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Trans. Nonferrous Met. Soc. China 24(2014) s134-s140

Transactions of Nonferrous Metals Society of China

www.tnmsc.cn

White luminescence of Ho³⁺/Tm³⁺/Yb³⁺-codoped CaWO₄ synthesized via citrate complex route assisted by microwave irradiation

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Received 18 June 2013; accepted 15 October 2013

Abstract: The nanocrystalline $Ho^{3+}/Tm^{3+}/Yb^{3+}$ co-doped CaWO₄ upconversion (UC) phosphors were successfully synthesized by a modified citrate complex method using microwave irradiation. The citrate complex precursors were heat-treated at temperature ranging from 300 to 700 °C for 3 h. Crystallization of the $Ho^{3+}/Tm^{3+}/Yb^{3+}$ co-doped CaWO₄ was detected at 400 °C, and entirely completed at 600 °C. The $Ho^{3+}/Tm^{3+}/Yb^{3+}$ co-doped CaWO₄ heat-treated at 600 °C showed primarily spherical and homogeneous morphology. Under the laser excitation of 980 nm, $Ho^{3+}/Tm^{3+}/Yb^{3+}$ co-doped CaWO₄ shows the bright white upconversion (UC) emission visible to the naked eye, which is composed of a blue emission at 475 nm from Tm^{3+} , and green and red emissions at 543 and 651 nm respectively from Ho^{3+} . The coordinates of $Ho^{3+}/Tm^{3+}/Yb^{3+}$ co-doped CaWO₄ in the Commission International De'eclairage (CIE) chromaticity diagram could be controlled from a cool to a warm white color depending on the Tm^{3+} and Ho^{3+} concentrations. The UC luminescent properties on Tm^{3+} and Ho^{3+} concentrations and related mechanism based on laser pump power were discussed in detail.

Key words: upconversion; CaWO4; microwave irradiation; white luminescence

1 Introduction

In recent years, research on upconversion (UC) materials, particularly the lanthanide-doped UC phosphors, has attracted much attention because of their unique properties that can convert low energy such as infrared (IR) radiation to high energy such as visible or UV light [1]. In particular, white UC luminescence has been extensively studied, because white luminescent UC phosphors can replace conventional lighting sources in optical devices and three-dimensional backlighting for color displays [2]. Also, white UC phosphors can be used as bio-medical probes with extended simultaneous detection, a capability unmatched by conventional bio-labeling [3]. For white UC luminescence, Er³⁺, Tm³⁺, and Ho³⁺ ions have been used as luminescent centers because they have unique electronic energy states, suitable for pumping by near infrared (NIR) radiation to generate desired visible emissions such as red, green, and blue colors [4]. In particular, Ho^{3+} and Tm^{3+} ions are considered candidates for white UC luminescent centers due to their unique UC properties such as yellow emission combined by green and red emissions in Ho^{3+} and blue emission from Tm^{3+} [5].

Displays and illuminations require UC luminescent materials that can emit controllable white colors with high efficiency. Also, these materials should have high chemical, physical, and mechanical stabilities. Although white UC luminescence was achieved with lanthanidedoped fluorides via combinations of blue emission from Tm³⁺ and green or red from Er³⁺ under NIR (generally 980 nm) excitation [6], fluorides have low physicochemical stabilities, which have made applications difficult in industry [7]. Therefore, it has become important to find new host materials with high stabilities and UC efficiency. Calcium tungstate (CaWO₄) with scheelite structure has been studied as a

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potential electro optic material because of its high density and stable physicochemical properties compared with other oxide materials [8]. However, the white UC luminescence in Tm^{3+} and Ho^{3+} -codoped CaWO₄ has yet to be researched.

In general, calcium tungstate phosphors were synthesized by conventional solid-state reaction method [9]. This approach usually requires heat-treatment at high temperatures for several hours and subsequent grinding. The grinding process damages the phosphor surfaces, resulting in the loss of emission intensity. In addition, calcium tungstate compounds with inhomogeneous composition might be easily formed because of high vapor pressure of WO₃ [10]. It was also shown that phosphors prepared by an wet chemical method have higher uniformity in particle size distribution with good crystallinity and exhibit higher photoluminescence intensity than those prepared by the solid-state reaction [11]. Thus, efforts had been made to develop alternative synthesis methods such as hydro-thermal method or sol-gel process.

Microwave irradiation as a heating source has been found and developed for a number of applications in chemical and ceramic processing [12]. Compared with the usual methods, microwave assisted synthesis has the advantage of shortening the reaction time, giving products with small particle size, narrow particle size distribution, and high purity, which can be attributed to fast homogeneous nucleation and easy dissolution of the gel [13]. In this work, we report the intense white UC luminescence of Tm³⁺ and Ho³⁺ co-doped CaWO₄ nanoparticle prepared by a citrate complex precursor using microwave irradiation. The precursors and powders are evaluated for the crystallization process, thermal decomposition and particle morphology. The color index of white UC emission is modulated by controlling the blue, green, and red components depending on the doping concentrations of Tm³⁺ and Ho³⁺ ions. The effects of Ho³⁺, Tm³⁺, and Yb³⁺ ions on the crystal structure of CaWO₄, photoluminescence properties, and possible UC mechanism are discussed in detail.

2 Experimental

2.1 Synthesis of Ho³⁺/Tm³⁺/Yb³⁺-codoped CaWO₄ powder

The $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ powders were synthesized by the complex citrate-gel method with microwave treatment. The starting materials were calcium nitrates (Ca(NO₃)₂·4H₂O, 99.99%; Junsei Chemical Co. Ltd., Japan), ammonium paratungstate pentahydrate ((NH₄)₁₀W₁₂O₄₁·5H₂O, 99.99%; Wako Chemical Co. Ltd., Japan), holmium nitrate hydrate (Ho(NO₃)₃·5H₂O, 99.99%; Alfa aesar), thulium nitrate hydrate (Tm(NO₃)₃·5H₂O, 99.99%; Alfa aesar) and ytterbium nitrate hydrate (Yb(NO₃)₃·6H₂O, 99.99%; Alfa aesar). They were used as the metallic cations and were dissolved in D.I. water with citric acid. The molar ratios of the metallic cations were as follows: $(1-x-y-z)Ca^{2+}+$ *x*Ho³⁺+*y*Tm³⁺+*z*Yb³⁺+W⁶⁺; *x*, *y*=0, 0.002, 0.005, 0.008, and 0.01; z=0.16. The solution was kept at 100 °C for 10 min under constant stirring until it became viscous. The solution was treated with microwave irradiation for 30 min in ambient atmosphere under constant stirring until the solution became a brown gel. No visible precipitation was observed during the heating process. As this solution condensed, the brown product was converted into powders after grinding with a Teflon bar. Thermal analysis was performed on this powder, hereinafter referred to as the precursor. After the microwave treatment, the obtained gel was heat treated in an oven at 250 °C for 24 h to remove organic substances and to evaporate moisture. Finally, the dried powders were calcined from 300 to 700 °C for 3 h in ambient atmosphere.

2.2 Characterization

The crystallization process of the polymeric precursor evaluated thermogravimetrywas by differential thermal analysis (TG-DTA, SETRAM, France), using a sample mass of about 8 mg and a heating rate of 5 °C/min. The existing phase in the particles after heat-treatment was identified by ordinary X-ray diffraction (XRD, Rigaku, Japan; Cu_a, λ =1.5046 Å) with a scan rate of 3 (°)/min. The microstructure and surface morphology of the nanocrystalline powders were observed by scanning electron microscope (SEM, JSM-35CF, JEOL) and transmission electron microscope (TEM, JEM 2010, JEOL). Roomtemperature UC luminescent spectra were evaluated with a photoluminescence spectrophotometer (LS55 with 100 mW laser diode, Perkin Elmer, USA) in the wavelength range from 400 to 750 nm under single-wavelength NIR laser excitation of 980 nm. The pump-power-dependence was calculated for irradiation power from 20 to 110 mW (SPEX, 1404P, France).

3 Results and discussion

3.1 Crystallization and phase evolution

The crystallization process of the precursor was evaluated by XRD, TG–DTA and electronic diffraction pattern (EDP). Figure 1 shows the phase identification of the $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ (0.5Ho³⁺, 0.5Tm³⁺ and 16Yb³⁺; mole fraction) according to heat-treatment temperature from 300 to 700 °C for 3 h using XRD. In Fig. 1(a), the Ho³⁺/Tm³⁺/Yb³⁺-codoped CaWO₄ powder heat-treated at 300 °C had amorphous and unreacted phases. Above 400 °C in Figs. 1(b)–(e), the powders could be identified as CaWO₄ phases, and unreacted or secondary phases were not detected. The XRD patterns of all the samples were in good agreement with the standard pattern of JCPDS (41-1431), indicating that the Ca²⁺ ions of CaWO₄ were successfully substituted by Ln^{3+} ions ($Ln = Ho^{3+}$, Tm^{3+} , and Yb^{3+}) up to 17% (mole fraction) without any charge compensator such as Li⁺ or Na⁺ ions. This agreement also means that the charge difference between the doped trivalent ions and bivalent host ions did not affect the CaWO₄ crystal structure.



Fig. 1 XRD patterns of $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ (0.5Ho³⁺, 0.5Tm³⁺ and 16Yb³⁺; mole fraction, %) precursors heat-treated at 300 (a), 400 (b), 500 (c), 600 (d) and 700 °C (e) for 3 h

Figure 2 shows the TG–DTA curves for the $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ (0.5Ho³⁺, 0.5Tm³⁺ and 16Yb³⁺) precursor. In Fig. 2, with the increase of temperature, the mass loss occurs in the TG curve up to 500 °C. Thereafter the mass remains constant, indicating that the decomposition of all organic materials continued in the precursor, their combustion and crystallization of CaWO₄ have been completed before 500 °C. No significant plateau, corresponding to well-defined intermediate products, appeared in the heating process. The DTA curve in Fig. 2 could be interpreted two physical meanings: 1) increase of DTA curve at 350 °C corresponds to initial decomposition of the precursor and formation of the nucleus of the Ho³⁺/Tm³⁺/Yb³⁺-codoped CaWO₄ nanoparticles and 2) exothermic peak at

440 °C corresponds to the crystallization of the $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄. Under 350 °C, the resultant particles were dark brown and porous in structure, denoting an amorphous phase. It is attributed to contain a lot of carbons and ignitable organics. When the temperature further increases above 350 °C, crystal nuclei begin to form, and consequently the primary crystallization process is completed accompanying the combustion of the residual carbons and ignitable organics.



Fig. 2 TG–DTA curves of $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ precursor in flowing air

Figure 3(a) shows TEM and electronic diffraction pattern (EDP) of the Ho³⁺/Tm³⁺/Yb³⁺-codoped CaWO₄ $(0.5Ho^{3+}, 0.5Tm^{3+} \text{ and } 16Yb^{3+}; \text{ mole fraction, }\%)$ powder heat-treated at 600 °C. The EDP of the powder sample heat-treated at 300 °C showed only diffuse hollow rings, corresponding to an amorphous phase. With increasing temperature, at 400 °C dotted rings were observed, signifying the nanocrystalline particle formation. The Ho3+/Tm3+/Yb3+-codoped CaWO4 (0.5 Ho3+, 0.5 Tm3+ and 16 Yb³⁺; mole fraction, %) heat-treated at 600 °C showed primarily spherical as shown in Fig 3(a). Figure 3(b) shows a surface morphology of the $Ho^{3+}/Tm^{3+}/Yb^{3+}$ codoped CaWO₄ powder heat-treated at 600 °C using SEM. The Ho³⁺/Tm³⁺/Yb³⁺-codoped CaWO₄ particles heat-treated at 600 °C show spherical and agglomerated particles of 30-50 nm, which corresponds to the TEM result of Fig. 3(a).

3.2 Upconversion and white luminescence

Figure 4 illustrates the upconversion (UC) luminescence of $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ heat-treated at 600 °C for 3 h and the variations of emission intensities with Tm^{3+}/Ho^{3+} concentration under excitation at 980 nm. As presented in Figs. 4(a) and 4(b), the



Fig. 3 TEM (a) and SEM (b) micrographs of nanocrystalline $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ (0.5Ho³⁺, 0.5Tm³⁺ and 16Yb³⁺; mole fraction, %) heat-treated at 600 °C for 3 h

Tm³⁺/Yb³⁺-codoped CaWO₄ has a strong blue emission peak near 470 nm induced by ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ transition with a weak red emission peak near 650 nm induced by ${}^{3}F_{2} \rightarrow$ ${}^{3}H_{6}$ transition [14]. Moreover, the Ho ${}^{3+}/Yb^{3+}$ -codoped CaWO₄ shows green (540 nm) and red (650 nm) emission peaks generated by 4F_4 , ${}^5S_2 \rightarrow {}^5I_8$ and ${}^5F_5 \rightarrow {}^5I_8$ transitions, respectively. The UC luminescence appears yellowish due to a combination of green and red emissions from Ho³⁺ [15]. At higher ratios of concentration between two dopants (Tm³⁺/Ho³⁺), the intensity of blue emission is higher than that of the green or red emission. However, as the Ho³⁺ concentration increases, the relative intensities of the green and red emission components increase. Therefore, the relative intensities of the blue, green, and red components can be controlled by modulating the Ho³⁺ and Tm³⁺ concentrations to display multicolor and white lighting.

Figure 5 shows commission international De'eclairage (CIE) chromaticity diagrams and the digital photographs of $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ heat-treated at 600 °C for 3 h. As shown in Fig. 5, the combination of RGB colors from Tm^{3+} and Ho^{3+} ions can



Fig. 4 UC luminescence of $\text{Ho}^{3+}/\text{Tm}^{3+}/\text{Yb}^{3+}$ -codoped CaWO₄ in 400–750 nm (a), variations of emission intensities with $\text{Tm}^{3+}/\text{Ho}^{3+}$ concentrations under excitation at 980 nm (b)



Fig. 5 CIE chromaticity diagram and digital photographs (inset) of $Tm^{3+}/Ho^{3+}/Yb^{3+}$ -codoped CaWO₄ according to Ho^{3+} and Tm^{3+} concentrations

generate a wide range of white emissions by modulating the Ho³⁺ and Tm³⁺ concentrations. The chromaticity coordinates (x, y) are obviously changed from the cool white to the warm white region as shown in the inset of Fig. 5. Tm³⁺/Yb³⁺-codoped CaWO₄ shows bright blue UC emission. The corresponding chromaticity coordinates are x=0.116 and y=0.082. However, 0.8% Tm³⁺/0.2% Ho³⁺-codoped CaWO₄ produces cool white UC emission plotted at x=0.255 and y=0.247. Moreover, with increasing ratio of Ho³⁺ to Tm³⁺, UC emissions gradually move to warm white emission at 0.2% Tm^{3+} / 0.8% Ho³⁺ (x=0.368, y=0.0.371). Finally, Ho³⁺/Yb³⁺codoped CaWO₄ shows bright yellow UC luminescence plotted at x=0.445, y=0.530. These results mean that a wide range of white UC emissions can be achieved by $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ by controlling the relative intensities of the blue, green, and red components according to the different Ho³⁺ and Tm³⁺ concentrations.

Figure 6(a) shows the logarithmically plotted UC emission intensities of CaWO₄ codoped with 0.5%Ho³⁺/0.5%Tm³⁺/16%Yb³⁺ as a function of laser pump power. For the unsaturated UC process, the number of photons required to populate the upper energy state can be explained using the following relation [16]:

$$I \propto P^n$$
 (1)

where *n* is the number of pumping photons required to excite the upper emitting state, *I* is the UC luminescent intensity, and *P* is the laser pumping power. The calculated slopes (*n*) were 2.80, 1.75, and 1.70 for blue, green, and red emissions, respectively. These results mean that the UC mechanism of blue emission can be populated by the three-photon process, while those of the green and red emissions by the two-photon process [17].

Based on this result, the possible UC emissions and

populating mechanisms in $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ are schematically presented in Fig. 6(b). For blue emission from Tm^{3+} , nonresonant energy transfer (ET) occurs from the ${}^{2}F_{5/2}$ state in the Yb³⁺ to the ${}^{3}H_{5}$ level in the Tm^{3+} , and/or the ground state absorption (GSA) process can be attributed to the ${}^{3}H_{6} \rightarrow {}^{3}H_{5}$ transition. Subsequent ${}^{3}H_{5} \rightarrow {}^{3}F_{4}$ transition can be generated by phonon-assisted nonradiative transition. Then, the ${}^{3}F_{3}$ state can be excited from the ${}^{3}F_{4}$ state via the excited state absorption (ESA) or energy transfer (ET), which can generate the ${}^{3}H_{4}$ state from the nonradiative transition. The ${}^{3}H_{4}$ state is further excited to the ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ transition generates the blue emission at around 470 nm [18].

Moreover, in the case of green and red emissions of Ho³⁺, the ground state absorption (GSA) (${}^{5}I_{8} \rightarrow {}^{5}I_{6}$) and energy transfer (ET) of ${}^{2}F_{5/2}$ (Yb³⁺)+ ${}^{5}I_{8}$ (Ho³⁺) \rightarrow ${}^{2}F_{7/2}(Yb^{3+})+{}^{5}I_{6}(Er^{3+})$ are responsible for the population at ${}^{5}I_{6}$ level in Ho³⁺. For the green emission, the ${}^{5}I_{6}$ state in Ho^{3+} involves two possible processes: 1) ESA: ${}^{5}I_{6} + a$ photon (980 nm) $\rightarrow {}^{5}F_{4}/{}^{5}S_{2}$ and/or 2) ET: ${}^{2}F_{5/2}$ (Yb³⁺) + ${}^{5}I_{6}$ (Ho³⁺) $\rightarrow {}^{2}F_{7/2}$ (Yb³⁺) + ${}^{5}F_{4}/{}^{5}S_{2}$ (Ho³⁺). The two possible processes generate the ${}^{5}F_{4}/{}^{5}S_{2}$ state of Ho³⁺, which then relaxes to the ground state at ${}^{5}I_{8}$ of Ho³⁺. As a result, the process produces green emission near 540 nm corresponding to ${}^{5}F_{4}/{}^{5}S_{2} \rightarrow {}^{5}I_{8}$ transitions [19]. In red emission, there are two possible UC mechanisms. First, the red emission is initiated through the population of the ${}^{5}I_{6}$ state. The ${}^{5}I_{6}$ state can be populated through ET and GSA processes from the ${}^{5}I_{8}$ state to the ${}^{5}I_{6}$ state. The relaxation of photons from the ${}^{5}I_{6}$ state to the ${}^{5}I_{7}$ state results in a nonradiative process. Then, the ${}^{5}F_{5}$ state can be populated through the ${}^{5}I_{7} \rightarrow {}^{5}F_{5}$ transition via the ESA or ET process from the ${}^{5}F_{5/2}$ (Yb³⁺) + ${}^{5}I_{7}$ (Ho³⁺) \rightarrow ${}^{5}F_{7/2}$ (Yb³⁺) + ${}^{5}F_{5}$ (Ho³⁺) transition. In the second process



Fig. 6 Effect of pump-power-dependent emission on working current from 20 to 110 mW for green, red, and blue UC emissions (a), and possible UC mechanism under excitation at 980 nm (b)

for the red emission, the ${}^{5}F_{5}$ state can be populated by the nonradiative transition from ${}^{5}F_{4}/{}^{5}S_{2} \rightarrow {}^{5}F_{5}$. Finally, the radiative process by relaxation from the ${}^{5}F_{5}$ state to the ground state of ${}^{5}I_{8}$ generates the red emission around 650 nm [20, 21].

4 Conclusions

1) The nanocrystalline $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ powders were successfully synthesized by a modified citrate complex method using microwave irradiation. Crystallization of the $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ was detected at 400 °C, and entirely completed at 600 °C.

2) Controllable white UC luminescence was successfully achieved from $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄. The blue, green, and red emissions as components of white UC emission can be controlled by modulating the Ho^{3+} and Tm^{3+} concentrations.

3) The calculated CIE coordinates can be located in the white region and can be changed from the cool to the warm white region. Therefore, it is concluded that $Ho^{3+}/Tm^{3+}/Yb^{3+}$ -codoped CaWO₄ can be a promising UC phosphor as a white light source for next-generation display devices and biomedical applications.

Acknowledgement

The research was supported by a grant from the LINC (Leaders in INdustry-university Cooperation) Program of Korea National University of Transportation in 2013.

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微波辐射辅助柠檬酸络合法制备的 Ho³⁺/Tm³⁺/Yb³⁺共掺杂 CaWO₄的白光性能

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摘 要: 采用微波辐射辅助柠檬酸络合法制备 Ho³⁺/Tm³⁺/Yb³⁺共掺杂 CaWO₄ 纳米晶升频转换荧光粉。将柠檬酸络 合物前驱体在 300~700 °C 热处理 3 h。Ho³⁺/Tm³⁺/Yb³⁺共掺杂 CaWO₄C 在 400 °C 时开始结晶,在 600 °C 时结晶完 成。经 600 °C 热处理的 Ho³⁺/Tm³⁺/Yb³⁺共掺杂 CaWO₄ 主要呈球形,且形态均匀。在 980 nm 的激光激发下, Ho³⁺/Tm³⁺/Yb³⁺共掺杂 CaWO₄ 纳米晶出现肉眼可见的明亮的白色升频转换发射,这种现象来自 Tm³⁺的 475 nm 蓝 光发射以及 Ho³⁺的 543 nm 绿光和 651 nm 红光发射。通过调整 Tm³⁺和 Ho³⁺的浓度可以控制 Ho³⁺/Tm³⁺/Yb³⁺共掺杂 CaWO₄ 的 CIE 色度图从冷到暖白色之间变化。讨论了 Tm³⁺和 Ho³⁺浓度对升频转换光性能的影响以及与激光泵 功率相关的影响机制。

关键词:升频转换; CaWO4; 波辐射; 白色发光

(Edited by Hua YANG)