Tunneling luminescence in long lasting afterglow of $SrAl_2O_4$:Eu,Dy

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ABSTRACT

A long lasting (afterglowing) luminescent material $SrAl_2O_4$: Eu^{2+}, Dy^{3+} was prepared by high temperature solid-state reaction method. The processes responsible for long lasting luminescence were studied by means of luminescence spectra, thermally stimulated luminescence and afterglow kinetics. Two processes are found to contribute in excited Eu $^{2+}$ creation – the thermally released electrons recombination and electron tunneling from trap to Eu^{3+}. The possible scheme of long lasting luminescence mechanism is proposed.

Keywords:
Long afterglow
Luminescence
Rare earth

1. Introduction

Compounds doped with divalent Eu ions, for example, $SrAl_2O_4$:Eu,Dy, $Sr_2MgSi_2O_7$:Eu have been widely studied [1–5] due to their notable luminescent properties – wide excitation spectrum, good quantum yield and long lasting luminescence (more than 10 h) in the blue-green region (depending on the host material). Thus these materials are promising for many practical applications such as modern lightening, signs, biological markers etc. A number of possible mechanisms responsible for long-lasting luminescence have been suggested in recent studies. The first mechanism proposed in [6] was based on idea that during excitation Eu^{2+} traps an electron, the Dy^{3+} acts as a hole trap and during excitation the Eu^{+} and Dy^{4+} are created in $SrAl_2O_4$:Eu,Dy. The thermal release of hole leds to its interaction with Eu^{+} and formation of excited Eu^{2+} luminescence centre that is responsible for luminescence observed. However one could note: (I) the Eu^{+} and Dy^{4+} ions in $SrAl_2O_4$ could not be chemically stable [7]; (II) the long lasting luminescence was still observed in $SrAl_2O_4$:Eu without Dy [8,9]; (III) band gap of $SrAl_2O_4$ is ~6,6 eV [10] whereas long lasting luminescence can be excited by photons below this energy [11]. Hence under excitation the main process could be ionization of dopants and/or defects followed by charge carriers trapping at other defects. Therefore the mechanism of long lasting luminescence described in [6] is incomplete and several other mechanisms for long lasting luminescence were suggested, [12] and references therein. The unifying idea of mechanisms suggested is that the long lasting luminescence is a thermally stimulated process, while in details the mechanisms differ. The discussion of long lasting luminescence details is mostly concentrated on the role of the trivalent rare earth co-dopant and the nature of the traps that are responsible for the long afterglow. It is clear the luminescence center in these compounds is the Eu^{2+} ion and the luminescence occurs due to the 5d-4f transition. The excited Eu^{2+} luminescence centre creation could be due to Eu^{3+} recombination with electron as it was proposed in [13,14]. This way for excited Eu^{2+} luminescence centre creation is supported by ESR data described in [15] – during excitation the concentration of Eu^{2+} was reduced and after excitation switching off concentration of Eu^{2+} rises. This result suggested the Eu^{3+} could be created during excitation. The evidence for Eu^{3+} creation under material irradiation by X-ray is described in [16], however as far as we know the information on Eu^{3+} presence in $SrAl_2O_4$:Eu,Dy is not complete. If the Eu^{2+} during excitation is oxidized to Eu^{3+} then the electron must be trapped at some other center. The nature of the trapping centers is yet unclear, as well as the role of co-dopants – adding another trivalent rare earth to the material enhances and prolongs the resulting luminescent afterglow. In this study several experiments were carried out to clear up details of $SrAl_2O_4$:Eu,Dy long lasting luminescence and we propose that there are two processes involved in the formation of excited Eu^{2+} luminescence centre– the Eu^{3+} recombination with thermally released electrons and the tunneling of electrons to the Eu^{3+}.

2. Experimental

$Sr_{0.97}Al_2O_4$:$Eu_{0.01}$, $Dy_{0.02}$ phosphors were prepared by solid state reaction method. The raw ingredients were aluminum nitrate ($Al(NO_3)_3$), strontium nitrate ($Sr(NO_3)_2$), dysprosium nitrate ($Dy(NO_3)_3$) and europium nitrate ($Eu(NO_3)_3$) synthesized at 1300 °C by usual solid-state reaction technique under a weak

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reductive atmosphere of active carbon, and boric acid was added to the mixture.

The structure of the prepared phosphors was observed by X-Ray diffraction method using Bruker AXS GmbH DS Advance diffractometer. The luminescence spectra of the obtained samples were measured using the Andor Shamrock B303-I spectrometer and excitation source was YAG:Nd laser LCS-DTL-382QT (266 nm, 8 ns). The afterglow spectra were recorded 30 s after the termination of excitation. The integration time for spectrum accumulation was 1ms. The luminescence decay profiles were also recorded using the same set of equipment. The excitation time was 50 s for luminescence decay profiles measurements.

For the thermally stimulated luminescence measurements the sample was cooled to the defined temperature in a helium cryostat in vacuum and excited by YAG:Nd laser LCS-DTL-382QT (266 nm, 8 ns) for 20 min to fill the traps. After that, the samples were heated at a rate of 2 deg/min. and the spectra were monitored by Andor Shamrock B303-I spectrometer.

3. Results and discussion

Fig. 1. shows the XRD pattern of the sample. We can observe that there is mainly $SrAl_2O_4$ phase, with a little admixture of $Sr_4Al_{14}O_{25}$, not exceeding 10% of the total sample composition.

The afterglow of $SrAl_2O_4$:Eu,Dy is a broad band with maximum at 529 nm (Fig. 2). This peak position and shape of band are close to those observed for $SrAl_2O_4$:Eu,Dy in [11,17], thus the luminescence observed is mainly from $SrAl_2O_4$ and possible contribution from other phase is negligible.The green long lasting luminescence (afterglow) was observed for time exceeding 10 h. The long lasting luminescence for $SrAl_2O_4$:Eu,Dy was excited at three different temperatures – at RT ($\sim$295 K), 240 K and 90 K and corresponding afterglow spectra recorded at the excitation temperatures are in Fig. 3. If the temperature of excitation is lowered, the intensity of luminescence decreases and for excitation at 90 K it is reduced by factor 3 relative to intensity for excitation at RT. The normalized spectra coincide well (inset in Fig. 3) indicating the peak position and shape of band are the same for all excitation temperatures. This is evidence that the luminescence centers as well as its surroundings are the same at RT and 90 K.

The spectra recorded under excitation at different temperatures are shown in Fig. 4. The spectra at 150 K and lower temperatures showed two well known luminescence bands [18] peaking at 529 and 446 nm.

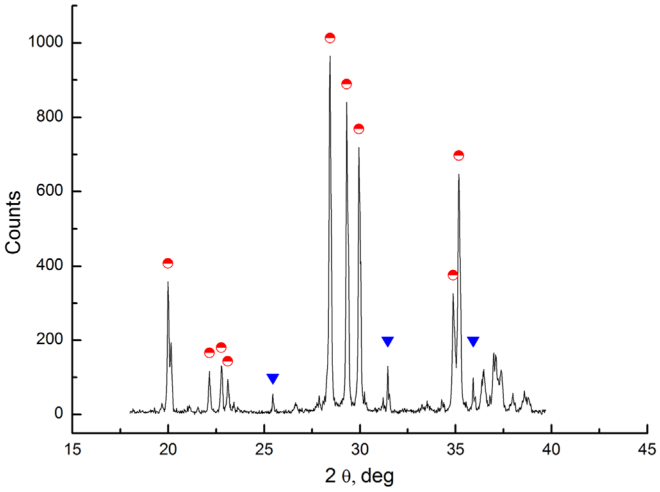

Fig. 1. XRD pattern of sample synthesized, the circles (half-filled) indicate main peaks of $SrAl_2O_4$ phase, triangles – peaks of $Sr_4Al_{14}O_{25}$ phase.

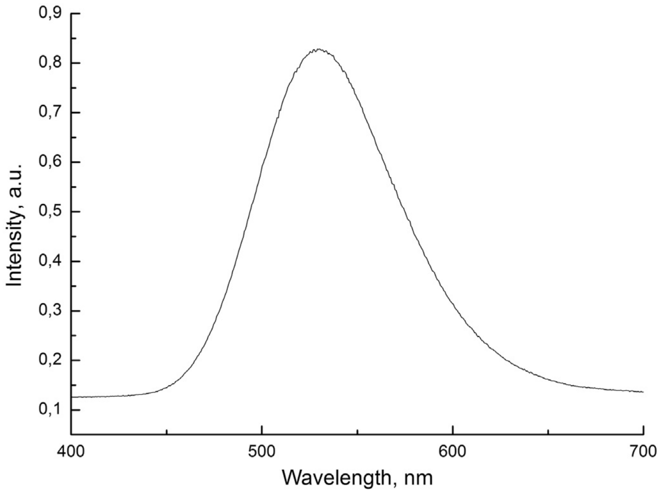

Fig. 2. Long lasting luminescence of SrAl2O4:Eu, Dy at RT.

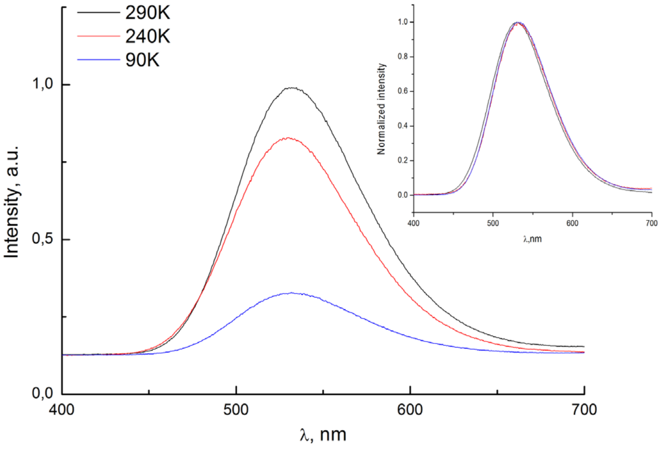

Fig. 3. Luminescence spectra at different temperatures. Inset – normalized luminescence, spectra coincide.

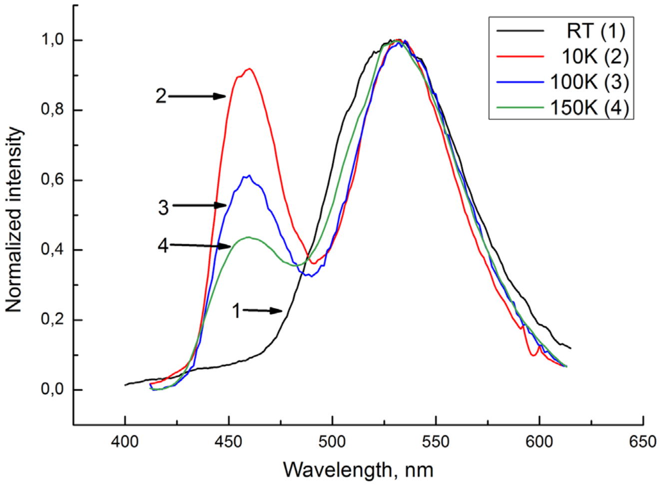

Fig. 4. Luminescence spectra under excitation at different temperatures.

Besides that, the luminescence bandwidth is larger at higher temperature due to phonon interaction. The afterglow spectra differ from those under excitation – the afterglow bands width did not change within 90–290 K and 446 nm band is not observed 30 seconds after termination of excitation. The luminescence band

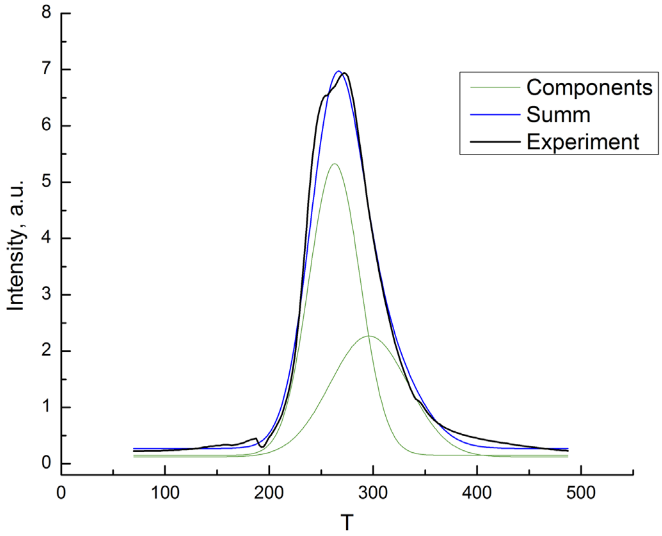

Fig. 5. Thermally stimulated luminescence of $SrAl_2O_4$:Eu,Dy and glow curve decomposition on possible main components.

peaking at 446 nm was not observed in afterglow spectra due to the short afterglow time.

The probability of thermal release of electrons and holes in $SrAl_2O_4$:Eu,Dy could be negligible at 90 K. To check the possible contribution of thermally stimulated processes the sample was excited at 70 K, then heated up (2 K/min) and thermally stimulated glow curve was recorded. The recorded glow curve in Fig. 5 shows that within 70–170 K there is no thermal release of electrons, but within 200–400 K multiple overlapping glow maxima are observed.

The glow curve is similar to that described in [17]. It indicates that there are two major traps having slightly different activation energies for charge release. However our attempt of glow curve decomposition on only two main components is not completely successful confirming that a larger number of traps could be involved. The activation energies of main components were roughly estimated using the empirical equation from [19]:

$$E=23kT_m \quad (1)$$

The estimated activation energies were 0.52 eV and 0.58 eV and they are close to those described in [12]. That means the luminescence observed for $SrAl_2O_4$:Eu, Dy sample excited at 90 K is not due to thermally released charges recombination on luminescence center. The electrons and holes in $SrAl_2O_4$:Eu,Dy studied at 90 K are localized at traps.

In the formation of excited Eu^{2+} luminescence centre both processes are involved – thermally released electron migration as well as electron tunnelling. The contribution of these processes is temperature dependent. The trap associated with Eu^{3+} is deeper than others [20] and it is possible that even at room temperature the last step could be electron tunneling to Eu^{3+} from this closely located trap.

The luminescence decay of excited luminescence centers created in tunnel processes depends on spatial distribution of defects involved and can often be described with the empirical Becquerel's law [21]

$$I(t) \propto t^{-\alpha}, \quad (2)$$

with the distinctive decay parameter

$$\alpha = \frac{\Delta \log(I(t))}{\Delta \log(t)}.$$

that is defined by the spatial distribution of the defects involved.

The decay of $SrAl_2O_4$:Eu,Dy luminescence excited at RT, 240 K and 90 K is shown in Fig. 6. The logarithmic plot of intensity

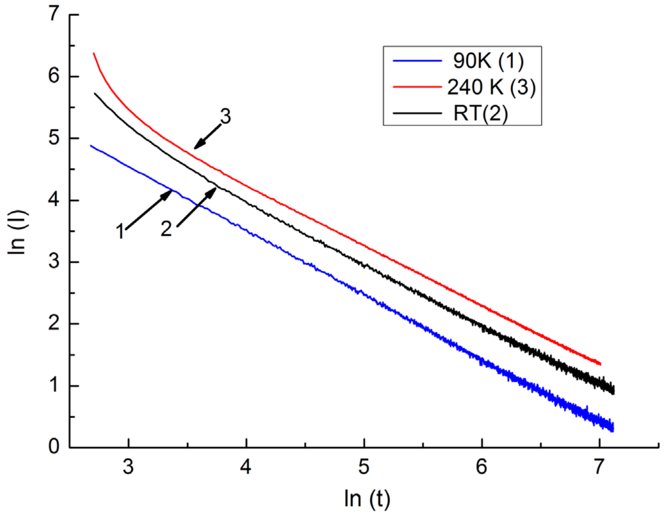

Fig. 6. The decay kinetics of the luminescence in logarithmic scale.

dependence on time can be well approximated by a straight line with the slope of approximately 1 for all three temperatures. This could be additional evidence for support of suggestion that the last step of excited Eu^{2+} luminescence centre formation at RT is electron tunneling. However the further study and analysis according to the description set out in [21,22] could be helpful for obtaining the stronger evidence that at RT the both processes thermal stimulation and tunneling occur simultaneously in $SrAl_2O_4$:Eu,Dy. The suggestion of tunnel process involvement in excited Eu^{2+} luminescence centre formation allows to clear the differences observed between afterglow luminescence spectra and the spectra recorded under excitation. The width of luminescence band at ~529 nm is temperature dependent in spectra under excitation due to luminescence centre interaction with phonons whereas the shape of luminescence band in afterglow spectra is not temperature dependent. This independence on temperature could be due to creation of excited Eu^{2+} luminescence centre via tunneling, since in this process the both states of electron (electron located at trap and electron at Eu^{2+} excited state) must have the same (or very close) energies. Therefore, the excited Eu^{2+} luminescence centre, created via tunneling could have the same surrounding (including phonon states) regardless of temperature. The decay of luminescence band peaking at 446 nm is faster than that peaking at 529 nm. Thus the 446 nm band was not observed in afterglow spectra recorded with 30 s delays after termination of excitation.

The scheme of suggested mechanism for long lasting luminescence is presented in Fig. 7.

We suggest that the thermally released electron during migration can be multifold trapped and released. The last step of electron migration can be either its direct trapping at Eu^{2+} excited state either trapping on a deeper level associated with Eu^{3+} and

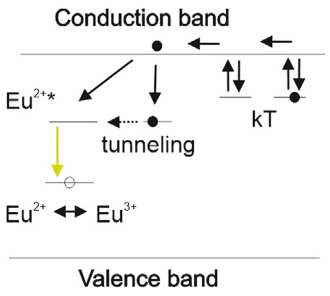

Fig. 7. The possible model for persistent luminescence in $SrAl_2O_4$: Eu, Dy.

followed by creation of excited Eu^{2+} luminescence centre via electron tunneling. The creation of excited Eu^{2+} luminescence centers via tunneling is the dominant process at low temperatures. The radiative decay of these centers is origin of luminescence observed. The mechanism described is simplified since: (I) the spatial distribution between luminescence center and the associated deep trap is not involved in scheme presented; (II) the glow curve gives strong evidence that more than two electron traps are present in the material. Therefore the further study, including numerical simulation and analysis, according to the description set out in [22,23] could be helpful for obtaining additional information on simultaneously active thermally stimulated and tunnelling processes in SrAl$_2$O$_4$:Eu,Dy.

4. Conclusions

The coincide of luminescence spectra for SrAl$_2$O$_4$:Eu,Dy excited at 290 K, 240 K and 90 K indicate that the luminescence center and its surrounding are the same at all the given temperatures. The absence of glow maxima within 70–170 K in thermally stimulated luminescence is strong evidence that both – electrons and holes are localized in traps and therefore tunneling process is responsible for the creation of excited Eu^{2+} luminescence centers. This is the dominant process within low temperature range. The thermally released charge migration is involved in excited Eu^{2+} luminescence centers creation at higher temperatures and it is possible the tunneling of electron could be the last step of process at higher temperatures as well. The possible scheme is presented for mechanism responsible for long lasting luminescence.

Acknowledgements

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