Recent progress in understanding the persistent luminescence in SrAl$_2$O$_4$:Eu,Dy

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ABSTRACT

Ever since the discovery of SrAl$_2$O$_4$:Eu,Dy persistent afterglow material, that can intensively glow up to 20 h, the mechanism of long-lasting luminescence has been a popular area of research. The research is focused on discovering the mechanism of persistent luminescence in order to prolong the duration and intensity of afterglow in a controlled way. Although most researchers agree on the general things, there are still many unclarities and ambiguities to discuss upon. This review paper briefly sketches in the highlights of past research on the luminescence mechanism in SrAl$_2$O$_4$:Eu,Dy, mainly focusing on the research conducted in the past decade dedicated to clearing these ambiguities. This paper provides an overview of the latest persistent luminescence mechanisms offered by researchers.

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 alumi-nates. Recently multiple unexplored fields of applica-tion 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 electrolytic oxi-dation coatings for protection and decoration [1]. A very intriguing application in persistent luminophores is the in-vivo medical imaging using luminescent nanoparticles [2–4].

The most commonly commercially used material for persistent luminescence applications is SrAl$_2$O$_4$:Eu,Dy. This material, if compared to others, is superior with its luminescence lifetime that greatly exceeds that of any other material known to date (over 20 h). The material is chemically stable, exhibits excellent photoresistance and a very bright afterglow [3]. Therefore, it is also widely studied. The knowledge of the processes contin-uing in the material is essential to improve the optical properties of the long-lasting aluminate luminophores for different applications. However, details of these pro-cesses are not clear, especially the nature and role of defects involved. Researchers are interested in study of defects that are involved in the luminescence process and the possibilities to control them in the process of synthesis in order to obtain the longest afterglow and good thermal stability The scientific literature about the luminescence processes continuing 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. This article highlights the latest discussions about the persistent luminescence mechanism in strontium aluminates.

SrAl$_2$O$_4$ as a host material

The long-lasting luminescence was an incompletely studied subject until the 1990s, although there were sev-eral luminescent materials known and used for multiple applications, such as glow in the dark watch dials and toys. For commercial applications mostly zinc sulphide with copper doping was used and, to achieve longer luminescence lifetimes and higher afterglow intensi-ties, they were sometimes co-doped with radioactive elements [5]. The era of intense long-lasting lumines-cent material research began with the discovery of SrAl$_2$O$_4$ doped with Eu. That was a great discovery, as the afterglow time and intensity exceeded the known compounds greatly. Not long after this discovery an improvement was made – by SrAl$_2$O$_4$:Eu co-doping with dysprosium, the already intensive and lengthy afterglow was enhanced even more and now could reach more than 10 h [6]. With this, the study of Eu activated alkaline earth materials and other compounds began – adding different aluminates, silicates and phos-phates to the list of persistent phosphors [7–11]. They all share the same blue–green emission colour, as they

all contain Eu^{2+} as the luminescence centre. Other emission colours are much less frequent, although there are a few materials that are non-Eu doped, but the afterglow time is significantly smaller [12,13]. The overall conclusion is that the number of known efficient compounds that exhibit a long-lasting afterglow is still quite low and $SrAl_2O_4$:Eu,Dy is still one of the best persistent luminescent materials that is available, judging by the afterglow duration and intensity.

Several strontium aluminate compounds is known. The $SrAl_2O_4$ is a stable compound 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°C and back to monoclinic at the same temperature during cooling [14]. $SrAl_2O_4$ has a tridymite structure constructed by corner-sharing AlO_4 tetrahedra that are tilted with respect to each other [15]. The occupation of Al^{3+} ions in the oxygen tetrahedra of the compound leaves a charge deficiency 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 tridymite 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 [16] (Figure 1).

The two crystallographically different sites for Sr^{2+} have different coordination numbers (i.e. 6 + 1), sim-ilar average Sr-O distances (i.e. 2.695 and 2.667 Å), but slightly different in individual Sr-O distances [18]. The two environments differ by a slight distortion of their 'square planes' [19]. When doping with Eu ions, it incorporates in the position of Sr ion [18,19].

The Sr^{2+} and Eu^{2+} ions are very similar in their ionic size [20] (1.21 and 1.20 Å, respectively) and the presence of Sr(I) and Sr(II) sites (6 and 7 coordinated) results in different symmetry and orientation around incorporated in these sites Eu ion leading to deviations in the luminescent properties for both sites.

It is also important to note the dopant incorporation in the matrix, as lattice disorders and substitutional ions introd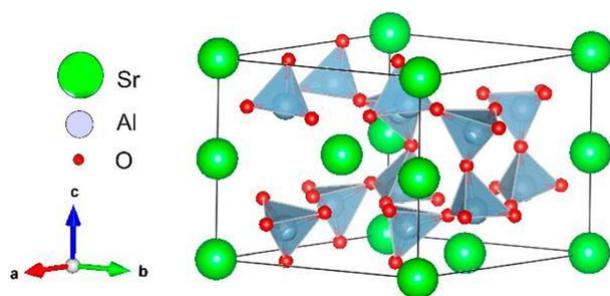uce localised states in the host matrix band gap by interrupting the long-range symmetry of the material. The examples of lattice imperfections in $SrAl_2O_4$ are:

- Sr vacancy (VSr) – 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 centre itself or attract some other defect for charge compensation
- Oxygen vacancy (VO) – 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 cen-tre itself or attract some other defect for charge compensation

There are other possibilities, like interstitial or substi-tutional ions, that can either be trapping centres them-selves or attract other defects for charge compensation. For example – if a Dy^{3+} would replace a Sr^{2+} ion, there would be 1+ charge incompatibility. This would either act as an electron trap or these defects could cooperate – 2 Dy^{3+} ions could need 3 sites of Sr^{2+} ions. The pos-sibility to trap an electron would also be dependent on the reduction and oxidation potential of the ion, as well as on the trapped electron energy level position in the host.

We have to note that the method of synthesis, concentration of dopants and the reductive atmosphere are very important factors in determining the creation of defects. Reduction of Eu^{2+} leads to the creation of oxygen vacancies and possibly some lattice distortions, excess Dy could lead to byproduct $DyAlO_3$ creation [21], the heating rate, boric acid content as well as other synthesis parameters can lead to a different amount of aggregation [22,23].

The dopant incorporation (Eu and Dy ions or dif-ferent) in different sites of the $SrAl_2O_4$ host is usu-ally determined by the ionic radii of the dopants and the host lattice components. From the literature it is known that the radii of the $SrAl_2O_4$ components and the dopants are as follows – see Table 1.

The information given in Table 1 gives ground to state that Eu^{2+}, Eu^{3+} and Dy^{3+} are very likely to be found in Sr^{2+} positions. This is also confirmed by EPR measurements in [19]. If we were to consider the two possible sites of Sr^{2+}, we could estimate that they are quite similar crystallographically [24] – therefore the dopant ions could be expected to occupy the sites more or less equally. EPR measurements confirm this state-ment in [19].

Also, one could note that Sr^{2+} and Eu^{2+} ions have really very close ionic radii. This can be used to explain the reason that Eu^{3+} ions incorporated in the Sr^{2+}

Figure 1. The crystal structure of $SrAl_2O_4$, drawn with VESTA [17].

Table 1. ionic radii of the $SrAl_2O_4$ and the dopants.

Ion	Ionic radius, A	Ion	Ionic radius, A
Eu^{2+}	1.2	Sr^{2+}	1.18
Eu^{3+}	0.95	Al^{3+}	0.53
Dy^{3+}	0.91	O^{2-}	1.4

sites of $SrAl_2O_4$ can be reduced to Eu^{2+} without any problems [19].

Clabau in an article [19] reports that the formation of by products $Sr_3Al_2O_6$ during the synthesis of $SrAl_2O_4$ as well as the thermoluminescence measurements indicate that $SrAl_2O_4$ tends to have strontium vacancies and oxygen vacancies due to the requirement of charge neutrality. Aluminium vacancies might exist as well, but would be energetically unfavourable to form because the Al–O bonds are short and strong. Owing to the requirement of charge neutrality and the absence of oxygen in the synthesis atmosphere, the co-doping with Dy^{3+} should enhance the cation deficiency [19].

The generally accepted opinion is that Eu^{2+} and Dy^{3+} ions substitute for Sr^{2+} in both sites. The additional Sr vacancies are introduced for excess charge compensation of incorporated trivalent ions. The unan-swered question is – what happens when Eu^{3+} is reduced? We know for sure, that before reduction Eu incorporates in the matrix in the trivalent form and the reduction leads to the formation of coexisting Eu^{2+} and Eu^{3+} species as well as some additional defects that are involved in the afterglow mechanism [25], but this matter still needs thorough research.

Role of lanthanides in long-lasting luminescence materials

Lanthanide ions, either in a divalent, trivalent, or, more rarely, tetravalent state, take a very important place among luminescence centres in crystalline phosphors – both long lasting and also fast fading luminescence have wide applications, for example, the Nd^{3+} narrow line of $4f^2 5d – 4f^3$ emission in laser crystals [26], $4f^7 5d^1 - 4f^8$ line transition of Tb^{3+} is used as one of the components for tube lighting [27], etc. Lanthanides are commonly referred to as rare earth activators, although several of them are not very rare. There are two types of lan-thanide luminescent transitions that might be of inter-est. Transitions between $4f^n$ levels are quite invariant in different compounds, and due to this invariance usually are observed as quite sharp and line-like absorption as well as emission. 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 absorption and emission spectra in different matrices [28]. The interesting properties of lanthanide ions arise from the fact that they possess a partially filled 4f shell that is shielded from the impact of crystal field of the host by outer shell electrons.

For real-life applications the colour of emission as well as the quantum efficiency and the thermal stability of the process play a crucial role. All these factors are closely related to the relative and absolute location of the lanthanide energy levels. For example, the position of the host-sensitive lowest 5d state relative to the host-invariant 4f states is important for the luminescence colour of the obtained strontium aluminate phosphor [18]. The absolute position of the 4f and 5d states relative to valence band and conduction band states also affects luminescence quenching and charge-trapping phenomena [29]. For example, if we talk about the possibility of trapped charge to be thermally released from a trapping centre, the energetical position of the trapping centre plays a crucial role. The approach for estimation of rare-earth ion levels positions in the host band scheme is presented in a number of articles by P. Dorenbos [29–31]. The main idea of this approach is that, if the positions of ground state and excited state levels are known for one rare-earth ion, then the positions of these levels can be estimated in the same host for any other rare-earth ion.

As for $SrAl_2O_4$:Eu,Dy, we are looking at the case of Eu^{2+}, that acts as a luminescence centre and its luminescent $4f^6 5d^1 \rightarrow 4f^7$ transition [31,32]. 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 [33–39]. The energetical displacement of an electron filled 5d level of Eu depends strongly on the configuration of its surroundings. The 5d – 4f transi-tions of rare-earth ions depends greatly on the sym-metry, coordination, covalence, bond length, site size and crystal field strength in which they reside, making it possible to tune the excitation and emission wave-length over a wide range by varying the composition and local crystal structure [39]. It is quite safe to say that exactly Eu^{2+} is playing the role of luminescence centre and the f-d transition is being shifted in dif-ferent crystal fields while still maintaining its shape, as it can be observed in Figure 2. The reasoning for this assertion is that this luminescence disappears in samples without Eu doping, the normalised lumines-cence bands have almost identical shapes – only the maximum position shifts due to differences in crys-tal field in different materials [39–41]. For example, Chernov et al. [42] reports, that the different crystalline
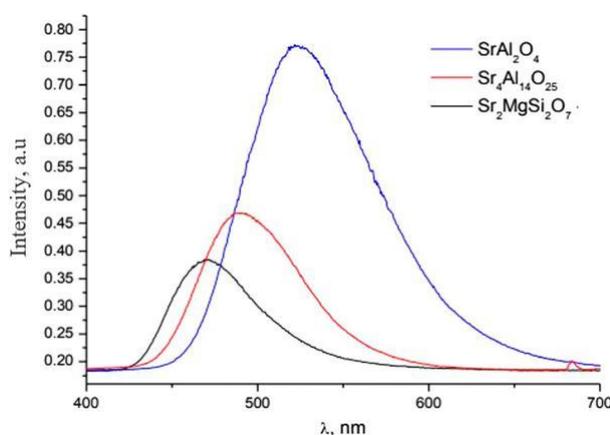

Figure 2. Eu^{2+} emission in different compounds.

structure of the hosts, orthorhombic for the case of $Sr_4Al_{14}O_{25}$ and monoclinic for $SrAl_2O_4$, gives rise to different crystallographic strontium sites for $SrAl_2O_4$ and $Sr_4Al_{14}O_{25}$ responsible for the Eu^{2+} $4f^6 5d^1 \rightarrow 4f^7$ emission and for the observed emission shifting to the shorter wavelengths. Zhang et al. [43] attribute this change in crystal structure and resultant shifting of emission maximum to the increase in the Al/Sr ratio. The size of the obtained particles can also contribute to the local crystal field of the luminescence centre, thus slightly shifting the maxima [44–46].

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, mak-ing the duration of afterglow much longer and much more intensive. The afterglow is present also without the Dy^{3+} co-doping [47]. Other rare earths have been used as co-activators as well, for example, Nd^{3+} [42] and Tm^{3+} [48]. This is the reason we can be sure to say that the luminescence centre in these compounds is Eu^{2+}, but Dy^{3+} somehow contributes to the trapping centres of the material. In the work of Rezende et al. [25] it is proposed, that the co-dopant ion can also influence the $[Eu^{2+}]/[Eu^{3+}]$ ratio obtained after the reduction process therefore stating that the co-dopants play an important role in the stabilisation of either of the Eu valences in the samples.

The photoluminescence that is characteristic to the trivalent rare earth co-activators in most cases is not observed, leading to a conclusion that direct excita-tion of trivalent rare earth is not involved, and nor is the energy transfer from Eu^{2+} to the trivalent rare earth. However, there are authors who claim to have observed photoluminescence of Dy^{3+} [49], however some authors claim to observe Dy^{3+} lines only in radi-oluminescence spectrum [50,51]. This indicates that maybe traces of Dy luminescence are present also in the $SrAl_2O_4:Eu^{2+},Dy^{3+}$ material, just hidden under the bright emission of Eu^{2+} and could be observed at different dopant concentrations. All these assertions do not lead to a clear answer about the Dy^{3+} role in the material.

Persistent luminescence models

Historical view

During these more than 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 a lack of full under-standing 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 are often based on trial and error methods.

The main models for long afterglow phosphors, that have been discussed until 2010 and their evolution is very briefly described in subchapters below, because, although it has been discussed also in previous research and review articles [18,52–54], the understanding of different possible mechanisms and the proof for or against them is crucial for the research conducted in recent past as well as the reader.

Matsuzawa model

The search for the mechanism began with the Mat-suzawa (the original patent of persistent luminescence in $SrAl_2O_4:Eu,Dy$) model [55]. In this publication, the long-lasting luminescence of $SrAl_2O_4:Eu,Dy$ with a model where Eu^+ ions are created during excitation is explained. The hole from Eu^{2+} is transferred to valence band (in other words, an electron from valence band is lifted to Eu^{2+}) and Eu^+ is created. Holes are then localised on Dy, that acts as a trapping centre, recharg-ing it to Dy^{4+}, and afterglow is determined by the thermal release of holes from the trapping centres and the following migration and recombination (Figure 3). The essence of the mechanism lays in the presumption that Eu^{2+} excitation is followed by hole delocalisation 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 release of a photon. The scheme of mechanism proposed by Matsuzawa is in Figure 3.

Aitasalo models

It was clear that Matsuzawa model needed improve-ments due to some physical inaccuracies, for example, the creation of Eu^+, that is energetically unfavourable. Aitasalo team consecutively proposed several con-sequent models for the long afterglow, by adding improvements to his previous works.

In this mechanism, it was assumed that under excitation the holes in valence band are created and the electron is localised at a trap level located within the band gap. The holes created are considered to be
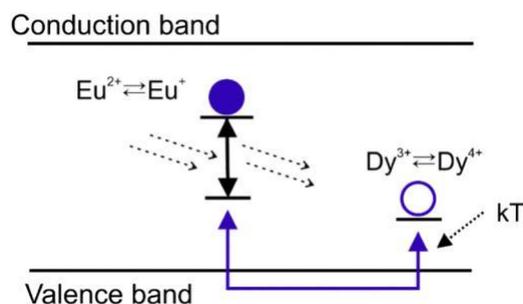

Figure 3. The Matsuzawa model for the long-lasting lumines-cence involving hole as free charge carrier.
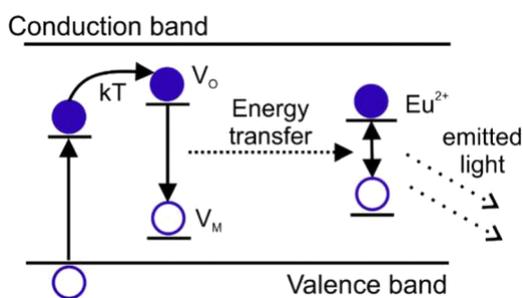
Figure 4. The Aitasalo model for the long-lasting luminescence involving indirect Eu^{2+} excitation.

the only free charge carriers, however the hole trapping at alkaline vacancies was assumed (Figure 4). There-fore, the proposed mechanism excluded the formation of Eu^+ and propose the possible thermally stimu-lated migration of electrons between somewhat dif-ferent traps until the electron and hole are localised at oxygen and alkaline vacancy complex. The elec-tron–hole recombination within this complex is fol-lowed by energy transfer process, that creates an excited Eu^{2+} ion. The energy transfer and oxygen and alkaline earth metal ion vacancy complexes play a crucial role in this mechanism. Also, the luminescence centre needs to be in close proximity to the vacancy complex for an efficient energy transfer process. However, it is not clear what the defects could be, for electron traps hav-ing the energy levels below to that of oxygen vacancy. This mechanism is good in the way that it does not limit the role of co-dopants to be charge-trapping centres. Aitasalo proposed that trivalent rare earth co-doping could possibly be responsible for a larger number of lattice defects – due to the charge compensation.

Later on Aitasalo proposed corrections on his previ-ous work, presenting an improved model [56]. As the previous models for mechanism of long-lasting lumi-nescence [56–58] received quite a lot of criticism on the physical accuracy, additional experiments were con-ducted to clarify the actual role of the co-dopants – this led to a conclusion, that Dy does not act as the trapping centre and the process could be more com-plex. A similar model was proposed by Dorenbos [59] involving some more 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 then be localised on defects – oxygen vacancies as well as trivalent rare-earth ions. The scheme of this model is in Figure 5.

Charge carriers can also migrate from one trap to another and finally migrate back to the luminescence centre, where excited Eu^{2+} transition to ground state creates the characteristic luminescence. Other authors have described a similar model [60].

The fourth work [61] on the topic of mecha-nism of persistent luminescence presented a very sim-ilar idea to that described in [56], that was also
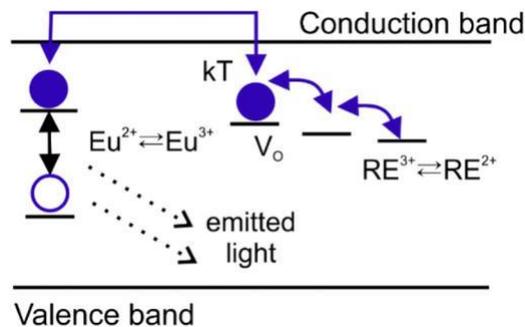

Figure 5. The model proposed by Aitasalo for the long-lasting luminescence involving Eu^{3+} accumulation during excitation.

verified by XANES (X-ray absorption near edge struc-ture) and EXAFS (Extended X-ray absorption fine structure) measurements that confirm Eu^{3+} accumu-lation during excitation. However, when explaining the mechanism, Aitasalo emphasises that there are doubts about Eu^{3+} presence, but Eu^{2+} and hole complexes might be more believable and the recombination of these complexes with the electron is the source of the long-lasting luminescence. The main difference from the previous model and that proposed by Dorenbos [59] is the involvement of several kinds of electron traps.

Quite a similar opinion was expressed by Holsa et al. – Holsa turned attention to the results of XANES measurements of $SrAl_2O_4$:Eu,Dy [17] and tried to observe any valence changes of dopants in the mate-rial during excitation and emission. He concluded that under excitation only the Eu^{2+}/Eu^{3+} oxidation hap-pens, therefore some changes to the known mod-els 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 sur-rounding thermal energy to the 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. Ther-mal energy can then liberate the charge carriers from the trapping centres and they can either be de-trapped or return to luminescence centre. The defects, that are claimed to be present in this material, are cation vacan-cies, oxygen vacancies and interstitial ions as well as the dopant ions [17]. The same conclusions were drawn by Qiu et al. [60], turning attention to the fact, that the trapping and de-trapping process from the trap levels can be repetitive.

Clabau model

Clabau suggested a model that involves electrons as the free charge carriers. To present proof for this hypothesis, electron paramagnetic resonance exper-iments were conducted. The experimental results
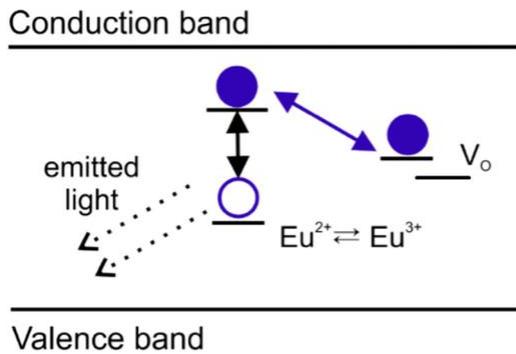
Figure 6. Clabau model for the long-lasting luminescence involving direct electron transition from luminescence centre to trapping centre.

Figure 7. Dorenbos model for the long lasting luminescence involving electron migration through conduction band.

showed that the concentration of Eu^{2+} ions changes during excitation and afterglow – it decreases in the excitation phase and increases during afterglow [19]. Therefore, Clabau presumed Eu^{2+} could be ionised – after Eu^{2+} excited state is formed during UV irradiation, thus Eu^{3+} is created. Electron migration from trapping centres to the luminescence centres 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. Schematic representation of this model is in Figure 6.

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 [59].

Dorenbos presented the locations of the Eu^{2+} d-bands in the band gap of $SrAl_2O_4$ matrix. The estimation of positions of dopant energy levels in $SrAl_2O_4$ material is discussed in [29–31]. The Eu^{3+} energy levels are located right beneath the bottom of the conduction band and Dy^{2+} level is located around 0.9 eV below the conduction band. 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 ionisation at room temperature is very prob-able. The electron migrates through the conduction band and 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+} centre. From there excited Eu^{2+} centre has two options – either it is again thermally excited to the conduction band or it can transit to the ground state with photon emission (Figure 7).

Latest discussion of luminescence processes in SrAl2O4

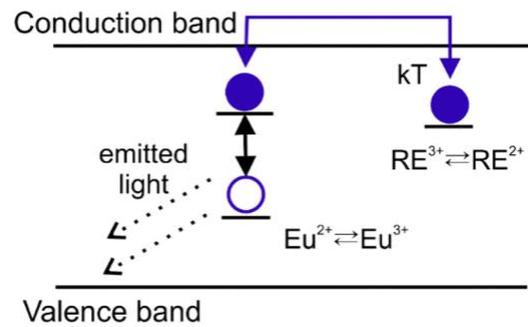The extensive work of scientists and researchers starting from the moment of the discovery of persistent

luminescence in rare earth doped strontium aluminates had made some progress in the understanding of afterglow mechanism, but more work needed to be done. Last decade was dedicated to more in-depth analysis about the material and the processes of charge carrier transfer, leading to the persistent luminescence. Therefore we will now take a look at the research that was conducted during the last decade and the conclusions that can be drawn from it.

All of the long afterglow mechanisms described above involve the generation of migrating charge carriers during excitation that are localised in trapping centres afterward [55–59,61,62]. The cause of persis-tent afterglow is thermally stimulated gradual charge release from trapping centres with resultant recombi-nation. The differences in these models concern (I) charge carriers – electrons or holes; (II) the charge carrier migration – does it happen through valence, conduction band or via levels of trapping centres; (III) the excitation of luminescence – does the charge car-rier directly transfers to the luminescence centre or the luminescence centre is excited with the aid of energy transfer process; (IV) the nature of trapping centres – intrinsic defects or co-activator (Figure 8). It is shown by TSL measurements that there are several different kinds of trapping centres in the material [18] but the exact nature of these trapping centres is not clear.

The analysis of the results that are described in sub-chapters 4.2. – 4.5. show that the most appropriate model for the explanation of persistent luminescence in $SrAl_2O_4$:Eu,Dy material is as follows: during excitation Eu^{3+} centres are created and electrons are localised in trapping centres. After the thermal release of electrons from trapping centres they recombine with Eu^{3+}, cre-ating excited Eu^{2+} and a radiative Eu^{2+} transition to ground state is the cause of luminescence.

There are some ambiguities in this model – does the electron recombination with Eu^{3+} occur only by thermal release of electrons from trapping centres; there is no evidence if the charge state change of co-activator Dy^{3+} can or cannot take place; as well as there is hardly any data about intrinsic luminescence of $SrAl_2O_4$ that could allow the identification of intrinsic
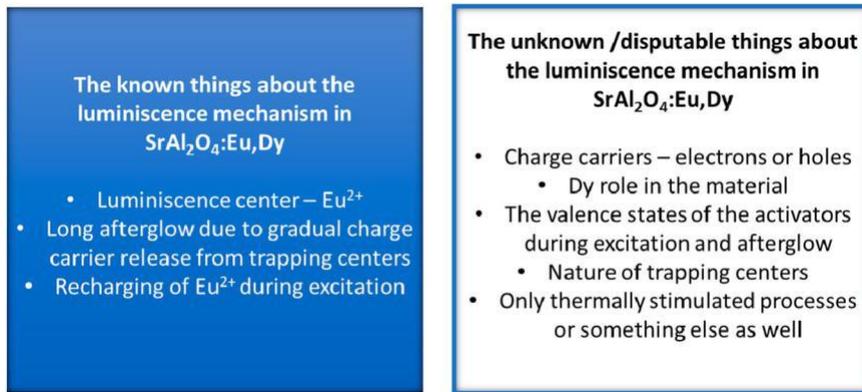
Figure 8. The known and unknown about the persistent luminescence mechanism in SrAl$_2$O$_4$:Eu,Dy.

defects. Therefore, more work had to be done to provide strong evidence for the mechanism.

In the last decade several more authors have put forward different ideas about the mechanism in the per-sistent SrAl$_2$O$_4$:Eu,Dy phosphor, but mostly scientists have invested their effort in finding proof that would support one or another of the mechanisms, that were offered before.

The mathematical approach

At this point, the mechanism where the electrons are considered to be the main charge carriers has become the predominant one and one of the reasons to assert this is the mathematical calculations of the band structure and the rare earth levels in the host band structure. J. Holsa et al., Nazarov et al., Zhai et al. and others have worked on the ab initio calculations of the structural and electronic properties of the material [15,24,63–70]. Several things have been confirmed by these calcula-tions. The most noticeable difference in the electronic properties of the material caused by doping is the appearance of impurity energy levels within the band gap [64].

The calculations give an estimate for the energy states of europium in the band gap, that can help greatly in the understanding the nature of charge carriers. Effi-cient electron transfer from the Eu^{2+} 5d states to the conduction band followed by trapping of electrons is required for the appearance of the persistent lumines-cence. The 5d states must be positioned close to or even within the conduction band in this material. However, the lowest Eu^{2+} 5d state has to be located below the conduction band, as the Eu^{2+} luminescence is experi-mentally observed. It has been shown that the lowest 4f states of europium are located at about 4.5–5 eV above the top of the valence band [15] (we have to note that this result is not fully compliant with the experimentally determined values). It is also confirmed that the Eu^{2+} 4f^7 ground state is located in the band gap. Experimen-tally determined Eu^{2+} excitation spectra are ranging from 200 to 450 nm and that would correspond to the excited state positions in the band gap [18]. The excited
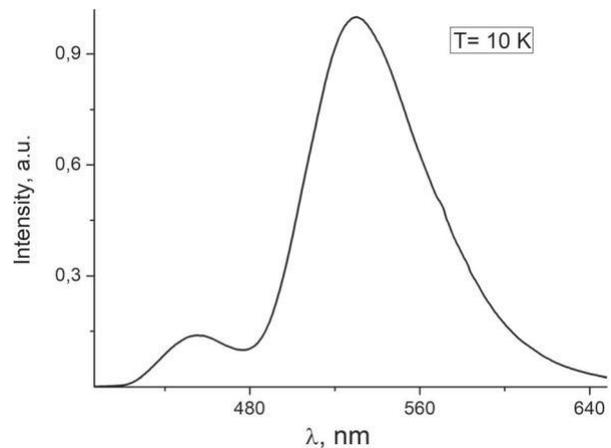

Figure 9. Photoluminescence of SrAl$_2$O$_4$:Eu,Dy at 10 K temperature.

electrons at the Eu^{2+} ions, which can be released to the conduction band, act as the primary charge carriers responsible for the persistent luminescence [24]. This has been accepted as a fact in the scientif ic commu-nity and holes are no longer regarded as potential main charge carriers.

Another thing that these theoretical calculations address, is the second luminescence band that is observable in the emission spectrum at the low-temperature range. [69,71] This band, peaking at 455 nm (Figure 9) (the position of the second band in different publications is slightly different, ranging from 440–455 nm) is relatively less intensive if com-pared to the 530 nm emission band and the intensity decreases with increasing temperatures until the band is thermally completely quenched at temperatures above 150 K [69,71]. The afterglow curves for both bands also differs – Bierwagen et al. shows two components in the decay – a slow and fast component. In the fast com-ponent, the amplitude in the blue maximum is nearly as high as in the green maximum whereas it is much weaker for the slower component [72].

There have been several assumptions for the possible origin of this second band, for example, charge transfer from oxygen to residual Eu^{3+} ion that takes place upon UV irradiation and is associated with hole trapping at

Sr^{2+} vacancies [19], a preferential orientation of the d orbitals of Eu^{2+} on Sr sites that appear to line up [73], anomalous low-temperature luminescence that origi-nates from a higher Eu^{2+} 5d state that may be observed due to the absence of high energy lattice vibrations at low temperatures [74].

The ab initio calculations together with XRD measurements have, however, shown that two crys-tallographic sites are available for the Sr^{2+} ions. The distances between sequential Sr^{2+} ions are alternat-ing by 3.9 and 4.6 Å, respectively. These two Sr sites have low local symmetry and differ in the coordina-tion numbers. The data presented here are in favour of a hypothesis that the emission bands originated from the Eu^{2+} ions located at two non-equivalent crystallo-graphic sites, when incorporating instead of Sr^{2+} ions, and this opinion is shared by experimental investiga-tions as well [46]. Calculations show, that both sites occur in almost equal amounts in the host lattice [15].

Separate investigation of bands behaviour at low temperatures shows the integrated intensity of one luminescence band (450 nm) is decreased while the other band's intensity (512 nm) is increased when the temperature is increased. That is why the existence of the non-radiative energy transfer between these two bands is proposed. This was explained more in-detail by Nazarov et al. [40] with the aid of adiabatic potentials of the two Sr sites. The Eu^{2+} ions entering the Sr II sites show broad emission at higher energy (at 450 nm), and those ions at the Sr I sites cause the lower energy band at 520 nm. Nazarov calculated the crystal field splitting for 5d states, obtaining 5 different energies. These ener-gies were in a good agreement with the excitation bands and also the two different emission bands. The lowest energy level that arises from 5d state crystal field split-ting in Sr I position – 3.1 eV is responsible for the green luminescence and lowest energy level in Sr II position – 3.3 eV is responsible for the blue luminescence. One can therefore conclude that at relatively high temperature the energy can be transferred from Eu^{2+} in the Sr II position to Eu^{2+} at the Sr I position, thus explaining the redistribution of emission intensities from both sites at different temperatures [15,64].

To summarise – there have been several opinions on the origin of the second luminescence band. The theoretical calculations that have been conducted in the last decade are in favour of the opinion that in $SrAl_2O_4$:Eu,Dy the 450 nm luminescence band arises from the Eu^{2+} incorporated in Sr II position.

Intrinsic defect role in the persistent luminescence mechanism

One of the most important tasks in completing the model of mechanism responsible for persistent lumi-nescence is the nature of defects, that act as trapping centres and the role of Dy co-doping that enhances the luminescence intensity and afterglow time greatly. To tailor the luminescent properties of the material to our needs, the trial and error method is not the best approach. It is sure to say that for more ef f icient commercial applications predictive modelling of the possible defect sites, although very difficult, would be superior to the empirical one.

Lately, several new research papers have been pub-lished that deal with the defects in the material and their role in the persistent afterglow.

Thermally stimulated luminescence glow curve analysis is used to study the trap depth and the results show similar glow curve maxima in both doped and undoped materials [75]. The multiple maxima of the TSL curve point to the presence of a number of stable electron traps able to retain charge over considerable periods, whereas the presence of closely spaced peaks implies closely spaced electron traps comprising shal-low, intermediate-energy and deep traps [76,77]. The idea of multiple, closely spaced trap levels has been implied in several other discussions on the mechanism of afterglow [18]. Hagemann et al. [78] have expressed the idea that the trap depth depends on the spatial distance to the Eu^{2+} centres, meaning that, depend-ing on the excess energy of the electron after reaching the excited state, electron can move further away from the emission centre and a trapping–de-trapping process can take place. It is now conf irmed, that $SrAl_2O_4$:Eu,Dy possesses a great variety of electron traps. The pop-ulation of these traps is dependent on the excitation wavelength and temperature [78].

Han et al. [79] have agreed on the wide distri-bution of trapping centres and continued the idea that distribution by a distance of co-dopant cations around luminescence centres can influence lumines-cent properties, meaning that for long-lasting lumines-cence phosphors traps there are more parameters to be considered than just energetical depth. He suggests that distance between Eu^{2+} and co-dopant should also be counted in and proposes that it might be done by using Morse potentials and treating the constituents of the crystal as potential wells and barriers, that can be widened and narrowed under different conditions. For example, trapped electrons can be released by climb-ing over potential barriers or just tunnelling through them under thermal stimulation, thus, previous mech-anisms would work the same. And thermal stimulation can be introduced either by direct stimulating electrons or by weakening barriers via enhancing lattice vibra-tion [79]. The idea of taking the dopant and co-dopant distances into account is very reasonable – because we can also observe, that dopant concentration influ-ences the efficiency of the afterglow. It can be seen that the PL intensity of emission from Eu^{2+} ions initially increases with the increase of dopant and co-dopant concentration. After it reaches the maximum value, a further increase in concentration makes the intensity

decrease, because of the concentration quenching effect [21,72,80,81].

When considering the possible origin of the trap-ping centres, it can not be excluded that similar defects to those in α-Al$_2$O$_3$ could be present in the strontium aluminate – F centres (oxygen vacancies occupied by two electrons or V$_O^0$), F$^+$ centres (oxygen vacancies occupied by one electron or V$_O^{+1}$ or), their aggregates such as F$_2$ centres (two associated oxygen vacancies occupied by four electrons), and the F$_2^+$ centres (two associated oxygen vacancies occupied by three electrons). Also, the vacancies of the two other main lat-tice constituents V$_{Sr}$ and V$_{Al}$ can be involved in the charge-trapping mechanism. Zhai et al. have expressed an opinion that all three Sr, Al and O vacancies might be involved in the charge-trapping process [67], whereas Chithambo et al. express the opinion, that the elec-tron trapping centres may be oxygen vacancies acting as F-centres or oxygen aggregates [76].

Vitola et al. have studied the TSL and X-ray excited emission spectra of undoped material to understand what defects exist in undoped SrAl$_2$O$_4$, that might be present in activated materials as well. The main conclu-sion from luminescence and TSL data analysis is that two main things contribute to the spectral properties – trace impurity metals, namely, Cr^{3+} and Mn^{4+}, that is close to impossible to get rid of in the synthesis process, and intrinsic defects – F- centres and F$_2$– centres lumi-nescence. Other authors also have noted, that impurity metals are present as contaminants in the strontium aluminate lattice, regardless of the preparation method [82] and that means they can also be responsible for trapping centre generation.

An extensive numerical study was conducted by Finley et al. [83] to determine the energetically most favourable defects, that might act as electron trapping centres. Experimental observations from thermolumi-nescence and electron paramagnetic resonance data support the presence of either cation or anion vacancies [19,83,84], therefore first principle calculations were conducted on monoclinic SrAl$_2$O$_4$ and SrAl$_2$O$_4$:Eu^{2+} to explore the presence of point defects due to cation and anion vacancies and their potential relationship to persistent luminescence. The team concludes that anion vacancies are present in both compositions, and energetically favourable in the crystal structure. Com-paring undoped and Eu doped materials it turns out, that when Eu^{2+} is present in the crystal structure, the trap depths shift to such energetic positions that are responsible for strontium aluminates exceptional lumi-nescent lifetime.

Dy role in the mechanism of persistent luminescence

The suggestions in previous reports of the Dy^{3+} ion role are rather different. It was proposed that Dy^{3+} traps a hole [55,78] while others proposed that the Dy^{3+} ions induce the formation of traps associated with a charge compensating defect [58,85], stabilising the traps [49] or act as an electron trapping centre itself [37,48,59,60]. While these conflicting opinions still exist, one thing is clear – Dy doping changes the environment surround-ing the Eu^{2+} ions in the SrAl$_2$O$_4$ host material [86] and generates some trapping centres [87].

First, let's look into the research of Zhai et al. [67]. This research states that in SrAl$_2$O$_4$ material Dy^{3+} ions substitute Sr^{2+} cations to form luminescent cen-tres in SrAl$_2$O$_4$. This statement comes from the fact, that SrAl$_2$O$_4$:Dy (without Eu doping) emits an after-glow. This is also stated by other authors, for example, Liepina et al. in [88] and Jamalaiah et al. in [84]. Char-acteristic Dy emission lines can also be observed in SrAl$_2$O$_4$:Eu,Dy under X-ray irradiation [89,90]. The other role of Dy^{3+} doping is to create a substitutional positive defect in the crystal lattice, that can act as an electron trap [91]. Owing to the requirement of charge neutrality, when two Dy^{3+} ions substitute for 2 Sr^{2+} ions additionally one Sr^{2+} vacancy is involved to bal-ance the charge of the phosphor, leading to the forma-tion of two positive defects – Dy^{3+} in Sr^{2+} site and one negative strontium vacancy [92]. V$_{Sr}$ is negative and could act as the hole trap. Extra electron and hole traps will be created in SrAl$_2$O$_4$ host when V$_O$, V$_{Sr}$ and V$_{Al}$ are present. The depths of these traps play a crucial role in determining the time of the material afterglow. Similar conclusions can be drawn from [69]. Moreover, Chithambo et al. [76] have assigned the largest TSL glow peak to the electron release from Dy trapping cen-tre, justifying it with the energetical distance $\sim$ 1 eV from conduction band for the Dy^{2+} supposed electron trapping state. It is interesting to note that in major-ity publications in the photoluminescence spectrum of SrAl$_2$O$_4$:Eu^{2+},Dy^{3+} only Eu^{2+} luminescence band is visible, not the Dy^{3+} luminescence – since these tran-sitions are forbidden and require excitation at the exact wavelengths of Dy absorption.

The other opinion is expressed by Liepina et al. [88]. In this research SrAl$_2$O$_4$:Dy material is studied through TSL, X-ray excited luminescence (Figure 10) and kinetics analysis and this gives rise to a claim that Dy might act as a hole trapping centre. There is quite a strong argument in favour of this claim – Dy^{3+} emission spectrum is observable also in afterglow [64] and TSL spectrum [84,88,93]. The Dy^{3+} characteris-tic lines, that are observable under X-ray irradiation SrAl$_2$O$_4$:Dy^{3+} are said to be created by electron return-ing to Dy^{4+} ion, thus creating an excited Dy^{3+} centre. The grounds for this claim is the TSL curves that indi-cate the same activation energies for trapped charge carriers that those of SrAl$_2$O$_4$:Eu,Dy. Since the persis-tent luminescence of SrAl$_2$O$_4$:Eu,Dy arises due to Eu^{3+} and electron recombination, it is possible only if dur-ing heating in TSL electrons are released. Therefore,
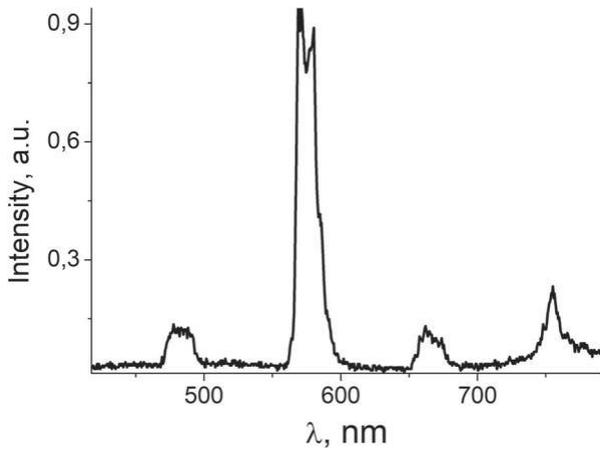
Figure 10. The SrAl$_2$O$_4$: Dy emission spectrum under X-ray irradiation.

the Dy^{3+} luminescence during TSL arises via released electron recombination with Dy^{4+}. Based on TSL and time-resolved spectral measurements the authors conclude 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. Therefore, it was concluded that under X-ray excitation the Eu^{2+} as well as Dy^{3+} each lost an electron and no evidence was obtained on Dy^{2+} creation. Thus, the electrons were trapped at host defects.

Qiu et al. [60] claim, that the trivalent co-dopant can introduce deeper electron trap centres. Other authors also state that the role of co-doped Dy^{3+} is to increase the number of vacancies and to alter the depth of the existing vacancies [49]. The role of Dy in SrAl$_2$O$_4$ is also discussed by Delgado et al. [49] also looking at the role of boron addition. The author states, that the role of the co-dopants, such as Dy^{3+} or B^{3+}, is not interfering directly in the mechanism by getting reduced or oxidised but stabilising the oxygen vacancies. These oxygen vacancies are located in the near surroundings of the photogenerated Eu^{3+} cations and are claimed to be responsible for the long phosphorescence by acting as electron trapping centres. The electron density of Dy^{3+} or B^{3+} is delocalised towards these oxygen vacancies, thus stabilising them [42]. The replacement of Sr^{2+} by Dy^{3+} in the host material induces defects on the crystal structure due to the size and charge differences. Furthermore, to compensate the charge difference, induced by the presence of Dy^{3+}, oxygen uptake may take place. The incorporation of oxygen into the lattice gives rise to more defects. Similar conclusions are drawn by Yoon et al. [22] who points out to additional TSL maxima due to oxygen vacancies, created by boron addition. We have to note that only few publications deal with the B^{3+} influence on the photoluminescent properties of SrAl$_2$O$_4$:Eu,Dy, however, it is quite often used in the synthesis process, therefore this is another thing that could lead us to a better understanding of the persistent luminescence process.

The XANES measurements of dopant valence

Laastusaari et al. and Korthout et al. have conducted a research on the valences of the dopants of SrAl$_2$O$_4$ material using XANES method [85,92]. The charging of the Eu^{2+} persistent luminescence could involve the excitation of an electron from the Eu^{2+} 4f ground levels via the 5d levels to the conduction band and migra-tion to trapping levels. This may create either the Eu^{3+} ion or the Eu^{2+}–h$^+$ pair Therefore the knowledge of the dopant valences during excitation might serve as a strong evidence for this claim. It was observed, that under excitation the ratio for Eu^{2+}/Eu^{3+} signal inten-sity changes – Eu^{3+} intensity increases, confirming the Eu^{2+} ionisation to Eu^{3+} with the liberation of an elec-tron [92], however there was no correlation observed between the Eu^{2+}/Eu^{3+} luminescence intensity ratio and the persistent luminescence intensity or duration, therefore it led the authors of this publication [85] to a conclusion, that the Eu^{2+}–h+ pair is formed dur-ing the charging rather than the Eu^{3+} ion. In this pair, the hole may be manifested as an O$^-$ ion adjacent to Eu^{2+} or could be located in a cation vacancy. As for the Dy valence measurements – no formation of Dy^{2+} or Dy^{4+} ion was detected during excitation, pointing out that it might not act as a trapping centre. But it is also possible, that Dy^{3+}-electron pair could be formed, which would allow the electron to become trapped without the reduction of the co-dopant ion. The pos-sibility that reduction of the Dy^{3+} does happen, but only for a minor fraction of the ions, can also not be excluded, and that could remain undetected by XANES measurement. [85,92].

Zeng model

As mentioned beforehand, recently several additional explanations for the trapping mechanism have been put forward. Taking in account the predominant view of electrons as free charge carriers, a study of TSL (thermally stimulated luminescence) glow curves, decay kinetics and OSL (optically stimulated luminiscence) was conducted for SrAl$_2$O$_4$:Eu and SrAl$_2$O$_4$:Eu,Dy by Zeng et al. [18]. This research team observed the presence of multiple electron trapping centres having different energetical depths. The elec-tron is promoted to the conduction band from Eu^{2+}, migrates through the conduction band and is trapped, for example, at oxygen vacancies. Electron can be thermally released and can contribute to forming the excited Eu^{2+} centre that can return to the ground state with photon emission. Doping of Dy is said to decrease the proportion of deep traps (over 0.65 eV). The traps are supposedly created by oxygen vacancies and the energies are distributed in a wide range. The more shal-low traps (with energetical depth less than 0.65 eV) can easily be emptied by the energy available in room temperature to conduction band by lattice vibrations,
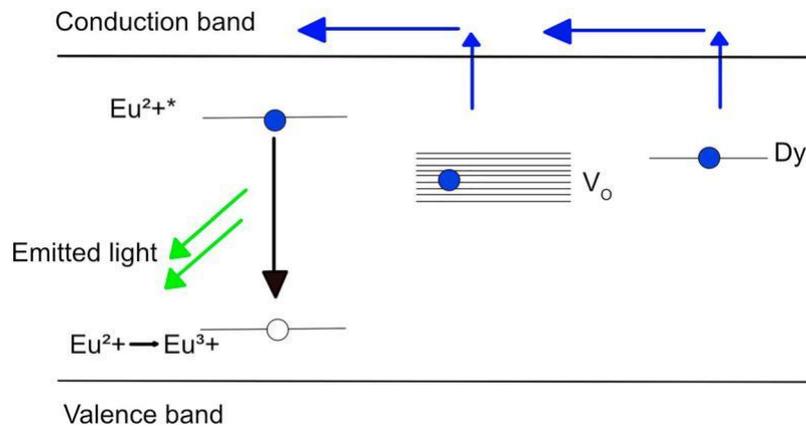
Figure 11. The mechanism proposed by Zeng for long lasting afterglow involving a distribution of vacancy related trapping centres.

however the thermal excitation of deeper traps at room temperature is much less probable. What is interest-ing – Dy is considered to be an electron trapping centre as well and if Dy introduces more shallow traps and decreases the proportion of deeper traps, that is a good explanation for the enhancement of luminescent prop-erties of $SrAl_2O_4$:Eu by Dy co-doping. The shallow trapping centres contribute to the intensity of after-glow, whereas the decrease in the number of deeper traps could shorten the duration of the afterglow. The schematic representation of this model is in Figure 11.

This model of long-lasting luminescence proposes a wide distribution of traps having different energetical depths, though it is not yet clear how the oxygen vacan-cies could form this wide distribution of traps. There are experimental research works, that deal with trap distri-bution and, although several different depth trapping centres are observed [68], but not an almost continu-ous distribution. Therefore this theory still needs to be confirmed. The other note – up to this day experimen-tal evidence of Dy^{2+} creation in $SrAl_2O_4$:Eu,Dy has not been provided.

Qu model

A very similar model has been proposed by Qu et al. [94] for $CaAl_2O_4$:Eu^{2+},Nd^{3+} material, that is structurally very similar to strontium aluminate mate-rial, Sr being replaced with another alkaline earth metal ion Ca and instead of the trivalent rare earth Dy, triva-lent Nd is used. It is proposed, that after the excitation and promotion to the conduction zone, the electrons can be trapped when they encounter the O vacancy or Nd dopant. Some trapped electrons can move back Eu, leading to persistent luminescence. Trivalent rare earth co-doping is considered to increase the lumines-cence intensity, because not only this co-dopant can offer additional electrons (by forming electron trap-ping centres, that can be emptied), but also introduce deeper electron trap centres. The authors claim, that it is not the wide distribution of oxygen vacancy energy levels, but the distribution of the 4f levels of trivalent rare earth, that plays a key role (Figure 12). Accord-ing to their calculations, trivalent ion introduces sev-eral 4f levels into the band gap that are distributed within a medium-energy range (> 0.4 eV). The lowest 4f level is located more than 1 eV below the conduc-tion band. The electron trapped in the lowest 4f level can move to only other nearby 4f levels with the assis-tance of thermal vibration and phonon coupling but cannot move directly to the conduction band with-out radiation. Therefore, the electron has to navigate between the 4f levels before having a chance to move back into the conduction band when it reaches the top

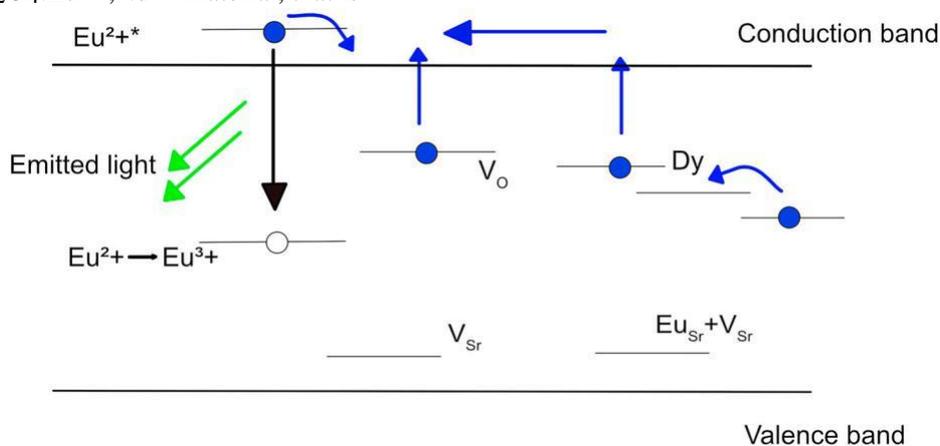**Figure 12.** The mechanism proposed by Qu for long lasting afterglow involving a distribution of trivalent rare earth related trapping centres.

4f levels or other higher trap centres like oxygen vacan-cies. Hence, to prolong the decay time, many empty energy levels with different energies distributed from shallow to deep positions in the band gap must be available. The authors claim, that the distribution of the trap centre levels is proportional to afterglow dura-tion. We have to note that a disputable claim is that Eu^{2+} 5d levels (excited Eu^{2+}) are in the conduction band.

Gnidakouong model

Similar to Qu model, Gnidakouong et al. [95] considers Dy and oxygen vacancies as electron trapping centres, but also introduces interstitial vacancies as another type of trapping centre. This research work was devoted to explaining the mechanoluminescence of the mate-rial, and also resulted in a suggestion for the persistent luminescence model. Electrons, after thermally being released into the conduction band are subsequently caught by the trivalent rare earth co-dopant (Dy^{3+}, creating a divalent Dy^{2+}), the oxygen vacancies (V_O) and the vacancies resulting from the lattice distortion – interstitial vacancies (V_C). Upon absorption of light from the excitation source, the electronic configuration of Eu^{2+} changes from $4f^7$ to $4f^65d^1$, after which the elec-tron can return to the ground state (Figure 13) or escape to the conduction band. There are three options from there. First, electrons can be caught by oxygen vacancy traps and this trap can be emptied in the afterglow pro-cess or through a mechanical stimulus. Electrons that are released in this way can reach ionised europium ions through the conduction band to form excited Eu^{2+}, resulting recombination will be accompanied by the light emission. Second, electrons released by the ionised europium are caught by dysprosium ions creating diva-lent ions de-trapped by the same route with the same effect as in the first case. Third, the carriers are caught by interstitial vacancies and are thermally released with the help of a mechanical stimulus. If an electron trapped in an interstice is very close to a luminescent centre, then the recombination can also occur through tunnelling.

We have to note that this model has several ambi-guities, because the predicted energetical position of V_C is below that of Eu^{2+} and would lead to trapping holes rather than electrons and the proposed tunnelling of electrons from V_C to Eu to form the excited cen-tre seems unclear –requiring a considerable change in electron energy.

Liepina model

The observation of low-temperature luminescence afterglow, that is mentioned in several articles [72,96] is not compatible with the idea of only thermal release of charge carriers from the trapping centres. Therefore, an extensive study was conducted on the luminescence processes in the low-temperature range [97]. Based on the measurements of decay kinetics, and due to the lack of TSL maxima in the low-temperature range, a persistent luminescence model involving electron tun-nelling from trapping centre to Eu^{3+} was proposed. It was suggested that the charge carriers are electrons and at low temperatures electron tunnelling is the domi-nant process in creation of excited Eu^{2+} centre, whereas in temperatures that offer enough thermal energy for the release of electrons, thermally stimulated process becomes dominant, however it is not excluded that the last step of electron migration could still be tunnelling process.

The thermally released electron during migration can be re-trapped and released multiple times. The last step of electron migration could be either its direct trapping at Eu^{2+} excited state or trapping at a deeper trap associated with Eu^{3+} that is followed by excited Eu^{2+} creation via tunnelling. The radiative decay of excited Eu^{2+} created via both processes is the ori-gin of observed luminescence. The mechanism is sim-plif ied – it is clear from the analysis of TSL glow curves that several trapping centres are involved. This goes in agreement with the above-mentioned Zhang
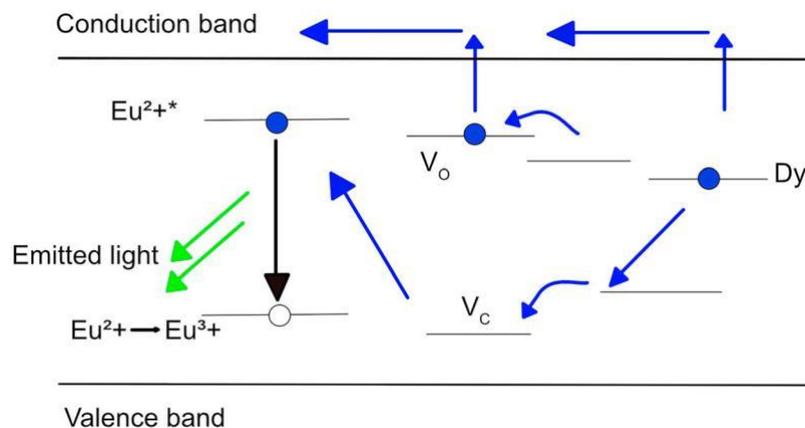

Figure 13. The mechanism proposed by Gnidakouong for long lasting afterglow involving interstitial vacancies as trapping centres.
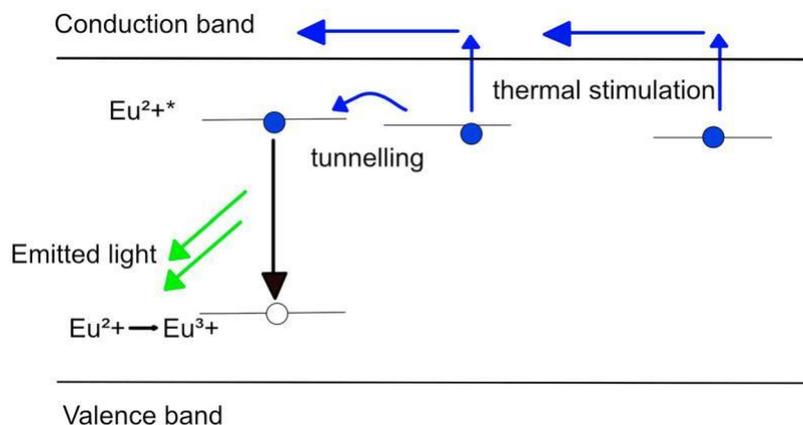
Figure 14. The mechanism for long lasting afterglow by Liepina involving electron tunnelling.

model. However, TSL measurements reveal that at room temperature and above the number of efficient traps involved is limited [97]. The schematic represen-tation of this model is in Figure 14.

Tunnelling luminescence was mentioned as a possible process for electron transition to luminescence cen-tre in $SrAl_2O_4$ material also by Chithambo et al. [76], based on the fact, that the phosphorescence that can be observed between irradiation and TSL measurement proceeds for periods much longer than required for the main peak to fade completely. Tunnelling between trap levels and luminescence centre together with thermally stimulated electron release has also been mentioned later in [98].

To conclude the discussion about different models, that were proposed in the last decade we can say, that a consensus has still not been found. However, proof to clear up some of the ambiguities has been found. For example, holes are no longer considered to be the charge carriers in $SrAl_2O_4$:Eu,Dy material. Several authors have found proof to the distribution of trapping cen-tres with different energetical depth. Charge migration from one trapping level to another is discussed in all of these models. Tunnelling from a closely located trap-ping centre to the luminescence centre as an addition to the thermally stimulated process has been shown. Therefore it is up to the reader to choose the most plau-sible model based on the proof and the unclarities for each mechanism that are described above.

Summary

Ever since the discovery of $SrAl_2O_4$:Eu,Dy long after-glow material, the model of long-lasting afterglow and the possibilities to enhance the intensity has been a pop-ular area of research due to the vast applications it pro-vides. During the last decade, researchers have mostly focused on finding experimental or theoretical proof that would back up or disprove any of the mechanisms, that were offered beforehand. The knowledge about

$SrAl_2O_4$:Eu,Dy and the charge carrier transfer pro-cesses in it has been improved during the last decade. A lot of attention was turned to the theoretical cal-culations, thus proving the crystal field splitting of 5d states in Eu and the two unidentical crystallographic positions that are responsible for the appearance of two emission maxima in low temperatures. An energeti-cal distribution of trapping centres has been discussed in several publications and a supplement to the ther-mally stimulated process has been acknowledged – the tunnelling process, that explains the afterglow in tem-peratures as low as 4 K. There still is more work to be done – although the role of Dy has been discussed in several publications and it is clear that it contributes to the creation of electron trapping centres, the exact nature of the trapping centres and Dy doping is yet to be understood. We also do not know, why Dy^{3+} emission is not visible in photoluminescence, but can be seen in radioluminescence and TSL measurements. However, it seems that we are getting much closer to fully understanding the processes that govern the long-lasting luminescence in Eu activated aluminate materials.

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