UNIVERSITY OF LATVIA

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ELECTRONIC EXCITATIONS AND PROCESSES IN LONG LASTING LUMINESCENCE MATERIAL $SrAl_2O_4$

SUMMARY OF DOCTORAL THESIS

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Annotation

Persistent luminescent material $SrAl_2O_4$: Eu^{2+}, Dy^{3+} is widely used and studied for energy efficient applications. However, the mechanism of the persistent luminescence mechanism and the role of co-dopant are not clear and the publications that are available on the mechanism are contradictory.

A study of $SrAl_2O_4$:Eu,Dy; $SrAl_2O_4$:Dy, and undoped $SrAl_2O_4$ material was conducted in order to clarify these ambiguities. Photoluminescence and radioluminescence spectral measurements were conducted at temperatures ranging from 10 K to room temperature. Thermally stimulated luminescence measurements were used to determine the trapping centre composition and depth in these materials.

Improvements for the mechanism of persistent luminescence have been suggested, that involve tunneling of electron from trapping center to Eu^{3+}, and the proof for stable Dy^{4+} existance in strontium aluminate has been presented. Intentionally undoped material luminescence has been observed, consisting of trace impurity and intrinsic defects luminescence.

The results of this work give new knowledge and improve the existing concepts of persistent luminescence in Eu activated strontium aluminates. They also open some possibilities for wider applications of long lasting phosphors.

Contents

1. Introduction

Long lasting luminescence (known also as persistent luminescence) has many well known applications – for example decorations, toys and emergency signs for cases of power shortage during an emergency, many of them are based on Eu doped strontium aluminates. Recently multiple unexplored fields of application have appeared, therefore intensifying the search for maximally efficient and long lasting luminescent materials. Road marks with luminescent paint are being developed, as well as plasma electrolitic oxidation coatings for protection and decoration. A very intriguing application in persistent luminophores is the in vivo medical imaging using luminescent nanoparticles [1-4].

The knowledge of the processes ongoing in the material are essential to improve the optical properties of the above mentioned long lasting aluminate luminophores for different applications. However details of these proceses are not clear, especially the nature and role of defects involved. We are interested in study of defects that are involved in the luminescence process and the posibilities to control them in the process of synthesis in order to obtain the longest afterglow and good thermal stability – so that the material is usable at different temperatures. The scientific literature about the luminescence processes ongoing in the material is not consentaneous – different models exist that could be responsible for the long afterglow and the defects that are involved are not clear. Also, there are very few articles on luminescent properties of undoped material, leaving a possibility for research in this direction. The main motivation for this work was to highlight details of the long lasting luminescence mechanism and to contribute to the knowledge of defects involved.

1.1 The aim of work

The synthesis of maximally efficient alkaline earth aluminate phosphor with a bright afterglow and long afterglow duration is limited with the lack of knowledge about the mechanism governing the persistent luminescence. There is some general knowledge of the process – it must involve some trapping centers and it involves thermally stimulated process, but many details remain unclear.

Therefore the aim of this work is the obtainement of new knowledge for understanding more about the persistent luminescence mechanism, including: the nature of the trapping centers, (hole or electron) and their depths, the trapping and detrapping mechanism as well as the origin of the trapping centers and the role of $SrAl_2O_4$ doping with Eu and Dy.

The following tasks were set:

1. **Conduct the experiments for study of $SrAl_2O_4$:Eu,Dy and $SrAl_2O_4$:Dy afterglow dependence on temperature.**
   This study can contribute in understanding details of afterglow mechanism including the charge transfer process.
2. **Record and compare the luminescence spectra under excitation, afterglow spectra and TSL spectra for $SrAl_2O_4$:Eu,Dy and $SrAl_2O_4$:Dy.**
   The co-activation with Dy increase the intensity and duration of afterglow, however it has not been determined whether it causes creation of new defects or increases the number of previous defects. It is unknown whether Dy is a charge trap.
3. **Study the intentionally undoped $SrAl_2O_4$ luminescence and TSL.**
   The luminescence of undoped $SrAl_2O_4$ was studied rarely and the defects in this undpped composition were not identified. Therefore the study can highlight whether the host defects contribute in afterglow.
4. **Summarize and analyze the results obtained in experiments to find out whether they contribute to a more complete understanding of the long-lasting luminescence mechanism.**

   This study can contribute in understanding details of afterglow mechanism including the charge transfer process.

1.2. The contribution of the author and the scientific novelty of work

The author has conducted the experiments that are connected with all of the described results except the XRD measurements. The interpretation of the experimental results has been done together with colleagues from Institute of Solid State Physics Radiation laboratory. The author has presented the work in multiple international and local conferences with oral and poster presentations. The author has taken part (as the main author and as one of the co-authors) in the making of several scientific publications.

The main results from this research are novel and the analysis of the results has given new knowledge about the ongoing processes in the material. The thesis of this work state novel results that have not yet been discussed before in scientific literature – tunneling luminescence as a part of the persistent luminescence process, proof for stable Dy^{4+} existance in strontium aluminate and observation of luminescence from unactivated $SrAl_2O_4$ material, leading to a conclusion that it is F-center luminescence.

These results are significant – they give new knowledge and improve the existing concepts of persistent luminescence in Eu activated strontium aluminates. They also open some possibilities for wider applications of long lasting phosphors.

1. Literature review

2.1. Structural properties of $SrAl_2O_4$

A number of strontium aluminate polymorphs is known. The $SrAl_2O_4$ is a stable compund in SrO-Al_2O_3 system. It has a stable monoclinic phase at room temperature, that transforms into hexagonal when heating at temperatures above 650 ^{0}C and back to monoclinic at the same temperature during cooling. $SrAl_2O_4$ has a tridymite structure constructed by corner sharing AlO_4 tetrahedra that are tilted with respect to each other (Fig. 2.1) [3, 4]. The occupation of Al^{3+} ions in the compound leaves a charge defficiancy that is then compensated by Sr^{2+} ion incorporation in the channels created within „rings" of corner shared AlO_4 tetrahedra, therefore it is called the stuffed tridimyte structure. There are two possible positions for Sr cations in this matrix. The structure of the low-temperature phase has a three-dimensional network of corner-sharing AlO_4 tetrahedra, which has channels in the a- and c- directions where the Sr^{2+} ions are located (Fig. 2.1). The two crystallographically different sites for Sr^{2+} have evidentical coordination numbers (i.e., 6 and 7), similar average Sr-O distances (i.e., 2.695 Å and 2.667 Å) and similar individual Sr-O distances. The two environments differ only by a slight distortion of their "square planes" [5]. When doping with Eu ions, it incorporates in the position of Sr.

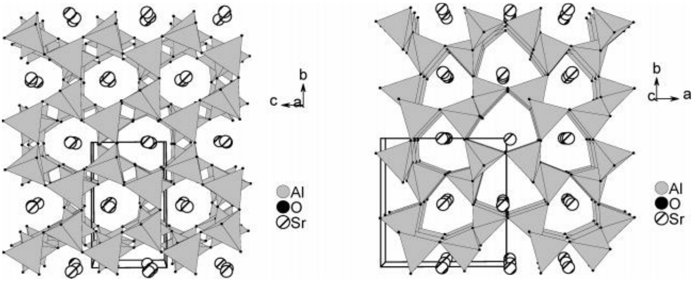

Fig. 2.1. The crystallographic structure of monoclinic phase of $SrAl_2O_4$ along the a- and c- directions. Image from [5].

The Sr^{2+} and Eu^{2+} ions are very similar in their ionic size - 1.21 and 1.20 Å, respectively) and the presence of Sr(I) and Sr(II) sites results in different symmetry and orientation around incorporated Eu ion leading to deviations in the luminiscent properties for both sites.

It is also important to note the dopant incorporation in the matrix, as lattice disorders and substitutional ions introduce localized states in the host matrix band gap by interrupting the long range symmetry of the material. An example of a lattice imperfection in $SrAl_2O_4$ are:

- Sr vacancy (V_{Sr}) – a point defect with 2- charge in respect to the lattice, as Sr is usually in 2+ form – thus its vacancy can be a hole trapping center itself or attract some other defect for charge compensation
- Oxygen vacancy (V_O) – a point defect with 2+ charge in respect to the lattice, as O is in 2- form - thus its vacancy can be an electron trapping center itself or attract some other defect for charge compensation

There are other possibilities, like interstitial or substitutional ions, that also can either be trapping centers themselves or attract other defects for charge compensation. The dopant incorporation (Eu and Dy ions or different) in different sites of the $SrAl_2O_4$ host is usually determined by the ionic radii of the dopants and the host lattice components

2.2. Luminescent properties of unactivated $SrAl_2O_4$

The band gap for unactivated $SrAl_2O_4$ is around 6.5 eV [6], therefore band to band excitation by visible light is not likely. But there are surely some defects present in the undoped material that might also be present in the material after doping. Therefore the knowledge of luminescence in undoped material could be useful in acknowledging the defects that participate in the long lasting luminescence process of the doped material. A large number of papers devoted to the investigation of long lasting luminescence of $SrAl_2O_4$:Eu,Dy do not contain any information on luminescence of undoped material as well as on nature of host intrinsic defects. Most articles do not deal with the undoped material at all. We found only several papers on luminescence of undoped $SrAl_2O_4$ and results described in these papers were contradictory.

In [7]A it is mentioned that the undoped $SrAl_2O_4$ is studied under UV excitation however no information of undoped $SrAl_2O_4$ luminescence was included in this publication. Some publications report that there is no detectable luminescence from undoped $SrAl_2O_4$ [8]. In another publication authors have detected sharp lines in the photoluminescence spectrum [9], not characteristic for intrinsic defects of a crystalline solid, the source of these lines could be trace amount of transition metals or rare earths present in the material. It is important to note that all these publications deal with luminescence at room temperature only, and emission might be different at low temperatures.

Even high purity strontium aluminates content some amount of trace metal, that can interfere with the acquisition of correct data about intentionally unactivated $SrAl_2O_4$. However, the luminescence of trace metals in different materials is well studied and the content of trace metals in pure $SrAl_2O_4$ is less than 0.1%, the influence of trace metals luminescence in determination of pure $SrAl_2O_4$ luminescence could be negligible, however might be detectable.

To deal with these unclarities and ambiguities, the author conducted a study on the luminescence of the undoped $SrAl_2O_4$ with different excitation sources and under different temperatures.

2.3. The properties of lanthanide ions in phosphors

Lanthanide ions, either in a divalent, trivalent, or, more rarely, tetravalent state, take a very important place among luminescence centers in crystalline phosphors – both long lasting and also fast fading luminescence have wide applications. Lanthanides are commonly referred to as rare earth activators, although several of them are not very rare. There are two types of lanthanide luminescent transitions that might be of interest. Transitions between $4f^n$ levels are quite invariant in different compounds, and usually quite sharp and line-like due to this invariance. Transitions between $4f^{(n-1)}5d$ and $4f^n$ configurations, however, do depend on the host matrix quite strongly, thus shifting the maximum of emission quite noticeably and also broadening the absorbtion and emission spectra [5]. The interesting properties of lanthanide ions arise from the fact that they posess a partially filled 4f shell that is shielded from the impact of crystallic field of the host by outer shell electrons.

As for $SrAl_2O_4$:Eu,Dy, we are looking at the case of Eu^{2+}, that acts as a luminiscence center due its luminescent 5d-4f transition [10]. All the luminescent materials from aluminate and silicate groups doped with Eu show a similar emission spectrum – a broad band with the maximum within blue – green region [10]. It is quite safe to say that exactly Eu^{2+} is playing the role of luminescence center and the emission band is shifted in different crystal fields while still maintaining its shape. The reasoning for this assertion is that this luminescence disappears in samples without Eu doping, the normalized luminescence bands have almost identical full widths at half maximum – only the maximum position shifts due to differences in crystal field in different materials.

The co-activation of the trivalent rare earth does not change the position of the luminescence emission band nor the shape of it – for $SrAl_2O_4:Eu^{2+},RE^{3+}$ it only contributes to the afterglow time and intensity, making the duration of the afterglow much longer and much more intensive. The afterglow is present also without the Dy^{3+} co-doping [11]. This is the reason we can be sure to say that the luminescence center in these compounds is Eu^{2+}, but Dy^{3+} somehow contributes to the trapping centers of the material. The photoluminescence that is characteristic to the trivalent rare earth coactivators is not observable, leading to a conclusion that direct excitation of rare earth is not involved, and nor is the energy transfer from Eu^{2+} to the trivalent rare earth.

2.4. Long lasting luminiscence models

During these over 20 years since the discovery of $SrAl_2O_4$:Eu many vast studies have been conducted to enhance the properties of long afterglow phosphors - prolong their persistent luminescence and improve the intensity. Despite this, there is still no comprehensive understanding of the mechanism of this phenomenon. This is the reason why the development of new materials and the enhancement of the properties of the known compounds is often based on trial and error methods. Different methods of synthesis have been used and studied [11]. The main models for long afterglow phosphorts and its evolution are shortly described in subchapters below.

2.4.1. Matsuzawa model

The search for the mechanism began with the Matsuzawa (the original patent of persistent luminiscence in $SrAl_2O_4$:Eu,Dy) model [12]. In this publication the long lasting luminescence mechanism of $SrAl_2O_4$:Eu,Dy is proposed. The essence of the mechanism lays in the presumption that the excitation of Eu^{2+} ion is followed by a hole delocalization from it and thus Eu^{+} is formed. The hole is trapped on Dy^{3+}, recharging it to Dy^{4+}. At a temperature that is high enough to release the trapped charges, the hole is released, migrates back to Eu^{+} and creates excited Eu^{2+}. The electron then returns to the ground state by the emission of a photon. The scheme of mechanism proposed by Matsuzawa is in Fig. 2.2.

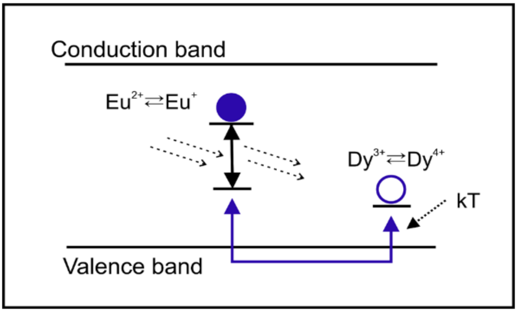

Fig. 2.2. The Matsuzawa model for the long lasting luminiscence involving hole as free charge carrier

The proposed mechanism recieved a lot of criticizm – the Eu^{+} state seems to be very unlikely to achieve – high energy would be needed [13]. Also, this mechanism does not explain the afterglow of $SrAl_2O_4$:Eu without Dy co-doping. Another counter-argument for this model is that some authors claim there is no change in the charge state of the co-dopant Dy during excitation as seen from EPR and XPS measurements [14].

2.4.2 Aitasalo model

It was clear that Matsuzawa model had to be modified due to the above mentioned shortcomings. The thermally stimulated luminiscence of Dy co-doped and non co-doped materials was studied and led to a conclusion, that co-doping does not alter the position of thermoluminiscence peak [15]. Thus one can to conclude that Dy does not act as the trapping center and the process could be more complex. Therefore Aitasalo modified the model four times and the last version is close to that proposed by Dorenbos [16] additionaly involving some details. The proposed processes are as follows - electron is thermally promoted from Eu^{2+} excited state to the conduction band, electron migrates through the conduction band and can be then localized on defects – oxygen vacancies as well as on trivalent rare earth ion. The scheme of this model is in Fig. 2.3

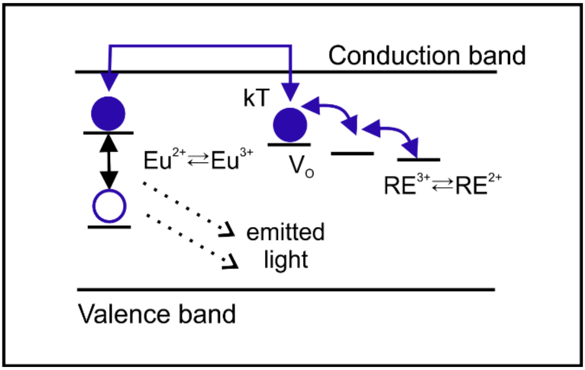

Fig. 2.3. The model proposed by Aitasalo for the long lasting luminiscence involving Eu^{3+} accumulation during excitation

Charge carriers can also migrate from one trap to another and finally migrate back to the luminescence center, where excited Eu^{2+} transition to ground state creates the characteristic luminescence.

2.4.3 Clabau model

Clabau suggested a model that involves electrons as the free charge carriers. To present the proof for this hypothesis, electron paramagnetic resonanse experiments were conducted. The experimental results showed that the concentration of Eu^{2+} ions changes – during excitation it decreases and during afterglow increases [17]. Therefore Clabau presumed Eu^{2+} could be ionized - after when, during UV irradiation, Eu^{2+} excited state is formed. Electron migration from trapping centers to the luminiscence centers in this model does not happen through the conduction band, but with the aid of a direct transition between traps, that can occur if the levels are located in close proximity to each other.

In this model there is a different approach to Dy role in the material – it is not regarded as a charge carrier trapping center, but as a stabilizing element for the oxygen vacancies – the presence of Dy^{3+} ions could modify electron density to an oxygen vacancy [17]. In this model oxygen vacancies are considered to be the electron trapping centers.

It is not actually clear, how Dy^{3+} could stabilize oxygen vacancies, because when Dy^{3+} replaces Sr^{2+} an uncompensated positive charge remains. This charge compensation could be achieved by creation of Sr vacancies. Therefore the hypothetical process where Dy^{3+} could be stabilising the creation of oxygen vacancies should be quite complicated. There are no experiments to be found in literature that validate this assumption.

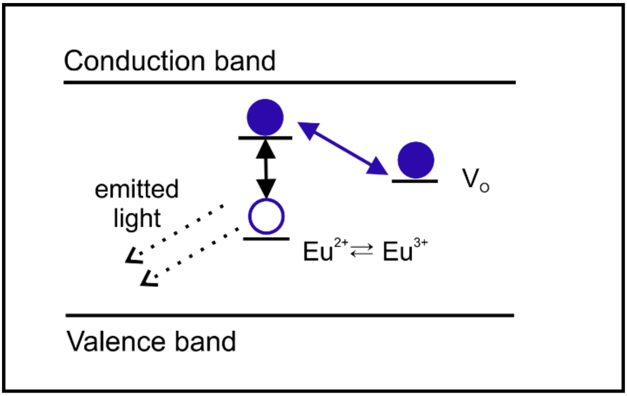

Fig. 2.4. Clabau model for the long lasting luminescence involving direct electron transition from luminiscence center to trapping center.

2.4.4 Dorenbos model

The study of excitation and luminescence processes of $SrAl_2O_4$:Eu,Dy completed by Dorenbos led to the new version of long lasting luminescence mechanism [16]. Dorenbos presented the locations of the Eu^{2+} 5d levels in the band gap of $SrAl_2O_4$ matrix. The Eu^{2+} energy levels are located right beneath the bottom of the conduction band and Dy^{3+} level is located around 0.9 eV below the conduction band. This information is consistent with the thermally stimulated luminescence measurements. In this model electron is thermally promoted from Eu^{2+} excited state to the conduction band, as the energy difference is small and therefore thermal ionization at room temperature is very probable. The electron from conduction band is trapped by Dy^{3+} thus recharging it to Dy^{2+}. Electron can be thermally released from Dy^{2+} and can contribute to forming the excited Eu^{2+}. The two possibilities for excited Eu^{2+} are – either it is again thermally ionized, either it can transit to the ground state with photon emission.

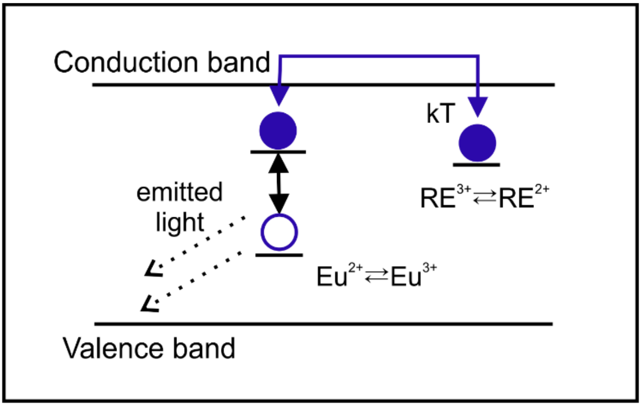

Fig. 2.5. Dorenbos model for the long lasting luminescence involving electron migration through conduction band

Based on this model Dorenbos later on also improved this version with mechanism that involves trapping and de-trapping events as part of the mechanism. This model has some problems as well – Dy or other co-dopant is needed and it would not explain the persistent luminiscence in non co-doped $SrAl_2O_4$: Eu.

2.4.5 Holsa model

Holsa turned attention to the results of XANES measurements of $SrAl_2O_4$:Eu Dy [18] and tried to observe any valence changes of dopands in the material during excitation and emission. He concluded that under excitation only the Eu^{2+}/Eu^{3+} oxidation happens, therefore proposed some changes to the known models are proposed. There is an assumption that in $SrAl_2O_4$:Eu,Dy UV radiation leads to the excitation of Eu^{2+}. The host matrix conduction band is close to the excited Eu^{2+} level therefore some electrons can escape from the excited levels of Eu^{2+} by the help of surrounding thermal energy to the conduction band. Clabau

[17] and Dorenbos [16] similarly have stated that electron from Eu^{2+} excited state is thermally transferred to conduction band. The electrons migrate through the conduction band and are eventually trapped on a defect level. The trivalent rare earth co-dopants can also act as electron traps. Thermal energy can then liberate the charge carriers from the trapping centers and they can either be de-trapped or return to luminescence center. The defects, that are claimed to be present in this material, are cation vacancies, oxygen vacancies and interstitial ions as well as the dopant ions. The cation vacancies can be created due to the evaporation of alkali earth metal oxide during the high temperature solid state reactions. Cation vacancies were involved also due to the charge compensation when a trivalent rare earth ion occupy divalent ion site in the host matrix while oxygen vacancies may be created due to the reducing atmosphere during material preparation. The introduction of oxygen and strontium vacancies as well as the Dy^{3+} ion creates electron traps essential for the persistent luminescence [18].

All of these long afterglow mechanisms involve the generation of migrating charge carriers during excitation that are localized in trapping centers afterwards. The cause of persistent afterglow is thermally stimulated gradual charge release from trapping centers with resultant recombination. The differences in these models concern (I) charge carriers – electrons or holes; (II) the charge carrier migration – does it happen through valence, or conduction band, or levels of trapping centers; (III) the excitation of luminescence - does the charge carrier directly transfers to the luminescence center or the luminescence center is excited with the aid of energy transfer process; (IV) the nature of trapping centers – intrinsic defects or co-activator.

The analysis of the results that are described in these publications show, that the most appropriate model for the explanation of $SrAl_2O_4$:Eu,Dy material is as follows: during excitation Eu^{3+} centers are created and electrons are localized in trapping centers. After the release of electrons from trapping centers they recombine with Eu^{3+}, creating the excited Eu^{2+} and a radiative Eu^{2+} transition to ground state is the cause of luminescence.

There are some shortcomings in the above described model – does the electron recombination with Eu^{3+} occur only by thermal release of electrons from trapping centers; there is no evidence if the charge state change of co-activator Dy^{3+} can or can not take place; there is absence of any data about intrinsic luminiscence of $SrAl_2O_4$ that could allow the identification of intrinsic defects.

2. Results and discussion

3.1. Methodology

For luminescence measurements at differrent temperatures two kinds of cryostats were used – liquid nitrogen cooled cryostat (working temperatures 90-450 K) and closed cycle helium cryostat (working temperature 9-300 K). For temperatures above room temperature a sample holder with heater was used. For all cases Lakeshore temperature controller was used for precise temperature logging and controlling.

The luminescence spectra as well as the luminescence kinetics and the TSL measurements were recorded with Andor Shamrock B303-I spectrograph (spectral resolution ~1nm) that is equipped with a CCD camera (Andor DU-401A-BV) at the exit port.Three different kinds of samples were preapred for this work – $SrAl_2O_4$ with Eu, Dy, $SrAl_2O_4$ with Dy and the undoped $SrAl_2O_4$ samples. All these samples were prepared with sol-gel method.

Strontium nitrate ($Sr(NO_3)_2$, purity 98%, Sigma Aldrich), aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H2O$, purity 99,6 %, VWR Prolabo Chemicals) were used as the starting materials for $SrAl_2O_4$. Urea (NH2CONH2, purity 99,5 %, Sigma Aldrich) was used as a chelating and a complexing agent. These chemicals were used without any further purification.

$Eu_2(NO_3)_3$ and $Dy(NO_3)_3$ were used for activators and were mixed with the precursor powders in order to obtain 1 mol% Eu and 1 mol% Dy concentration in the samples. The appropriate amount of $Sr(NO_3)_2$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water. After the $Sr(NO_3)_2$ and the $Al(NO_3)_3 \cdot 9H_2O$ were dissolved completely, an appropriate amount of urea was added to the solution (the molar ration of all metals ions and urea was 1:20, respectively). Also an appropriate amount of deionized water was added so the molar concentration of all metals ions in the solution would be 0.2 M. Then this mixture was heated at 90 °C until white gel was formed. When the gel consistence was obtained, then this gel was heated at 400 °C in an open oven for 2 hours for nitric oxides elimination and white powder was obtained. After synthesis, obtained sample was calcined at 1200 °C for 2 hours in reductive atmosphere and white powders were obtained [19].

The structure of all our strontium aluminate samples before and after the reducing heat treatment was characterized by X-ray powder diffraction. In the present study the PANalytical X'Pert Pro diffractometer was used for structure determaination of the syhthesized materials as well as the determination of crystallite sizes. This diffractometer is equipped with X-ray tube with Cu anode, operating at cathode voltage of 45 kV and current of 40 mA , producing Cu Kα radiation (1.5418 Å).

For the crystallite size estimation Rietveld method was used, that considers both the full width at half maximum (FWHM) of the diffraction pattern as well as the instrumental circumstances of the measurement. The estimated grain size from the XRD data was 30-50 nm.

The analysis of obtained XRD patterns of $SrAl_2O_4$ powder and the comparison of these XRD patterns with data from International Centre for Diffraction Data (ICDD) Inorganic Crystal Structure Database [00-034-0379] confirms the dominant phase of all the samples is monoclinic $SrAl_2O_4$, and content of other phases, if present, is below 10%. However in some samples traces of $SrAl_4O_7$ were present. Therefore is expected that processes responsible for luminescence of synthesized material can be mainly governed by $SrAl_2O_4$ monoclinic phase in undoped and doped samples.

3.2. Luminescence of $SrAl_2O_4$:Eu,Dy

The photoluminescence spectrum of $SrAl_2O_4$:Eu,Dy sample at room temperature as well as the afterglow spectrum of $SrAl_2O_4$:Eu,Dy is a broad band with maximum at 529 nm. The peak position and shape is in agreement with those observed by other researchers for $SrAl_2O_4$:Eu,Dy [11], thus the luminescence observed is mainly from $SrAl_2O_4$:Eu,Dy monoclinic phase and possible contribution from other phase is negligible. The luminescence center for this emission is Eu^{2+} and it emerges from the 5f-4d allowed radiative transition as stated in [10]. The green persistent luminescence afterglow of this sample can be observed for time exceeding 10 h.

The sample was cooled down to low temperatures using nitrogen cryostat for a measurement of thermally stimulated luminiescence. What was observed was quite surprising – the luminiscence afterglow intensity when cooling down the sample was still large enough to be clearly detectable. That leads to a discussion – if only thermally stimulated processes take place in the sample to ensure the persistent luminiscence – could there possibly be enough thermal energy at 90 K temperature for the charge carriers de-trapping process? That most definitely seemed like a matter worth looking into.

To begin with dealing with the above mentioned question, the long lasting luminescence for $SrAl_2O_4$:Eu,Dy was excited at three different temperatures – at RT (~295 K), 240 K and 90 K and the afterglow was observed at each of these temperatures, Fig. 3.1. When lowering the temperature of excitation, we can observe that the intensity of afterglow luminescence decreases relative to the intensity of afterglow luminescence excited at room temperature, afterglow luminescence excited at 90 K is reduced.

To compare the spectral distribution, all the afterglow spectra were normalized – it is visible that the peaks at different temperatures coincide well (inset in Fig. 3.1.) - this means that the maximum position and shapes of emission bands are very close for all three excitation temperatures. Therefore it can be stated that the luminescence center as well as its surroundings are the same at room temperature, 240 K and 90 K.

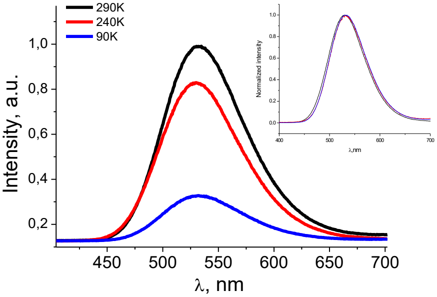

Fig. 3.1. Luminescence afterglow spectra at different temperatures. Inset – normalized luminescence spectra coincide.

The probability of thermal release of charge carriers - electrons and holes in $SrAl_2O_4$:Eu,Dy might be negligible at 90 K, as was already discussed before. This statement needed some proof. Therefore, in order to check the possible contribution of thermally stimulated processes in the afterglow, the sample was excited with X-rays to fill up traps at 10 K for 20 minutes, then heated up (2 K/min) while recording the emission spectra where, after processing the obtained data, thermally stimulated glow curve was acquired at the maximum of emission. The acquired glow curve in Fig. 3.2. shows two overlapping glow maxima within 200 – 400 K and a minor peak at around 135 K, below that temperature there are no evident peaks, meaning no thermal release of electrons (Fig. 3.2.).

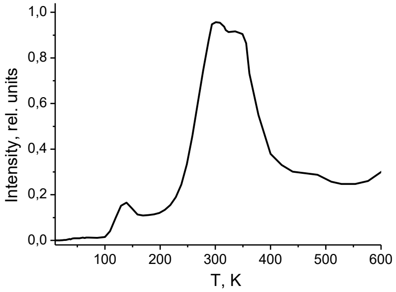

Fig. 3.2. Thermally stimulated luminescence glow curve of $SrAl_2O_4$:Eu,Dy

The luminescence spectra within glow peaks are the same as recorded for afterglow, indicating the luminescence center is Eu^{2+}. The two intense glow maxima indicate two kinds of charge carrier traps with a slight shift in activation energies for charge release relative one to another.

The estimated activation energies were around 0.52 eV and 0.59 eV. These activation energies are close to those described in [11]. Thus we can assume that the luminescence that is detected for $SrAl_2O_4$:Eu,Dy sample excited at 90 K is not due to thermally released charges recombination on luminescence center [20] - the electrons and holes in $SrAl_2O_4$:Eu,Dy at 90 K are localized at traps and do not have enough thermal energy to be released from them. Therefore it can be concluded that one of the processes that is involved in the long afterglow mechanism is electron tunneling from trap to the Eu^{3+} thus creating the excited Eu^{2+}.

Based on the results of thermally stimulated luminescence measurements and the emission spectra the author puts forward a hypothesis - in the formation of excited Eu^{2+} luminiscence center both processes are involved - 1) thermally released electron migration through conduction band that, possibly after multiple trapping-detrapping processes, returns to Eu^{3+}, creating the excited Eu^{2+}, as well as 2) electron tunneling to Eu^{3+} from closely located trapping centers, thus creating the excited Eu^{2+} also. The ratio of the contribution of these processes to the whole afterglow mechanism is temperature dependent. The study of long lasting luminescence dependence on excitation temperature [21] showed that in $SrAl_2O_4$:Eu,Dy the electron traps in proximity of Eu probably are deeper than these well separated spatially. If the electron trapping center that is associated with Eu^{3+} is slightly deeper than others, the electron life time at this trap must be longer than at shalower traps and thus it is possible that even at room temperature the last step of the process could be electron tunneling to Eu^{3+} from trapping center that is located in close proximity to the luminescence center.

The luminescence intensity dependence on time for excited luminescence centers created in tunnel processes depends on spatial distribution of defects involved and can often be described with the empirical Becquerels law [22]. This is defined by the spatial distribution of the defects involved. Therefore, the decay kinetics could give additional evidence to confirm the presence of tunneling processes in the material. For this a measurement of luminescence decay kinetics was conducted.

The luminescence decay of $SrAl_2O_4$:Eu,Dy excited at 90 K temperature can be seen in Fig. 3.3. The plot of intensity as a function of time, both in logarithmic scale, is well approximated by a straight line with the slope of approximately 1 – this result goes together well with the Becquerels law. This therefore can be considered as additional evidence to support that at 90 K the Eu^{2+} excited state formation occurs via electron tunneling. Since the tunneling of electron is independent on temperature it can take place also at a higher temperature. This process can be similar to that described by Kotomin for diffusion controlled tunneling [22].

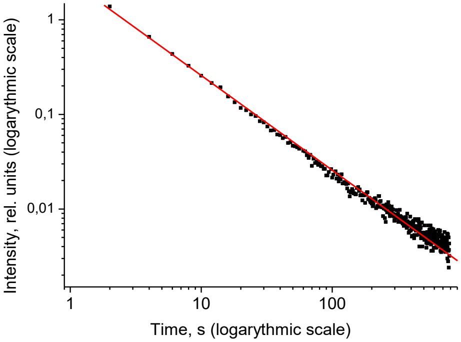

Fig. 3. 3. The decay kinetics of $SrAl_2O_4$:Eu, Dy luminescence afterglow excited at 90 K in logarithmic scale

All the above mentioned evidences leads us to suggesting some upgrade of the long afterglow mechanism models that are available in the publications. We suggest that the charge carriers are electrons and at low temperature, e.g. 90 K, the electron tunneling is dominant process in creation of excited Eu^{2+} center. In turn, at high enough temperature the electrons were released from traps. The thermally released electron during migration can be re-trapped and released multiple times. The last step of electron migration could be its direct trapping at Eu^{2+} excited state either trapping at deeper trap associated with Eu^{3+} that is followed by Eu^{2+} excited state creation via tunneling.

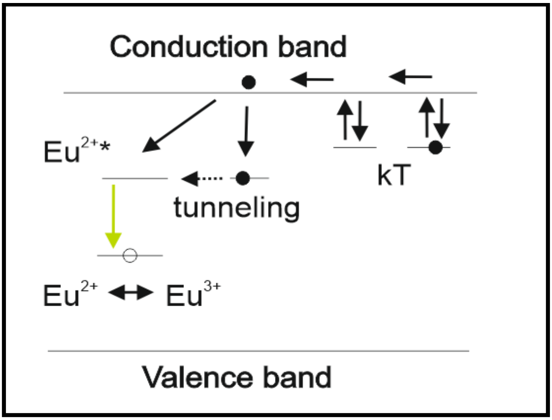

Fig. 3.4. The possible model for persistent luminescence in $SrAl_2O_4$: Eu,Dy

The radiative decay of excited Eu^{2+} centres created via both processes is the origin of observed luminescence. The scheme of proposed mechanism is in Fig. 3.4. The described mechanism is simplified as the glow curve gives strong evidence that two electron traps were involved and spatial distribution between Eu^{3+} and its associated electron traps could somewhat differ.

This discovery is actually of major importance towards the applicability of persistent luminophores in outdoor situations. The ambient air temperatures during winter time in Latvia can make this luminophore lose over 90% of its intensity in coldest times due to thermally stimulated process efficiency decrease. And that is a major drawback for the possible outdoor applications, for example, glowing roadsigns that do not work in winter would not be something that anybody would be interested in. Therefore – if it was possible to improve the ratio of temperature independant tunneling luminescence process versus the thermally stimulated process, that could improve the situation greatly.

3.3. Low temperature studies of $SrAl_2O_4$

A large number of researches of persistent phosphors have been conducted for temperature range around room temperature and above due to the possible applications of material. The studies of luminescence processes in $SrAl_2O_4$:Eu,Dy at low temperatures are not frequently found in publications as the afterglow is weak or not observed below 240 K after photoexcitation and mainly photoluminescence is investigated, turning less attention to X-ray excited afterglow. Therefore the attention was turned to the studies of low temperature luminescence in $SrAl_2O_4$ material.

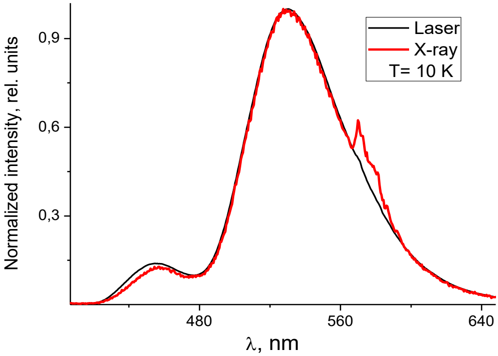

Fig. 3.5. Photoluminescence (266 nm) and X-ray excited $SrAl_2O_4$:Eu,Dy luminescence spectra at 10 K temperature

The emission spectrum of $SrAl_2O_4$:Eu,Dy at 10 K under X-ray excitation was recorded (Fig. 3.5.) and compared to the photoluminescence spectrum under 266 nm excitation at 10 K. The luminescence spectra of X-ray excited $SrAl_2O_4$:Eu,Dy reveals additional luminescence peaks overlapping with Eu^{2+} band. Literature study reveals that these additional bands could possibly be attributed to Eu^{3+} luminescence or Dy^{3+} luminescence. The three Dy^{3+} luminescence bands are mentioned in [14], whereas one Dy^{3+} band is mentioned in [23, 24]. Dy^{3+} and Eu^{3+} ions have emission peaks in relatively close positions, therefore additional experiment is needed to confirm the origin of these lines.

3.4. Luminescence of $SrAl_2O_4$:Dy

The author carried out the study of the strontium aluminate doped only with Dy to confirm the origin of emission line groups in $SrAl_2O_4$:Eu,Dy. The emission spectrum of $SrAl_2O_4$:Dy sample under X-ray excitation can be seen in Fig. 3.5.

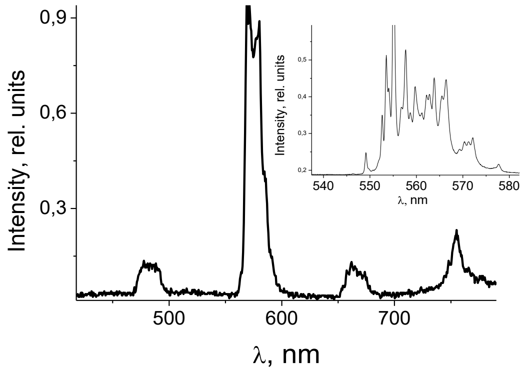

Fig. 3.5. Luminescence spectrum under X-ray excitation of $SrAl_2O_4$:Dy sample at 10 K

There are four luminescence bands centered at ~ 483 nm, 576 nm 664 nm and 754 nm. The emission bands shapes reveals a possible contribution from multiple closely located and partially overlapping lines. These lines are barely resolved at room temperature, therefore the spectrum was recorded at 10 K. The spectrum for more intense band at ~ 576 nm in higher resolution is shown in inset in Fig. 3.5, and it reveals a group of emission lines. Since the interaction of Dy^{3+} with host matrix is weak [25] the luminescence spectra of Dy^{3+} ion should be similar in a number of materials and the spectrum can be compared with luminescence of Eu^{3+} in YAG:Dy [25] and GdAlO3:Dy [26]. In these spectra, the sets of overlapping Eu^{3+} emission lines are in regions 460 – 500 nm, 550 – 610 nm and a low intensity band at 677 nm and this is very close to that observed in our experiment and the shapes of bands are similar to those recorded in our eksperiment. Based on that, one must conclude that the $SrAl_2O_4$:Dy under X-ray excitation exhibits dominantly Dy^{3+} luminescence. The comparison of luminescence spectra of $SrAl_2O_4$:Eu,Dy and $SrAl_2O_4$:Dy reveals that in luminescence spectrum of $SrAl_2O_4$:Eu,Dy the position of lines within 568 – 600 nm exactly matches the position of more intense lines in luminescence spectrum of $SrAl_2O_4$:Dy. Therefore it is shown that under X-ray excitation in $SrAl_2O_4$:Eu,Dy both – dopant Eu^{2+} and co-dopant Dy^{3+} are excited and contribute in luminescence spectrum.

It is worth noting the intensity of Dy^{3+} luminescence at RT is more than twice of that at 10 K, indicating that at 10 K only a fraction of X-ray generated electrons and holes undergoes recombination at Dy^{3+}. It can be assumed, that the other fraction of charge carriers are trapped at defects, for it confirmation the measurements of TSL were conducted (Fig 3.6).

The sample was excited by X-ray at 10 K for 20 minutes. TSL glow curve of $SrAl_2O_4$:Dy was recorded and three major glow peaks are observed at 110 K, 270 K and 532 K.

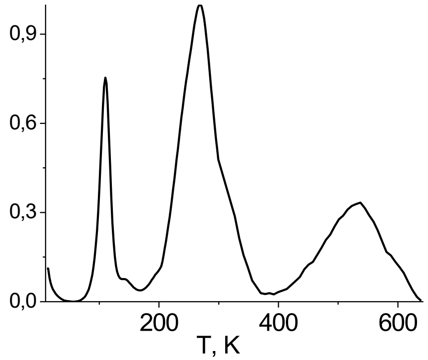

Fig. 3.6. X-ray induced TSL of $SrAl_2O_4$:Dy sample.

The luminescence spectra in all the glow peaks coincide with the emission spectrum under X-ray excitation at 10 K (Fig. 3.5), meaning that only Dy^{3+} luminescence bands were observed in TSL without the contribution from any other luminescence. There is one more thing in the TSL glow curve that requires clarification - the low temperature part of the measurement shows gradual decrease in the glow intensity within 10 – 60 K. The origin of this decrease might be a glow peak at very low temperature or creation of excited Dy^{3+} from another descending source. Therefore the time dependences of luminiscence intensity decrease at 10 K and during time interval necessary for sample heating from 10 K to 50 K were recorded. The luminescence intensity decay coincide well for both experiments – in TSL record within 10 – 50 K and time dependence of luminescence decay at 10 K and this excludes the thermostimulated process. This is evidence that there is not an additional TSL maximum in the low temperature range. Therefore, one can assume there are no shallow traps, which release charges within the temperature range 10-60 K [27]. It is important to point out the absence of glow peaks in the very low temperature range. Thus the origin of the afterglow recorded at 10 K is due to the creation of excited Dy^{3+} luminescence centers via electron tunneling. Similar afterglow revealing Eu^{2+} luminescence is observed for $SrAl_2O_4$:Eu,Dy at 10 K, indicating the same tunneling process takes place.

The thermally stimulated glow curves, if we compare the $SrAl_2O_4$:Eu,Dy and $SrAl_2O_4$:Dy sample, are different one from another, as expected, but some things are worth noting (see Fig. 3.2. and Fig. 3.6.). The TSL peak at the region 100-150 K was observed in $SrAl_2O_4$:Dy and $SrAl_2O_4$:Eu,Dy as well as in undoped $SrAl_2O_4$ (subchapter 3.6) therefore it could possibly be attributed to intrinsic defects.

It is generally accepted that during afterglow the excited Eu^{2+} center is created via Eu^{3+} recombination with electron [17]. Therefore, the glow peaks correspond to the thermal release of electrons from traps and the excited Dy^{3+} centers can appear in TSL experiment due to Dy^{4+} recombination with electrons. The electrons were trapped at host defects; possibly at distorted oxygen tetrahedra of AlO_4 [28]. These terahedrons could be distorted by the rare earth ions and this distortion is slightly different for Eu^{2+} and Dy^{3+}. This difference is responsible for a slight glow peak position shift if compared $SrAl_2O_4$:Eu,Dy and $SrAl_2O_4$:Dy. The important conditions for electron tunneling are: (I) the electron wave functions must overlap for electron initial and final state; (II) the energy of electron in initial and final state is equal. Experiments and corresponding calculations give confirmation that electron traps are located close to Eu^{3+} [20] and Dy^{4+} [28]. This suggests that wave function overlapping can take place and it is favorable for electron tunneling. The estimated energy levels for Eu and Dy ions in $SrAl_2O_4$ differ [16,17], therefore one can suggest the depth of electron traps could differ also. On the other hand it seems that initially both Eu and Dy in $SrAl_2O_4$ incorporate in charge states 3+ and the thermal treatment under reducing atmosphere leads to the formation of Eu^{2+}, but not to the reduction of Dy^{3+}. The initial incorporation of Eu^{3+} and Dy^{3+} in $SrAl_2O_4$ requires charge compensation by host defects and since the charge states of both dopants are the same, the same host defects can be created. The electron traps - distorted tetrahedra of AlO_4 - are similar, however, not identical due to different Eu^{3+} and

Dy^{3+} ion sizes and differently located energy levels of trapped electrons. The main problem for electron tunneling is the positions of energy levels of electron trap and the excited state of luminescence center. It can be noted the Eu^{2+} excitation spectrum is a complex wide band covering range from 2.76 eV up to 4,96 eV (450 nm – 250 nm), the high frequency side of this band is due to charge transfer from oxygen to Eu, the low frequency side is determined by split 4f and 5d states of Eu, therefore, in accordance with ab initio calculations for two different cation sites [4, 29] there is a number of mutually close located energy levels within ~ 1 eV interval. The study of Eu^{3+} doped YAG showed that there are 7 energy levels in the range 3.024 – 3.815 eV (with a difference of 0.79 eV) [24,30]. This suggests that the similar closely located Eu^{3+} levels could be present in $SrAl_2O_4$ as well. The excited state levels for Dy can be also splitted and cover some energy range in band gap. Therefore, if the energy of electron located at a trap is within the mentioned energy range of Eu and Dy ions energy levels, the tunneling probability is substantial.

The prior discussion leads to the conclusion that observed luminescence bands peaking at 457 nm, 526 nm and ~572 nm in afterglow spectrum for $SrAl_2O_4$:Dy and at 520 nm band for $SrAl_2O_4$:Eu, Dy at 10 K arises from decay of excited Eu^{2+} and Dy^{3+} centers created via electron tunneling from host trap to Eu^{3+} and Dy^{4+} ions [20].

Another discovery when measuring $SrAl_2O_4$:Dy emission at 10 K temperature is the afterglow of this material at 576 nm (the more intense lines of Dy^{3+} luminescence). The afterglow intensity as well as its decay kinetics are excitation duration time dependent.

The luminescence kinetics dependence on excitation time is additional evidence to the fact that during excitation accumulation of trapped charges takes place. The TSL and afterglow are strong evidences that under X-ray irradiation the Dy^{3+} ions undergo a charge state change. However, as described in [14] estimation of possible charge states of Dy in $SrAl_2O_4$ led the author of this publication to conclusion that Dy^{4+} and Dy^{2+} cannot exist in $SrAl_2O_4$. It should be pointed out that in the study of $SrAl_2O_4$:Eu,Dy under X-ray irradiation at 120 K the change of Eu^{2+} charge was observed, not any change of Dy^{3+} charge [14]. There has been a lot of discussion on this matter in literature overall and the results of our experiments are important since them strongly proves that electrons are trapped on some center that is not Dy and during irradiation by X-ray Dy^{3+} converts to Dy^{4+}.

3.5. The $SrAl_2O_4$:Eu,Dy luminescence dependence on duration of X-ray excitation

The author recorded the emission spectra of $SrAl_2O_4$:Eu,Dy under X-ray excitation and during TSL measurement as well as the afterglow spectra. The luminescence spectra of sample $SrAl_2O_4$:Eu,Dy at room temperature for different excitation time are shown in Fig. 3.7. The spectra reveal the intense Eu^{2+} luminescence band peaking at 526 nm, and three Dy^{3+} luminescence bands peaking at 576 nm, 664 nm, 754 nm. The Dy lines are not visible in photoluminescence spectrum. The Dy^{3+} band peaking at 483 nm is not resolved due to overlapping with intense and a wide Eu^{2+} luminescence band. The shape of the spectrum changes during excitation and this could be due to gradual filling of traps by charge carriers. The luminescence intensity dependence on excitation time for several excitation intensities of X-Ray were recorded at RT and was observed that Eu^{2+} luminescence intensity saturation is delayed relative to the beginning of excitation.

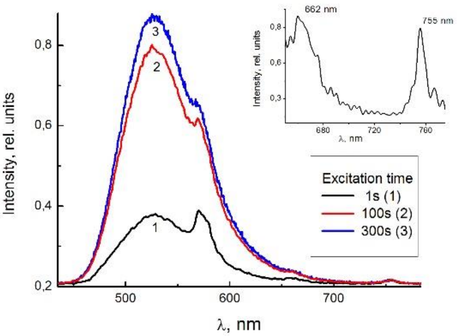

Fig. 3.7. Luminescence spectra of $SrAl_2O_4$:Eu,Dy for different excitation duration at room temperature. Inset the 630 – 800 nm range in extended scale

The analysis of luminescence spectra in Fig. 3.7. allowed to estimate that the changes of Dy^{3+} luminescence intensity during excitation are opposite to that observed for Eu^{2+} luminescence. The reason of this change is yet unclear and additional investigation is necessary. However, the results are evidence that traps filling affect the Dy^{3+} excitation, possibly these electron traps could be somewhat associated with Dy [28].

3.6. Luminescence of undoped $SrAl_2O_4$

Intentionally undoped $SrAl_2O_4$ luminescence spectra at different temperatures were recorded. Fig. 3.8. shows photoluminescence spectra of the undoped sample under two different wavelengths of laser excitation at 10 K temperature.

Although the luminescence is not strong, there is a clearly distinguishable wide asymmetrical shape band that can be decomposed to two bands peaking at 2.32 eV and 2.8 eV (534 and 442 nm) under 219 nm excitation and a 652 nm narrow peak under 311 nm excitation. This narrow line probably is emission from Mn^{4+} since in [31] is shown that these transient metal ions in $SrAl_2O_4$ polymorphs are responsible for lines within 652-657 nm and Mn is known as trace element in aluminum. As mentioned in [31], traces of transition metals are present even in material that has been synthesized from high purity grade precursor materials.

In search of the defects that are responsible for bands at 534 nm and 442 nm, the available information on defect luminescence in Al_2O_3 was checked. The luminescence of F– centers in pure α - Al_2O_3 is at ~440 nm (2.8 eV) [32], in turn the luminescence of F_2– centers is at 517 nm (2.4 eV) [33]. Important is to note that the F_2– centers luminescence band position is found to be very close, even the same in both α - Al_2O_3 and γ - Al_2O_3 showing weak influence from the structure. There is a strong possibility, that in the $SrAl_2O_4$ material these defects might be present as well and the F– centers and F_2– centers could be responsible for luminescence bands peaking at 442 nm and 534 nm.

The photoluminescence intensity at RT is low and equipment used was not sensitive enough for spectrum recording.

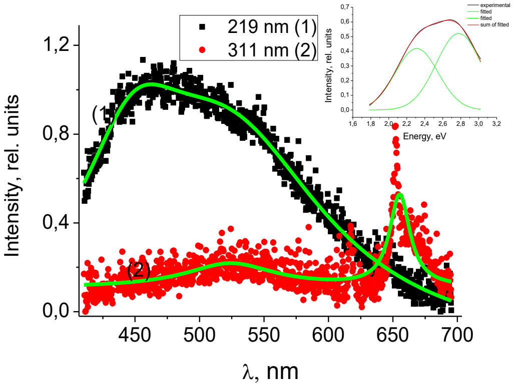

Fig. 3.8. Photoluminescence spectra of undoped $SrAl_2O_4$ at 10 K under different excitation wavelengths. Inset – fitted two peaks

The excitation spectrum of photoluminescence (Fig. 3.9.) shows excitation energies within 3.8 – 5.9 eV (~ 330 – 210 nm). These energies are well below the band gap of $SrAl_2O_4$ matrix. The band gap of $SrAl_2O_4$ is estimated to be around 6.5 eV [6], meaning that under laser excitation electron – hole pairs over the band gap were not created – therefore one can assume the presence of some defect levels in the band gap. Our equipment limits photoluminescence excitation spectra recording at wavelengths above 340 nm.

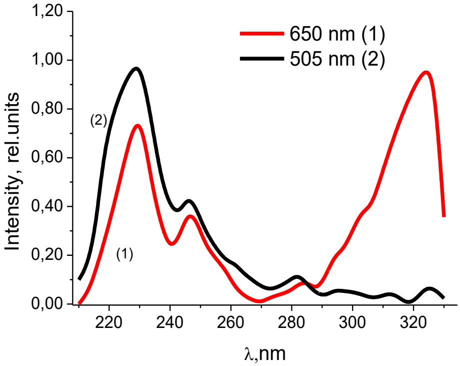

Fig. 3.9. Excitation spectra in two maxima of undoped $SrAl_2O_4$ emission

The 652 nm narrow band luminescence excitation peak close to the 325 nm could be related to Mn^{4+} excitation [31]. The two excitation peaks at ~230 nm and ~ 246 nm are common for the broad luminescence band at 500 nm and for the narrow band at 652 nm. Since the F– centers are probably responsible for the broad band luminescence and Mn^{4+} - for the narrow band at 652 nm, the same excitation bands for both exclude the direct excitation of these centers, it can be assumed that energy transfer takes place. The possible hypothesis would be as follows. The initial step of excitation could be the charge transfer between oxygen and F– or F_2– center (excitation band peaking at ~229 nm), similar to that described for α-Al_2O_3 by Surdo et. al [32]. The other excitation band peaking at ~246 nm possibly is of the same nature, since both F– and F_2– centers could be involved. The step where energy is transferred to Mn^{4+} needs a separate study. Therefore the photoluminescence spectra and corresponding excitation spectra show the intrinsic defects and trace impurity is present in $SrAl_2O_4$ sample. It will be noted the F- type centers can act as electron traps, however the F- center interaction with hole followed by F^+-formation could not be excluded. It is proposed the intrinsic defects are presented in rare earth doped $SrAl_2O_4$ also and incorporation of Eu^{3+} as well as followed reduction to Eu^{2+} can strongly depend on presence of F type centers.

The excitation of undoped $SrAl_2O_4$ by 219 nm and 311 nm result in different luminescence spectra (Fig. 3.9.) The main differences are in the longer wavelength region of the spectra and in the luminescence intensity. In turn, under X-ray irradiation the luminescence spectrum at 10 K is more intense than that of photoluminescence and it was possible record the spectra at different temperatures (Fig. 3.10.). There are clearly distinguishable maxima at 442 and 534 nm (similar that those in photoluminescence under laser excitation of 266 nm). These luminescence bands decrease in intensity due to thermal quenching at RT. The wide and intense luminescence band at low temperatures was recorded within 650 nm – 900 nm. This band quenches at RT; however, above 150 K a narrow band at 692 nm and a side band at 713 nm are revealed. The relative narrow luminescence bands of Cr^{3+} are known to be within 650 – 850 nm for several aluminates as well as for Al_2O_4. Therefore the narrow bands recorded at 692 nm and 713 nm under X-ray irradiation are due to spin-forbidden ^2E – $^4A_2$ transition in Cr^{3+}, at low temperature these narrow bands are strongly overlapped with more intense 790 nm band. The Cr usually present in aluminum, therefore Cr can be incorporated in $SrAl_2O_4$ from $Al(NO_3)_3 \cdot 9H_2O$ that is used as the raw material in synthesis. The 790 nm band might also be attributed to Cr luminescence and this consideration is based on fact that in alkaline earth aluminate crystals Cr^{3+} ion substitutes two different crystallographic sites, that were already mentioned, if substituting for Sr^{2+} [34], and can substitute Al^{3+} as well, because the ionic radii of all the ions are quite similar. Therefore the X – ray excited luminescence confirms the presence of intrinsic defects responsible for overlapping bands between ~350 – 600 nm as well as presence of trace impurities in undoped $SrAl_2O_4$.

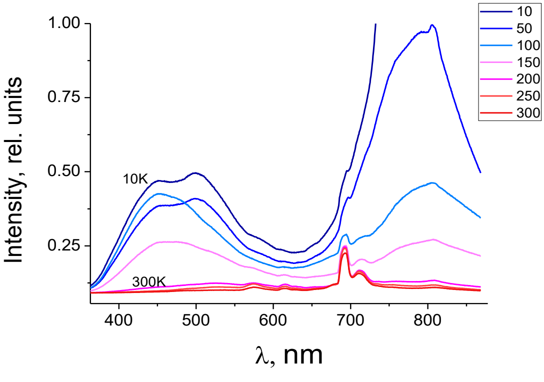

Fig. 3.10. X-ray induced luminescence of undoped $SrAl_2O_4$ at different temperatures (10-300 K).

The electron – hole pairs were created in $SrAl_2O_4$ under X – ray irradiation and at low temperatures these charge carriers could be trapped, thus the TSL measurements were conducted. The TSL curves show a well resolved maximum at 100 K, that appears also in the $SrAl_2O_4$: Eu,Dy and $SrAl_2O_4$:Dy material, although it is shifted to ~135 K in $SrAl_2O_4$:Eu,Dy. This can be attributed to the electrons release from intrinsic defects of the $SrAl_2O_4$ crystal. The weak glow peak was at ~260 K, at the same temperature the glow peak is in the rare earth doped $SrAl_2O_4$ [27]. The third well resolved peak is located above RT at around 400 K. This is also visible in the Eu and Dy doped material [27], although this peak is slightly shifted to lower temperatures when adding the dopants. As glow peaks at the similar temperatures were observed in rare earth doped and undoped $SrAl_2O_4$, we would like to state that the defects that act as trapping centers in the long lasting luminescence of $SrAl_2O_4$:Eu,Dy are intrinsic defects nearby to dopant, not the dopant impurities directly. The Dy co-doping clearly shifts the TSL peak at 400 K to lower temperature [27], suggesting that intrinsic defects could be perturbed by dopant or by trace impurities, thus contributing to more intensive afterglow.

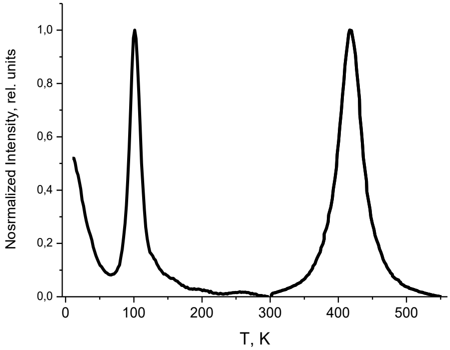

Fig. 3.11. TSL measurement for undoped $SrAl_2O_4$ at 790 nm (two measurements: 10-300 K and 300-700 K)

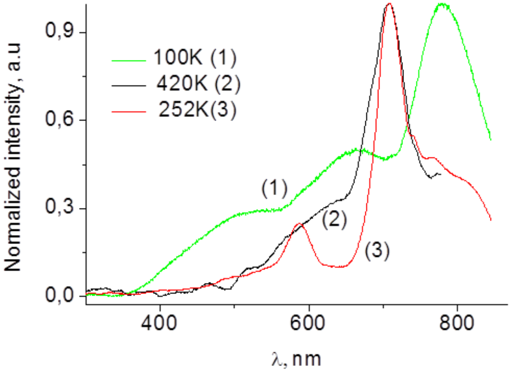

Fig. 3.12. Luminescence spectra undoped $SrAl_2O_4$ during TSL measurement at 100, 252 and 420 K.

Also, it is possible to see that the 790 nm peak exhibits an afterglow at low temperatures (Fig. 3.11.). It has already been stated in this work beforehand that tunneling luminescence is present in $SrAl_2O_4$ and this afterglow of Cr^{3+} might also be related to creation of excited Cr^{3+} via electron tunneling [19].

The luminescence spectra within glow peaks at 100, 252 and 420K (Fig. 3.12.), are different, however all of them can be explained with Cr and intrinsic defect luminescence. The spectrum recorded within 100 K glow peak reveals three broad luminescence bands peaking at 780 nm, 660 nm and around 500 nm. The long wavelength band is from Cr^{3+} spin-allowed transition $^4T_2 – ^4A_2$ and the band at ~660 nm might be due to Cr^{3+} $^4T_2 – ^4A_1$ transition, however other origin of this band cannot be excluded. The luminescence band peaking around 500 nm seems complex one however a good deconvolution on the components was not possible due to the strong overlaping with the 660 nm band. As the luminescence band around 500 nm covers the same spectral range as X-ray induced luminescence bands of F– and F_2– centers, it could be that luminescence band around 500 nm is emerging from F– type centers. The support for this assumption is that F– centers luminescence was not quenched at 100 K.

Within glow curve peaking at 252 K the before mentioned narrow Cr^{3+} luminescence bands are also dominant. The origin of luminescence band peaking at ~ 590 nm is unclear. Thus the narrow Cr^{3+} bands in TSL spectra above 150 K are dominant and origin of this luminescence is the electron recombination with Cr^{4+}. The spectrum within glow curve above RT (420 K) shows similar features as the 252 K spectrum – with the Cr^{3+} emission as the dominant peak.

To summarize – the spectral measurements of undoped $SrAl_2O_4$ material under X-ray excitation up to RT show a clearly distinguishable luminescence. The luminescence of undoped $SrAl_2O_4$ consists of two main parts – trace impurity metals, namely, Mn^{4+} and Cr^{3+} luminescence, and luminescence of intrinsic defects – F- centers and F_2- centers. There is a strong possibility, that in the rare earth doped $SrAl_2O_4$ material these defects might be present as well and we propose that the presence of these defects is stimulating the Eu^{3+} ion incorporation. TSL shows two strong glow peaks – a peak under RT at around 100 K, emerging from intrinsic defects of the $SrAl_2O_4$ crystal and this peak also present in the doped materials, as well as a peak above RT at ~420 K, that might be attributed to the defects perturbed by trace impurities, and it is also present in the doped material, but its position depends on the dopant incorporated.

3. Conclusions

The study of luminescence of $SrAl_2O_4$, $SrAl_2O_4$:Dy and $SrAl_2O_4$:Eu,Dy was conducted at different temperatures under photoexcitation as well as under X-ray excitation. The analysis of results obtained allows draw out the following conclusions.

1. The luminescence spectra for $SrAl_2O_4$: Eu, Dy excited at room temperature, 90 K and 10 K are alike - this indicates the luminescence center and its surroundings are the same at all temperatures studied.
2. The absence of glow maxima in $SrAl_2O_4$:Eu,Dy within the temperature range 10 – 50 K in thermally stimulated luminescence is strong evidence that electrons and holes are localized in traps and the origin of observed Eu, Dy and Cr ions afterglow luminescence within this temperature range is creation of excited corresponding ions via electron tunneling process. This process is dominant within the low temperature range.
3. The thermally released charge migration is involved in excited Eu^{2+} creation at higher temperatures and it is possible the tunneling of electron could be the last step of process even at higher temperature. The possible scheme is presented for mechanism responsible for long lasting luminescence: thermally released electron during migration can be multifold trapped and released. The last step of electron migration could be its direct trapping at Eu^{2+} excited state either trapping at deeper trap associated with Eu^{3+} and followed by excited Eu^{2+} creation via tunneling. The radiative decay of this excited Eu^{2+} is the origin of persistent luminescence.
4. The line groups visible under X-ray excitation in $SrAl_2O_4$:Eu, Dy material along with the typical Eu^{2+} broad emission band are attributed to Dy^{3+} luminescence.
5. Both Eu and Dy luminescence peaks are observed in the afterglow and within glow curves of TSL measurement. Based on TSL and time resolved spectral measurements it is concluded, that under X-ray irradiation Eu^{2+} and Dy^{3+} serve as hole traps and the Eu^{3+} as well as Dy^{4+} are accumulated. Electron traps are located relative to Eu^{3+} and Dy^{4+} in such way, that electron tunneling probability is substantial.
6. The afterglow in low temperatures, TSL measurements and the charging of luminescence intensity imply that electron tunneling is present in both $SrAl_2O_4$:Eu,Dy and $SrAl_2O_4$:Dy, and luminescence afterglow at 10 K arises from decay of excited Eu^{2+} and Dy^{3+} centers created via electron tunneling from host trap to Eu^{3+} and Dy^{4+} ions.
7. The undoped $SrAl_2O_4$ material exhibits clearly distinguishable luminescence under X-ray excitation up to room temperature. The luminescence of undoped $SrAl_2O_4$ consists of two main parts – trace impurity metals, namely, Mn^{4+} and

Cr^{3+} luminescence, and intrinsic defects luminescence – F- centers and F_2-centers. The intensities of broad bands of F-centers luminescence are low at room temperature due to partial quenching and therefore the narrow luminescence bands of Cr^{3+} are dominant. There is a strong possibility that these defects in the undoped $SrAl_2O_4$ material might be present in the rare earth doped $SrAl_2O_4$ as well and the author proposes that the presence of these defects is stimulating the Eu^{3+} ion incorporation.

8. TSL shows two strong glow peaks – a peak at ~ 100 K, emerging from intrinsic defects of the $SrAl_2O_4$ crystal and this peak, although shifted, is also presented in the doped materials, as well as a peak above RT at ~ 420 K, that might be attributed to the defects perturbed by trace impurities, and it is also present in the doped material, but the peak position depends on the dopant incorporated.

4. Thesis

1. The excited Eu^{2+} luminescence centers can be created in $SrAl_2O_4$:Eu,Dy via electron tunneling from a trap to Eu^{3+}. This led to the improvement of mechanisms stated in scientific publications for $SrAl_2O_4$:Eu,Dy persistent luminescence.

The new proposition is: thermally released electron during migration can be multifold trapped and released. The last step of electron migration could be its direct trapping at Eu^{2+} excited state either trapping at deeper trap associated with Eu^{3+} and followed by Eu^{2+} excited state creation via tunneling. The radiative decay of this state is origin of persistent luminescence.

2. Under X-ray irradiation Eu^{2+} and Dy^{3+} serve as hole traps and the Eu^{3+} as well as Dy^{4+} are accumulated. Electron traps are located relative to Eu^{3+} and Dy^{4+} in such way, that electron tunneling probability is substantial.

Luminescence afterglow at 10 K arises from decay of excited Eu^{2+} and Dy^{3+} centers created via electron tunneling from host trap to Eu^{3+} and Dy^{4+} ions.

3. The undoped $SrAl_2O_4$ material exhibits clearly distinguishable luminescence under X-ray excitation up to room temperature. The luminescence of intentionally undoped $SrAl_2O_4$ consists of two main parts – trace impurity metals, namely, Mn^{4+} and Cr^{3+} luminescence, and intrinsic defects luminescence: F - centers and F_2 – centers.

The experimental data and scientific proof of thesis 1. has been published in [20].
The experimental data and scientific proof of thesis 2. has been published in [27].
The experimental data and scientific proof of thesis 3. has been published in [19].

5. List of conferences and publications

6.1. Publications in chronological order

- **Vitola V.**, Millers D., Smits K., Bite I., Zolotarjovs A. The search for defects in undoped $SrAl_2O_4$ material, Optical Materials 87 (2019), 48-52.
- Bite I., Krieke G., Zolotarjovs A., Laganovska K., **Liepina V**., Smits K., Grigorjeva L., Millers D., Skuja L. Novel Method of Phosphorescent Strontium Aluminate Coating Preparation on Aluminium Materials and Design 160 (2018), 794 – 802 .
- **Liepina V**., Millers D., Smits K., Zolotarjovs A. X-ray excited luminescence of $SrAl_2O_4$:Eu,Dy at low temperatures, Journal of Physics and Chemistry of Solids, 115 (2018), 381-385.
- **Liepina V**., Millers D., Smits K. Tunneling luminescence in long lasting afterglow of $SrAl_2O_4$:Eu,Dy, Journal of Luminescence, 185 (2017).
- **Liepina V**., Smits K., Millers D., Grigorjeva L., Monty C. The luminescent properties of persistent strontium aluminate phosphor prepared by solar induced solid state synthesis, IOP Conference Series Materials Science and Engineering (2012).

6.2. International conferences in chronological order

- Search for defects in $SrAl_2O_4$:Eu,Dy material, Vitola Virginija, Millers D, Smits K, Zolotarjovs A, Bite I, International Conference Functional materials and nanotechnologies, 2018, October 2 -5, Riga, Latvia.
- X-ray excited luminescence of $SrAl_2O_4$:Eu,Dy at low temperatures, Vitola Virginija, Millers D, Smits K, Zolotarjovs A, 7th International workshop on Photoluminescence in Rare Earths: Photonic Materials and Devices, 2017, November 30 – December 2, Rome, Italia (oral presentation).
- Low temperature luminescence studies in $SrAl_2O_4$:Eu,Dy, Vitola Virginija, Millers D, Smits K, Zolotarjovs A, Functional Materials and nanotechnologies 2017, April 24 – 27, Tartu, Estonia (oral presentation).
- Tunnelling luminescence studies in $SrAl_2O_4$:Eu,Dy, Vitola Virginija, Millers D, Smits K, Zolotarjovs A, International Young Scientists Conference Developments in Optics and Communications 2017, April 6 - 7, Riga, Latvia.
- The luminescent properties of persistent strontium aluminate phosphor prepared by solar induced solid state synthesis, Liepina Virginija, K.Smits, L.Grigorjeva, D.Millers, C. Monty, International Conference Functional Materials and nanotechnologies 2012, April 17 - 20, Riga, Latvia.

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