Rare-earth (RE) ions present numerous well-defined electronic transitions involving their 4f and 5d shells, and the RE-related materials have been applied in solid-state lasers, plasma display panels (PDPs), biolabeling, and so on [6–8]. Wang et al. [9] employed NaYF$_4$:Yb,Er up-conversion nanoparticles as a novel fluorescent label for the detection of latent fingerprints with high sensitivity and broad applicability. As for 1D nanomaterials, Yang et al. [10] prepared nearly monodispersed and well-defined Gd$_2$O$_3$:Eu$^{3+}$ nanorods and microrods through hydrothermal reaction followed by conventional annealing, and explored their size-dependent photoluminescence for potential application in high-performance phosphors. Ethylene
diamine tetraacetic acid (EDTA) is well known to have strong ability to coordinate with metal ions with its four carboxyl groups (-COOH) and two nitrogen atoms, and has been tested to be useful in the morphology/structure modification and surface functionalization of an inorganic material [11]. Employing Na$_2$EDTA as a capping reagent, Huang et al. [12] synthesized 1D nanobelts and nanorods of YVO$_4$ via a facile hydrothermal route, and morphology-dependent luminescence of the Eu$^{3+}$ doped YVO$_4$ was also investigated.

One-dimensional rare-earth orthophosphates (REPO$_n$) may find applications in phosphor displays and lighting, waveguide devices, fluorescence labels for biological detection, and solid-state lasers [13,14]. Gd$^{3+}$ ion is well known to be strongly paramagnetic since it has the largest number (seven) of unpaired electrons in the lanthanide family, and is frequently used in the phosphor field as a sensitizer to improve excitation absorption and to enhance activator luminescence through energy transfer [15,16]. Therefore, gadolinium phosphate as a host lattice may combine the luminescence of the activator and the magnetic properties of Gd$^{3+}$ [17]. Gadolinium phosphate has two basic structures depending on the extent of hydration, with the hydrous phase (GdPO$_4$·nH$_2$O) belonging to the rhabdophane type (hexagonal system, space group Pnma) and the anhydrous one (GdPO$_4$) belonging to the monazite type (monoclinic, space group P2$_1$/n). Huang et al. [18] developed a low-temperature solution approach to prepare hexagonal GdPO$_4$·H$_2$O nanorods with hydrogel-like property and proposed its utilization in encapsulation and drug release. Yu et al. [19] prepared monoclinic GdPO$_4$·Eu$^{3+}$ nanowires and nanorods via hydrothermal reaction and compared their luminescence properties. Through a melt–quenching method, Guo et al. [20] fabricated transparent glass ceramics containing GdPO$_4$:Eu/Tb crystallites and manifested their possible application in lighting and luminescence fields. It is noteworthy that gadolinium phosphates were mostly investigated for the anhydrous monoclinic phase, since water of hydration always induces serious luminescence quenching. Layered hydroxyl nitrate (LHN) compounds, exemplified by the group of RE$_2$(OH)$_2$NO$_3$·nH$_2$O, are attracting keen research interest during recent years owing to their unique layered structures and the rich electronic, optical, magnetic, and catalytic functionalities of the lanthanide (Ln) elements. We established in this work a new technique to generate (Gd$_{0.95}$RE$_{0.05}$)PO$_4$·nH$_2$O (RE = Eu, Tb) nanowires, employing nanosheets (thickness 3–5 nm) of the LHN as a sacrificial precursor, monoammonium phosphate (NH$_4$H$_2$PO$_4$) as the phosphate source, and EDTA as a morphology modifier. It was also found that calcining the hydrated hexagonal nanowires at 500 °C did not bring obvious change to the morphology and phase purity but substantially enhanced their luminescence owing to dehydration. The effects of EDTA content, hydrothermal temperature on phase structure, morphology and photoluminescence of the nanowires were systematically studied, and the energy transfer from Gd$^{3+}$ to Eu$^{3+}$ and Tb$^{3+}$ was also discussed.

### 2. Experimental details

#### 2.1. Synthesis of LHN nanosheets and conversion into (Gd$_{0.95}$RE$_{0.05}$)PO$_4$·nH$_2$O (RE = Eu, Tb) nanowires

The starting gadolinium, europium, and terbium sources were Gd$_2$O$_3$, Eu$_2$O$_3$, and Tb$_4$O$_7$ (99.99% pure, Huizhou Ruier Rare-Chem. Hi Tech. Co. Ltd., Huizhou, China), and the nitrate solution of RE was prepared by dissolving the corresponding oxide with a proper amount of nitric acid. The reagents of ammonium water, EDTA (C$_{10}$H$_{16}$N$_2$O$_8$), and monoammonium phosphate (NH$_4$H$_2$PO$_4$) were analytical grade products from Shenyang Chemical Reagent Factory (Shenyang, China).

The LHN precursor was produced via titrating nitrate solution of the rare-earth with ammonium water (1 mol/L) at ~4 °C [21]. For the phase conversion synthesis of phosphate, 0.5 mmol of LHN was dispersed in ~70 mL of deionized water, to which 1 mL of ammonium water (1 mol/L) at ~4 °C was added followed by magnetic stirring for 30 min and addition of a certain amount of EDTA. The resultant suspension was transferred into a Teflon-lined stainless steel autoclave of 100 mL capacity after magnetic mixing for 10 min, and the tightly sealed autoclave was then put into an electric oven preheated to a certain temperature for 24 h of reaction. After natural cooling to room temperature, the hydrothermal product was collected via centrifugation, washed with distilled water three times to remove by-products, rinsed with absolute ethanol, and was finally dried in air at 70 °C for 24 h to yield a white powder for characterization and further processing. The effects of reaction parameters (Table 1) were studied with (Gd$_{0.95}$Eu$_{0.05}$)PO$_4$ as an example.

#### 2.2. Characterization techniques

Crystal phases were identified by X-ray diffraction (XRD, Model PW3040/60, Philips, Eindhoven, The Netherlands, operated at 40 kV/40 mA), using nickel-filtered Cu-Kα radiation. The samples were scanned in a 2θ range of 5°–80° with a step size of 0.02° and a scan rate of 2°/min. The lattice parameters were refined using the powder X-ray diffraction (PXRD) data.

| Sample | Reaction time (h) | R = EDTA/(Gd$_{0.95}$Eu$_{0.05}$) | Reaction temperature (°C) |
|--------|------------------|----------------------------------|---------------------------|
| S1     | 0.5              | 0.5                              | Room temp.                |
| S2     | 3                | 0.5                              | 150                       |
| S3     | 6                | 0.5                              | 150                       |
| S4     | 12               | 0.5                              | 150                       |
| S5     | 24               | 0.5                              | 150                       |
| S6     | 48               | 0.5                              | 150                       |
| S7     | 24               | 0                      | 150                       |
| S8     | 24               | 0.25                            | 150                       |
| S9     | 24               | 0.75                            | 150                       |
| S10    | 24               | 0.5                              | 120                       |
| S11    | 24               | 0.5                              | 180                       |
| S12    | 24               | 0.5                              | 200                       |

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radiation ($\lambda = 0.15406 \text{ nm}$) and a scanning speed of 4.0° 2θ per minute. Morphology and microstructure of the products were analyzed by field emission scanning electron microscopy (FE-SEM, Model JSM-7001F, JEOL, Tokyo, Japan) at an accelerating voltage of 15 kV and transmission electron microscopy (TEM, FEM-3000F, JEOL) at 200 kV. Fourier transform infrared spectroscopy (FTIR, Nicolet i55, Thermal Fisher Scientific, New York, NY, USA) was combined with the standard KBr sample preparation method. Thermogravimetry (TG, Model TAS-200, Rigaku, Tokyo, Japan) of the powder was carried out in flowing oxygen gas with a heating rate of 10 °C/min. Photoluminescence spectroscopy and fluorescence decay kinetics of the phosphors were analyzed at room temperature with an FP-8600 fluorospectrophotometer (JASCO, Tokyo, Japan).

3. Results and discussion

3.1. Characterization and formation mechanism of the nanowires

Powder XRD analysis of the precursor (Figure 1) revealed a series of diffraction peaks that are characteristic of layered $\text{Ln}_n(\text{OH})_2\text{NO}_3\cdot n\text{H}_2\text{O}$ (LHN) [21–25]. The crystal structure of LHN is built up via alternative stacking of the hydroxide main layers ($ab$ plane) and exchangeable interlayer $\text{NO}_3^-$ along the $c$-axis. The occurrence of non-(00 $l$) diffractions thus indicates that the hydroxide layers are long-range ordered while the significantly broadened 00 $l$ diffractions are owing to the thinness of the nanosheets, which are confirmed later by TEM analysis. The LHN diffractions are no longer observable for sample S1, implying that the hydroxide main layers have collapsed even after short (30 min) interaction with $\text{NH}_4\text{H}_2\text{PO}_4$ at room temperature, as also seen from the results of morphology analysis (Figure 2). The broadened and diffuse diffraction peaks of S1 cannot be indexed to any crystalline form of rare-earth orthophosphate, due to the high water content and significantly nanocrystalline nature of the product [26]. Hexagonal $\text{GdPO}_4\cdot 1.5\text{H}_2\text{O}$ (JCPDS File No. 00–021–0037, space group $P3_1$) crystallized in sample S2 via consumption of the unidentified phase of S1, despite a short hydrothermal reaction of 3 h. Better crystallinity (gradually sharper XRD diffractions) was achieved for the hexagonal phosphate by prolonging the hydrothermal reaction up to 12 h (S2–S4). Though the 24 h product (S5) was retained as pure hexagonal phase, the 48 h product (S6) crystallized with a minor amount of monoclinic phosphate (JCPDS No. 01–083–0657, space group: $P2_1/n$) as impurity. The phase transition can be interpreted in view of thermodynamics, that is, the less stable hexagonal phase possesses higher free energy, which can be released to generate the stable monoclinic phase during prolonged hydrothermal reaction [27].

SEM and TEM images of the original LHN are presented in Figure 2(a) and (b), respectively. Micro-sized assemblies composed of LHN nanosheets (sputtered with gold for electrical conductivity) were clearly seen in Figure 2(a), while thicknesses of ~4 nm were observed for the primary nanosheets in Figure 2(b). Selected area electron diffraction (SAED, the inset in Figure 2(b)) clearly revealed the (220) and (620) planes, confirming that the hydroxide layers are well ordered as found via XRD. Interaction of LHN with the phosphate species dissociated from $\text{NH}_4\text{H}_2\text{PO}_4$ at room temperature (sample S1) tends to disintegrate the hydroxide main layers into small particles (Figure 2(d)), though skeletons of the micron-sized assemblies were largely retained (Figure 2(c)). High-resolution TEM (HR-TEM) analysis (inset in Figure 2(d)) revealed that S1 has a crystalline structure, as evidenced by the well resolved lattice fringes with an inter-planar spacing of ~0.392 nm. Short-range crystallization (~10 nm) was thus proposed to be the reason for the significantly broadened XRD peaks of S1 in Figure 1. Though the 3 h product (S2, Figure 2(e)) presents aggregates of needle-like particles, the 6 h product (S3, Figure 2(f)) and 24 h product (S5, Figure 2(g)) exclusively consist of monodispersed spicules. Longer reaction time favors Ostwald ripening and thus a more uniform particle morphology. Low-magnification TEM observation of S5 (Figure 2(h)) revealed that the particles have a length of about 300 nm and a width of about 10 nm. In view of the large aspect ratio (~30), the products can be ranked as nanowires. HR-TEM analysis (inset (1) in Figure 2(h)) indicates that each individual nanowire is well-crystallized with the (100) fringes running along the growth direction and spaced by 0.607 nm, and the (101) fringes can also be observed with a spacing of 0.442 nm. It can thus be figured out that the nanowire grows up along the [001] direction, as indicated by the arrow in the inset. Fourier transform of

![Figure 1. Powder XRD patterns for the original LHN and the products of S1 (anion exchange at room temperature for 30 min) and S2–S6 (hydrothermally reacted at 150 °C for 3, 6, 12, 24, and 48 h, respectively). The black dots in the XRD pattern of S9 denote monoclinic phosphate.](image-url)
also their skeletons (S1), which favors a more uniform morphology and better dispersion of the \((\text{Gd}_{0.95}\text{Eu}_{0.05})\text{PO}_4\cdot1.5\text{H}_2\text{O}\) product.

The effects of EDTA on phase structure and morphology of the hydrothermal products were studied via the lattice fringe yielded well-defined diffraction spots (inset (2) in Figure 2(h)), indicating a single crystalline nature of each nanowire. One conceivable advantage of this sacrificial precursor route is that the rare-earth cations are gradually released from the LHN nanosheets and also their skeletons (S1), which favors a more uniform morphology and better dispersion of the \((\text{Gd}_{0.95}\text{Eu}_{0.05})\text{PO}_4\cdot1.5\text{H}_2\text{O}\) product.

The effects of EDTA on phase structure and morphology of the hydrothermal products were studied via Figure 2. FE-SEM (a), (c), (e), (f), (g) and TEM (b), (d), (h) micrographs showing morphologies of the LHN (a), (b) and the four typical samples of S1 (c), (d), S2 (e), S3 (f), and S5 (g), (h). The insets in (b), (d), (h) are the corresponding SAED pattern, HR-TEM lattice image, and Fourier transform diffraction pattern, respectively. Samples S2, S3, and S5 were synthesized with an EDTA/(Gd\text{$_{0.95}$Eu$_{0.05}$})$^{3+}$ molar ratio (R) of 0.5.
product, but did not alter phase purity (S8, S5, and S9, Figure 3). The significant effects of EDTA can also be perceived through comparing morphologies of the products shown in Figure 4, where it is seen that the sample synthesized without EDTA (Figure 4(a), (b)) consists of agglomerates entangled from underdeveloped acicular particles while that made with a small amount of EDTA (R = 0.25) is composed of much better dispersed nanowires/nanorods with an aspect ratio of ~10 (Figure 4(c)). Increasing the ratio R to 0.5 led to monodispersed nanowires (Figure 2(g)), while significantly longer rods with larger diameters (aspect ratio: ~20–30) appeared in the product at the even larger R value of 0.75 (Figure 4(d)).

The phase structure and crystal shape of a hydrothermal product are known to be synergistically determined by additives and crystallization habit [29]. Lanthanide orthophosphates possess extremely low water solubility (solubility product is on the order of 10^{-25} to 10^{-27}) [30], and accordingly, the S1 product would dissociate in an extremely low degree according to the following equation:

\[
(Gd/Eu)PO_4 \cdot nH_2O \leftrightarrow (Gd/Eu)^{3+} + PO_4^{3-} + nH_2O
\]

The addition of EDTA lowers the concentration of Gd^{3+}/Eu^{3+} in the solution through chelation and thus right-shifts the equation, which speeds up the process of Ostwald ripening to yield the larger and better dispersed nanowires shown in Figures 4 and 2(g). Meanwhile,
residing at the distorted $D_2$ crystallographic sites (Figure 5(b)) [33]. Each phosphate group (PO$_4$ tetrahedron) in the structure is coordinated to six Gd$^{3+}$ to form P-Gd octahedron (Figure 5(c)), where the P atom assumes a C$_2$ point symmetry [34]. The crystal structure contains $-\text{Gd}^{3+}-\text{PO}_4^{-}-\text{Gd}^{3+}$- chains running along the c axis to form open tunnels, where hydration water is accommodated (Figure 5(d)). Murphy et al. previously reported that the activation energy for the growth of hexagonal LnPO$_4$ along the c-axis is lower than that perpendicular to the c-axis [35], which may account for the crystallization of [001]-oriented (Gd,Eu)PO$_4\cdot n$H$_2$O nanowires in this work (inset (1) in Figure 2(h)).

The effects of hydrothermal temperature on phase structure and morphology of the nanowires were investigated in Figure 6 and Figure S1, respectively. It was found from Figure 6 that the 120–180 °C products are all of the hexagonal phase while the even higher temperature of 200 °C induced partial crystallization of monoclinic phosphate (denoted with black dots). The reason is similar to that discussed for the effects of reaction time (Figure 1). Although SEM (Figure S1(a), (b)) and TEM (Figure S1(d), (e)) observations revealed that the nanowires are less uniform in length and width for samples S10 and S11, SAED (insets in Figure S1(d), (e)) indicated that each individual wire is of single crystalline. Through morphology comparison, it is clear that 150 °C is the optimal hydrothermal temperature to generate nearly monodispersed nanowires.

### 3.2. Thermal behaviors of the nanowires

Thermal behaviors of the nanowires were investigated with sample S5 as example. Figure 7 compares XRD patterns of the original nanowires (Figure 7(a)) and those calcined under flowing O$_2$ at various...
temperatures for 2 h. It is seen that the hexagonal crystal structure can be well retained up to 500 °C (Figure 7(b)) while calcination to 600 °C led to partial crystallization of the monoclinic phase (JCPDS No. 01–083–0657; space group: P2_1/n; labeled in Figure 7(c) with black dots). TG analysis (Figure S2) showed that the sample completely dehydrates up to 570 °C via two major stages, with the first one (up to ~150 °C) due to evaporation of surface-adsorbed water, and the second one (150–570 °C) owing to the removal of hydration water. It can thus be inferred from Figure 7(c) and Figure S2 that complete dehydration tends to collapse the hexagonal structure or, in other words, the metastable hexagonal phase is stabilized by hydration water. The n value of the (Gd_{0.95}Eu_{0.05})PO_4·nH_2O nanowires was determined to be around 1.0 from the total weight loss of 6.76%. Calcining to 900 °C caused full crystallization of the monoclinic phase (Figure 7(e)), and the higher temperature products (up to 1200 °C) remained as monoclinic phosphate. Improved crystallinity owing to crystal perfection and crystallite growth was observed with increasing temperature of calcination, as evidenced by the successively sharper and stronger XRD diffractions (Figure 7(f)–(h)). The monoclinic (Gd_{0.95}Eu_{0.05})PO_4 powders had average crystallite sizes of ~29, 37, 78, and 90 nm after calcination at 900, 1000, 1100, and 1200 °C, respectively, as estimated from the width of the (120) diffraction peak using the Scherrer formula.

Figure 8 compares FTIR spectra of the nanowires before and after calcination, from which it can be seen that dehydration weakens the characteristic vibrations of water molecules (ν_1 and ν_3 at 3457 cm⁻¹ and ν_2 at 1624 cm⁻¹). A characteristic profile of orthophosphate groups under C_2 symmetry is observed in the IR spectra of the hexagonal phase (Figure 8(a), (b)). For C_2 symmetry, each of the four absorption bands (ν_1, ν_2, ν_3, and ν_4) of PO_4^3⁻ is theoretically active [34], as observed in this work for the P-O symmetric stretching (ν_1, A) vibration as a weak band at ~964 cm⁻¹, the P-O antisymmetric stretching (ν_2, A + 2B) as an intense band centered at ~1072 cm⁻¹, and the O-P-O antisymmetric deformation (ν_4, A + 2B) bands in the 500–700 cm⁻¹ region. The ν_2 vibration is nonetheless too weak to be recorded, which is coinciding with the report of Hezel and Ross [34]. The hexagonal to monoclinic phase conversion changes the crystallographic sites of PO_4^3⁻ into the lower symmetry of C_1, which allows better resolved vibrations [36], as can be seen from Figure 8(c, d). The vibration region of PO_4^3⁻ anions in the monoclinic (Gd_{0.95}Eu_{0.05})PO_4 calcined at 1200 °C presents ν_1 vibration as a sharp band at ~964 cm⁻¹, ν_1 vibration as a sharp band at ~493 cm⁻¹, ν_2 stretching band as five observable components at ~1008, 1037, 1048, 1071, and 1106 cm⁻¹, and ν_4 vibration as several shallow absorptions with frequencies at ~549, 576, 584, and 629 cm⁻¹. The above observations agree with the results of Kijkowska [36].

Figure S3 shows typical FE-SEM morphologies of the calcination products. Although calcination at 500 °C did not affect phase purity of the hexagonal (Gd_{0.95}Eu_{0.05})PO_4·nH_2O compound, a slight collapse of the nanowires happened (Figure S3(a)). Calcining to 600 °C induced substantial destruction of the 1D morphology, mainly owing to dehydration. The original nanowire morphologies are hardly observable for the 900 and 1000 °C products because of the re-constructive type hexagonal→monoclinic phase transition. Abrupt particle coarsening took place at 1100 °C, which corresponds well to the results of crystallite analysis (37.6 and 77.5 nm at 1000 and 1100 °C, respectively).

The Tb³⁺ doped nanowires of (Gd_{0.95}Tb_{0.05})PO_4·nH_2O were also synthesized under the conditions used for sample S5. XRD analysis (Figure S4) and FE-SEM...
predicts that the $^5D_0 \rightarrow ^7F_{2,4}$ magnetic dipole transition is permitted while the $^5D_0 \rightarrow ^7F_{0,2,4}$ electric dipole transition is forbidden, and the latter is allowed only on condition that the Eu$^{3+}$ ions occupy a site without an inversion center [37,38]. As mentioned above, the Eu$^{3+}$ ions are expected to replace Gd$^{3+}$ to inherit the centrosymmetric $D_2$ point symmetry in hexagonal (Gd$^{0.95}$Eu$^{0.05}$)PO$_4$ and (Gd$^{0.95}$Eu$^{0.05}$)PO$_4$·$n$H$_2$O. The abnormally strong $^5D_0 \rightarrow ^7F_{2,4}$ emissions observed for the above two phosphates (Figure 9) may be understood from the $\Omega$ intensity parameter. It is known that the intensities of the $^5D_0 \rightarrow ^7F_{2}$ and $^5D_0 \rightarrow ^7F_{4}$ transitions are governed by the effective operators of $\Omega^2U(2)$ and $\Omega^4U(4)$, respectively, where $U(\lambda)$ is the unit tensor operator [39]. Nanomaterials generally show lattice distortions, unlike bulk crystals, and hence it is plausible to say that in this work the Eu$^{3+}$ activators have a lower site symmetry distorted from $D_2$. The distortion may make the ligand field-/polarizability-related parameters larger, and thus enlarges the $\Omega^2,4$ parameters to lead to the strong $^5D_0 \rightarrow ^7F_{2,4}$ electric dipole transitions [40].

The excitation and emission behaviors of Tb$^{3+}$ in the hexagonal phosphates of (Gd$^{0.95}$Tb$^{0.05}$)PO$_4$·$n$H$_2$O and (Gd$^{0.95}$Tb$^{0.05}$)PO$_4$ are studied in Figure 10. The excitation spectra of the two samples recorded by monitoring the $^5D_4 \rightarrow ^7F_{5}$ green emission at 546 nm consist of two bands in the short UV region (up to 300 nm) for the low-spin inter-configurational $4f^8\rightarrow 4f^75d^1$ transition of Tb$^{3+}$ (LS, at ~211 nm) and the $8S_{7/2}\rightarrow 6I_J$ intra-4f$^7$ transition of Gd$^{3+}$ (at ~272 nm) [23]. The other bands in the longer UV region of 300–400 nm arise from intra-4f$^8$ excitation transitions of Tb$^{3+}$, as labeled in the figure. The whole excitation spectrum is dominated by the LS transition at 211 nm. The PL spectra obtained under 211 nm excitation consist of emissions ranging from 500 to 750 nm, which are associated with transitions from the excited $^5D_0$ state to the $^7F_J$ ($J = 1$–4) ground states of Eu$^{3+}$ as labeled in the figure, with the $^5D_0 \rightarrow ^7F_4$ transition (~697 nm) being the most prominent. Intensity of both the PLE and PL bands were greatly enhanced by calcination at 500 °C, owing to significant dehydration (Figure S2) and elimination of luminescence-quenching defects such as surface dangling bonds and particularly hydroxyls [5].

The relative intensities of transitions from the $^7D_0$ excited state to the different $J$ levels of the ground state depend on the site symmetry of Eu$^{3+}$ and can be described in terms of the Judd-Ofelt theory, which observation (Figure S5) indicated that (Gd$^{0.95}$Tb$^{0.05}$)PO$_4$·$n$H$_2$O similarly crystallized as hexagonal nanowires, and phase purity and the 1D morphology were well retained after 500 °C calcination.

### 3.3. Optical properties of the (Gd$^{0.95}$Eu$^{0.05}$)PO$_4$ and (Gd$^{0.95}$Tb$^{0.05}$)PO$_4$ phosphate phosphors

Since calcination at 600 °C induced partial crystallization of the monoclinic phase and substantial destruction of the 1D morphology of the nanowires, the Eu/Tb-doped hexagonal nanowires were annealed at 500 °C to investigate their luminescence properties. Figure 9 shows photoluminescence excitation (PLE) and photoluminescence (PL) spectra for the hexagonal (Gd$^{0.95}$Eu$^{0.05}$)PO$_4$·$n$H$_2$O and (Gd$^{0.95}$Eu$^{0.05}$)PO$_4$. The band observed at ~240 nm in the PLE spectra corresponds to the excitation of electrons from the 2p orbital of O$^{2-}$ in the PO$_4$$^{3-}$ group to the 4f orbital of Eu$^{3+}$, which is known as charge transfer. The weak shoulder at ~272 nm is attributed to the $^8S_{7/2}\rightarrow ^{1}D_J$ intra-4f$^6$ transition of Gd$^{3+}$. The intra-4f$^6$ transitions of Eu$^{3+}$ were observed at ~318 nm for the $^7F_{0,1}\rightarrow ^1H_{1,0}$, 363 nm for the $^7F_{0,1}\rightarrow ^3D_0$, 378 nm for the $^7F_{0,1}\rightarrow ^1L_J$, 396 nm for the $^7F_{0,1}\rightarrow ^3L_J$, and 448 nm for the $^7F_{0,1}\rightarrow ^3D_2$ transitions, as labeled in the figure. Upon UV excitation at 240 nm, the two hexagonal phosphates exhibit transitions ranging from 500 to 750 nm, which are associated with transitions from the excited $^5D_0$ state to the $^7F_J$ ($J = 1$–4) ground states of Eu$^{3+}$ as labeled in the figure, with the $^5D_0 \rightarrow ^7F_4$ transition (~697 nm) being the most prominent. Intensity of both the PLE and PL bands were greatly enhanced by calcination at 500 °C, owing to significant dehydration (Figure S2) and elimination of luminescence-quenching defects such as surface dangling bonds and particularly hydroxyls [5].

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The excitation and emission behaviors of Tb$^{3+}$ in the hexagonal phosphates of (Gd$^{0.95}$Tb$^{0.05}$)PO$_4$·$n$H$_2$O and (Gd$^{0.95}$Tb$^{0.05}$)PO$_4$ are studied in Figure 10. The excitation spectra of the two samples recorded by monitoring the $^5D_4 \rightarrow ^7F_{5}$ green emission at 546 nm consist of two bands in the short UV region (up to 300 nm) for the low-spin inter-configurational $4f^8\rightarrow 4f^75d^1$ transition of Tb$^{3+}$ (LS, at ~211 nm) and the $^8S_{7/2}\rightarrow ^{4}F_4$ intra-4f$^7$ transition of Gd$^{3+}$ (at ~272 nm) [23]. The other bands in the longer UV region of 300–400 nm arise from intra-4f$^8$ excitation transitions of Tb$^{3+}$, as labeled in the figure. The whole excitation spectrum is dominated by the LS transition at 211 nm. The PL spectra obtained under 211 nm excitation consist of emissions ranging from 450 to 700 nm, which are associated with transitions from the excited $^5D_4$ state to the $^7F_J$ ($J = 3$–6) ground states. The strongest emission is located at ~546 nm ($^5D_4 \rightarrow ^7F_4$ transition), typical of a green color. The hexagonal (Gd$^{0.95}$Eu$^{0.05}$)PO$_4$ and

![Figure 9. PLE and PL spectra of sample S5 and its product calcined at 500 °C. CT stands for charge transfer.](image1)

![Figure 10. PLE and PL spectra of (Gd$^{0.95}$Tb$^{0.05}$)PO$_4$·$n$H$_2$O and its product calcined at 500 °C.](image2)
with the single-exponential function of $I = A \exp(-t/\tau) + B$, where $\tau$ is the fluorescence lifetime, $t$ the delay time, $I$ the relative intensity, and $A$ and $B$ are constants. It is seen from Figure S8(a) that the lifetime of Eu$^{3+}$ was increased continuously from ~3.66 to 6.70 ms by calcination up to 1100 °C and then decreased to ~4.66 ms after 1200 °C calcination. The constant increase is primarily owing to the removal of luminescence-quenching defects and surface species, while the subsequent decrease is mainly due to increased effective refractive index of the phosphor by significant crystallite/particle coarsening [43]. Slight lifetime elongation by calcination was also observed for the Tb$^{3+}$ emission. The emission of Eu$^{3+}$ under 240 nm excitation was calculated from Figures 9 and 11 to have Commission internationale de l’éclairage (CIE) chromaticity coordinates of around (0.63, 0.36) for the 150 °C hydrothermal and 500 °C calcination products, (0.62, 0.36) for the 900 °C, (0.62, 0.38) for the 1000 °C, and (0.61, 0.39) for the 1100 and 1200 °C calcination products (Figure 12(a)–(f)). The color coordinates slightly yet steadily shift to the orange color region for the sample calcined at a higher temperature (a–f, arrow direction), owing to faster intensity increase of the 5D0→7F1 orange-red emission than the 5D0→7F2,4 red emissions as inferred from the intensity ratio of these transitions (Figure S9). The two Tb$^{3+}$ containing samples were calculated to have the same CIE chromaticity coordinates of about (0.37, 0.54), falling in the green area of the diagram (points g and h).

4. Conclusions

Hexagonal (Gd$_{0.95}$RE$_{0.05}$)PO$_4$·nH$_2$O (RE = Eu, Tb) nanowires have been hydrothermally converted from the nanosheets of layered rare-earth hydroxyl nitrate. The nanowires were determined to grow along the [001] orientation (Gd$_{0.95}$Tb$_{0.05}$)PO$_4$ anhydrous nanowires, with enhanced luminescence and favorable dispersity, may find applications in the fields such as biolabeling, optoelectronics, and sensing [41].

PLE/PL spectra of the calcination-derived (Gd$_{0.95}$Eu$_{0.05}$)PO$_4$ monoclinic phosphates are presented in Figure 11. It is seen that both the excitation and emission intensities steadily increase with increasing temperature of calcination. The increment from 1000 to 1100 °C is the most prominent, which corresponds well to the greatly enhanced crystallization observed from Figure 7. In monoclinic GdPO$_4$, Yaiphaba et al. reported that the Eu$^{3+}$ ion is surrounded by nine oxygen atoms to form EuO$_9$ with different Eu-O bond lengths, residing at the highly asymmetric $C_1$ site [42]. This agrees with the presence of $^3D_2\rightarrow^7F_9$ transition (inset in Figure 11).

The energy transfer from Gd$^{3+}$ to Eu$^{3+}$ was analyzed for the 1000 °C sample through exciting the $^8S_{7/2}\rightarrow^4I_J$ transition of Gd$^{3+}$ at 272 nm, and the resultant PL spectrum, which consists of the characteristic $^3D_0\rightarrow^7F_J$ ($J = 1–4$) emissions of Eu$^{3+}$, is shown in Figure S6(a). The process of energy transfer involved in Eu$^{3+}$ emission is schematically shown in Figure S6(b). That is, exciting the (Gd$_{0.95}$Eu$_{0.05}$)PO$_4$ phosphor at 272 nm raises electrons from the $^8S_{7/2}$ ground state to the $^4I_J$ energy level of Gd$^{3+}$, followed by relaxation to the $^9P_{7/2}$ level. The $^9P_{7/2}$ electrons first relax to the higher $^9D_J$ ($J = 1, 2, 3$) excited states of Eu$^{3+}$, followed by further relaxation to the lowest-lying $^3D_0$ excited level in a rapid non-radiative way. Subsequently, f–f transitions of Eu$^{3+}$ take place from the $^3D_0$ state to the $^7F_J$ ($J = 0, 1, 2, 3, 4$) ground states. Tb$^{3+}$ emissions enabled by Gd$^{3+}$→Tb$^{3+}$ energy transfer were similarly achieved, as seen in Figure S7(a), (b).

Fluorescence decay kinetics of the 593 nm red emission of Eu$^{3+}$ and the 546 nm emission of Tb$^{3+}$ have been investigated under 240 nm (for Eu$^{3+}$) and 211 nm (for Tb$^{3+}$) excitations, and the results are presented in Figure S8(a) and (b), respectively. The decay curves can be well fitted with the single-exponential function of $I = A \exp(-t/\tau) + B$, where $\tau$ is the fluorescence lifetime, $t$ the delay time, $I$ the relative intensity, and $A$ and $B$ are constants. It is seen from Figure S8(a) that the lifetime of Eu$^{3+}$ was increased continuously from ~3.66 to 6.70 ms by calcination up to 1100 °C and then decreased to ~4.66 ms after 1200 °C calcination. The constant increase is primarily owing to the removal of luminescence-quenching defects and surface species, while the subsequent decrease is mainly due to increased effective refractive index of the phosphor by significant crystallite/particle coarsening [43]. Slight lifetime elongation by calcination was also observed for the Tb$^{3+}$ emission. The emission of Eu$^{3+}$ under 240 nm excitation was calculated from Figures 9 and 11 to have Commission internationale de l’éclairage (CIE) chromaticity coordinates of around (0.63, 0.36) for the 150 °C hydrothermal and 500 °C calcination products, (0.62, 0.36) for the 900 °C, (0.62, 0.38) for the 1000 °C, and (0.61, 0.39) for the 1100 and 1200 °C calcination products (Figure 12(a)–(f)). The color coordinates slightly yet steadily shift to the orange color region for the sample calcined at a higher temperature (a–f, arrow direction), owing to faster intensity increase of the 5D0→7F1 orange-red emission than the 5D0→7F2,4 red emissions as inferred from the intensity ratio of these transitions (Figure S9). The two Tb$^{3+}$ containing samples were calculated to have the same CIE chromaticity coordinates of about (0.37, 0.54), falling in the green area of the diagram (points g and h).
crystallographic direction, and EDTA was found to play a decisive role in morphology evolution of the nanowires. Both the hexagonal structure and nanowire morphology can be retained after calcination at 500 °C, and monoclinic (Gd$_{0.95}$Eu$_{0.05}$)PO$_4$ emerges as a pure phase at 900 °C. The Eu$^{3+}$ and Tb$^{3+}$ activators exhibit their characteristic $^{3}D_{0}→^{7}F_j$ and $^{3}D_{0}→^{7}F_j$ emissions under excitation with peak wavelengths of the O$_2$→Eu$^{3+}$ charge transfer and low-spin 4F$^5$→4F$^5$S$^0$ transition bands, respectively. The abnormally strong $^{3}D_{0}→^{7}F_j$, electric dipole Eu$^{3+}$ emission in the hexagonal phosphates was ascribed to the site distortion. Exciting the Gd$^{3+}$ ions in the host lattice with the $^{8}S_{7/2}→^{6}I_{7/2}$ transition at ~272 nm also produces the characteristic emissions of Eu$^{3+}$ and Tb$^{3+}$, owing to Gd$^{3+}$→Eu$^{3+}$/Tb$^{3+}$ energy transfer.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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