Optical Materials 36 (2014) 1660–1664

Contents lists available at ScienceDirect

Optical Materials

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

Energy transfer in solid solutions $Zn_xMg_{1-x}WO_4$

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ARTICLE INFO

Article history:
Available online 10 January 2014

Keywords:
Zinc tungstate
Magnesium tungstate
Solid solutions
Luminescence
Energy transfer
Scintillating bolometers

ABSTRACT

It is shown that the light output of $Zn_xMg_{1-x}WO_4$ solid solutions has a maximum at $x = 0.5$ under X-ray excitation. Excitation spectra of exciton emission under vacuum ultraviolet excitation also show the increase of the probability of exciton creation by the geminate e–h pairs for the intermediate values of x. Numerical simulation of the relaxation of hot electrons and holes demonstrates that the observed effects are due to the decrease of the mean distance between thermalized charge carriers.

1. Introduction

An enhancement of scintillation light yield can be achieved by the transition from pure compounds to solid solutions of inorganic insulators. This effect has been shown recently for several compounds, e.g. $(Lu_xY_{1-x})AlO_3$:Ce [1], $Y_3(Al_xGa_{1-x})_5O_{12}$:Ce [2], $(Lu_xGd_{1-x})_2SiO_5$:Ce [3], $(Lu_xSc_{1-x})BO_3$:Ce [4], $(Lu_xGd_{1-x})_3(Al_yGa_{1-y})_5O_{12}$:Ce [5], $BaBr_{2-x}I_x$:Eu [6], $(Lu_xY_{1-x})BO_3$:Eu [7], CsBrI [8], $Lu_3Al_{5-x}Sc_xO_{12}$ [9]. One of the possible explanations of the observed enhancement is the decrease of the thermalization length of hot charge carriers at the stage of energy relaxation after the absorption of excitation quanta [1]. The decrease of thermalization length is supposed to be due to non-uniform distribution of substituted ions with the formation of clusters constructed from one of the component or due to the modulation of the bottom of conduction band and of the top of valence band by electronic states of randomly distributed substituted ions [1]. In both cases the increase of the efficiency of recombination and energy transfer to the emission centers can be achieved. Most of the solutions mentioned above are doped with rare earth ions. Rare-earth ions were often chosen to achieve high light yield and fast response. However the solid solutions with the dopant emission are not optimal for the study of the effect of thermalization length modification. The effect may be masked by the following effects, which also influence the efficiency of dopant emission in the solid solutions: (I) Location of the dopant energy levels within the forbidden gap depends on the concentration of one component x. For instance in $Gd_3(Al_xGa_{1-x})_5O_{12}$:Ce the lowest 5d state of Ce^{3+} moves very close to the bottom of conduction band or even into the conduction band, when x value approaches 0 [10,11]. In this case the emission of Ce^{3+} ion is quenched due to the thermal ionization of the emission center. (II) Dopants are sometimes incorporated inhomogeneously into solid solutions due to the mismatch in the ionic radii of dopant and substituted cations. For instance in case of $(Lu_xY_{1-x})AlO_3$:Ce cerium ions (ionic radius of $Ce^{3+} = 1.143$ Å) occupy rather Y^{3+} (ionic radius = 1.02 Å) sites rather than Lu^{3+} (ionic radius = 0.98 Å) sites. (III) Phase composition might vary with the ratio of components of a solid solution. For instance the second phase is found in $(Lu_xY_{1-x})BO_3$:Eu for $x > 0.5$, and its presence substantially modifies the energy transfer processes [7].

In order to study modification of energy transfer processes in solid solutions exclusively as a function of thermalization length of charge carriers we have to avoid the influence of all mentioned effects and choose solid solutions with the following properties: (I) Emission centers should be of intrinsic origin, e.g. emission of self-trapped excitons (STE). In case of the STE emission the process of energy transfer to the emission centers implies the efficiency of exciton creation from separated electrons and holes. (II) The parentage of the states responsible for the intrinsic emission should not be affected by the changing composition of the solid solution. (III) Solid solutions with a single phase should be selected. Solid solutions of $Zn_xMg_{1-x}WO_4$ meet all of these requirements. $ZnWO_4$

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http://dx.doi.org/10.1016/j.optmat.2013.12.039

and $MgWO_4$ crystals belong to the wolframite type of crystal structure (space group C_{2h}) and demonstrate intensive luminescence due to emission of excitons self-trapped on WO_6 complexes. Recent calculations of the band structure demonstrated only negligible contribution from ***s*** electronic states of Mg and Zn cation in the formation of the bottom of the conduction band [12–15]. The solid solutions $Zn_xMg_{1-x}WO_4$ are also interesting for potential applications, since $ZnWO_4$ and $MgWO_4$ are considered as perspective scintillators for cryogenic scintillating bolometers [16,17].

In the present paper we have studied the dependence of exciton creation efficiency in $Zn_xMg_{1-x}WO_4$ on the relative concentration of the cations, which is determined by the value of x. The numerical simulation of exciton production under VUV excitation has been performed in order to demonstrate that the observed dependence of luminescence excitation spectra on x is determined by the modification of thermalization length. The influence of the exciton creation efficiency on the light output under X-ray excitation has been studied as well.

2. Experimental details

Solid-phase synthesis method was used to obtain the charge for the single crystal growth. Initial oxides for the charge were ZnO (99.995%), MgO (99.95%) and WO_3 (99.995%). The crystals were grown by Czochralski method from platinum crucibles using the high-frequency heating. The growth has been carried out on the seed of $ZnWO_4$ single crystal, which was oriented along the direction [010]. As a result the set of single crystals were grown with general formula $Zn_xMg_{1-x}WO_4$ where $x = 0.3$, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1. Phase composition was controlled by X-ray phase analysis and single phase of wolframite was detected in all of the grown crystals. Ratio between Zn, Mg and W in the crystals has been controlled using the scanning electron microscopy. $MgWO_4$ single crystal was grown from the melted flux solution by pulling on the rotating seed from the platinum crucible [17]. Na_2WO_4 was used as a solvent during the growth. The concentrations of contaminating impurities were determined by atomic emission spectral analysis. The data on the impurities detected in the investigated samples are summarized in Table 1.

The relative light output was measured on the special test bench for the samples with 2 mm thickness under X-ray irradiation (anode voltage 200 kV, current 1 mA). A laboratory set-up was used for the measurements of luminescence spectra under X-ray excitation as well as of luminescence excitation spectra and decay curves under UV radiation (photon energies 3.5–5.5 eV). Measured excitation spectra have not been corrected for the instrument function of this set-up. For some of the studied samples the measurements of luminescence excitation spectra were performed using synchrotron radiation in UV and VUV energy regions at the SUPERLUMI station (energy region 3.7–20 eV) at DESY (Hamburg) [18] and at the branch-line FINEST (energy region 15–45 eV) at MAX-lab, Lund [19]. In these cases the measured spectra were corrected using sodium salicylate. All measurements have been carried out at the room temperature on the freshly cleaved plane surfaces of the samples, which correspond to the crystallographic plane {0 1 0}.

Table 1
The concentration of contaminating impurities in the $Zn_xMg_{1-x}WO_4$ according to the data of atomic emission spectral analysis presented in weight ppm.

x	Impurities concentration (ppm)							
	Fe	Si	Cr	Sn	Ni	Mo	Pb	Al
1	2	5	2	<2	1	10	1	2
0.9	2	5	2.5	<2	1	5	10	2
0.8	2	5	2	<2	<1	10	<1	4
0.7	1.5	10	2	<2	<1	10	10	5
0.6	0.8	5	2	<2	<1	5	<1	2
0.5	1	5	2.5	<2	<1	5	<1	2
0.4	1	10	<2	<2	2	<2	<1	2
0.3	1	10	<2	<2	2	<2	<1	1
0	10	10	<2	<2	2	<2	<1	<1

3. Experimental results

The luminescence spectra of $Zn_xMg_{1-x}WO_4$ under X-ray excitation are presented in Fig. 1. The observed single band peaking at 495 nm is connected with the STE emission [20]. The maximum and the width of emission band are almost independent on the value of x. The characteristic decay times are of few tens of µs. These values slightly increase with the decrease of x from 28 µs for $ZnWO_4$ ($x = 1$) to 35 µs for $Zn_{0.5}Mg_{0.5}WO_4$ ($x = 0.5$) and up to 39 µs for $MgWO_4$ ($x = 0$) under excitation in the region of direct creation of STEs ($E_{ex} = 4.1$–4.4 eV). Therefore the characteristics of STE emission are similar for all studied crystals indicating insignificant influence from electronic states of substituted cations on the STE excited and relaxed states. It also confirms the negligible contribution of cation electronic states on the formation of the energy bands in the vicinity of the bandgap, which was predicted by band structure calculations [12–15].

The data on the light output under X-ray excitation are presented in Fig. 2. For the samples with $x = 0.3$ and 0.8 measurements were not performed because the size of grown boules did not allow to cut the samples with the dimensions required for the test bench. The gradual increase of the light output is observed for the solid solutions with the maximum at $x = 0.5$. For the crystal with $x = 0.5$ the light output is increased in ~1.5 times relatively to $ZnWO_4$ and in ~2.1 times relatively to $MgWO_4$. The data on the relative scintillation light output under α-particles excitation are also presented for $MgWO_4$ and $ZnWO_4$ according to [21] and they are in a good correspondence to the values of relative light output obtained by us. Taking into account that the absolute value of scintillation light yield of $ZnWO_4$ is 21,500 ph/MeV [22], the light yield up to ~32,000 ph/MeV may be expected for $Zn_{0.5}Mg_{0.5}WO_4$ at room temperature. Since the tungstates attract attention as scintillators, the opportunity of the light yield enhancement for their solid solutions is very tempting.

Obtained results demonstrate that the increase of light output in the solid solutions is a characteristic not only for RE-doped compounds (see Section 1) but also for compounds with intrinsic STE

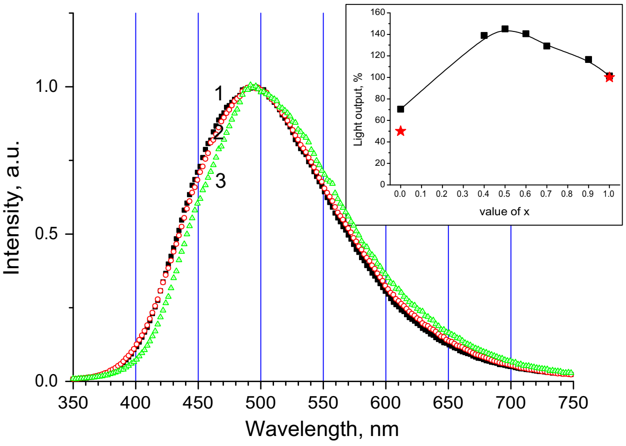

Fig. 1. Emission spectra of $Zn_xMg_{1-x}WO_4$ under X-ray excitation for $x = 1$ (curve 1), 0.5 (curve 2) and 0 (curve 3). In the inset: light output of $Zn_xMg_{1-x}WO_4$ under X-ray excitation. Data on the relative scintillation light output of $MgWO_4$ and $ZnWO_4$ under excitation with α-particles are presented with circles according to [21].