

Photochromic effect of $\text{HoPO}_4\text{:Li}^+$ powder

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Li^+ -doped HoPO_4 powders with a pure tetragonal phase are successfully synthesized by the co-precipitation method. It exhibits an obvious color change under sunlight and tri-phosphor fluorescent light illumination. The introduction of Li^+ ions into HoPO_4 can further enhance its photochromic property effectively. The doped Li^+ ions induce changes in the crystal structure. The spectral characteristics and thus photochromic properties of HoPO_4 are explored. The improved HoPO_4 powder, when used as a photochromic material, has wide-ranging prospects in security, decoration, and other applications.

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Photochromic materials have been widely investigated because of their potential technological applications in displays and large-area optical devices^[1,2].

Recently another kind of photochromic material, i.e., rare-earth (RE) compounds, has also attracted interest. The color change for RE-based compounds is due to the light absorbed or reflected by the compounds, and from neither an excitation/luminescence emission process nor a photo-induced change in the material microstructure^[3]. It is well-known that RE ions have unique and extraordinary luminescence properties such as narrow emission lines covering the short wavelength (ultraviolet) to visible region, until the near-infrared region^[4]. Therefore, trivalent RE (i.e., RE^{3+})-ion-doped luminescent materials receive much attention due to their extensive applications^[5]. Considering that many RE ions also have discrete absorption bands in the visible range, photochromism of RE-based compounds is also possible under illumination from discrete and broad spectral distribution light sources, especially tri-phosphor fluorescent light and sunlight.

Among the RE ions, Ho^{3+} is promising for photochromic applications, because it exhibits several important electronic transitions in the visible range^[6]. Recently an investigation has also suggested that HoPO_4 crystals can display different colors under exposure to the Sun and a tri-phosphor fluorescent lamp^[3]. Therefore, HoPO_4 is likely to be developed into a photochromic material for practical applications as a security pigment and a decoration material if the photochromic properties are further improved.

The effect of Li^+ doping on the luminescence properties has been investigated in many phosphors such as in $\text{SrTiO}_3\text{:Pr}^{3+}$ ^[7] and $\text{Gd}_{2-x}\text{Y}_x\text{O}_3\text{:Eu}^{3+}$ ^[8]. This fact reveals that Li^+ addition remarkably affects the crystallinity, morphology, as well as the photoluminescent efficiency of the phosphors. In this work, Li^+ ions are introduced into the HoPO_4 in an attempt to improve its color-change properties. The Li^+ ions induced changes of the crystal

structure, and the absorption properties of HoPO_4 have been investigated in detail.

$\text{HoPO}_4\text{:xLi}$ ($x = 0.0, 0.1, 0.2,$ and 0.3 in mole fraction) crystals was prepared using the co-precipitation method followed by heat treatment. $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $\text{LiCl} \cdot \text{H}_2\text{O}$ aqueous solutions were dissolved in distilled water according to the designed mole ratio. The dissolved $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$, and $\text{LiCl} \cdot \text{H}_2\text{O}$ aqueous solutions were marked as Solutions A–C, respectively. The mole ratio of $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to $\text{NH}_4\text{H}_2\text{PO}_4$ was kept as 1 : 1.1 while different mole contents of $\text{LiCl} \cdot \text{H}_2\text{O}$ were introduced according to the designed mole ratio during the co-precipitation process. Earthy yellow precipitates were obtained by dumping slowly Solution A and then Solution C into Solution B under constant stirring with a glass rod. The precursors without washing were stewed for 48 h. After drying at 150°C for 24 h, earthy yellow pigments were obtained. Then they were sintered at 1000°C for 4 h to get the final products. To explore the influence of doped Li^+ ions on the spectral characteristics of Ho^{3+} in HoPO_4 , Eu^{3+} -doped YPO_4 powders of different Li^+ content were also prepared with the same method, so as to probe changes of the local environment of Ho^{3+} in the lanthanum phosphate host.

The structure of the samples were identified by X-ray diffraction (XRD) on a Bruker D8 Advance instrument using a Cu tube with $K\alpha$ radiation of 0.15406 nm in the 2θ range of 10° – 80° . The microstructure was analyzed using a JSM-6610 scanning electron microscope (SEM). The absorption spectra were recorded using diffuse reflectance spectroscopy (a Varian Cary 10 UV-Vis spectrophotometer with a DRA-CA-30I diffuse reflectance accessory). All experiments were carried out at room temperature. The Eu^{3+} probing spectra were measured using a Perkin–Elmer LS-50 luminescence spectrometer under an excitation of 396 nm produced by a xenon flash lamp.

Figure 1 shows the XRD patterns of the HoPO_4 crystals doped with different Li^+ concentrations. Figure 1 reveals

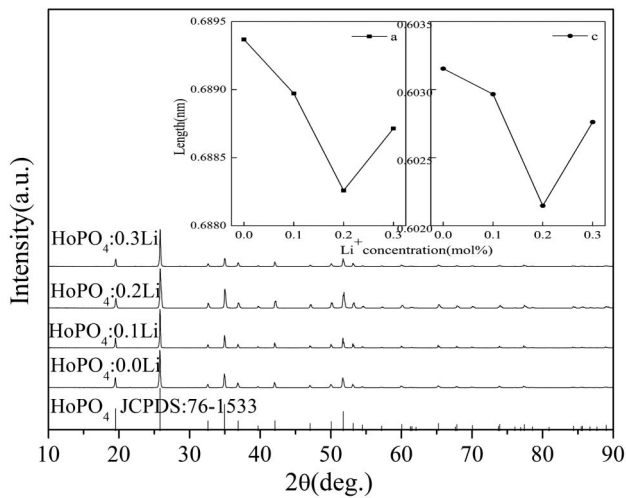


Fig. 1. XRD patterns of $\text{HoPO}_4:x\text{Li}^+$ crystals ($x = 0.0, 0.1, 0.2$, and 0.3); inset, Li^+ concentration dependence of unit cell parameters.

that all the diffraction peaks can be readily indexed to the tetragonal structure of HoPO_4 according to JCPDS-76-1533, indicating that Li^+ ions has been embedded into the crystal lattice of HoPO_4 . The cell parameters of the samples are calculated using the XRD data (Fig. 1, inset). The inset in Fig. 1 reflects that the values of lattice parameters initially decrease with the increasing Li^+ ion concentration, and then increase at higher Li^+ ion concentration. It is believed that Li^+ ions usually occupy interstitial sites in the lanthanum phosphate host. In our work, however, Li^+ ions of relatively high concentration are introduced. This means that some of the Li^+ ions occupy Ho^{3+} sites, causing a substantial contraction of the unit cell. As a result, the lattice parameters decrease with the increasing Li^+ ion concentration in our work. At higher Li^+ ion concentrations (>20 mol%), the Li^+ ions no longer occupy Ho^{3+} sites and only occupy interstitial regions because of the large charge imbalance. Therefore, the values of the lattice parameters begin to increase.

At present, great effort has been devoted to investigating the internal impact of metal-ion doping on nanocrystallite size and shape. It has been reported the Ti-doped CeO_2 makes nanoparticles become more perfect (spherical) with increasing TiO_2 content^[9]. This may be an efficient method to modify the shape, size, and phase of crystals by metal ion doping^[10]. Figure 2 shows the SEM images of HoPO_4 powders with different concentrations of Li^+ ion doping. Notably, after Li^+ ion doping, the shape and size of the HoPO_4 crystals were remarkably modified. Figure 2(a) shows the shape is irregular and the size is very small. With Li^+ ion doping, the particles have a large size variation and tend to form flake particles. This phenomenon indicates that the introduction of Li^+ ions reduces the eutectic melting point and thereby promotes crystal growth and aggregation of the particles, resulting in an increase of the grain size of the powder.

The photochromic phenomenon of HoPO_4 is due to its efficient light absorption in a discrete wavelength range.

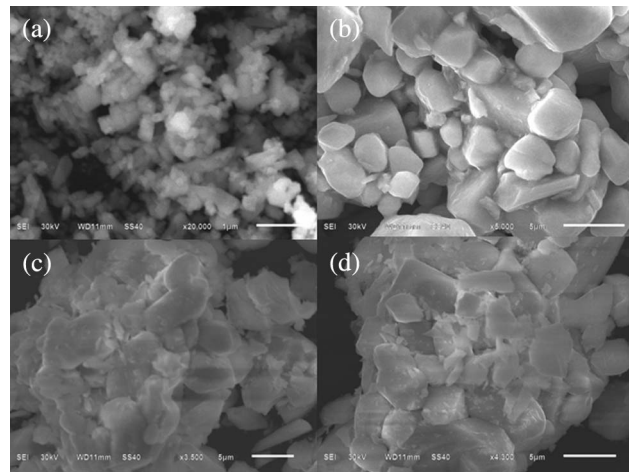


Fig. 2. SEM images of $\text{HoPO}_4:x\text{Li}^+$ powder; (a) $x = 0.0$; (b) $x = 0.1$; (c) $x = 0.2$; (d) $x = 0.3$.

As is known to researchers, sunlight is a light source of a broad spectral distribution, while a tri-phosphor fluorescent lamp has a discrete spectral distribution in the blue, green, and red region. The color is the same when a common material is set aside under the sun and under the tri-phosphor fluorescent lamp. Unlike common materials, HoPO_4 powders have strong and discrete absorption bands in the visible region. Thus under illumination of a specific light source, part of the light will be absorbed and the rest will be reflected. The wavelength distributions of the sun and the tri-phosphor fluorescent lamp are different. Consequently, the wavelengths reflected by the HoPO_4 crystals will also be different. As a result, the HoPO_4 powder will exhibit different colors under illumination of the two different light sources.

Figure 3(a) is the diffuse reflection spectra of HoPO_4 powder. It exhibits several stronger absorption bands in the visible region (from 360 to 760 nm). The formation of the absorption bands of HoPO_4 powders is attributed to the $4f-4f$ transitions of Ho^{3+} ions from the ground state to different excited states. The four main absorption

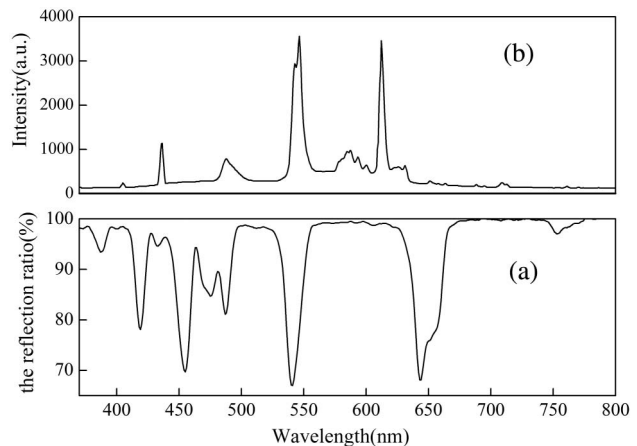


Fig. 3. (a) Diffuse reflection spectrum of HoPO_4 powder; (b) emission spectrum of the tri-phosphor fluorescent lamp.

bands are centered at 419.5, 457, 541, and 661 nm, which are assigned 5I_8 to $(^5G, ^3G)_5$, 5G_6 , $^5S_2(^5F_4)$, and 5F_5 transitions, respectively^[11]. Figure 3(b) shows a typical spectrum of the tri-phosphor fluorescent lamp. From the spectrum we can see that there are three main and strong emission peaks, which are located at 435, 545, and 610 nm, respectively. The other emissions have a relatively weak intensity.

The HoPO_4 powder presents a pink color under a tri-phosphor fluorescent lamp and then earthy yellow under sunlight. The color change of HoPO_4 powder under illumination of a tri-phosphor fluorescent lamp can be easily understood by a comparison of the emission spectrum of the tri-phosphor fluorescent lamp with the diffuse reflection spectrum of HoPO_4 powder in Fig. 3. Figure 3 shows that the HoPO_4 powder has a strong absorption band at 541 nm, of which the reflective absorption coefficient is almost 67%. This means that most of the green light at 545 nm that is emitted by the tri-phosphor fluorescent lamp can be absorbed. In the blue region, a part of the blue light emitted by the tri-phosphor fluorescent lamp can also be absorbed. However, the red emission centered at 611 nm is hardly absorbed because of the mismatch between the absorption wavelength of HoPO_4 and the emission wavelength of the tri-phosphor fluorescent lamp in the red region. Therefore, the reflected weak blue light plus the strong red light will present a pink color when the HoPO_4 powder is exposed to the tri-phosphor fluorescent lamp. The color illuminated by sunlight can also be analyzed by the same method and it is found that the HoPO_4 powder presents an earth yellow after part of the light is absorbed.

Obviously, the photochromic effect of HoPO_4 powder relies on its absorption efficiency. The larger the absorption efficiency, the more remarkable the photochromic effect will be. Thus in order to improve the photochromic effect of HoPO_4 powder, we attempted to introduce Li^+ ions into the HoPO_4 powder. Figure 4 is the diffuse reflection spectra of the $\text{HoPO}_4:x\text{Li}^+$ crystals ($x = 0.0, 0.1, 0.2,$

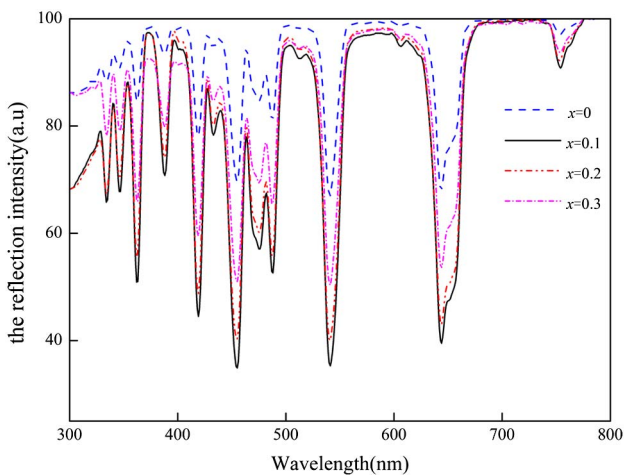


Fig. 4. Diffuse spectrum of $\text{HoPO}_4:x\text{Li}^+$ ($x = 0.0, 0.1, 0.2,$ and 0.3).

and 0.3). From the spectra, we can see the absorption intensity increases with x increasing from 0 to 0.1, then decreases at higher Li^+ ion doping concentrations. By comparison, it is obvious to see that doping by using Li^+ ions can improve the absorption efficiency of HoPO_4 .

To explore Li^+ -ion-induced spectral properties and thus the photochromic properties, powders of $\text{Eu}_{0.05}\text{Y}_{0.95}\text{PO}_4:x\text{Li}^+$ were prepared with the same method, in order to detect the variation of local environment by Eu^{3+} spectroscopy. As researchers know, yttrium orthophosphate^[12] and holmium orthophosphate both have a tetragonal structure and their space groups are the same [$I4_1/amd$]. Therefore, the Li^+ -doping-induced variation of the local environment in HoPO_4 can be reflect by Eu^{3+} spectroscopy in a Li^+ -doped YPO_4 host to some extent. The emission spectra (normalized at 592 nm) of $\text{Eu}_{0.05}\text{Y}_{0.95}\text{PO}_4$ and $\text{Eu}_{0.05}\text{Y}_{0.95}\text{PO}_4:0.1\text{Li}^+$ under 396 nm excitation are shown in Fig. 5, inset. The emission spectra of $\text{Eu}_{0.05}\text{Y}_{0.95}\text{PO}_4:x\text{Li}^+$ mainly consist of a sharp peak at approximately 592 nm along with a weaker peak at approximately 617 nm. The 592 and 617 nm emissions are attributed to the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions of Eu^{3+} , respectively.

The $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} ion is a hypersensitive electronic transition, which is markedly affected by the coordination environment of Eu^{3+} , whereas the $^5D_0 \rightarrow ^7F_1$ transition is the magnetic dipole transition and is much less sensitive to the coordination environment^[13-16]. Therefore, the relative intensity ratio T termed the symmetry ratio, which is defined as $^5D_0 \rightarrow ^7F_1 / ^5D_0 \rightarrow ^7F_2$, gives a measure of the degree of distortion from the inversion symmetry of the local environment surrounding the Eu^{3+} ions in the host matrix^[12,17]. A smaller value of T means a lower local symmetry of the luminescence center and thus possibly higher luminescence intensity. The T value as a function of Li^+ concentration is shown in Fig. 5. The result suggests the local symmetry of luminescence centers in lattice decreases with x increasing from 0 to 0.1, then

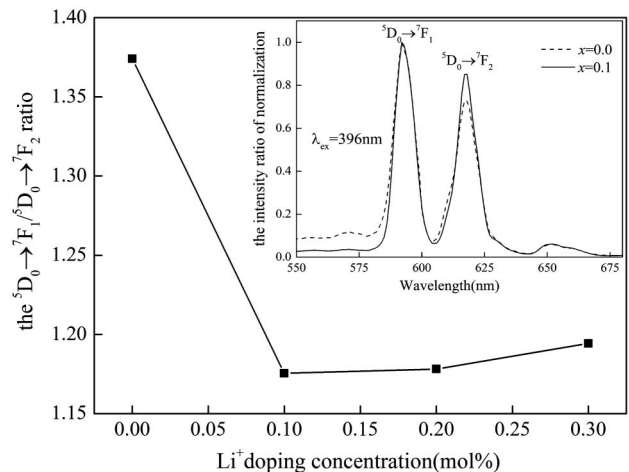


Fig. 5. Ratio of $^5D_0 \rightarrow ^7F_1 / ^5D_0 \rightarrow ^7F_2$ as a function of Li^+ content; inset, emission spectra of $\text{Eu}_{0.05}\text{Y}_{0.95}\text{PO}_4:x\text{Li}^+$ ($x = 0.0$ and 0.1) under 396 nm excitation.

increases at higher Li⁺-ion-doping concentration. Clearly the doping of Li⁺ will change the symmetry of the local environment of Eu³⁺^[12,18]. Considering the same crystalline structure between YPO₄ and HoPO₄, the Li⁺-ion-induced decrease of local symmetry will also take place in HoPO₄. Therefore, it is reasonable to believe that the doped Li⁺ ions in HoPO₄ of suitable concentration decrease the local symmetry of the luminescence centers in the lattice.

This suggests that when Li⁺ ions are doped into HoPO₄, Li⁺ ions may occupy sites in or diffuse to various interstitial sites in the HoPO₄ lattice, making the change of Coulomb interactions and Ho–O bond slightly distorted. The Ho–O bond distortion alters the local symmetry of the crystal field around Ho³⁺. The intra-4*f* electronic transitions that are parity-forbidden in principle become partially allowed, increasing the intra-4*f* electronic transition probability of the RE³⁺ ions^[19]. As a result, there is enhancement of the absorption intensity of Ho³⁺ ions in accordance with Li⁺ doping.

Li⁺ ions might occupy both interstitial sites and Ho³⁺ sites, which depends on the Li⁺-ion-doping concentration. Both kinds of Li⁺ ion in HoPO₄ will give rise to the formation of a defective structure^[18] and thus decrease the local symmetry environment of the Ho³⁺ ions. Thus the doped Li⁺ ions of proper concentration will enhance the electronic dipole transition probability of Ho³⁺ and intensify its absorption cross section, which has been proved by Eu³⁺ probing spectroscopy. However, the absorption intensity of the powder tends to decrease when the doped Li⁺ concentration is beyond 10%. Presumably, the doped Li⁺ ions induced an enhancement of the electronic dipole transition probability of Ho³⁺ by changing its local environment, which is no longer significant at a Li⁺ doping concentration over 10%. As shown in Fig. 5, the symmetry ratio of Eu³⁺ no longer decreases but slight increases when the Ho³⁺ concentration is over 10%. These results mean that the absorption cross section of Ho³⁺ will not effectively be enhanced when the Ho³⁺ concentration is over 10%. The Ho³⁺ concentration per unit volume will decrease with the increase of the Li⁺ ion content, leading to the decrease of the absorption intensity. As a result, the photochromic effect begins to deteriorate at higher Li⁺ doping concentration.

In conclusion, a series of HoPO₄:*x*Li⁺ powders are prepared using the co-precipitation method. It is believed that the doped Li⁺ ions of proper concentration arouse the variation of the asymmetry and covalency at the Ho³⁺ sites, leading to the enhancement of the 4*f*–4*f* transition of Ho³⁺ and therefore improvement of the photochromic effect. This work indicates that the

HoPO₄:*x*Li⁺ powders at *x* = 0.1 presents the most significant color change under illumination of sunlight and tri-phosphor fluorescent light. The improved HoPO₄ powder has potential wide applications for use as a photochromic pigment in the fields of security and decoration.

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