Effects of composition modulation on the luminescence properties of Eu\(^{3+}\) doped Li\(_{1-x}\)Ag\(_x\)Lu(MoO\(_4\))\(_2\) solid-solution phosphors†

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Double molybdate scheelite-type solid-solution phosphors Li\(_{1-x}\)Ag\(_x\)Lu\(_{1-y}\)(MoO\(_4\))\(_2\):yEu\(^{3+}\) were synthesized by the solid state reaction method, and their crystal structures and luminescence properties were investigated in detail. The composition modulation and structural evolution of this series of samples were studied and the selected AgEu(MoO\(_4\))\(_2\), AgLu(MoO\(_4\))\(_2\), LiLu(MoO\(_4\))\(_2\) and LiEu(MoO\(_4\))\(_2\) phases were analyzed based on the Rietveld refinement. Depending on the variation of the Li/Ag ratio in Li\(_{1-x}\)Ag\(_x\)Lu\(_{1-y}\)(MoO\(_4\))\(_2\):yEu\(^{3+}\) phosphors, the difference in the luminescence properties of Li\(_{1-x}\)Ag\(_x\)Lu\(_{1-y}\)(MoO\(_4\))\(_2\):yEu\(^{3+}\) phosphors was ascribed to two factors, one reason could be assigned to the coupling effect and the non-radiative transition between the energy levels of Li\(_{1-x}\)Ag\(_x\)Lu(MoO\(_4\))\(_2\) matrices and the activator Eu\(^{3+}\), another could be due to the near ultraviolet energy absorption and transmission efficiency between the charge-transfer (CT) band of O\(_2\)-Mo\(^6+\) and the 4f → 4f emission transitions of Eu\(^{3+}\). The ultraviolet-visible diffuse reflection spectra (UV-vis DRS) and Raman spectra analysis were also used to verify the above mechanism.

1. Introduction

Double molybdate scheelite-type compounds can be written as M\(^2\)Ln\(^{11}\)(MoO\(_4\))\(_2\). From the viewpoint of the structure and physical–chemical properties, most of these double molybdates are mainly classified into scheelite-type, wolframite-type, and pseudo-scheelite-type, respectively. In the past few decades, Eu\(^{3+}\)-activated molybdates with scheelite-type structures have drawn much attention as potential red-emitting phosphor candidates for white light-emitting diodes (W-LEDs). These materials usually have a broad and intense charge-transfer (CT) band in the UV region except for the intrinsic good stability and low synthetic temperature. The excitation intensity of Eu\(^{3+}\) in molybdates around 394 and 464 nm is significantly enhanced compared with that of Eu\(^{3+}\) in other hosts. Our previous work on the upconversion (UC) luminescence properties of molybdate Li\(_{1-x}\)Ag\(_x\)Lu(MoO\(_4\))\(_2\):Eu\(^{3+}\) verified that the variation of the nonradiative transition rates (\(W_{\text{nr}}\)) originating from the Li/Ag ratio played an important role in the enhancement of the UC emission. Herein, new molybdate Li\(_{1-x}\)Ag\(_x\)Lu(MoO\(_4\))\(_2\):Eu\(^{3+}\) have been proposed, and we wonder whether such a host can also enhance the photo-luminescence intensities of Eu\(^{3+}\) depending on different chemical compositions, and it will give new insights into the modification of the luminescence properties of scheelite-type molybdate phosphors.

Recently, many reports have shown that the dopant of the alkali-metal Li\(^+\) ion in the Eu\(^{3+}\)-activated molybdate materials can enhance the Eu\(^{3+}\) emission intensity. For instance, Wang reported that the luminescence intensity of CaMoO\(_4\):Eu\(^{3+}\)/Li\(^+\) phosphor under excitation at 395 nm increased gradually with more Eu\(^{3+}\)/Li\(^+\) substitution for Ca\(^2+\), till the composition turned into LiEuMoO\(_4\). Liu discussed the dependence of the red emission intensity on the Eu\(^{3+}\) concentration (\(x\)) in a range of molybdate phosphors under excitation at 393 nm. Moreover, as for the phosphors Ca\(_{1-x}\)A\(_x\)MoO\(_4\):Eu\(^{3+}\) [A = K\(^+\), Na\(^+\) ...
and Li\(^{+}\)), the emission intensity increases significantly with increasing contents of Eu\(^{3+}\) and alkali-metal ions, and Li\(^{+}\) ions have the best effect in this series. Therefore, the effect of alkali-metal Li\(^{+}\) ions on the luminescence properties of Eu\(^{3+}\)-activated molybdates has been widely reported in the recent years.\(^{10-15}\) It was found that the alkali-metal Li\(^{+}\) ion could not only enhance the luminescence intensity and improve the color purity but also change the CT band of O\(^{2-}\)–Mo\(^{6+}\) of the molybdate phosphors. However, the effects of alkali-metal Li\(^{+}\) ions on the luminescence properties for molybdate host matrices are still not clear enough.

In this work, the crystal structures of Li\(_{1-x}\)Ag\(_{x}\)Lu\(_{1-y}\)(MoO\(_4\))\(_2\); yEu\(^{3+}\) solid-solution phosphors have been comparatively investigated, and four new phases of AgEu(MoO\(_4\))\(_2\), AgLu(MoO\(_4\))\(_2\), LiLu(MoO\(_4\))\(_2\) and LiEu(MoO\(_4\))\(_2\) have been firstly identified. It is found that the dopant of Li\(^{+}\) ions can alter the spectral profiles of the excitation spectra of Li\(_{1-x}\)Ag\(_{x}\)Lu(MoO\(_4\))\(_2\);0.05Eu\(^{3+}\) phosphors, and the potential mechanism on the different luminescence properties has been analyzed based on the ultraviolet-visible diffuse reflection spectra (UV-vis DRS), and Raman spectra analysis.

2. Experimental section

2.1. Materials and synthesis

Li\(_{1-x}\)Ag\(_{x}\)Lu\(_{1-y}\)(MoO\(_4\))\(_2\);yEu\(^{3+}\) phosphors were synthesized by the high temperature solid-state reaction. Li\(_2\)CO\(_3\) (A.R.), AgNO\(_3\) (A.R.), Mo\(_2\)O\(_3\) (A.R.), Lu\(_2\)O\(_3\) (99.99%) and Eu\(_2\)O\(_3\) (99.99%) were selected as the starting materials. The stoichiometric mixtures or heterogeneous mixtures were filled into porcelain crucibles and then calcined in a mu–furnace at 750 °C for 12 h. The products obtained were found to be white or pink polycrystalline powder.

2.2. Characterization

The phase structures of the as-synthesized materials were determined by using a Rigaku D/max-RB X-ray diffractometer (Tokyo, Japan) with a Cu K\(_\alpha\) (40 kV, 100 mA) incident source in the 5–120° 2\(\theta\) range (0.02°, 2\(\theta\) step size and 1 s per step). The crystallinity and morphology of the as-prepared phosphor samples were studied using a scanning electron microscope (SEM, Hitachi S-4800). The photoluminescence emission (PL) and excitation (PLE) spectra were recorded using a Hitachi F-7000 spectrophotometer with a 150 W Xe lamp as the excitation source under a working voltage of 400 V. The low-temperature PL spectra at 77 K were measured using the same FLS920 fluorescence spectrophotometer with a Xe900 lamp, and the sample temperature was varied using a temperature controller (Oxford, CRY TEMP). The decay curves were recorded on the same Edinburgh instrument (FLS920) with an nF900 flash lamp used as the excitation resource. The quantum efficiency (QE) was measured using an Absolute Photoluminescence Quantum Yield Measurement System (C9920-02, Hamamatsu-Photonics) with an integrating sphere at room temperature.

The ultraviolet-visible diffuse reflection spectra (UV-vis DRS) were recorded on a UV–Vis–NIR spectrophotometer (UV-3600, Shimadzu). BaSO\(_4\) served as a reference standard. The Raman spectra were recorded on a LabRAM Aramis micro-Raman spectrometer (HORIBA Jobin Yvon, France) with an excitation laser beam at 633 nm. The measurements were taken in backscattering configuration using a microscope with a 50\(^{\times}\) objective and a laser focal spot of ~1 \(\mu\)m.

3. Results and discussion

3.1. Phase analysis and crystal structure

Previous studies give some contradictory statements about the symmetry of the LiEu(MoO\(_4\))\(_2\) compound.\(^{16-19}\) For example, Chiu et al.\(^{16}\) proposed that LiEu(MoO\(_4\))\(_2\) is triclinic with the P\(_1\) space group and with two molecular units per unit-cell, but Guo et al.\(^{17}\) and Zaushutsyn et al.\(^{18}\) suggested that LiEu(MoO\(_4\))\(_2\) belongs to the tetragonal crystal system with the space group I\(_4\)/a and showed that all peaks coincide with the peaks of tetragonal AgEu(MoO\(_4\))\(_2\) (PDF 53-0040) and tetragonal LiEu(MoO\(_4\))\(_2\) (PDF 52-1848). To solve this discrepancy, Chimitova et al.\(^{19}\) made a collection of available structural parameters of Aln(MoO\(_4\))\(_2\) binary molybdates and suggested the relationship between the ionic radii ratio \(t = R_{\text{ion}}/R_{\text{a}}\) and the symmetry generated by different combinations of Ln and A atoms. Based on this, one can find that LiEu(MoO\(_4\))\(_2\) should have a I\(_4\)/a space group because it has \(t = 0.863\) and all compounds with \(t\) in the range 0.805–1.341 have a tetragonal unit cell with I\(_4\)/a or I\(_4\) space groups and not a triclinic P\(_1\) space group. In addition, the analysis of the crystal structure of LiEu(MoO\(_4\))\(_2\) with the P\(_1\) space group showed some problems: (1) bond lengths Mo–O are in a very wide range of 1.8587(1)–2.3452(1) Å and the upper limit of this range is unusual for the Mo–O bond; (2) the volume of the primitive part of a unit cell is two times greater than the volume of the primitive cell of a hypothetical I\(_4\)/a cell but the superstructure peaks were not observed in the pattern; (3) [Li/Eu]O\(_4\) polyhedra are very distorted. Thus, all of these facts allowed us to suggest that LiEu(MoO\(_4\))\(_2\) is in fact a tetragonal crystal system with a space group I\(_4\)/a.

Therefore, in order to give direct evidence on the phase formation and crystal structure of the LiEu(MoO\(_4\))\(_2\) structural evolution of the related Li\(_{1-x}\)Ag\(_{x}\)Lu\(_{1-y}\)(MoO\(_4\))\(_2\);yEu\(^{3+}\) phosphors is discussed in this paper. The four endpoint host compounds AgEu(MoO\(_4\))\(_2\), AgLu(MoO\(_4\))\(_2\), LiLu(MoO\(_4\))\(_2\) and LiEu(MoO\(_4\))\(_2\) of this series of solid-solutions Li\(_{1-x}\)Ag\(_{x}\)Lu\(_{1-y}\)(MoO\(_4\))\(_2\);yEu\(^{3+}\) were selected to reveal the detailed characteristics of the structure. Profile fitting and the following Rietveld refinements of the four compounds were performed by using TOPAS 4.2.\(^{20}\) Almost all their peaks were indexed by a tetragonal cell [I\(_4\)/a] with parameters close to AgLa(MoO\(_4\))\(_2\) based on the profile fitting results.\(^{21}\) Therefore the crystal structure of AgLa(MoO\(_4\))\(_2\) was taken as the starting model for Rietveld refinement. The Rietveld plots for four samples are shown in Fig. 1a–d, respectively, and the main parameters of processing and refinement are
It is found that the refinement was stable and gives low R-factors (Table 1). The coordinates of atoms and main bond lengths are in Tables S1 and S2† respectively, which verified the structural occupancy of the different cations in this system. And the crystallographic information files (CIF) for AgEu(MO₄)₂, AgLu(MO₄)₂, LiLu(MO₄)₂ and LiEu(MO₄)₂ compounds are also given in ESI.† The above Rietveld refinement results suggest its real symmetry of I₄₁/a in all the studied compounds.

According to the crystallographic information, the crystal structures of MLn(MO₄)₂ (M = Ag, Li; Ln = Lu, Eu) were well analysed. As for this kind of scheelite-type double molybdate shown in Fig. 2, the Eu³⁺ and alkali metal Li⁺ ions arbitrarily substitute for Lu³⁺ and Ag⁺ ions in the host lattice, respectively. Moreover, the positions of the Lu³⁺ and Ag⁺ ions are randomly distributed in the host of AgLu(MO₄)₂. Hence, in the MLn(MO₄)₂ (M = Ag, Li; Ln = Lu, Eu) crystal structures, the four oxygen atoms surround the Mo⁶⁺ ions to form an isolated [MO₄]²⁻ tetrahedron, while the cations of Li⁺, Ag⁺, Lu³⁺, Eu³⁺ are arbitrarily distributed among the isolated [MO₄]²⁻ tetrahedra and replace each other, as also given in Fig. 2. Furthermore, since four endpoint components AgEu(MO₄)₂, AgLu(MO₄)₂, LiLu(MO₄)₂ and LiEu(MO₄)₂ share the same crystal structure, i.e., tetragonal with the same space group of I₄₁/a, the solid solution phase of these samples also maintained a tetragonal crystal structure. In this work, the components AgEu(MO₄)₂ and LiLu(MO₄)₂ were selected as matrices, and Eu³⁺ acts as a good red emission activator ion.

The solid solutions of AgLu₁₋ₓEuₓ(MO₄)₂ (x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) and LiLu₁₋ₓEuₓ(MO₄)₂ (x = 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) samples were prepared, and their XRD patterns are given in Fig. S1 and S2 in the ESI.† It was found that almost all the diffraction peaks of the products can be readily indexed to the pure tetragonal phase, and no impurity phase was found. Fig. 3 gives the linear dependence

![Fig. 1 Difference Rietveld plots of (a) AgLu(MO₄)₂; (b) AgEu(MO₄)₂; (c) LiLu(MO₄)₂; (d) LiEu(MO₄)₂.](image)

![Fig. 2 The typical crystal structures of MLn(MO₄)₂ (M = Ag, Li; Ln = Lu, Eu).](image)

![Fig. 3 Linear dependence of unit cell volume (V) as a function of x values of AgLu₁₋ₓEuₓ(MO₄)₂ (x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) and LiLu₁₋ₓEuₓ(MO₄)₂ (x = 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0).](image)

### Table 1 Main parameters of processing and refinement of the selected AgEu(MO₄)₂, AgLu(MO₄)₂, LiLu(MO₄)₂ and LiEu(MO₄)₂ samples

<table>
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<th>Compound</th>
<th>AgEu(MO₄)₂</th>
<th>AgLu(MO₄)₂</th>
<th>LiLu(MO₄)₂</th>
<th>LiEu(MO₄)₂</th>
</tr>
</thead>
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<td>Sp. Gr.</td>
<td>I₄₁/a</td>
<td>I₄₁/a</td>
<td>I₄₁/a</td>
<td>I₄₁/a</td>
</tr>
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<td>a, Å</td>
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<td>5.26334(2)</td>
<td>5.10332(11)</td>
<td>5.20263(2)</td>
</tr>
<tr>
<td>c, Å</td>
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<td>11.5433(6)</td>
<td>11.0829(3)</td>
<td>11.33824(5)</td>
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<tr>
<td>V, Å³</td>
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<td>319.782(3)</td>
<td>288.642(2)</td>
<td>306.896(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>2θ interval, °</td>
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<td>5–120</td>
<td>5–120</td>
<td>5–120</td>
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<td>117</td>
</tr>
<tr>
<td>No. of refined parameters</td>
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<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Rwp, %</td>
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<td>1.66</td>
<td>11.79</td>
<td>1.15</td>
</tr>
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<td>Rp, %</td>
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<td>1.11</td>
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<td>Rmerge, %</td>
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</tr>
<tr>
<td>Rfd, %</td>
<td>1.84</td>
<td>3.86</td>
<td>2.45</td>
<td>2.75</td>
</tr>
<tr>
<td>RE, %</td>
<td>1.30</td>
<td>0.26</td>
<td>0.90</td>
<td>0.34</td>
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of unit cell volume ($V$) as function of $x$ values in AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ ($x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8$ and $1.0$) and LiLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ ($x = 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$). As can be seen, the crystal structure remained the same though the Eu/Lu ratio in the host is different, which also indicates that Lu$^{3+}$ can be substituted for Eu$^{3+}$, forming a total range of continuous solid solutions of molybdates. There are evident shifts of the diffraction peaks depending on the different Eu/Lu ratios, as shown in the inset of Fig. S1 and S2. This is attributed to the different ionic radii of Eu$^{3+}$ (1.066) and Lu$^{3+}$ (0.977) in the eight coordination, also implying that AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ ($x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$) and LiLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ ($x = 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$) solid solutions are successfully synthesized and the lattice parameters can be modulated. Moreover, as $x$ values vary from 0 to 1.0, the volumes of the unit cell rise in linear dependence from 304.5 to 319.4 Å$^3$ in the AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ phosphors and from 288.6 to 306.6 Å$^3$ in the LiLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ phosphors, as shown in Fig. 3, which obey Vegard’s law. The unit cell parameters of AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ ($x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$) and LiLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ ($x = 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$) solid solutions are also shown in Tables 2 and 3, respectively. These results attest that the crystalline structure achieves continuous variation and retains the same tetragonality though the $x$ values vary from 0 to 1.0.

Except for the variation of the Eu/Lu ratio, the crystalline structure of MLn(MoO$_4$)$_2$ (M = Ag, Li; Ln = Lu, Eu) series can also remain unchanged depending on the Ag/Li ratio. Thus, Li$_x$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) were chosen as typical phosphors suggesting the influence of different Ag/Li ratios on the structure and luminescence properties. AgLu(MoO$_4$)$_2$ and LiLu(MoO$_4$)$_2$ share the same tetragonal crystal structure with the same space group of $I4_1/a$, as shown in Fig. 1. Based on the different Li/Ag ratios in the Li$_x$Ag$_{1-x}$Lu(MoO$_4$)$_2$ host, the crystal structure remained because of the similar characteristics of Ag$^+$ and Li$^+$, as given in the XRD patterns in Fig. 4(a). It also shows that Ag$^+$ can be replaced with Li$^+$, forming a full-range of continuous solid solutions of molybdates. There are also obvious shifts of the diffraction peaks due to the different Li/Ag ratios as shown in the inset of Fig. 4(a), since the ionic radii of Li$^+$ (0.92 Å) and Ag$^+$ (1.28 Å) are different in the eight coordination, also meaning that Li$_x$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ solid-solution phosphors were successfully synthesized and the cell parameters can be well modulated. In addition, the tetragonality ($c/2a$) of this series of Li$_x$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ samples as a function of $x$ is plotted as shown in Fig. 4(b). Due to the different ionic radii of Li$^+$ (0.92) and Ag$^+$ (1.28) in the eight coordination, the tetragonality $c/2a$ ratio declines in linear dependence from 1.10041 to 1.08594 as $x$ values vary from 0 to 1.

### Table 2 The unit cell parameters of AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ ($x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$)

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$</th>
<th>$c$</th>
<th>$V$ (Å$^3$)</th>
</tr>
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<tbody>
<tr>
<td>0.01</td>
<td>5.1720(7)</td>
<td>11.3841(7)</td>
<td>304.5(3)</td>
</tr>
<tr>
<td>0.1</td>
<td>5.1892(9)</td>
<td>11.4042(9)</td>
<td>307.1(0)</td>
</tr>
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<td>0.2</td>
<td>5.1905(3)</td>
<td>11.4072(1)</td>
<td>307.3(3)</td>
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<td>0.4</td>
<td>5.2141(1)</td>
<td>11.4402(7)</td>
<td>311.0(3)</td>
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<td>0.6</td>
<td>5.2258(2)</td>
<td>11.4720(3)</td>
<td>313.2(9)</td>
</tr>
<tr>
<td>0.8</td>
<td>5.2555(9)</td>
<td>11.5088(0)</td>
<td>317.8(9)</td>
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<tr>
<td>1</td>
<td>5.2610(1)</td>
<td>11.5418(4)</td>
<td>319.4(6)</td>
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### Table 3 The unit cell parameters of LiLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ ($x = 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$)

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$</th>
<th>$c$</th>
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<tr>
<td>0.01</td>
<td>5.1039(5)</td>
<td>11.0802(0)</td>
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<td>5.1236(4)</td>
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<td>11.1817(4)</td>
<td>295.7(2)</td>
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</tr>
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<td>0.8</td>
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<td>11.2780(3)</td>
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<td>5.2006(0)</td>
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<td>306.6(4)</td>
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1.0, and the volume of the unit cell also reduces in linear dependence from 305.5 to 289.3 Å³, which also obey Vegard’s law. The results are also shown in Table 4.

Fig. 5 shows the SEM images of the selected Li₁₋ₓAgₓLu₀.₉₅(MoO₄)₂:₀.₀₅Eu³⁺ (x = 0, 0.2, 0.5 and 1.0) phosphors. From the SEM images, we can find some irregular rectangle particles with the diameters of 1–2 μm, and the morphology and size don’t change a lot depending on the different Li/Ag ratios. Hence we can assume that the observed variation of spectral profiles is mainly due to the changes of covalent properties of the Li/Ag compounds, not the crystallinity and morphology of the as-prepared phosphors.

3.2. Luminescence properties of Eu³⁺ doped MLu(MoO₄)₂ phosphors

Fig. 6(a) shows the PL spectra of AgLu₁₋ₓEuₓ(MoO₄)₂ (x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8, 0.8 and 1.0) phosphors, and the inset of (a) shows the dependence of PL intensities on the Eu³⁺ doping concentration.

Table 4 The unit cell parameters of LiₓAg₁₋ₓLu₀.₉₅(MoO₄)₂:₀.₀₅Eu³⁺ (x = 0, 0.2, 0.4, 0.6, 0.8, 1.0)

<table>
<thead>
<tr>
<th>x</th>
<th>a</th>
<th>c</th>
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<td>1</td>
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Fig. 6 The PL (a) (λex = 464 nm) and PLE (b) (λem = 615 nm) spectra of AgLu₁₋ₓEuₓ(MoO₄)₂ (x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0) phosphors, and the inset of (a) shows the dependence of PL intensities on the Eu³⁺ doping concentration.

5D₀ → ⁷F₂, suggesting that the Eu³⁺ occupies the lattice site of the noncentrosymmetric environment in the present phases, while another group of relatively weak orange emission lines at 593 nm are due to the magnetic dipole transitions of ⁵D₀ → ⁷F₃. Other transitions from the ⁵Dₓ excited levels to ⁷Fₗ ground states of Eu³⁺, for instance, both ⁵D₀ → ⁷F₄ transition located at 650–700 nm and the ⁵D₁ → ⁷Fₗ transition located at 500–570 nm are very weak. Moreover, as shown in Fig. 6(a), with an increasing Eu³⁺ content, the luminescence intensity of AgLu₁₋ₓEuₓ(MoO₄)₂ (x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) red phosphors increased gradually. When the Eu³⁺ content is 1.0, the luminescence intensity is saturated, and the Eu³⁺ has no quenching concentration in the AgLu(MoO₄)₂ host. Being monitored at 615 nm attributed to the ⁵D₀ → ⁷F₂ emission of Eu³⁺ ions, the PLE spectra of the selected compositions of AgLu₁₋ₓEuₓ(MoO₄)₂ (x = 0.01, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) are shown in Fig. 6(b). The PLE spectra consist of two parts, one is composed of the broad band ranging from 200 to ~400 nm, which is assigned as the charge-transfer (CT) transition originating from oxygen to molybdenum and europium (i.e., ligand to metal CT).22,23 Compared to the CT band of
O$^{2-}$–Mo$^{6+}$, the CT band of O$^{2-}$–Eu$^{3+}$ is located in the short ultraviolet wavelength region (250–320 nm) in the double molybdate phosphors, therefore, the long wavelength region of the broad band is mainly ascribed to the CT band of O$^{2-}$–Mo$^{6+}$, as shown in Fig. 6(b). It is also found that the observed CT band is obviously di


different from the CT band of Eu$^{3+}$ in the ZnWO$_4$ and CdWO$_4$ hosts. With the increase of the Eu$^{3+}$ concentration in the matrix, the long wavelength region of the broad band is shifting, the CT band of O$^{2-}$–Mo$^{6+}$ move to the left, that is to say, the near ultraviolet light absorption range of the AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ phosphors tends to become narrow. This phenomenon suggests energy transfer appearing between the CT band of O$^{2-}$–Mo$^{6+}$ in the [MoO$_4$]$^{2-}$ and the luminescence center Eu$^{3+}$ through the oxygen ligand. Another part in the PLE spectra contains a series of sharp peaks ranging from ~400 to 550 nm, which is ascribed to the characteristic intra-configurational 4f → 4f emissive transitions of Eu$^{3+}$: sharp $^7F_0$ → $^5I_6$ transition at 394 nm, $^7F_0$ → $^5D_2$ transition at 464 nm, and the $^7F_1$ → $^5D_1$ transition at 534 nm. However, parts of sharp line transitions were not clearly observed in the excitation spectra, which could be due to the overlap of the CT band with that of the molybdate group. With increasing Eu$^{3+}$ concentrations, the intensities of the sharp peak intensity of AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ ($x = 0.01$, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) phosphors are enhanced, which is consistent with the PL intensity shown in Fig. 6(a).

Similarly, Fig. 7(a) shows the PL spectra of LiLu$_{1-x}$(MoO$_4$)$_2$:xEu$^{3+}$ ($x = 0.01$, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) phosphors under the excitation at 396 nm near ultraviolet light. It is found that the strongest red emission line is peaked at 618 nm and the optimum Eu$^{3+}$ content is 0.8. Being monitored at 618 nm, the PLE spectra of this series of samples are shown in Fig. 7(b). The PLE spectra also consist of two parts, one is corresponding to the broad band ranging from 200 to 360 nm, and another part contains a series of sharp peaks ranging from 360 to 550 nm, which is the same as the result shown in the above Fig. 6. With increasing Eu$^{3+}$ concentrations, the broad absorption band becomes much stronger, which is due to the effect of the CT band of O$^{2-}$–Mo$^{6+}$ and O$^{2-}$–Eu$^{3+}$. We also think that this should be related to the energy transfer between the CT band of O$^{2-}$–Mo$^{6+}$ and the luminescence center Eu$^{3+}$.

By comparing the results shown in Fig. 6 and 7, the spectral profiles of the PLE spectra of AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ and LiLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ phosphors are quite different. The near ultraviolet light absorption range of AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ phosphors is much greater than that of LiLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ phosphors. However, the near ultraviolet energy absorption and transmission efficiency of the AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ phosphors are higher than that of the AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ phosphors. As we know, continuous solid solutions can be obtained from the MLn(MoO$_4$)$_2$ (M = Ag, Li; Ln = Lu, Eu) compounds, and the luminescence intensities of AgLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ and LiLu$_{1-x}$Eu$_x$(MoO$_4$)$_2$ phosphors both tend to be saturated with increasing Eu$^{3+}$ concentrations. Thus, Li$_{0.8}$Ag$_{0.2}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ was selected by changing the Ag/Li ratio, in order to study the effect of Ag/Li ratio composition modulation on the luminescence properties.

Fig. 8(a) and (b) show the PL spectra of Li$_{1-x}$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0) phosphors under different excitation wavelengths of 394 nm and 464 nm. The strongest red emission line all peaked at 615 nm suggesting that the Ag/Li ratio does not change the noncentrosymmetric environment of the luminescence center Eu$^{3+}$ in the present system. As shown in Fig. 8(a), the luminescence intensities of Li$_{1-x}$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ phosphors is enhanced with increasing Li$^+$ concentrations under excitation wavelength of 394 nm, and the Li$_{1-x}$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ phosphor has the strongest luminescence intensity. As shown in Fig. 8(b), under excitation at 464 nm, the luminescence intensities of Li$_{1-x}$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ are also enhanced with increasing Li$^+$ concentrations, the Li$_{0.8}$Ag$_{0.2}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ phosphor has the strongest luminescence
gives the PL spectrum at 77 K of AgLu0.95(MoO4)2:0.05Eu3+ and (MoO4)2:0.05Eu3+ (transitions of Eu3+).

To understand the local symmetry/environments at Eu3+ sites, the Fig. 8 shows the normalized excitation spectra in the range of 200–420 nm.

and 1.0) phosphors, and the insets in (a) and (b) show the dependence (c: \(\lambda_{\text{em}} = 615 \text{ nm} \)) of LiAg1–xLu(x=0, 0.2, 0.4, 0.6, 0.8, 1.0) phosphors monitored at 615 nm. With the increase of Li+ concentrations in the matrix, the CT band of O2–Mo6+ of the broad band is shifting to the left, the near ultraviolet energy absorption and transmission effects are clearly found from the normalized excitation spectra. That’s to say, the luminescence intensities of the molybdate phosphors are not only related to the coupling nonradiative transition probabilities of the phonons but also associated with near ultraviolet energy absorption and transmission efficiency between the CT band of O2–Mo6+ and the 4f \(\rightarrow\) 4f emissive transitions of Eu3+.

In order to improve the spectral resolution and better understand the local symmetry/environments at Eu3+ sites, the low temperature measurement of the PL spectra is essential and some interesting results can be demonstrated.27,28 Fig. 9 gives the PL spectrum at 77 K of AgLu0.95(MoO4)2:0.05Eu3+ and the comparison of PL spectra at 77 K of Li1Ag1–xLu(x=0, 0.2, 0.5, 0.8, 1.0) phosphors in the range of 570–600 nm.

Intensity. The absolute quantum efficiency (QE) of the selected LiEu(MoO4)2 is about 24% under excitation at 460 nm.

Fig. 8(c) shows the PLE spectra of five samples with selected compositions of Li2Ag1–xLu(x=0, 0.2, 0.4, 0.6, 0.8, 1.0) phosphors monitored at 615 nm. With the increase of Li+ concentrations in the matrix, the CT band of O2–Mo6+ of the broad band is shifting to the left, the near ultraviolet light absorption range of Li2Ag1–xLu(x=0, 0.2, 0.4, 0.6, 0.8, 1.0) phosphors becomes much narrower but the near ultraviolet energy absorption and transmission efficiency becomes greater. As a comparison, the broad absorption band is becoming much stronger. As given in the inset of Fig. 8(c), such a variation can be clearly found from the normalized excitation spectra. That’s to say, the luminescence intensities of the molybdate phosphors are not only related to the coupling nonradiative transition probabilities of the phonons but also associated with near ultraviolet energy absorption and transmission efficiency between the CT band of O2–Mo6+ and the 4f \(\rightarrow\) 4f emissive transitions of Eu3+.

In order to improve the spectral resolution and better understand the local symmetry/environments at Eu3+ sites, the low temperature measurement of the PL spectra is essential and some interesting results can be demonstrated.27,28 Fig. 9 gives the PL spectrum at 77 K of AgLu0.95(MoO4)2:0.05Eu3+ and the comparison of PL spectra at 77 K of Li1Ag1–xLu(x=0, 0.2, 0.5, 0.8, 1.0) phosphors in the range of 570–600 nm.
In order to further discuss the mechanism on the effect of Ag/Li ratio composition modulation on the luminescence properties, the UV-vis DRS of phosphors Li$_{1-x}$Ag$_x$Lu$_{1-y}$Eu$_{y}$ (MoO$_4$)$_2$ ($x = 0, 1.0; y = 0, 0.6, 1.0$) and undoped hosts Li$_{1-x}$Ag$_x$Lu$_{1-y}$ (MoO$_4$)$_2$ ($x = 0, 1.0$) were measured and calculated, respectively, and the relationship between the absorption coefficient and the photon energy is shown in Fig. 11. As shown in Fig. 11, it is found that the obvious difference of the band gaps ($E_g$) is not ascribed to the substitution of Lu$^{3+}$ for Eu$^{3+}$, but the result of Li$^+$ substitution for Ag$^+$. As can be seen from Fig. 11, the band gaps of Li$_{1-x}$Ag$_x$Lu$_{1-y}$ (MoO$_4$)$_2$ ($x = 0, 1.0$) are obviously different, which should be due to the different electronegativity values of Li$^+$ (0.91) and Ag$^+$ (1.87). Therefore, it will lead to the different covalent properties of the host crystal lattice. On the basis of Pankove’s and Hao’s suggestion,$^{31,32}$ the reflection spectrum was expressed as the following eqn (1):

\[(\alpha h \nu)^2 \propto h \nu \]

where $\alpha$ represented the reflection coefficient, $h$ is the Planck's constant, and $\nu$ is the frequency of light. Therefore, the band gap value ($E_g$) was measured from the low energy edge (the long wavelength edge) of the absorption band in the reflection spectrum. The $E_g$ values of Li$_{1-x}$Ag$_x$Lu$_{1-y}$ (MoO$_4$)$_2$ ($x = 0, 1.0$) were determined to be 3.08 eV, and 3.58 eV, respectively. Thus, as shown in Fig. 11, the increasing $E_g$ value was expected to enhance the Eu$^{3+}$ emission due to the decrease of covalent properties of the host lattice. To find out the difference between Eu$^{3+}$ emission and excitation intensities in this series of Li$_{1-x}$Ag$_x$Lu$_{1-y}$ (MoO$_4$)$_2$, their relationships among the ionic polarizations, deformation abilities of the ions and band gap have also been introduced.$^7$ At the same time, the relationship between the band gap value ($E_g$) and Eu$^{3+}$ luminescence intensity has been well studied, as shown in Fig. 12. It is commonly recognized that the band gap is closely related to the polarization ability of cations and the deformation ability of ions. Particularly, the polarization ability of cations has been taken into account. The greater the cationic polarization ability is, the stronger the covalent bond links to the anion, which in turn results in the narrower band gap. In order to give a further comprehension of the increasing $E_g$ value extension with the increasing $x$ values of the Li$_{1-x}$Ag$_x$Lu$_{0.95}$ (MoO$_4$)$_2$:0.05Eu$^{3+}$ ($x = 0, 0.2, 0.5, 0.8, 1.0$) phosphors, the following expression has been proposed, as given in eqn (2):

\[\Phi_{\text{eff}} = Z_{\text{eff}} / r \]

The effective ionic potential ($\Phi_{\text{eff}}$) is introduced to measure the polarization ability of cations (Fig. 12). The function $Z_{\text{eff}}$ is called the effective cationic nuclear charge, and $r$ is the cationic radius in the corresponding ligand field.$^{33}$ Based on this equation, the effective cationic nuclear charge results of Ag$^+$ and Li$^+$ are $\Phi_{\text{Ag}} = 3.63$ and $\Phi_{\text{Li}} = 1.41$, respectively, which indicate that the polarization ability of Ag$^+$ is much greater than that of Li$^+$. As shown in Fig. 12, oxygen ions have more deformation in the AgLu$_0.95$(MoO$_4$)$_2$:0.05Eu$^{3+}$ system compared to that of the LiLu$_0.95$(MoO$_4$)$_2$:0.05Eu$^{3+}$ system, which will lead to
the enhancement of covalent properties of the Ag–O bond. Hence, in the Li$_{x}$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ (x = 0, 0.2, 0.5, 0.8, 1.0) phosphors, when Ag$^+$ is replaced with Li$^+$, the band gaps of the Li$_{x}$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$ host become wider. Besides, the deformation ability of ions should be also considered. Since the Li$_{x}$Ag$_{1-x}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ (x = 0, 0.2, 0.5, 0.8, 1.0) phosphors share the same Mo–O bond, the difference between the deformation abilities of Li$^+$ and Ag$^+$ is primarily discussed. Based on the theory on Lewis hard and soft acids and bases, Li$^+$ is difficult to be deformed since it possesses a two electron configuration and only its orbitals have two electrons with small ionic radius and high charge density. Therefore, Li$^+$ belongs to the hard acid. While Ag$^+$ has the eighteen electron configuration and its outer shell layer contains 4d$^{10}$ orbital with large ionic radius and low charge density, Ag$^+$ is easy to deform and it is called the soft acid. Hence, based on the above analysis, the arrows show the moving direction of the electron cloud, as shown in Fig. 12, which is also regarded as the effect of electron cloud expansion, and the deformation ability of Ag$^+$ is greater than that of Li$^+$, which will generate the phenomenon that the Ag$^+$ feeds back much more electron cloud to the Mo–O bond in the AgLu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ system than that of Li$^+$ in the LiLu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ system. Thus the covalent properties of the Mo–O bond in the AgLu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ system is much greater than that of the LiLu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ system.

Fig. 13 gives the Raman spectra of AgLu(MoO$_4$)$_2$ and LiLu(MoO$_4$)$_2$ host materials excited at 633 nm. As we can also observe from Fig. 13 that the Raman spectra of the bands at 318, 403, 790, and 880 cm$^{-1}$ can be divided into two groups, which show the clear multiplets of the stretching $\nu$(Mo–O) vibrations in the range of 750–1000 cm$^{-1}$ and the bending vibrations in the range of 300–450 cm$^{-1}$. Moreover, the theory on lattice relaxation and multiphonon transitions has been well established. In the case of rare-earth luminescence centers, the coupling between centers and the lattice is relatively weak because the 4f electrons are shielded by 5s and 5p electrons. If the doped concentrations of rare earth ions and the maximum phonon energy remain the same, the nonradiative transition probabilities ($W_{NR}$) of the matrices will influence the rare earth ion emission intensity. The formula for the nonradiative rate is given by the following eqn (3):\[ W_{NR} = C \left[ \frac{1}{\exp \left( \frac{\hbar \nu}{kT} \right) - 1} \right] \exp \left( \frac{\Delta E}{\hbar \nu} \right) \exp \left( \frac{\Delta E \ln \epsilon}{\hbar \nu} \right) \] where $\Delta E$ is the measure of the relative offset between these levels; $\epsilon$ accounts for the exact nature of the ion-phonon coupling and is insensitive as $\ln(\epsilon)$ in the formula; the constant $C$ depends on the phonon density of the matrix. $\nu_p$ refers to the maximum phonon frequency of the host. It is known that the influence of crystal lattice on the rare earth ion luminescence mainly depends on the phonon. For the sake of discussing the impact of different matrices on the Eu$^{3+}$ emission intensity, eqn (4) is introduced. From Fig. 13, the maximum phonon energy of AgLu(MoO$_4$)$_2$ and LiLu(MoO$_4$)$_2$ hosts show no difference, and then the values of $\epsilon$ and $C$ should only be considered. With regard to the present molybdate matrices, the intensity of ion-phonon coupling ($\epsilon$) depends on the impact of Li$^+$ or Ag$^+$ on the tetrahedron [MoO$_4$]$^{2-}$. Due to the difference of the deformation ability of ions mentioned above, the polarization ability of $\nu$(O–Mo$^{2-}$) in the tetrahedron [MoO$_4$]$^{2-}$ to the rare earth Eu$^{3+}$ becomes stronger and the intensity of ion-phonon coupling ($\epsilon$) is greater in the AgLu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$.
system. Furthermore, according to Debye approximation, the following eqn (4) can be achieved:

$$C \propto \rho(w)^{5/3}$$

(4)

where $\rho(w)$ is the phonon density of state of the matrix. Thus, a larger phonon density will lead to a larger $C$, implying a greater $W_{NR}$ and a weaker Eu$^{3+}$ emission intensity. As shown in Fig. 13, the maximum phonon frequency peak (880 cm$^{-1}$) in the LiLu(MoO$_4$)$_2$ host material has a smaller area and weaker intensity than that in the AgLu(MoO$_4$)$_2$ host material. Therefore, the maximum energy phonon density is defined as the specific value of the integrated intensity of the maximum phonon vibration peak and the integrated intensity of the host Raman scattering curve. After calculation, the maximum energy phonon density of AgLu(MoO$_4$)$_2$ and LiLu(MoO$_4$)$_2$ are 0.6221 and 0.5597, respectively. Then, the AgLu(MoO$_4$)$_2$ host has greater values of $C$ and $R$ than that of the LiLu(MoO$_4$)$_2$ host. Based on eqn (4), the nonradiative transition probabilities ($W_{NR}$) in the AgLu(MoO$_4$)$_2$ are greater than that of LiLu(MoO$_4$)$_2$, and then it is reasonable to find that the Eu$^{3+}$ emission intensity of the AgLu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ system is weaker than that of LiLu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$.

In all, the interpretation has been proposed on the reason that the Eu$^{3+}$ emission intensity of the AgLu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ system is weaker than that of the LiLu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ system. According to Fig. 12, the lower edge of the matrix conduction band is much closer to the excitation band energy level of Eu$^{3+}$ and it may have some kind of coupling which will produce a kind of energy loss (nonradiative transition), leading to diminishing Eu$^{3+}$ emission intensity. As mentioned previously, the $E_g$ values of AgLu(MoO$_4$)$_2$ and LiLu(MoO$_4$)$_2$ are 3.08 eV and 3.58 eV, respectively, thus the band gap of the Li$_{1-x}$Ag$_x$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ will be much closer to the energy level gap 2.67–3.14 eV (394–464 nm) of the activator Eu$^{3+}$ with increasing Ag/Li ratios. As a result, there may be a part of the coupling between two energy levels of AgLu(MoO$_4$)$_2$ and the activator Eu$^{3+}$. This phenomenon also exists in the Eu$^{3+}$ doped molybdate matrix systems. However, since the Li-contained material has a wider band gap than that of the Ag-based material, we can only know the excited state of Eu$^{3+}$ is much closer to the conduction band of Ag$^+$. According to Boltzmann distribution, we can qualitatively know that the excited state electron number of Eu$^{3+}$ distributes more to the conduction band of Ag$^+$, which will cause possible energy loss, leading to the lower Eu$^{3+}$ emission intensity. But we cannot confirm the absolute position of the Eu$^{3+}$ level in the band gaps for the two different kinds materials, thus the specific numerical values of the energy difference between excited state of Eu$^{3+}$ and the conduction band of Ag$^+$ or Li$^+$ is by far unclear. Hence, the energy coupling between the AgLu(MoO$_4$)$_2$ matrix and Eu$^{3+}$ was weakened when Li$^+$ was introduced into the Li$_{1-x}$Ag$_x$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ phosphors.

As for the excitation spectra of Li$_{1-x}$Ag$_x$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ ($x = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$) phosphors, both the $7F_0 \rightarrow 5L_6$ transition at 394 nm and $7F_0 \rightarrow 5D_2$ transition at 464 nm, are not only closely related to the energy coupling (the nonradiative transition) but also most associated with the near ultraviolet energy absorption and transmission efficiency between the CT band of O$^{2-}$–Mo$^{6+}$ and the 4f $\rightarrow$ 4f emissive transitions of Eu$^{3+}$. As a typical rare earth activated photoluminescence process, the electrons in the Eu$^{3+}$ absorb some energy, transferring from the ground state $7F_0$ to the excited state, then always revert to the original equilibrium state, completing the photoluminescence process. However, the emission process of molybdate matrix luminescent materials is mainly completed through two processes, the electrons in a higher excited state will transfer to the lower excited state $3D_2$ via the energy transfer or nonradiative transitions appear and go back to the ground state $7F_j$ ($j = 0, 1, 2, 3, 4, 5, 6$) by coupling of the CT band of O$^{2-}$–Mo$^{6+}$, and another way is through the electron phonon relaxation process of rare earth energy levels, relaxing from a higher excited state to excited state $5D_0$. Both the processes will finally get back to the ground state $7F_j$ ($j = 0, 1, 2, 3, 4, 5, 6$) from excited states $5D_0$ and the Eu$^{3+}$ emission is achieved. For the $7F_0 \rightarrow 5L_6$ transition and the $7F_0 \rightarrow 5D_2$ transition, the photoluminescence process is mainly through the coupling of the CT band of O$^{2-}$–Mo$^{6+}$, however, this process contains both the energy transfer and energy coupling loss from the CT band of O$^{2-}$–Mo$^{6+}$ to Eu$^{3+}$ energy levels, and the energy loss process will lead to a higher nonradiative transition probability. Thus, via composition modulation in the Li$_{1-x}$Ag$_x$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ ($x = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$) phosphors, the PLE and PL intensity of the Li$_{0.8}$Ag$_{0.2}$Lu$_{0.95}$(MoO$_4$)$_2$:0.05Eu$^{3+}$ phosphor is the strongest one, which is due to the balance of the energy transfer and the coupling nonradiative transition between the CT band of O$^{2-}$–Mo$^{6+}$ and Eu$^{3+}$ energy levels.

4. Conclusion

In conclusion, the double molybdate solid-solution phosphors Li$_{1-x}$Ag$_x$Lu$_{1-y}$(MoO$_4$)$_2$:yEu$^{3+}$ were designed and reported in this paper. The crystal structure and phase formation of the Li$_{1-x}$Ag$_x$Lu$_{1-y}$(MoO$_4$)$_2$:yEu$^{3+}$ solid solutions were discussed in detail. With increasing Li/Ag ratios, the nonradiative transition between two energy levels of the Li$_{1-x}$Ag$_x$Lu$_{1-y}$(MoO$_4$)$_2$ host and the activator Eu$^{3+}$ has been weakened since the band gaps of the host were enlarged, and then the Eu$^{3+}$ emission intensities were enhanced. A model on the evaluation of the polarization ability of cations has been built to explore the relationship between the Eu$^{3+}$ energy level and the host. The luminescence intensity of molybdate matrix materials is not only related to the coupling nonradiative transition probabilities of the phonons but also associated with near ultraviolet energy absorption and transmission efficiency between the CT band of O$^{2-}$–Mo$^{6+}$ and the 4f $\rightarrow$ 4f emissive transitions of Eu$^{3+}$. These results could shed light on the research and understanding of luminescence intensity and efficiency enhancement in Eu$^{3+}$ doped luminescent materials.
Acknowledgements

The present work was supported by the National Natural Science Foundations of China (Grant No. 51272242, 51572023, 51511130035), Natural Science Foundations of Beijing (2132050), the Program for New Century Excellent Talents in University of Ministry of Education of China (NCET-12-0950), Beijing Nova Program (Z13110300413047), Beijing Youth Excellent Talent Program (YETP0635), the Funds of the State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (RERU2015022), and the excellent tutor section of the Fundamental Research Funds for the Central Universities of China University of Geosciences, Beijing (2-9-2015-028). This work was also partly supported by the Russian Foundation for Basic Research (Grant No. 15-52-53080 GFEN_a).

Notes and references

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