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Novel Red-Orange Phosphors Na$_2$BaMg(PO$_4$)$_2$:Pr$^{3+}$: Synthesis, Crystal Structure and Photoluminescence Performance

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Abstract: A series of new red-orange emission phosphors Na$_2$BaMg(PO$_4$)$_2$:Pr$^{3+}$ were synthesised by a high-temperature solid-state reaction. The crystal structure and photoluminescence properties of these samples were characterised by X-ray diffraction and spectroscopic measurements. This compound holds $P\bar{3}m1$ space group of the trigonal system with the lattice parameters of hexagonal cell $a = 0.5304(3)$ nm and $c = 0.6989(3)$ nm. The phosphor emits the strongest peak at 606 nm when excited by 449 nm. The average Commission Internationale de l’Eclairage chromaticity coordinates calculated for the phosphors are (0.52, 0.46). The results demonstrate the potential application of these phosphors in solid-state lighting and other fields.

Keywords: Na$_2$BaMg(PO$_4$)$_2$; Phosphor; Photoluminescence; Pr$^{3+}$; Solid-State Reaction Method.

1 Introduction

The next generation of solid-state lighting, i.e. white light-emitting diodes (LEDs), has attracted significant attention recently due to their potential application in many areas [1–5]. They exhibit many advantages over the present incandescent and halogen lamps with regard to reliability, power efficiency, long lifetime and environment [6–11]. One way by which white light can be produced is by the combination of blue GaN-based LED with yellow-emitting phosphor. However, due to lack of warm-colour component, the poor chromatic aberration and bad white light performance will happen for the blue LED and yellow phosphor. Therefore, in order to eliminate this problem, in this work, a series of red-orange emitting Na$_2$BaMg(PO$_4$)$_2$:Pr$^{3+}$ phosphors were synthesised for the first time. The luminescent properties are investigated through 449 nm blue light excitation, which matches well with high-efficiency emitting at 449 nm of GaN-based LED chips. The results are discussed.

2 Experimental

The powder samples of Na$_2$BaMg(PO$_4$)$_2$:Pr$^{3+}$ were prepared by a traditional solid-state method. The raw materials were Na$_2$CO$_3$ (A.R.), BaCO$_3$ (A.R.), Mg(OH)$_2$·4MgCO$_3$·5H$_2$O (A.R.) (Chengdu Kelong Chemical Reagent Company, Chengdu, China), NH$_4$H$_2$PO$_4$ (A.R.) and Pr$_2$O$_3$ (99.99 %) (Aladdin Industrial Corporation, Shanghai, China). Stochiometric amounts of reactants were weighed out and well ground, then pre-sintered at 400 °C for 2 h and fired at 1000 °C for 3 h. The resulting samples were cooled down to room temperature and pulverised for further measurements.

The crystalline structure of the phosphor was examined using a XRD-7000 X-ray diffractometer (Shimadzu, Japan) with Cu Kα at $\lambda = 0.15406$ nm as the incident radiation. The morphology of the typical sample was examined using scanning electron microscopy (SEM; MIRA3, TESCAN). The excitation and emission spectra were measured by using a F-4600 spectrofluorometer (Hitachi, Japan) with a 450 W Xe lamp as the excitation light source. The photoluminescence decay curve was recorded using a FLS-980 fluorescence spectrophotometer (Edinburgh Instruments, England) equipped with both continuous and pulsed xenon lamps as the light source. All the data were collected in air at room temperature.

3 Results and Discussion

3.1 Crystal Structure

Figure 1 shows the XRD patterns of Pr$^{3+}$-doped and undoped Na$_2$BaMg(PO$_4$)$_2$. The main diffraction peaks are indexed well with the space group of $P\bar{3}m1$ which is isostructural to the mineral glaserite K$_3$Na(SO$_4$)$_2$ [12]. The structure can be depicted as the stacking along the [001] direction of equivalent [MgP$_2$O$_8$]$^{4-}$ mixed layers of corner sharing MgO$_6$ octahedron which is connected to six PO$_4$ tetrahedra while each tetrahedra is linked to only three octahedra. The Na$^+$ ions are sited in large cavities bound to the layers and the Ba$^{2+}$ ions are found...
within the interlayer space. There is a charge compensation problem with the Pr\(^{3+}\) ions doped Na\(_2\)BaMg(PO\(_4\))\(_2\). Based on the effective ionic radii and electronegativity of cations with different coordination numbers, it might be proposed that Pr\(^{3+}\) ion occupies preferably the Ba\(^{2+}\) site. The required charge compensations for the occupation of Pr\(^{3+}\) ions could be more complicated due to three kinds of cations (Na\(^{+}\), Ba\(^{2+}\) and Mg\(^{2+}\)) in the lattices. This can probably be obtained by the following possible mechanism: the positive charge due to Pr\(^{3+}\) ion substitute for Ba\(^{2+}\) may be combined with the cation vacancy to form the dipole complexes of [(PrBa\(^{3+}\)\(^{-}\) − V\(_{\text{Ba}}\)]\(^{\ast}\). In fact, because of the reaction at high temperature, the Pr\(^{3+}\) ions are not excluded into the Na\(^{+}\) or Mg\(^{2+}\) sites, thus forming the dipole complexes of [(Pr\(_{\text{Ba}}\)\(^{3+}\)\(^{-}\) − V\(_{\text{Na}}\)] and [(Pr\(_{\text{Ba}}\)\(^{3+}\)\(^{-}\) − V\(_{\text{Mg}}\)] respectively. This is very common in other components because of the charge compensation mechanism. For example, trivalent rare-earth (RE\(^{3+}\)) ions doped apatite structure phosphate [13]. In addition, the possible negative charge compensation related to interstitial oxygen here is difficult because this mechanism usually occurs in the case of the high RE-doping [14]. And usually, in oxides, the reaction energy to create the interstitial oxygen is higher than that of cation vacancy [15]. Moreover, it should be noted that due to Pr\(^{3+}\) and host cations having different electrical charges, ionic radii and coordination number, the diffraction intensities, diffraction peak positions and lattice constants of Na\(_2\)BaMg(PO\(_4\))\(_2\)·Pr\(^{3+}\) should be changed with the increasing Pr\(^{3+}\) content, but it is hard to find these differences from Figure 1. The crystal data are collected in Table 1 which are calculated by using the Jade software and XRD experimental data. From Table 1, the cell angles (α, γ) are invariable. The lattice parameters a, c and cell volume of the Na\(_2\)BaMg(PO\(_4\))\(_2\)·Pr\(^{3+}\) are reduced slightly with the increase of doping concentration of Pr\(^{3+}\). Thus, the crystalline density will increase a little. Even so, the change of the cell parameters is very small. The reason is that the doping concentration is very low and is not enough to cause significant change in lattice properties.

### 3.2 SEM Image of Na\(_2\)BaMg(PO\(_4\))\(_2\)·Pr\(^{3+}\)

The typical SEM image is shown in Figure 2. From Figure 2, it is revealed that the surface morphology of the representative sample (0.5 mol% of Pr\(^{3+}\) doping case) is irregular. It is made of numerous micron-sized particles. These particulate sizes of Na\(_2\)BaMg(PO\(_4\))\(_2\)·Pr\(^{3+}\) are mainly in the range of 10–60 μm.

### 3.3 Photoluminescence Properties

Figure 3 presents the excitation and emission spectra of the undoped and doped samples. The excitation spectra of Na\(_2\)BaMg(PO\(_4\))\(_2\)·Pr\(^{3+}\) powders indicate two broad charge transfer bands at 200–280 nm and 310–420 nm, respectively. This is due to the charge transfer from Pr\(^{3+}\), Na\(^{+}\), Ba\(^{2+}\), Mg\(^{2+}\), P\(^{5+}\) to O\(^{2-}\). There are three adjacent peaks at around 449, 468, and 480 nm in the excitation spectra of Na\(_2\)xBaMg(PO\(_4\))\(_2\)·xPr\(^{3+}\), corresponding to the transitions from the ground state 3H\(_4\) to the multiplets 3P\(_2\), 3P\(_1\), and 3P\(_0\), respectively.

<table>
<thead>
<tr>
<th>x</th>
<th>0</th>
<th>0.5%</th>
<th>1.0%</th>
<th>1.5%</th>
<th>2.0%</th>
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<tbody>
<tr>
<td>a (nm)</td>
<td>0.53066</td>
<td>0.53043</td>
<td>0.53042</td>
<td>0.53023</td>
<td>0.53018</td>
</tr>
<tr>
<td>c (nm)</td>
<td>0.69921</td>
<td>0.69919</td>
<td>0.69897</td>
<td>0.69871</td>
<td>0.69867</td>
</tr>
<tr>
<td>α (degree)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>γ (degree)</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Z</td>
<td>1</td>
<td>1</td>
<td>1</td>
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</tr>
<tr>
<td>Volume (nm(^3))</td>
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<td>0.25554</td>
<td>0.25545</td>
<td>0.25518</td>
<td>0.25512</td>
</tr>
<tr>
<td>Density (\rho_{\text{cal.}}) (10(^3)kg/m(^3))</td>
<td>2.5450</td>
<td>2.5473</td>
<td>2.5482</td>
<td>2.5510</td>
<td>2.5516</td>
</tr>
</tbody>
</table>
respectively. Considering 449 nm as the strongest peak, it could be used as a potential red-orange phosphor for the fabrication of white LED with a commercial blue LED chip (430–480 nm).

The characteristic emission peaks of Pr\(^{3+}\) are observed at 528 nm (\(\text{P}_0 \rightarrow \text{H}_1\)), 552 nm (\(\text{P}_0 \rightarrow \text{H}_2\)), 606 nm (\(\text{D}_0 \rightarrow \text{H}_1\)), 611 nm (\(\text{P}_0 \rightarrow \text{H}_1\)), 644 nm (\(\text{P}_0 \rightarrow \text{F}_2\)) and 722 nm (\(\text{P}_0 \rightarrow \text{F}_3\)) for Na\(_2\)BaMg(PO\(_4\))\(_2\):Pr\(^{3+}\) phosphors. As shown in Figure 3, the emission intensity at 606 nm increases with the increasing doped concentration from 0 to 0.005, and decreases with the increasing doped concentration from 0.005 to 0.015. The maximum of luminescent intensity lies at \(x = 0.005\) in the range of 0–0.015, and then increases until \(x = 0.02\). The concentration quenching for the fluorescence of Na\(_2\)BaMg(PO\(_4\))\(_2\):Pr\(^{3+}\) occurs when \(x\) value is higher than 0.02. The quenching of the emission of Pr\(^{3+}\) in Na\(_2\)BaMg(PO\(_4\))\(_2\):Pr\(^{3+}\) might be due to the following reason: the distances between the activators are shortened, and the energy transfer between the adjacent Pr\(^{3+}\) ions in the host Na\(_2\)BaMg(PO\(_4\))\(_2\) occurs with the higher probability of non-radiation transition, which enables the excitation energy to be consumed and results in the quenching of the emission of Pr\(^{3+}\).

### 3.4 The Commission Internationale d’Eclairage Chromaticity Coordinates

As shown in Figure 4, the Commission Internationale d’Eclairage (CIE) average chromaticity coordinates (0.52, 0.46) of Na\(_2\)BaMg(PO\(_4\))\(_2\):Pr\(^{3+}\) with different concentrations (\(x\) = 0.2 mol%, 0.5 mol%, 1.0 mol%, 1.5 mol%, 2.0 mol%, 2.5 mol%, and 3.0 mol%) of \(x\)-Pr-doped Na\(_2\)BaMg(PO\(_4\))\(_2\) phosphors are obtained from the calculations of optical spectra and intensity data. It is clearly observed that the colour of the as-prepared samples is in the red-orange region. The chromaticity coordinates \((x, y)\) and correlated colour temperatures data of all Na\(_2\)BaMg(PO\(_4\))\(_2\):Pr\(^{3+}\) samples are shown in Table 2.

### 3.5 The Decay Curve

Figure 5 shows the typical fluorescence decay pattern in Na\(_{1.999}\)BaMg(PO\(_4\))\(_2\):0.005Pr\(^{3+}\). The fluorescence decay is often given by the multi-exponential or non-exponential decay equation.
decay equation. In this work, the decay curve is non-exponential and well fitted into a three-exponential function
\[ I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} \] (1)
in which \( \tau_1, \tau_2 \) and \( \tau_3 \) are time constants and \( A_1, A_2 \) and \( A_3 \) are coefficients. The average lifetime can be calculated by using the equation,
\[ \langle \tau \rangle = \frac{A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3} \] (2)

As can be seen, the average lifetime in \( \text{Na}_{1.995}\text{BaMg(PO}_4)\text{2:0.005Pr}^{3+} \) is 73.32 \( \mu \text{s} \) which is caused by the radiation relaxation channels and reduction of the 1D lifetime in the \( \text{Na}_{1.995}\text{BaMg(PO}_4)\text{2:0.005Pr}^{3+} \) phosphor. Interestingly, in the experiment, the Pr\(^{3+}\) ions instead of the Na\(^+\) sites are designed, but in the high temperature synthesis condition, a small amount of Pr\(^{3+}\) may replace other ions (such as Ba\(^{2+}\), Mg\(^{2+}\) sites) or occupy the interstitial sites. The three-exponential function indicates that the Pr\(^{3+}\) ions occupy two additional positions besides the Na\(^+\) site. The conclusion here is to verify the correctness of the previously mentioned defect model.

4 Conclusions

A series of Pr\(^{3+}\)-activated \( \text{Na}_{2}\text{BaMg(PO}_4)\text{2:Pr}^{3+} \) phosphors are synthesised with the solid-state reaction method. From the powder X-ray diffraction studies, the phosphor samples are indexed to trigonal symmetry structure with irregular surface morphology. The synthesised phosphors can be efficiently excited by 449 nm which are well matched with the emission of the blue LED chips. The emission intensity can be arrived at a maximum when the doping content is 0.005 \%Pr\(^{3+}\) in \( \text{Na}_2\text{BaMg(PO}_4)\text{2:Pr}^{3+} \). The fluorescence decay time (73.32 \( \mu \text{s} \)) in \( \text{Na}_{1.995}\text{BaMg(PO}_4)\text{2:0.005Pr}^{3+} \) is obtained. The CIE average chromaticity coordinates of the as-prepared phosphors are in the red-orange colour region.

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References