Optical Materials 66 (2017) 447–452

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Investigation of luminescence from LuAG: Mn^{4+} for physiological temperature sensing

Fei Li, Jiajia Cai, FengFeng Chi, Yonghu Chen*, Changkui Duan, Min Yin

Department of Physics, University of Science and Technology of China, Hefei 230026, China

ARTICLE INFO

Article history:
Received 18 January 2017
Received in revised form
24 February 2017
Accepted 26 February 2017

Keywords:
Sol–gel processes
Lifetime
Thermal properties
Optical thermometry

ABSTRACT

Optical thermometry based on luminescent materials has garnered much attention due to its many advantages. But higher sensitivity is still expected in physiological temperature range which is of special significance in medicine and biology. For this purpose, quadrivalent manganese doped lutetium aluminum garnet, $Lu_3Al_5O_{12}$: Mn^{4+}, or simply LuAG: Mn^{4+}, has been successfully synthesized by sol-gel method and its temperature dependent luminescence has been investigated in the present work. Compared to the common red emission phosphors $Y_3Al_5O_{12}$: Mn^{4+} (YAG:Mn^{4+}) with same structure, LuAG:Mn^{4+} has a stronger crystal field strength and a higher thermal-quenching activation energy (ΔE) of 5732 cm^{-1}. Rapid thermal quenching of the Mn^{4+} luminescence occurred above room temperature around 90 °C for our LuAG:Mn^{4+} sample. Temperature dependent decay curves of Mn^{4+} emission from LuAG:Mn^{4+} revealed that an extraordinary high sensitivity can be achieved from luminescence lifetime measurements covering physiological temperature range with a sensitivity of 3.75% K^{-1} at 38 °C.

1. Introduction

Nowadays, transition metal ions and rare earth ions doped phosphors of various kinds have witnessed an increasingly widespread popularity for their application in diverse fields such as LED [1,2], bio-cultivation [3,4], and temperature sensing [5–7]. Employed in temperature sensing, luminescence-based thermometers have the advantages of noninvasiveness, accuracy, fast response, high spatial resolution, and environmental applicability [8]. Several temperature-dependent fluorescent properties of phosphors, such as changes in transition energy [8], lifetime [9] and intensity [10], can be used as the main metrics in temperature measurements. To date, several luminescent materials have been explored and developed as optical thermometers. For instance, as the commonly used temperature materials, lanthanide doped upconversion luminescent materials are based on fluorescence intensity ratio technique [9–11], which can work in a wide temperature range with a relatively high sensitivity [12]. However, materials and performance for sensing in the physiological temperature range (298–318 K) of special interests of medicine and biology are still need to be explored and improved [8,12].

As well-known, transition metal doped luminescence materials exhibit a strong electron–phonon coupling [13], which usually makes their emissions easily thermally quenched, as observed, for instances, in $YAlO_3$:Mn^{4+} [14] and $BaGe_4O_9$:Mn^{4+} [15]. Therefore, temperature sensitive luminescence can be expected from these kinds of materials. Moreover, as cheap and easy-to-obtain raw materials [16,17], Mn^{4+} doped red phosphors have received increasing attention these years. In this work, we focus on the application prospect of Mn^{4+} doped phosphors in thermometers. As a novel red phosphor previously reported, YAG: Mn^{4+} [17] has a thermal-quenching activation energy as high as 2230 cm^{-1} [13]. On the other hand, it is also found in $RE_2Sn_2O_7$:Mn^{4+}($RE^{3+} = Y^{3+}$, Lu^{3+} or Gd^{3+}) that crystal field strength of Mn^{4+} enhanced with the decrease of RE^{3+} ionic radius and Mn^{4+}-O^{2-} distance, as expected from the electrostatic point charge model [18]. Generally, thermal-quenching activation energy (ΔE), as well as crystal field strength, could increase with metal-ligand distance decreased [19,20] and while larger thermal-quenching activation energy (ΔE) usually means higher temperature sensitivity [12,15]. Therefore we choose lutetium aluminum garnet (LuAG) as host for Mn^{4+} doping, in consideration of the smaller ionic radius of Lu^{3+} than Y^{3+} and shorter Mn^{4+}-O^{2-} distance in LuAG:Mn^{4+}. A stronger crystal field strength and a higher thermal-quenching activation energy (ΔE) are expected in LuAG: Mn^{4+} than in YAG: Mn^{4+}, which could possibly leads to a better temperature sensing performance.

* Corresponding author.
E-mail address: yhuchen@ustc.edu.cn (Y. Chen).

http://dx.doi.org/10.1016/j.optmat.2017.02.054
0925-3467/

Accordingly, temperature dependent luminescence is recorded to characterize LuAG: Mn^{4+}. A spectral blue-shift of Mn^{4+} emission is also observed, evidencing the stronger crystal field strength in LuAG host. A strong thermal quenching of the luminescence occur at above 90 °C. However, a remarkable high temperature sensitivity is registered in physiological temperature range when using decay time as indicator of temperature, recommending it as a promising candidate for thermometry applications in medicine and biology.

2. Experiments

The lutetium aluminum garnet doped with quadrivalent manganese, LuAG:Mn^{4+} was synthesized by sol-gel method [21,22]. As reported in YAG, Mn^{4+} ions can better enter the YAG crystal lattice when additional charge compensator is applied, e.g., Mg^{2+} [23]. Besides, large amount of additional Mg^{2+} ions can be used to improve the Mn^{4+} emissions in YAG:Mn^{4+} and an optimal formula $Y_3Al_{4.959}Mn_{0.001}Mg_{0.04}O_{12}$ was found in the previous work [17]. Therefore, a similar formula $Lu_3Al_{4.959}Mn_{0.001}Mg_{0.04}O_{12}$ was used for the present preparation of LuAG:Mn^{4+} in consideration of the structural similarity between YAG and LuAG. Lutetium oxide (Lu_2O_3, A. R.), aluminum nitrate ($Al(NO_3)_3$, A. R.), manganous carbonate $MnCO_3$ (99.99%) and basic magnesium carbonate $Mg_2(OH)_2CO_3$ were used as starting materials. Firstly, the stoichiometric amount of Lu_2O_3, $MnCO_3$ and $Mg_2(OH)_2CO_3$ were dissolved into hot diluted nitric acid. Then the required amounts of aluminum nitrate $Al(NO_3)_3$ and citric acid ($C_6H_8O_7.H_2O$) (citric acid: metal ion = 2:1) were added and dissolved into the above solution. The mixture was stirred and heated in water bath of 80 °C. After several hours of heating and stirring, yellow gel was formed. Subsequently, the gel was heated at 180 °C for 4 h in drying oven to get white gel. The white gel were thoroughly ground in an agate mortar and then be annealed at 600 °C for 4 h in a muffle furnace in air to remove the residual carbon. Finally, the obtained powders were calcinated for 4 h at 1000 °C in air to yield the final product of LuAG:Mn^{4+}.

The crystal structures of LuAG:Mn^{4+} was analyzed by a MXPAHF rotating anode X-ray diffractometer using Cu K_α radiation (λ = 0.15418 nm). The XRD profiles were collected in the range $10° < 2\theta < 70°$. Photoluminescence excitation spectra, emission spectra and the decay curves at different temperatures were characterized on a HITACHI 850 fluorescence spectrometer with a 150 W Xe lamp as excitation source. The signal was analyzed using an EG&G 7265 DSP lock-in amplifier. The decay curves of the sample were measured at each temperature using a Tektronix TDS2024 digital storage oscilloscope. The temperature of the sample fixed on a copper post was controlled over the range of 34–110 °C using a temperature controller (FOTEK MT48-V-E, Taipei) with a type-K thermocouple and a heating tube.

3. Results and discussion

3.1. Phase and crystal structure analysis

Fig. 1 shows the XRD patterns of the obtained LuAG:Mn^{4+} sample in comparison with the standard data of LuAG(PDF#74-1368). The two XRD patterns match well and no redundant crystal phases are observable in our sample, indicating that the pure phase LuAG:Mn^{4+} has been obtained. The Al^{3+} in LuAG have two kinds of sites, one is octahedral point symmetry (coordination number CN = 6) and the other is tetragonal point symmetry (CN = 4); and the Lu^{3+} has only one site with D_2 point symmetry (CN = 8) [24]. Because of the similar revised effective ionic radii of Al^{3+} (r = 0.535 Å, CN = 6) and Mn^{4+} (r = 0.530 Å, CN = 6) and the stronger ligand-field stabilization energy of Mn^{4+} in the hexa-

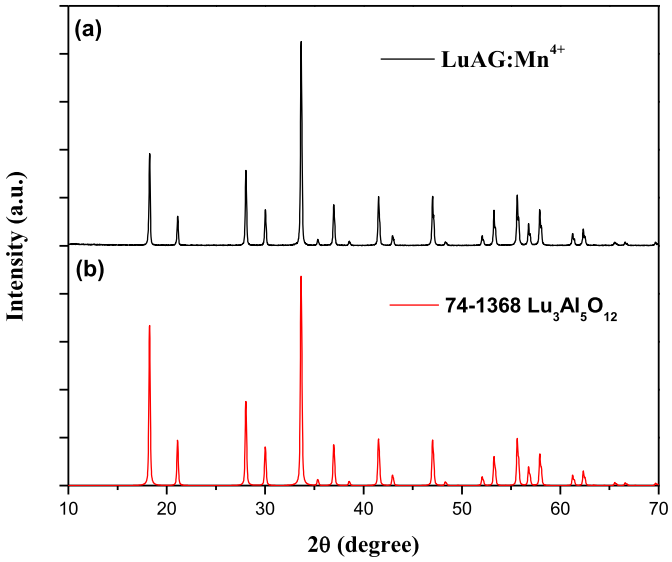

Fig. 1. Powder XRD patterns of LuAG:Mn^{4+} sample (a) and the standard data of LuAG (PDF#74-1368).

coordination [17,25], Mn^{4+} are most likely to incorporate themselves into octahedral positions of Al^{3+} ions [23]. Obviously, the structure of LuAG crystal has almost no change when Al^{3+} is substituted by Mn^{4+} and/or Mg^{2+}.

3.2. Photoluminescence analysis

The room temperature photoluminescence emission (PL) spectra and the excitation (PLE) spectra of LuAG:Mn^{4+} and YAG:Mn^{4+} (from Ref. [17]) phosphors are both presented in Fig. 2(b) and (c), respectively. Though the two samples have similar spectral shape for Mn^{4+} luminescence, an obvious blue shift is observed from YAG:Mn^{4+} to LuAG:Mn^{4+} in both the emission and the excitation spectra. When excited by 355 nm the PL spectrum of LuAG:Mn^{4+} contains two emission bands with the stronger band centered at 666 nm and another centered around 638 nm. The two bands can be attributed to $^2E \rightarrow {}^4A_2$ transitions of Mn^{4+} ions. However, there is only one octahedral site of Al^{3+} for Mn^{4+} substitution, excluding the possibility of luminescence from different sites. Actually, the two bands can be attributed to the phonon-assisted Stokes and the anti-Stokes $^2E \rightarrow {}^4A_2$ transitions. It is reported that due to the parity- and spin-forbidden nature of the $^2E \rightarrow {}^4A_2$ transition, the emission intensity of the zero-phonon line (ZPL) of $^2E_g \rightarrow {}^4A_2$ would be rather weak and the phonon-assisted vibronic transitions usually dominate the emission of Mn^{4+} [26], and the Stokes and anti-Stokes of $^2E \rightarrow {}^4A_2$ transition would be prominent. The PLE spectra of LuAG:Mn^4 monitoring 666 nm emission consist of two strong excitation bands centered at 345 and 480 nm, respectively. The excitation band located in blue region is assigned to $^4A_2 \rightarrow {}^4T_2$ transitions of Mn^{4+}. And the broad excitation band located in UV region (345 nm) can be assigned to $^4A_2 \rightarrow {}^4T_1$ and $^4A_2 \rightarrow {}^2T_1$ transitions, of which $^4A_2 \rightarrow {}^4T_1$ transition plays a dominant role and $^4A_2 \rightarrow {}^2T_1$ transition can be ignored. The above assignment of the excitation bands is supported by the fact that the $^4A_2 \rightarrow {}^4T_1$ and the $^4A_2 \rightarrow {}^4T_2$ transitions are spin-allowed and the transition $^4A_2 \rightarrow {}^2T_1$ is spin-forbidden according to the spin selection rule of $\Delta S = 0$. However, the spin-forbidden transition $^4A_2 \rightarrow {}^2T_1$ is still be found in some cases of Mn-incorporated phosphors, such as $CaAl_{12}O_{19}$: Mn^{4+}, $SrMgAl_{10}O_{17}$: Mn^{4+} [27].

The splitting of the Mn^{4+} ($3d^3$) energy levels in an octahedral