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**The modulated structure and frequency upconversion properties of
 $\text{CaLa}_2(\text{MoO}_4)_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ phosphors prepared by microwave synthesis**

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Abstract

$\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ phosphors with the doping concentrations of Ho^{3+} and Yb^{3+} ($x = \text{Ho}^{3+} + \text{Yb}^{3+}$, $\text{Ho}^{3+} = 0.05$; $\text{Yb}^{3+} = 0.35, 0.40, 0.45$ and 0.50) have been successfully synthesized by the microwave sol-gel method. The modulated and averaged crystal structures of $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ molybdates have been found by Rietveld method, and the upconversion photoluminescence properties have been investigated. The synthesized particles, being formed after the heat-treatment at 900°C for 16 h, showed a highly crystallized state. Under the excitation at 980 nm, $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ particles exhibited strong 545- and 655-nm emission bands in the green and red regions. When the $\text{Yb}^{3+}:\text{Ho}^{3+}$ ratios are 9:1 and 10:1, the UC intensity of $\text{CaLa}_{1.5}(\text{MoO}_4)_4:\text{Yb}_{0.45}/\text{Ho}_{0.05}$ and $\text{CaLa}_{1.45}(\text{MoO}_4)_4:\text{Yb}_{0.50}/\text{Ho}_{0.05}$ particles is the highest for different bands. The CIE coordinates calculated for $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ phosphors are related to the yellow color field. The Raman spectrum of undoped $\text{CaLa}_2(\text{MoO}_4)_4$ has revealed about 13 narrow lines. The strongest band observed at 906 cm^{-1} was assigned to the ν_1 symmetric stretching vibration of MoO_4 tetrahedrons. The spectra of the samples doped with Ho and Yb obtained under the 514.5 nm excitation were dominated by Ho^{3+} luminescence over the wavenumber range of $>700\text{ cm}^{-1}$ preventing the recording of the Raman spectra.

1. Introduction

Presently, applications of photoluminescence materials have actively evolved in such fields as fluorescent lamps, cathode ray tubes, solid-state laser, amplifiers for fiber optics communication and new optoelectronic devices [1-5]. Recently, the synthesis and the luminescence properties of upconversion (UC) particles have attracted considerable attention, and they are considered as potentially active components in new optoelectronic devices and luminescent labels for imaging and biodetection assays, which overcome the limitations in traditional photoluminescence materials [6-14]. Among oxide compounds, complex molybdates are very attractive as hosts for rare earth luminescent ions because of a high chemical stability, comparatively low synthesis temperature and excellent spectroscopic characteristics [15-22].

The wide family of double molybdates/tungstates $MLn_2(MoO_4)_{4(1-m)}(WO_4)_{4m}$ ($M = Ba, Sr, Ca$; $Ln = Y^{3+}$ or rare earth elements; $0 \leq m \leq 1$) with a scheelite-like structure has been recently discovered as efficient host materials, and the photoluminescent properties have been evaluated for several host/ activator [23-32]. Other properties of the compounds, however, are less studied. As to the $MLn_2(MoO_4)_4$ crystals, up to now, the structure has been obtained only for $CaEu_2(MoO_4)_4$ that is $(3 + 2)$ -dimensionally modulated and crystallized in tetragonal superspace group $I4_1/a(\alpha\beta 0)00(-\beta\alpha 0)00$ [28]. The structure is formed by MoO_4 tetrahedrons and $(A)O_8$ square antiprism, $A = Ca, Eu$ or vacancy, and the variation of the occupancy factor of the A position was considered as a driving force for the structure modulation. As it can be reasonably supposed, the trivalent rare-earth ions in the disordered scheelite-type structure could be partially substituted by different Ln^{3+} ions. The ions are efficiently doped into the crystal lattice due to the similarity of Ln^{3+} ion radii, and that releases the restriction on the acceptable doping level. Among rare earth ions, the Ho^{3+} ion is suitable for converting infrared to visible light through the UC process due to its appropriate electronic energy level configuration. Co-doped Yb^{3+} and Ho^{3+} ions can remarkably enhance the UC efficiency by the energy transfer from Yb^{3+} to Ho^{3+} . The Yb^{3+} ion, as a sensitizer, can be effectively excited by an incident light source energy. This energy is transferred to the

activator from which the radiation can be emitted. The Ho^{3+} ion activator is the luminescence center of the UC particles, while the sensitizer enhances the UC luminescence efficiency [6,7,13,33–37].

The present study is aimed at the structural and spectroscopic evaluation of $\text{CaLa}_2(\text{MoO}_4)_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ phosphors. Earlier, these rare-earth doped molybdates were reported as host materials in several phosphors [23-26,30]. Nevertheless, the structural and vibrational properties remain unknown. The $\text{Ho}^{3+}/\text{Yb}^{3+}$ -doping effects and UC characteristics of $\text{CaLa}_2(\text{MoO}_4)_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ phosphors are also unclear. The microwave sol-gel technology is selected for the sample preparation [13,20,30-32,37]. Usually, complex molybdates are prepared by a solid-state method that requires high temperatures, a lengthy heating process and subsequent grinding, which may occasionally result in a loss of the emission intensity. The sol-gel process possesses such advantages as particle shape homogeneity, low calcination temperature and a small particle size, and a narrow particle size distribution promising for good luminescent characteristics. However, the long gelation time is a typical disadvantage of the sol-gel process. As compared to the traditional methods, microwave synthesis is characterized by a very short reaction time, small-size particles, narrow particle size distribution and a high purity of the final polycrystalline products. Microwave heating is delivered to the material surface by radiant and/or convection heating which is transferred to the bulk of the material via conduction [38,39]. Thus, the microwave sol-gel process is a cost-effective method that provides its high homogeneity with an easy scale-up, and it is emerging as a viable alternative approach for the synthesis of high-quality luminescent materials in short time periods. Previously, this synthesis route was tested by our team for different complex molybdates and tungstates, and successfully provided powder products with a homogeneous particle size distribution and uniform morphology [30-32,37].

2. Experimental

In this study, stoichiometric amounts of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99 %, Sigma-Aldrich, USA), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99 %, Sigma-Aldrich, USA), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (99%, Alfa Aesar, USA),

$\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich, USA), $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9%, Sigma-Aldrich, USA), citric acid (99.5%, Daejung Chemicals, Korea), NH_4OH (A.R.), ethylene glycol (A.R.) and distilled water were used to prepare $\text{CaLa}_{2-x}(\text{MoO}_4)_4 \cdot \text{Yb}_y/\text{Ho}_z$ ($y = 0, 0.35, 0.40, 0.45$ and 0.50 ; $z = 0, 0.05$; $x = y + z$) compositions. The $\text{CaLa}_{2-x}(\text{MoO}_4)_4 \cdot \text{Yb}_y/\text{Ho}_z$ sample notations and compositions are shown in Table 1.

To prepare pure $\text{CaLa}_2(\text{MoO}_4)_4$, 0.4 mol% $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 0.229 mol% $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ were dissolved in 20 mL of ethylene glycol and 80 mL of 5M NH_4OH under vigorous stirring and heating. Subsequently, 0.8 mol% $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and citric acid (with a molar ratio of citric acid to the total metal ions of 2:1) were dissolved in 100 mL of distilled water under vigorous stirring and heating. Then, the solutions were mixed together under vigorous stirring and heating at 80-100°C. At the end, highly transparent solutions were obtained and adjusted to pH = 7-8 by the addition of NH_4OH or citric acid. To prepare $\text{CaLa}_{1.6}(\text{MoO}_4)_4 \cdot \text{Yb}_{0.35}/\text{Ho}_{0.05}$, the mixture of 0.64 mol% $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.14 mol% $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.02 mol% $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was used for the creation of the rare-earth-carrying solution. To prepare $\text{CaLa}_{1.55}(\text{MoO}_4)_4 \cdot \text{Yb}_{0.40}/\text{Ho}_{0.05}$, the mixture of 0.62 mol% $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.16 mol% $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.02 mol% $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was employed for the creation of the rare-earth-carrying solution. To prepare $\text{CaLa}_{1.50}(\text{MoO}_4)_4 \cdot \text{Yb}_{0.45}/\text{Ho}_{0.05}$, the mixture of 0.6 mol% $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.18 mol% $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.02 mol% $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was used for the creation of the rare-earth-carrying solution. To prepare $\text{CaLa}_{1.45}(\text{MoO}_4)_4 \cdot \text{Yb}_{0.50}/\text{Ho}_{0.05}$, the rare-earth-containing solution was generated using 0.58 mol% $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.2 mol% $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and 0.02 mol% $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

The transparent solutions were placed for 30 min into a microwave oven operating at the frequency of 2.45 GHz and the maximum output-power of 1250 W. The microwave reaction working cycle was being controlled very precisely between 40 s on and 20 s off for 15 min followed by a further treatment of 30 s on and 30 s off for 15 min. Ethylene glycol was evaporated slowly at its boiling point of 197°C, and this solvent is a suitable medium for the microwave process.

Respectively, if ethylene glycol is used as a solvent, the reactions proceed at their boiling point temperature. When microwave radiation is supplied to the ethylene-glycol-based solution, the components dissolved in the ethylene glycol can couple. The charged particles vibrate in the electric field interdependently when a large amount of microwave radiation is supplied to the solution. The samples were being treated with ultrasonic radiation for 10 min to produce a light yellow transparent sol. After this stage, the light yellow transparent sols were dried at 120°C in a dry oven to obtain black dried gels. The black dried gels were being ground and heat-treated at 900°C for 16 h in the air after several steps at 300°C for 12 h, at 400°C for 1 h, at 500°C for 1 h, at 600 °C for 2 h, 700°C for 2 h, 800°C for 2 h with a 100°C interval. Finally, the white particles were obtained for $\text{CaLa}_2(\text{MoO}_4)_4$ and pink particles were obtained for the doped compositions.

The structural properties of the synthesized particles were evaluated using XRD (D/MAX 2200, Rigaku, Japan) with the scans over the range of $2\theta = 5\text{-}110^\circ$. The microstructure and surface morphology were observed using SEM/EDS (JSM-5600, JEOL, Japan). The PL spectra were recorded using a spectrophotometer (Perkin Elmer LS55, UK) at room temperature. The pump power dependence of the UC emission intensity was measured on the working power from 20 to 110 mW. Commission Internationale de l'Eclairage (CIE) chromaticity for the color coordinates of the synthesized phosphors was evaluated. Raman spectra measurements were made using a LabRam Aramis (Horiba Jobin-Yvon, France) set up at the spectral resolution of 2 cm^{-1} . The 514.5-nm line of an Ar ion laser was used for the excitation; the power on the samples was kept at the 0.5-mW level to prevent the possible sample decomposition.

2. Results and discussion

The XRD pattern recorded from $\text{CaLa}_2(\text{MoO}_4)_4$ is shown in Fig. 1. The diffraction peaks are sharp and that confirms high powder crystallinity. The XRD patterns obtained from doped samples are similar to that shown in Fig. 1. Previously, it was found that all compounds in $\text{CaGd}_{2(1-x)}\text{Eu}_{2x}(\text{MoO}_4)_4$ series are (3 + 2)D incommensurately modulated with superspace group $I4_1/a(\alpha,\beta,0)00(-\beta,\alpha,0)00$ [27,28]. On the analogy, it is suggested that compounds CaLa_2 .

$x(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ also have their structure modulation. Therefore, first of all, the Le Bail decomposition was applied using the JANA2006 software to prove the incommensurability of the compounds under investigation [40]. The refinements were stable and gave low R-factors. The obtained structural parameters are shown in Table 2. All peaks in each pattern were accounted by one phase which verifies all samples high phase purity.

As far as it is not possible to calculate the vibrational spectra from a modulated crystal structure, the averaged crystal structures were refined for all compounds. The related diffraction patterns are shown in Figs. 1S-5S. The Rietveld refinement was performed using package TOPAS 4.2 [41]. The refinements were stable and gave reasonable R-factors, as shown in Table 3. The atom coordinates and the main bond lengths can be found in Tables 1S and 2S, respectively. The averaged structure of $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ crystals is shown in Fig. 2. In the structure, the site containing Ca/La/Yb/Ho ions or a vacancy is coordinated by eight oxygen ions, and partial cation occupations are governed by chemical composition. The Mo^{6+} ions are coordinated by four O^{2-} ions. (Fig. 2). The unit cell volume tendency to growth on the averaged ion radii La/Yb/Ho increase, as shown in Fig. 3, proves the suggested chemical formula of the solutions. This result confirms the persistence of the designed chemical composition during the microwave sol-gel synthesis. It is emphasized that the microwave sol-gel process provides the energy, uniform to the bulk of the material, so that the fine particles with a controlled morphology can be fabricated for a short time [38,39]. The method is a cost-efficient way to provide homogeneous double molybdate products with an easy scale-up potential, and it is a viable alternative for the rapid synthesis of UC particles.

The SEM images of the doped molybdate samples are shown in Fig. 4. The formation of homogeneously agglomerated particles with the size of 1-3 μm is evident. Generally, the coalescent particle morphology is an indicator of the grains active interdiffusion that, as a rule, provides high chemical and structural homogeneity of the oxide products [10,37,44-47]. The well faceted tetragonal microcrystal forms were not found, and domination of the irregular particle forms may be induced due to a comparatively short time of the high-temperature annealing at 600-900°C, when

the equilibrium microcrystal shapes have no time to be generated. Specifically for molybdates, it is known that efficient MoO₃ oxide evaporation is possible in the air over the temperature range of 600-900°C, and this factor additionally stimulates the formation of faceted molybdate particles [15,16,46,47]. Thus, the faceted tetragonal microparticle formation of CaLa_{2-x}(MoO₄)₄:Yb_y/Ho_z compounds could be reasonably supposed on a further 600-900°C increase of the annealing time.

The UC photoluminescence emission spectra of the as-prepared (a) CaLa_{1.6}(MoO₄)₄:Yb_{0.35}/Ho_{0.05}, (b) CaLa_{1.55}(MoO₄)₄:Yb_{0.40}/Ho_{0.05}, (c) CaLa_{1.5}(MoO₄)₄:Yb_{0.45}/Ho_{0.05}, and (d) CaLa_{1.45}(MoO₄)₄:Yb_{0.50}/Ho_{0.05} particles excited by 980 nm at 24°C are shown in Fig. 5. The samples exhibited yellow emissions based on the combination of strong emission bands at 545-nm and 655-nm in green and red spectral regions, respectively. The strong 545-nm emission band in the green region corresponds to the ⁵S₂/⁵F₄ → ⁵I₈ transition in Ho³⁺ ions, while the strong emission 655-nm band in the red region appears due to the ⁵F₅ → ⁵I₈ transition in Ho³⁺ ions. The Ho³⁺ ion activator is the luminescence center in these UC particles, and the Yb³⁺ sensitizer enhances the UC luminescence efficiency. The UC intensity is dependent on the Yb³⁺:Ho³⁺ ratio in samples (a) 7:1, (b) 8:1, (c) 9:1 and (d) 10:1. When the Yb³⁺:Ho³⁺ ratios are 9:1 and 10:1, the UC intensity of (c) CaLa_{1.5}(MoO₄)₄:Yb_{0.45}/Ho_{0.05} and (d) CaLa_{1.45}(MoO₄)₄:Yb_{0.50}/Ho_{0.05} particles is the highest for different bands.

The logarithmic scale dependence of the UC emission intensities at 545 and 655 nm on the working pump power over the range from 20 to 110 mW in the CaLa_{1.50}(MoO₄)₄:Yb_{0.45}/Ho_{0.05} sample is shown in Fig. 6. In the UC process, the UC emission intensity is proportional to the slope *n* value of the irradiation pumping power, where *n* is the number of pumping photons required to produce UC emission [48]:

$$I \propto P^n$$

$$\text{Ln}I \propto n\text{Ln}P$$

where n value is the number of the pumping photons required to excite the upper emitting state, I is the UC luminescent intensity and P is the laser pumping power. The calculations show the slopes of $n = 1.70$ and 1.85 for green emission at 525 and 550 nm, and 1.55 for red emission at 655 nm, respectively. This result provides that the UC mechanism of the green and red emissions can be explained by a two-photon UC process in $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped phosphors [11,35]. Comparing the power dependences obtained for the molybdate under study, we note that they indicate on-level optimal conditions for upconversion close to those obtained in a number of other matrices produced by various technologies. Only $\text{NaLa}(\text{MoO}_4)_2:\text{Ho},\text{Yb}$ phosphor was more optimal with slope very close to 2 for both spectral components of upconversion luminescence [49].

Based on the results of pump power dependence, the known schematic energy level diagrams of Ho^{3+} (activator) and Yb^{3+} (sensitizer) ions in the as-prepared $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ samples and the UC mechanisms, accounting for the green and red emissions during 980 nm laser excitation, are shown in Fig. 7 [13,37]. The UC emissions are generated by a two photon process through excited state absorption (ESA) and energy transfer (ET). Initially, the Yb^{3+} ion sensitizer is excited from the $^2\text{F}_{7/2}$ level to the $^2\text{F}_{5/2}$ level under the excitation at 980 nm, and, then, transfers its energy to Ho^{3+} ions. The Ho^{3+} ions are populated from the $^5\text{I}_8$ ground state to $^5\text{I}_6$ excited state. This is a phonon-assisted energy transfer process because of the energy mismatch between $^2\text{F}_{5/2}$ level of Yb^{3+} and $^5\text{I}_6$ level of Ho^{3+} . Secondly, the Ho^{3+} in $^5\text{I}_6$ level is excited to $^5\text{S}_2$ or $^5\text{F}_4$ levels by the next energy transfer from Yb^{3+} . In addition, the $^5\text{S}_2/^5\text{F}_4$ level of Ho^{3+} can be populated through the excited state absorption. Finally, the green emission at ~ 545 nm, corresponding to $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_8$ transition, takes place. For the red emission, the population of the $^5\text{F}_5$ level is generated by two different channels. One channel is that Ho^{3+} in the $^5\text{S}_2/^5\text{F}_4$ level state relaxes non-radiatively to the $^5\text{F}_5$ level. Another channel is closely related to the $^5\text{I}_7$ level populated by non-radiative relaxation from the $^5\text{I}_6$ excited state. The Ho^{3+} in the $^5\text{I}_7$ level is excited to the $^5\text{F}_5$ level by the energy transfer from Yb^{3+} and relaxed to the $^5\text{F}_5$ level. Therefore, the red emission around 655 nm corresponds to the $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transition.

The CIE chromaticity diagram showing the color coordinates of the $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ phosphors is shown in Fig. 8. Here, the points related to the emission from samples (a) $\text{CaLa}_{1.6}(\text{MoO}_4)_4:\text{Yb}_{0.35}/\text{Ho}_{0.05}$, (b) $\text{CaLa}_{1.55}(\text{MoO}_4)_4:\text{Yb}_{0.40}/\text{Ho}_{0.05}$, (c) $\text{CaLa}_{1.5}(\text{MoO}_4)_4:\text{Yb}_{0.45}/\text{Ho}_{0.05}$, and (d) $\text{CaLa}_{1.45}(\text{MoO}_4)_4:\text{Yb}_{0.50}/\text{Ho}_{0.05}$ are inserted. The yellow emission color coordinates of the samples are well matched with the standard equal energy point. This result provides the achievement of the attractive yellow UC emissions for the potentially active components in new optoelectronic devices and luminescent devices.

The Raman spectra recorded from the $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ samples under the 514.5 nm excitation are shown in Fig. 9. In general, the spectra are similar at wavenumbers $<950\text{ cm}^{-1}$. In doped samples, however, the new wide bands superimposed on the spectrum of $\text{CaLa}_2(\text{MoO}_4)_4$ are evident over the wavenumber range of $>750\text{ cm}^{-1}$. As it will be shown in the following, the features should be attributed to the photoluminescence of Ho^{3+} ions. Besides, the low-wavenumber lines in doped samples are shifted to higher wavenumbers.

The Raman spectrum recorded from $\text{CaLa}_2(\text{MoO}_4)_4$ is shown in Fig. 10. About 13 narrow Raman lines were revealed by the experimental spectral decomposition, as it is depicted in Figs. 6S and 7S, and the total set of Raman lines found in $\text{CaLa}_2(\text{MoO}_4)_4$ is shown in Table 4. The Raman spectrum of $\text{CaLa}_2(\text{MoO}_4)_4$ possesses strong lines at low $<440\text{ cm}^{-1}$ and high $\sim 900\text{ cm}^{-1}$ wavenumbers with a wide empty gap of $440\text{-}700\text{ cm}^{-1}$ that is typical of molybdates with MoO_4 tetrahedrons [17,18,24,50-54]. The doped samples spectra contain the Raman contribution that is similar to the Raman spectrum of undoped $\text{CaLa}_2(\text{MoO}_4)_4$. Surprisingly, no radical changes in Raman contribution to these spectra were observed up to the rare-earth elements doping as high as 0.55.

The vibrational representation for the tetragonal phase at the Brillouin zone center for pure $\text{CaLa}_2(\text{MoO}_4)_4$ is:

$$\Gamma_{\text{vibr}} = 3A_g + 6B_g + 6E_g + 6A_u + 3B_u + 6E_u,$$

acoustic and optic modes:

$$\Gamma_{\text{acoustic}} = A_u + E_u,$$

$$\Gamma_{\text{optic}} = 3A_g + 6B_g + 6E_g + 5A_u + 5E_u,$$

infrared and Raman active modes are:

$$\Gamma_{\text{raman}} = 3A_g + 6B_g + 6E_g, \Gamma_{\text{infrared}} = 5A_u + 5E_u.$$

The vibrational representation for the doped molybdates $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ is:

$$\Gamma_{\text{vibr}} = 3A_g + 8B_g + 8E_g + 8A_u + 3B_u + 8E_u,$$

acoustic and optic modes:

$$\Gamma_{\text{acoustic}} = A_u + E_u,$$

$$\Gamma_{\text{optic}} = 3A_g + 8B_g + 8E_g + 7A_u + 7E_u,$$

infrared and Raman active modes are:

$$\Gamma_{\text{raman}} = 3A_g + 8B_g + 8E_g, \Gamma_{\text{infrared}} = 7A_u + 7E_u.$$

To calculate the $\text{CaLa}_2(\text{MoO}_4)_4$ vibrational spectrum, the simulation package LADY was used [55]. The atomic vibration values were obtained using the modified random-element-isodisplacement model [56]. Only the pair-wise interactions and bond-stretching force constants

$A = \frac{\partial^2 E}{\partial R^2}$ (E – energy, R – bond length) are considered. To find the model parameters, a special

optimization program was written and tested for several compounds [54,57-61]. The model parameters obtained for $\text{CaLa}_2(\text{MoO}_4)_4$ are shown in Table 5. The calculations show that only 3 Raman active modes should exist in the range of $>700 \text{ cm}^{-1}$ and 12 Raman active modes could be found in the range of $<500 \text{ cm}^{-1}$. The strong high-wavenumber band at 906 cm^{-1} is assigned to the ν_1 symmetric stretching vibration of a MoO_4 tetrahedron; other active lines can be assigned to the ν_3 MoO_4 vibrations [62]. The ν_2 and ν_4 , and MoO_4 bending modes are observed in the range of $300 - 450 \text{ cm}^{-1}$. Generally, the frequency of ν_2 vibration should be lower than the frequency of ν_4 vibration [62]. The calculated lanthanum vibrations are located at low wavenumbers of $<200 \text{ cm}^{-1}$.

This part of experimental spectra can not be uniquely decomposed. Taking into account the fact, that masses of La, Ho and Yb atoms are much larger than those of Ca, Mo and O, additional lines in

Raman spectra of doped $\text{CaLa}_2(\text{MoO}_4)_4$ should appear in the range of $<150 \text{ cm}^{-1}$. As can be seen from Fig. 10, there are no significant changes over the low frequency range of the Raman signal in doped crystals that is in the agreement with the supposition. Extra Raman and IR experiments are required for the observation of La, Ho and Yb related lines in the range below 150 cm^{-1} .

In the higher frequency range, Raman spectrum experiences are overlaid by the luminescence from $^5\text{S}_2$ and $^5\text{F}_4$ states of Ho^{3+} ion. The residual luminescence spectra of the samples a-d obtained by the subtraction of undoped $\text{CaLa}_2(\text{MoO}_4)_4$ spectra from the net spectra are presented in Fig. 8S, in comparison with the reference luminescence spectrum of Ho^{3+} ion in $\text{HoAl}_3(\text{BO}_3)_4$ [63]. All these spectra occupy the same spectral region, that admits their luminescent origin, and the difference in the peak structures within this luminescent band is due to the difference in the crystal field splitting between molybdates $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ and the reference crystal.

3. Conclusions

UC $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ phosphors with the doping concentrations of Ho^{3+} and Yb^{3+} can be successfully synthesized by the microwave sol-gel method combined with short-time high-temperature calcination. This synthesis route needs a shorter total time and provides a very uniform final powder product. The synthesized particles, being formed after the heat-treatment at 900°C for 16 h, were well crystallized and showed a uniform morphology with the particle sizes of 1-3 μm . Under the excitation at 980 nm, the $\text{CaLa}_{1.6}(\text{MoO}_4)_4:\text{Yb}_{0.35}/\text{Ho}_{0.05}$, $\text{CaLa}_{1.55}(\text{MoO}_4)_4:\text{Yb}_{0.40}/\text{Ho}_{0.05}$, $\text{CaLa}_{1.5}(\text{MoO}_4)_4:\text{Yb}_{0.45}/\text{Ho}_{0.05}$ and $\text{CaLa}_{1.45}(\text{MoO}_4)_4:\text{Yb}_{0.50}/\text{Ho}_{0.05}$ particles exhibited two strong emission bands at 545 and 655 nm emission band in the green-yellow region, which were assigned to the $^5\text{S}_2/{}^5\text{F}_4 \rightarrow {}^5\text{I}_8$ and $^5\text{F}_5 \rightarrow {}^5\text{I}_8$ transitions, respectively. The experimental Raman spectra of undoped $\text{CaLa}_2(\text{MoO}_4)_4$ are in good agreement with the calculations. The 514.5 nm excited spectra of the samples doped with Ho and Yb are dominated by Ho luminescence, and this factor should be considered in the Raman spectra analysis. Thus, the experiments confirm the efficient frequency upconversion process in the $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ phosphor, the representative member of the

$MLn_2(MoO_4)_{4(1-m)}(WO_4)_{4m}$ family. The microwave synthesis combined with short-time annealing provides good cation ordering that was verified by the first structure determination of $CaLa_2(MoO_4)_4$. This synthesis route could be widely used for other complex compounds from the $MLn_2(MoO_4)_{4(1-m)}(WO_4)_{4m}$ family.

Acknowledgments: This study was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2014-046024). VVA, ASA and ASO are partially supported by the Ministry of Education and Science of the Russian Federation.

Supporting Information Available: The Rietveld patterns, atom coordinates, Raman spectra decomposition, emission spectra of the $CaLa_{2-x}(MoO_4)_4:Yb_y/Ho_z$ samples.

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Table 1. Chemical compositions and notations of the doped samples

Samples	Yb ³⁺ (y)	Ho ³⁺ (z)	$x = \text{Yb}^{3+} + \text{Ho}^{3+}$	Yb ³⁺ :Ho ³⁺
CaLa _{1.60} (MoO ₄) ₄ :Yb _y /Ho _z (a)	0.35	0.05	0.40	7:1
CaLa _{1.55} (MoO ₄) ₄ :Yb _y /Ho _z (b)	0.40	0.05	0.45	8:1
CaLa _{1.50} (MoO ₄) ₄ :Yb _y /Ho _z (c)	0.45	0.05	0.50	9:1
CaLa _{1.45} (MoO ₄) ₄ :Yb _y /Ho _z (d)	0.50	0.05	0.55	10:1

Table 2. Main parameters and processing of Le Bail fitting of the CaLa_{2-x}(MoO₄)₄:Yb_y/Ho_z samples by using (3+1)D modulation

Compound	CaLa ₂ (MoO ₄) ₄	CaLa _{1.6} (MoO ₄) ₄ : Yb _{0.35} /Ho _{0.05}	CaLa _{1.55} (MoO ₄) ₄ : Yb _{0.40} /Ho _{0.05}	CaLa _{1.5} (MoO ₄) ₄ : Yb _{0.45} /Ho _{0.05}	CaLa _{1.45} (MoO ₄) ₄ : Yb _{0.50} /Ho _{0.05}
Sp.Gr.	$I4_1/a(\alpha,\beta,0)00$ $(-\beta,\alpha,0)00$	$I4_1/a(\alpha,\beta,0)00$ $(-\beta,\alpha,0)00$	$I4_1/a(\alpha,\beta,0)00$ $(-\beta,\alpha,0)00$	$I4_1/a(\alpha,\beta,0)00$ $(-\beta,\alpha,0)00$	$I4_1/a(\alpha,\beta,0)00$ $(-\beta,\alpha,0)00$
q-vector	[0.5809(2), 0.8588(2), 0]	[0.5649(2), 0.8476(2), 0]	[0.5649(2), 0.8487(2), 0]	[0.5611(1), 0.8429(2), 0]	[0.5588(2), 0.8425(2), 0]
<i>a</i> , Å	5.3374(1)	5.30312(7)	5.30265(9)	5.30011(8)	5.2994(1)
<i>c</i> , Å	11.8291(4)	11.7175(2)	11.7144(3)	11.7054(3)	11.7161(4)
<i>V</i> , Å ³	336.99(2)	329.53(1)	329.39(1)	328.83(1)	329.03(1)
2θ-range, °	5-110	5-110	5-110	5-110	5-110
<i>R</i> _{wp} , %	16.57	15.71	15.59	15.89	15.85
<i>R</i> _p , %	11.52	11.11	10.89	11.01	10.77
<i>R</i> _{exp} , %	12.68	11.62	10.78	11.31	11.33

Table 3. Main parameters of processing and Rietveld refinement the $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ samples by using averaged crystal structure

Compound	$\text{CaLa}_2(\text{MoO}_4)_4$	$\text{CaLa}_{1.6}(\text{MoO}_4)_4$: $\text{Yb}_{0.35}/\text{Ho}_{0.05}$	$\text{CaLa}_{1.55}(\text{MoO}_4)_4$: $\text{Yb}_{0.40}/\text{Ho}_{0.05}$	$\text{CaLa}_{1.5}(\text{MoO}_4)_4$: $\text{Yb}_{0.45}/\text{Ho}_{0.05}$	$\text{CaLa}_{1.45}(\text{MoO}_4)_4$: $\text{Yb}_{0.50}/\text{Ho}_{0.05}$
Sp.Gr.	$I4_1/a$	$I4_1/a$	$I4_1/a$	$I4_1/a$	$I4_1/a$
a , Å	5.3371(3)	5.30300(9)	5.3021(1)	5.2996(1)	5.2684(1)
c , Å	11.8290(6)	11.7162(2)	11.7118(4)	11.7047(3)	11.7130(4)
V , Å ³	336.93(4)	329.48(1)	329.24(2)	328.74(2)	328.82(2)
2θ -range, °	5-110	5-110	5-110	5-110	5-110
No. of reflections	107	106	106	106	106
No. of refined parameters	7	7	7	7	7
R_{wp} , %	21.99	17.51	18.46	18.64	18.17
R_p , %	15.15	12.20	12.68	12.64	12.11
R_{exp} , %	12.65	11.60	10.76	11.28	11.31
χ^2	1.74	1.51	1.72	1.65	1.61
R_B , %	3.60	2.60	2.55	2.26	1.65

Table 4. Calculated and experimental wavenumber values of the Raman lines observed in $\text{CaLa}_2(\text{MoO}_4)_4$

Number	Notation	ω , cm^{-1} (calc.)	ω , cm^{-1} (exp.)
1	A_g	906	958 906
2	E_g	889	885 868
3	B_g	879	828 762
4	E_g	396	393
5	B_g	377	377
6	E_g	326	333
7	A_g	321	317
8	B_g	308	305
9	B_g	285	251
10	A_g	201	193
11	E_g	179	
12	E_g	114	
13	B_g	84	
14	B_g	43	
15	E_g	40	

Table 5. Parameters of the interatomic interaction potential

Interaction	Radii of interaction, Å	λ , aJ/Å ²	ρ , Å
Ca – O	0.0 – 2.70	394.63	0.4408
La – O	0.0 – 2.70	349.80	0.2996
Mo – O	0.0 – 1.80	295.59	0.4192
O – O	0.0 – 2.79	419.29	0.4145
O – O	2.80 – 3.00	392.86	0.3774

Captions

Fig. 1. The difference profile plot of $\text{CaLa}_2(\text{MoO}_4)_4$. Red dots - experimental pattern (Y_{obs}), black line - calculated pattern (Y_{calc}), grey line - difference ($Y_{\text{obs}} - Y_{\text{calc}}$), green sticks - main Bragg peaks, purple - modulated peaks. The inset shows a zoomed part of the difference plot, and the numbers in brackets show the reflection indices in notation $(3+2)D$.

Fig. 2. The averaged crystal structure of $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ in space group $I4_1/a$. The unit cell is outlined.

Fig. 3. The linear dependence of the $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ cell volume on the averaged ion radii ($\text{La}_{2-x}\text{Yb}_y\text{Ho}_z$).

Fig. 4: Scanning electron microscopy images of the synthesized (a) $\text{CaLa}_{1.6}(\text{MoO}_4)_4:\text{Yb}_{0.35}/\text{Ho}_{0.05}$, (b) $\text{CaLa}_{1.55}(\text{MoO}_4)_4:\text{Yb}_{0.40}/\text{Ho}_{0.05}$, (c) $\text{CaLa}_{1.5}(\text{MoO}_4)_4:\text{Yb}_{0.45}/\text{Ho}_{0.05}$, and (d) $\text{CaLa}_{1.55}(\text{MoO}_4)_4:\text{Yb}_{0.50}\text{Ho}_{0.05}$ particles.

Fig. 5: The upconversion photoluminescence emission spectra of (a) $\text{CaLa}_{1.6}(\text{MoO}_4)_4:\text{Yb}_{0.35}/\text{Ho}_{0.05}$, (b) $\text{CaLa}_{1.55}(\text{MoO}_4)_4:\text{Yb}_{0.40}/\text{Ho}_{0.05}$, (c) $\text{CaLa}_{1.5}(\text{MoO}_4)_4:\text{Yb}_{0.45}/\text{Ho}_{0.05}$, and (d) $\text{CaLa}_{1.45}(\text{MoO}_4)_4:\text{Yb}_{0.50}/\text{Ho}_{0.05}$ particles excited under 980 nm at room temperature.

Fig. 6. The logarithmic scale dependence of the upconversion emission intensity on the pump power in the range from 20 to 110 mW at 545 and 655 nm in the $\text{CaLa}_{1.50}(\text{MoO}_4)_4:\text{Yb}_{0.05}/\text{Ho}_{0.45}$ sample.

Fig. 7. The schematic energy level diagrams of Yb^{3+} (sensitizer) and Ho^{3+} ions (activator) ions in the $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ system and the upconversion mechanisms of the green and red emissions under 980-nm laser excitation.

Fig. 8. The CIE chromaticity diagram showing the color coordinates of the $\text{CaLa}_{2-x}(\text{MoO}_4)_4:\text{Yb}_y/\text{Ho}_z$ phosphors. The yellow emission for samples (a) $\text{CaLa}_{1.6}(\text{MoO}_4)_4:\text{Yb}_{0.35}/\text{Ho}_{0.05}$, (b) $\text{CaLa}_{1.55}(\text{MoO}_4)_4:\text{Yb}_{0.40}/\text{Ho}_{0.05}$, (c) $\text{CaLa}_{1.5}(\text{MoO}_4)_4:\text{Yb}_{0.45}/\text{Ho}_{0.05}$, and (d) $\text{CaLa}_{1.55}(\text{MoO}_4)_4:\text{Yb}_{0.50}/\text{Ho}_{0.05}$ is shown in the insert.

Fig. 9. The Raman spectra of the synthesized (a) pure $\text{CaLa}_2(\text{MoO}_4)_4$ (b) $\text{CaLa}_{1.6}(\text{MoO}_4)_4:\text{Yb}_{0.35}/\text{Ho}_{0.05}$, (c) $\text{CaLa}_{1.55}(\text{MoO}_4)_4:\text{Yb}_{0.40}/\text{Ho}_{0.05}$, (d) $\text{CaLa}_{1.5}(\text{MoO}_4)_4:\text{Yb}_{0.45}/\text{Ho}_{0.05}$, and (e) $\text{CaLa}_{1.45}(\text{MoO}_4)_4:\text{Yb}_{0.50}/\text{Ho}_{0.05}$ particles excited by the 514.5-nm line of an Ar ion laser at 0.5 mW.

Fig. 10. $\text{CaLa}_2(\text{MoO}_4)_4$ Raman spectrum.

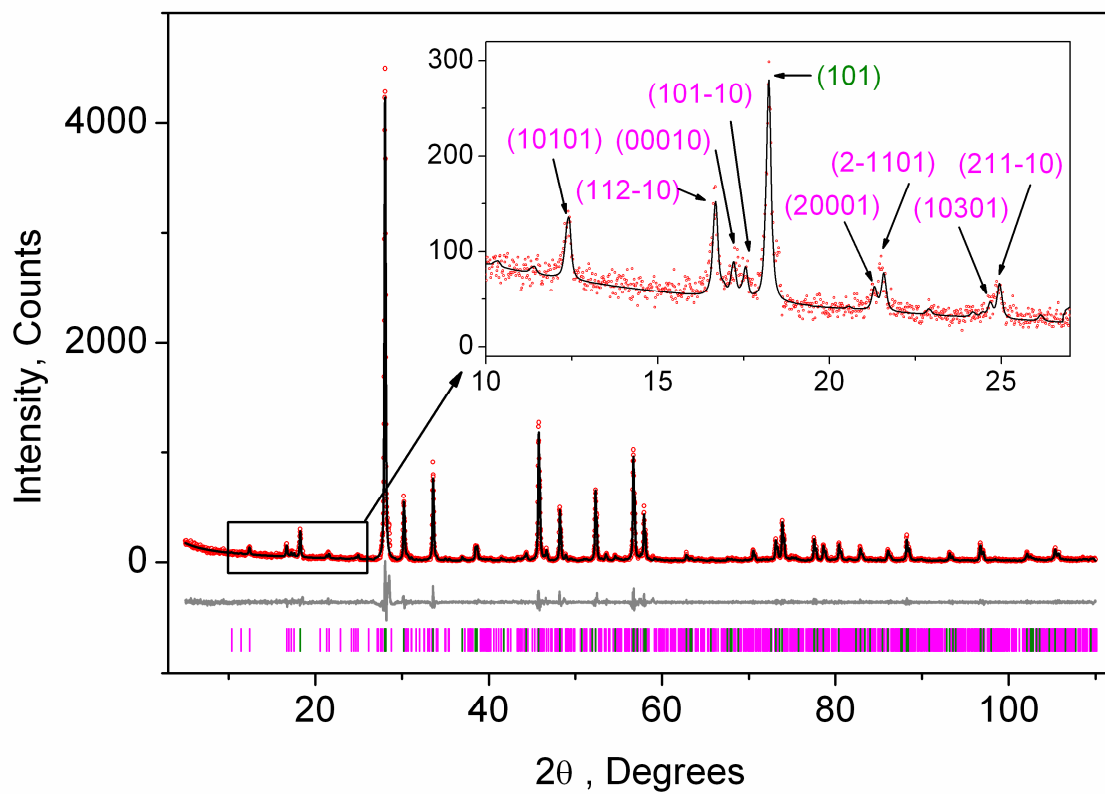


Fig. 1.

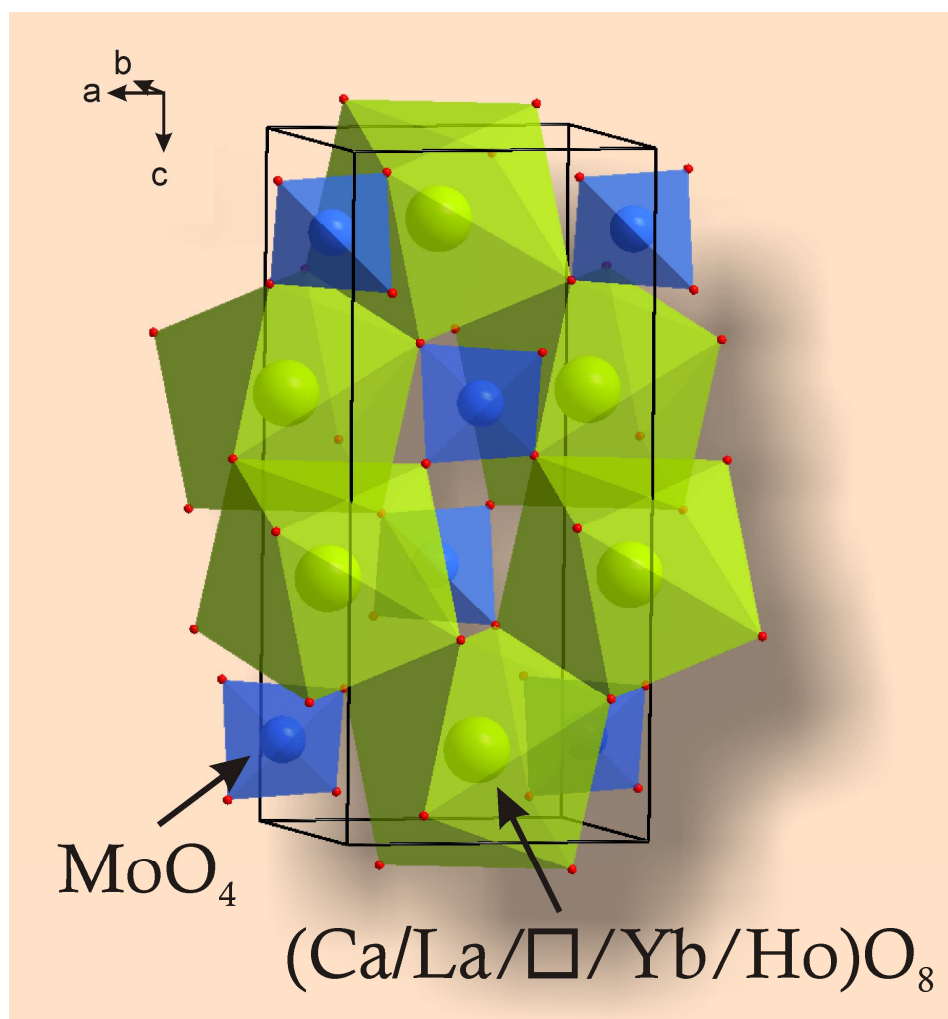


Fig. 2.

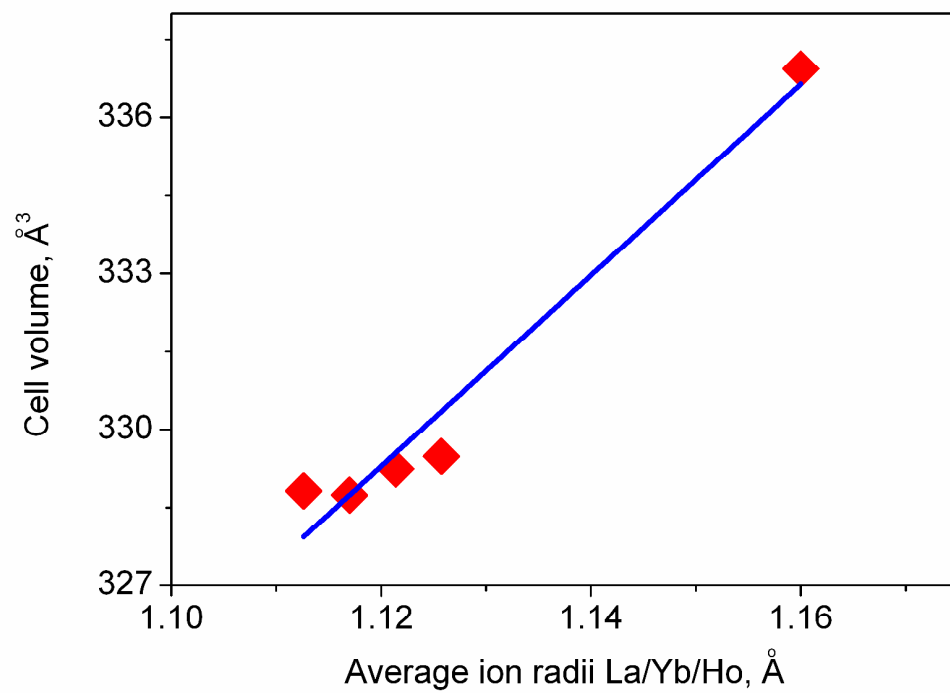


Fig. 3.

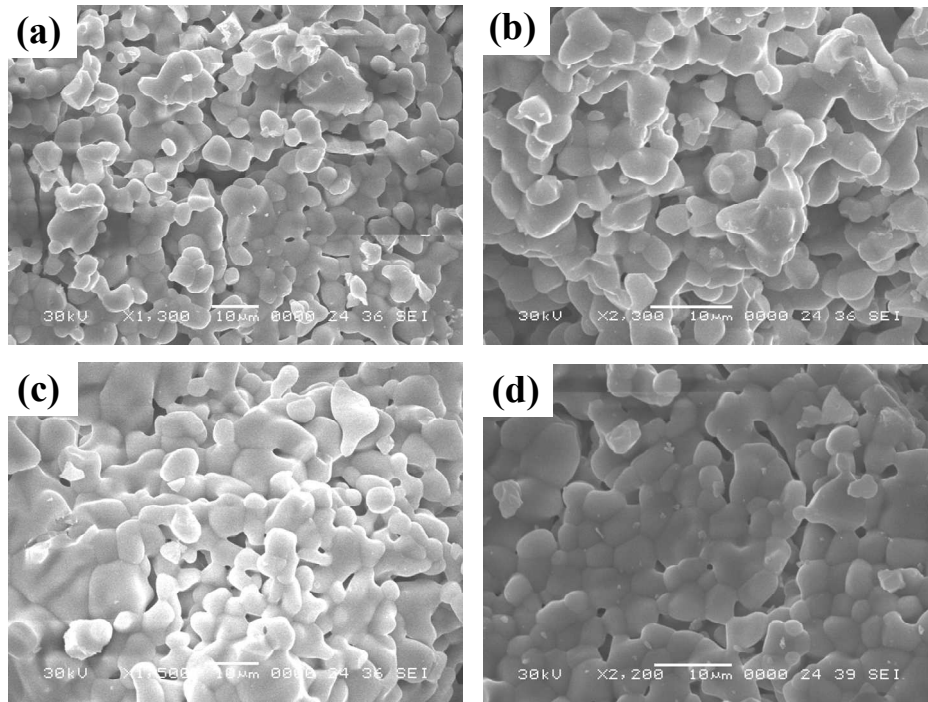


Fig. 4.

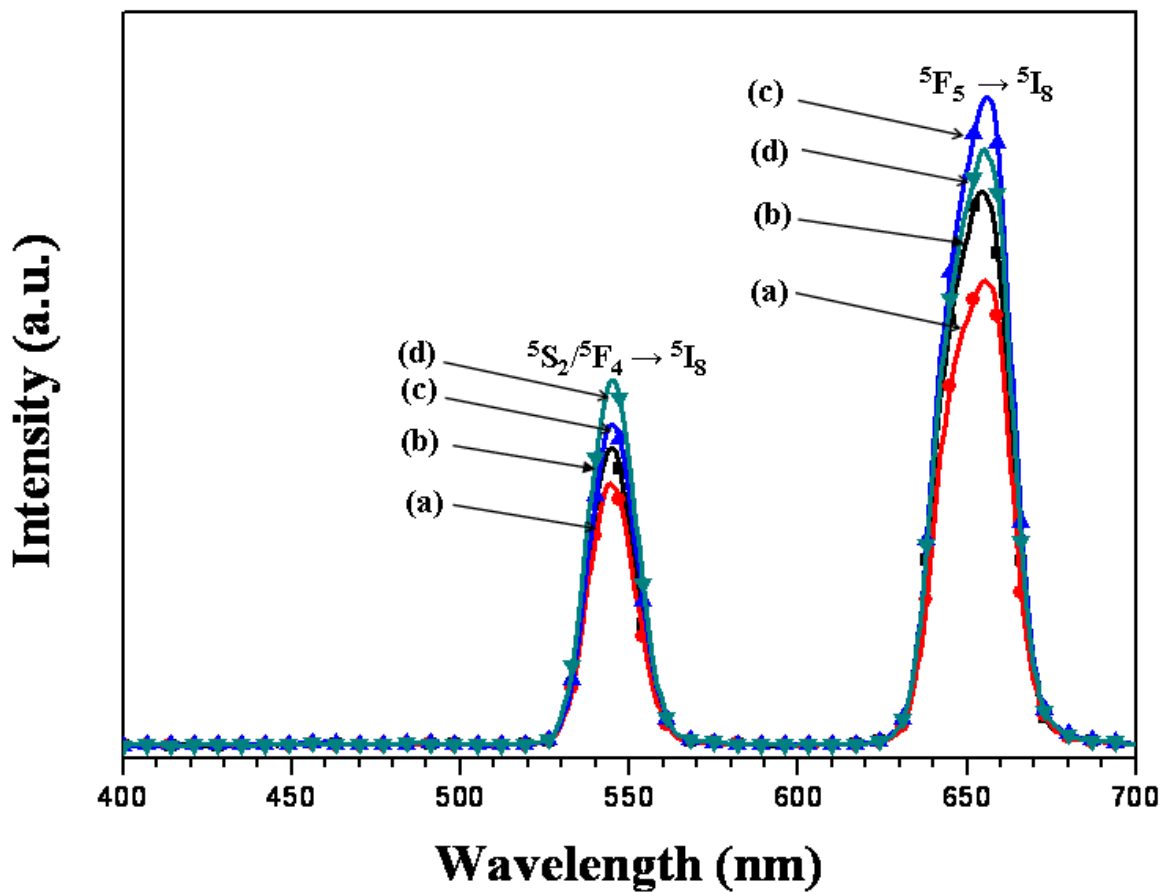


Fig. 5.

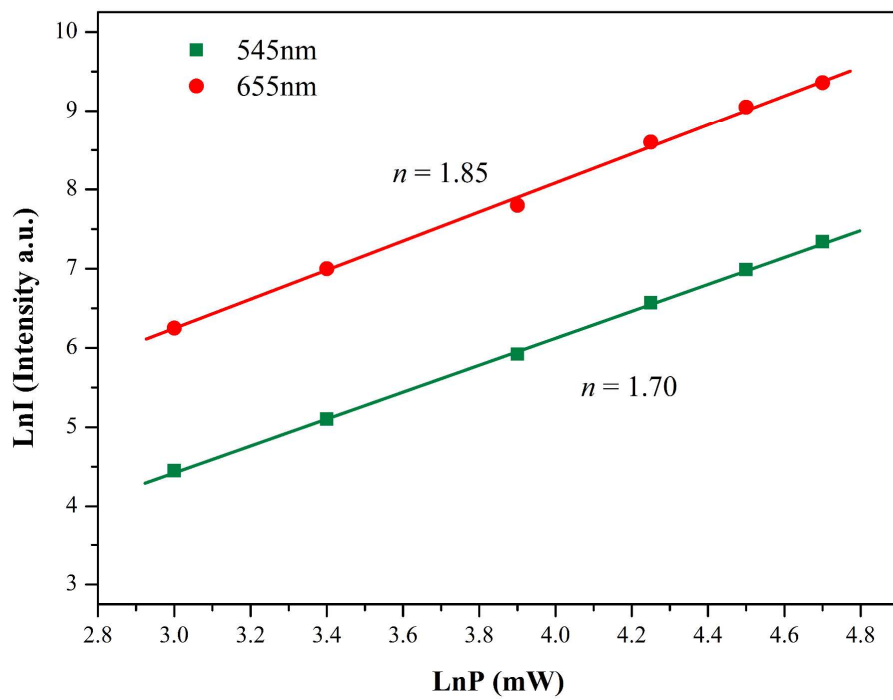


Fig. 6.

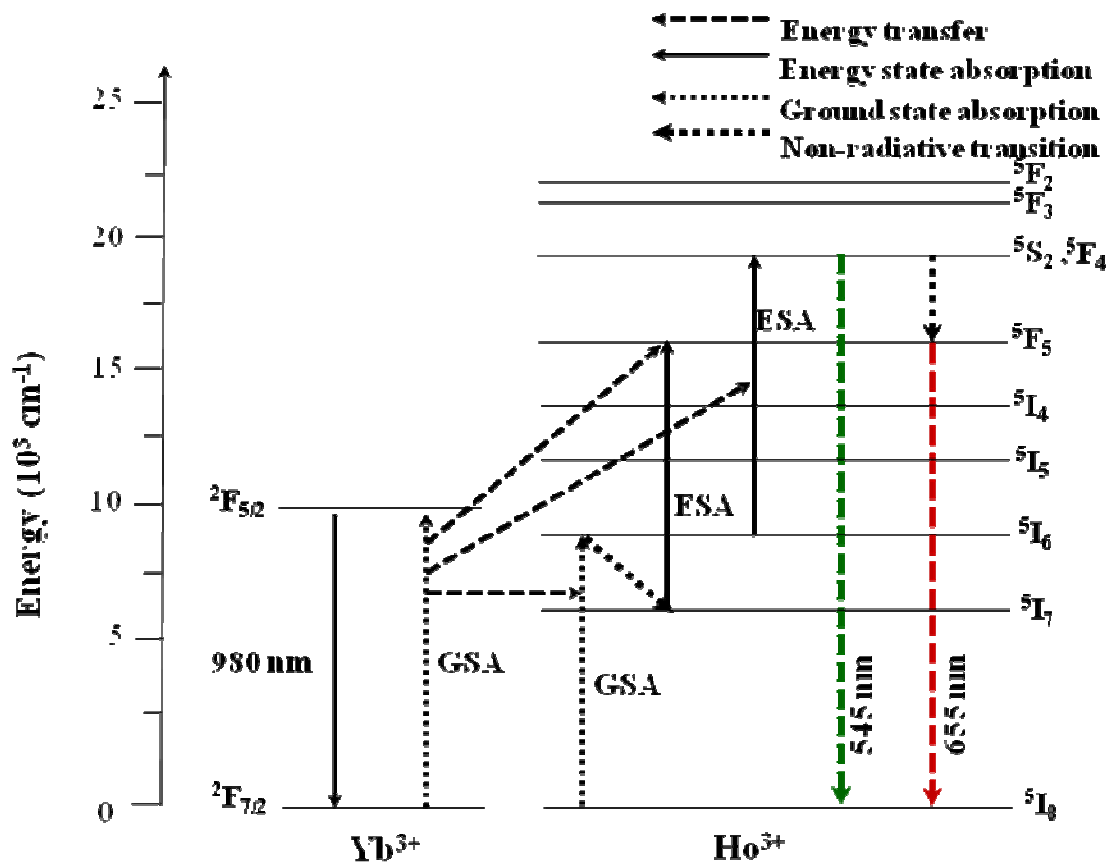


Fig. 7.

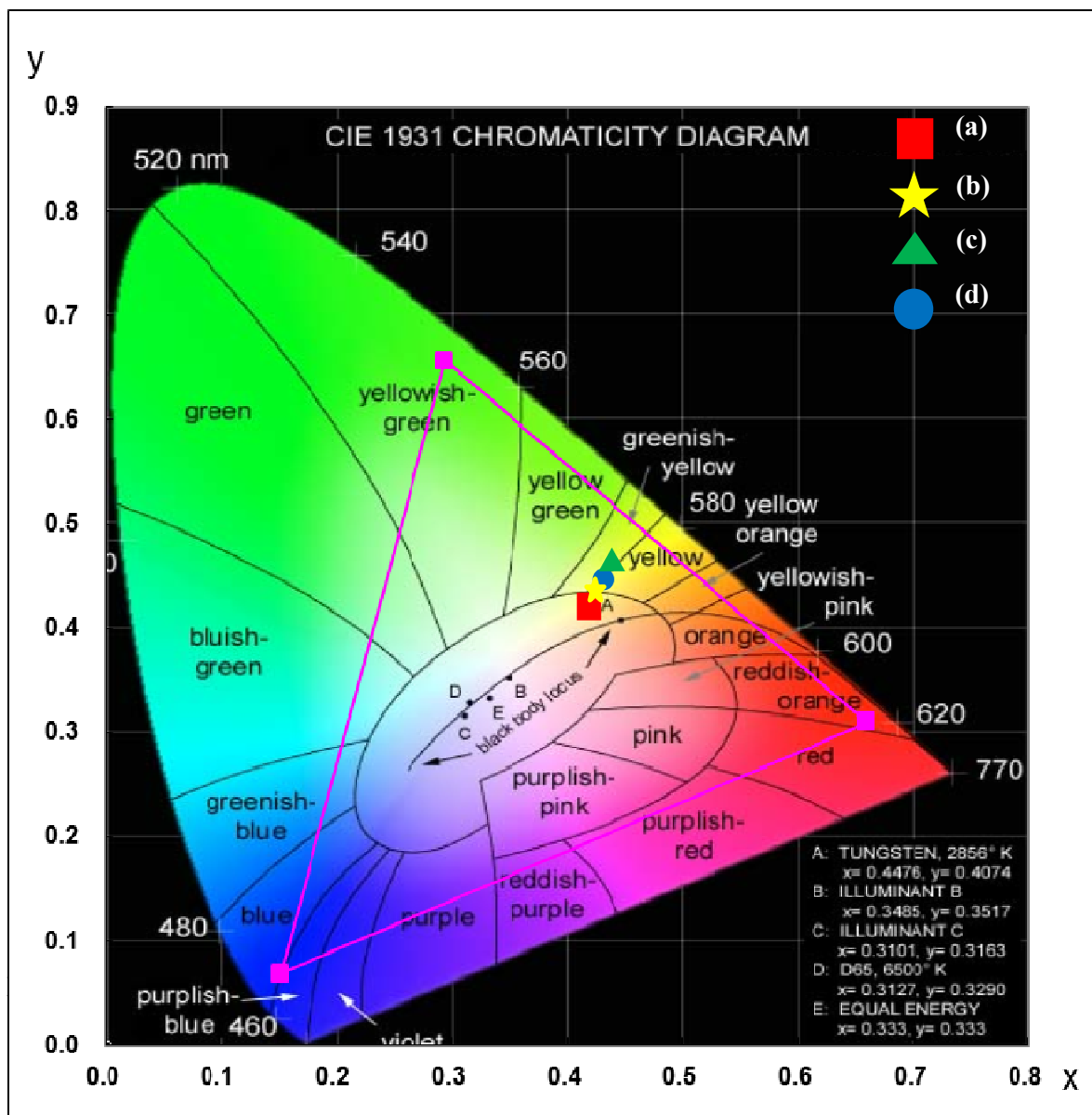


Fig. 8.

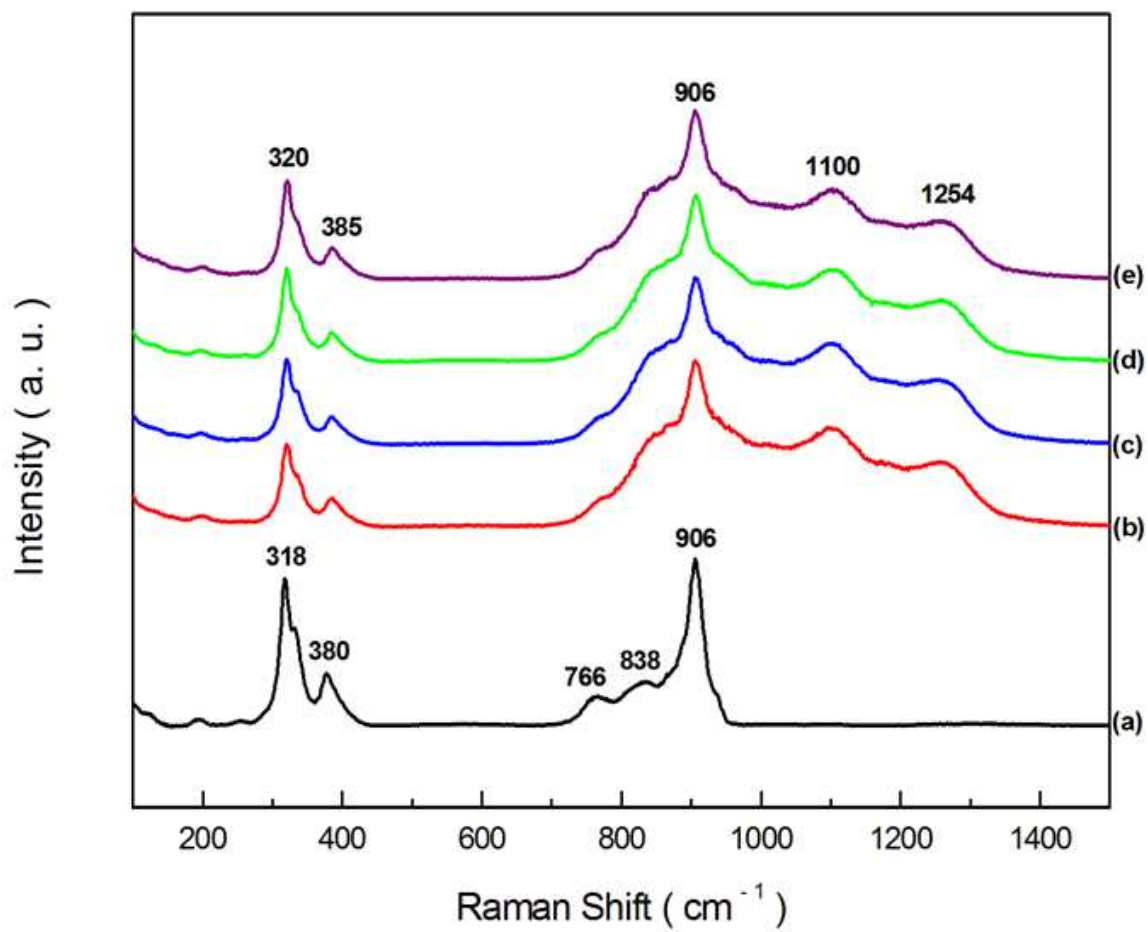


Fig. 9.

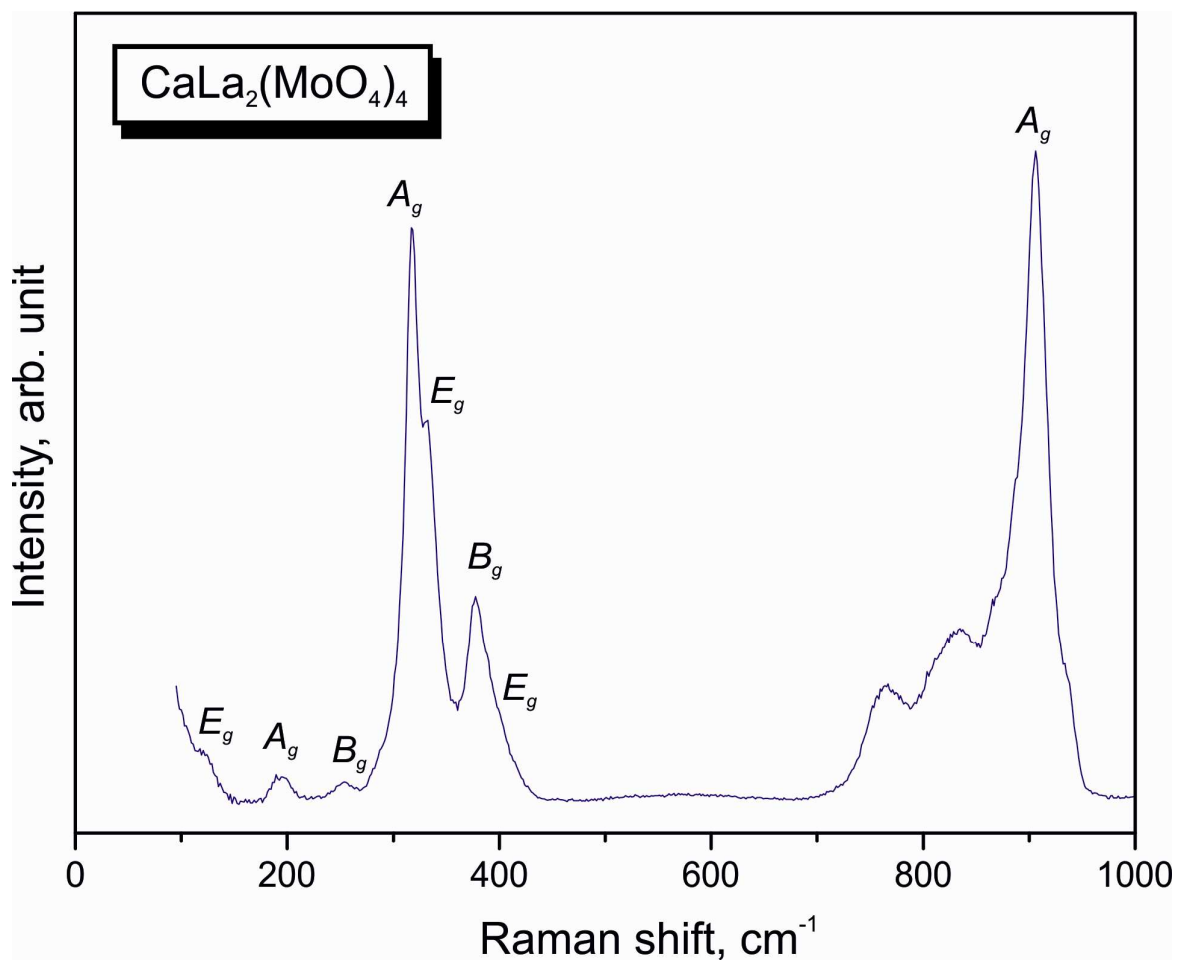
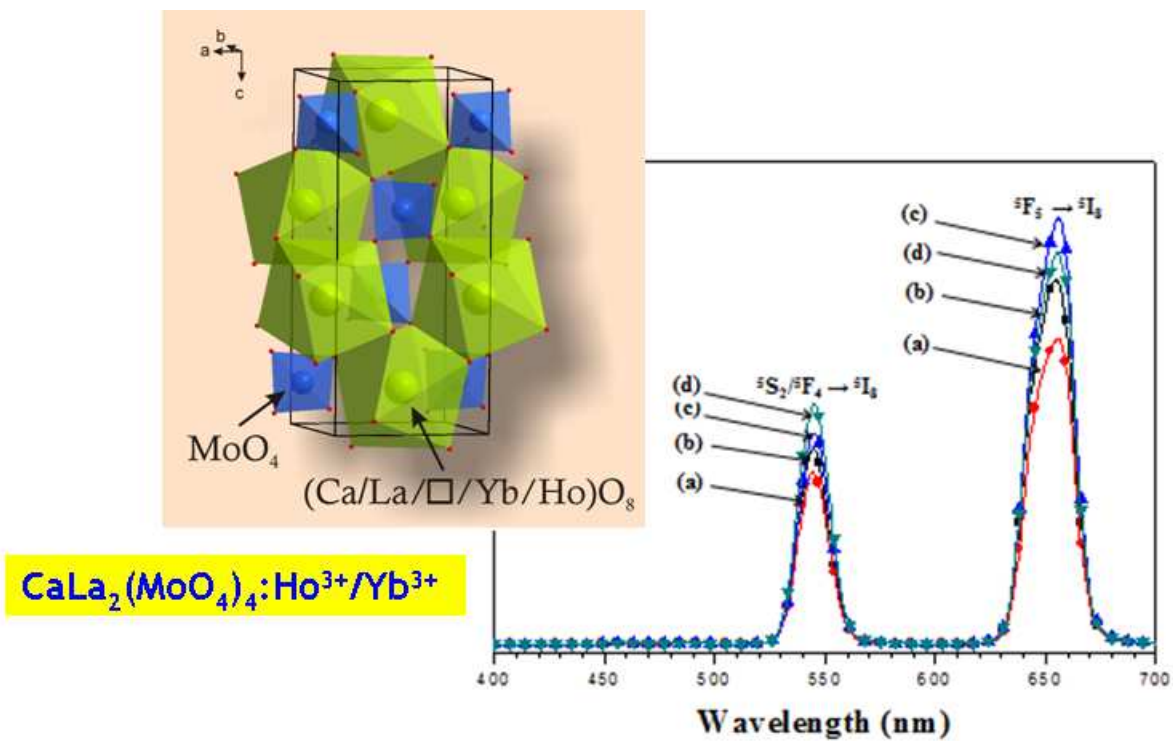


Fig. 10.

TOC image



The modulated structure and frequency upconversion properties of $\text{CaLa}_2(\text{MoO}_4)_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ phosphors are carried out.