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Persistent luminescence phenomena in materials doped with rare earth ions

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Abstract

The luminescent efficiency of rare earth ions is usually drastically lowered when defects are present in the host lattice. Persistent luminescence is the most recent rare earth application based on lattice defects. Typical materials are the Eu^{2+}-doped alkaline earth aluminates, $M\mathrm{Al_2O_4}$:Eu^{2+} (M = Ca and Sr). The trivalent R^{3+} ions as co-dopants enhance greatly the duration and intensity of persistent luminescence. As a result of very slow thermal bleaching of the excitation energy from the lattice defects acting as traps, the new persistent luminescent materials yield luminescence still visible to naked eye for more than 10 h. Despite the seemingly simple stoichiometry and structure of these materials, the determination of persistent luminescence mechanism(s) presents a very complicated problem. This report presents in detail some of the factors affecting the luminescence properties of the Eu^{2+}-, R^{3+}-doped $M\mathrm{Al_2O_4}$. The possible mechanisms involved with different defect centers and interactions between them and the emitting Eu^{2+} ion are discussed based on the results of systematic investigations carried out on the preparation, composition, structure and different luminescence properties.

1. Introduction

Rare earths (R) are used extensively in luminescent materials which employ practically any kind of energy as the excitation source. Non-doped rare earth compounds with well-defined stoichiometry can be employed, but most frequently the rare earths enter as dopants into different host matrices. In order to avoid any decrease in efficiency, a very good homogeneity is then required of the crystal lattice. In most cases, the efficiency of luminescence is drastically lowered when any kind of lattice defect is found in the host lattice. One of the consequences of the presence of lattice defects is the long afterglow which is exhibited by some potentially efficient luminescent materials. This feature is usually considered disadvantageous among the properties of a phosphor when the practical applications are considered [1]. Accordingly, the luminescence applications based on lattice defects are rare. Despite the usually undesired afterglow, the persistent luminescence materials have already been used since tens of years. The material used so far, copper- and cobalt-doped ZnS is, however, extremely sensitive to moisture [2]. Moreover, the duration of the afterglow is of the order of a few hours only and because of the potentially hazardous use of radioactive elements (e.g. Pm^{3+}) as an auxiliary excitation source these materials are environmentally hazardous.

The use of the rare earth luminescence in persistent luminescence materials is one of the latest application of the rare earth elements (Table 1). Since the mid-1990s a completely new generation of persistent luminescent phosphors has been developed and partly entered into the commercial market [3]. These new phosphors originally included only the Eu^{2+}-doped alkaline earth aluminates, $M\mathrm{Al_2O_4}$:Eu^{2+} (M = Ca and Sr) [4–6], but other, more complex aluminates,

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Table 1
Applications of rare earth luminescence

Application	R's used	Excitation	Critical features
Lighting	Eu^{2+}, Eu^{3+}, Tb^{3+}	UV-radiation	Chemical stability, UV-absorption
TV/cathode ray tubes	Eu^{2+}, Eu^{3+}	Electrons	Chemical stability, fast luminescence
Scintillators	Ce^{3+}	γ-/X-rays	Absorption of radiation, fast luminescence
Electroluminescence	Ce^{3+}, Tb^{3+}, Eu^{3+}	Electric field	Energy conversion, fast luminescence
IR-vis conversion	Yb^{3+}, Er^{3+}, Tm^{3+}, Ho^{3+}	IR-radiation	Energy transfer
Photostimulated luminescence	Ce^{3+}, Eu^{2+}	X-rays	Trap formation, depth of traps
Laser	Nd^{3+}, Yb^{3+}	(UV-)radiation	Chemical stability, laser action
Fiber optics	Er^{3+}	IR-radiation	Transparency
Persistent luminescence	Eu^{2+}; Nd^{3+}/Dy^{3+}	Thermal energy	Depth of traps

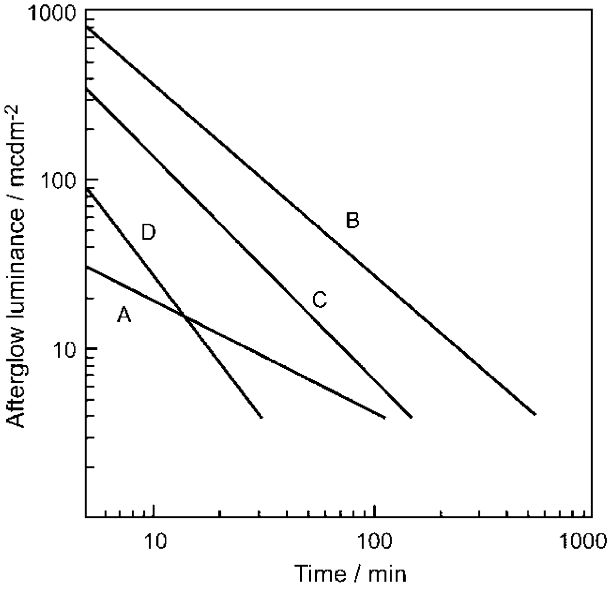

Fig. 1. Comparison of the persistent luminescence lifetimes of A: $SrAl_2O_4:Eu^{2+}$, B: $SrAl_2O_4:Eu^{2+},Dy^{3+}$, C: $SrAl_2O_4:Eu^{2+},Nd^{3+}$ and D: ZnS:Cu,Co [24].

e.g. Eu^{2+}- or Ce^{3+}-doped melilite-based aluminosilicates ($Ca_2Al_2SiO_7:Eu^{2+}$, $CaYAl_3O_7:Eu^{2+},Dy^{3+}$, etc. [7–10]) have been studied. Other ceramic materials of interest include calcium magnesium triple silicates ($Ca_3MgSi_2O_8:Eu^{2+},Dy^{3+}$ [11]) as well as Mn^{2+}-doped zinc gallate ($ZnGa_2O_4:Mn^{2+}$ [12]). Eu^{2+}-doped silicate or borate glasses have been investigated extensively as well [13–23]. The Eu^{2+}-doped alkaline earth aluminates remain, however, most important persistent phosphors, especially because the afterglow is greatly enhanced by co-doping with some R^{3+}-ions as Dy^{3+} and Nd^{3+} [24–29]. The new persistent luminescent materials much superior to ZnS:Cu,Co (Fig. 1) yield luminescence still visible to naked eye for more than 10 h in the dark after exposure to radiation (sunlight, UV radiation, fluorescent lamp, etc.). These materials are used e.g. in traffic signs, emergency signage, watches and clocks as well as in textile printing.

The overall mechanism of the persistent luminescence is now quite well agreed on to involve the formation of traps followed by a subsequent thermal bleaching of the traps and emission from the Eu^{2+} sites. Despite the seemingly simple stoichiometry and structure of the alkaline earth aluminates, the determination of persistent luminescence mechanisms seems to present a very complicated problem. Accordingly, no general agreement has been achieved on the detailed mechanisms involved and several interesting and even exciting mechanisms have been proposed. Especially, the mechanisms resulting in the prolonged and enhanced afterglow when R^{3+} ions have been introduced into $MAl_2O_4:Eu^{2+}$ as co-dopants are either ignored or are contradictory [30–34].

In this report, after presenting an initial review on the status on the field, the factors affecting the luminescence properties of the $MAl_2O_4:Eu^{2+}$ phosphors are described in detail. The possible mechanisms involved with different defect centers and interactions between them and the emitting Eu^{2+} ion are discussed based on the results of systematic investigations carried out on the preparation, composition, structure and different luminescence properties (UV-, laser-, persistent luminescence and thermoluminescence (TL)) of the Eu^{2+}-, R^{3+}-doped alkaline earth aluminates. The understanding of the mechanisms of the persistent luminescence is crucial if new, even more efficient materials were to be developed in a systematic way. In order to successfully treat with this task, multidisciplinary investigations including solid-state chemistry and physics, materials science and different spectroscopic methods are required.

2. Experimental

The polycrystalline Eu^{2+} (and Na^+ and R^{3+})-doped alkaline earth aluminates were prepared by a solid-state reaction between aluminium oxide, Al_2O_3, calcium (or strontium) carbonate, $CaCO_3$ (or $SrCO_3$), sodium carbonate, Na_2CO_3, and rare earth oxide, R_2O_3 (4 N), powders. The mixtures were annealed in a reducing ($N_2 + 12\%\ H_2$) atmosphere at 1250°C (or 1300°C) for 6 (or 4) h, respectively. B_2O_3 (1 mol%) was used as a flux.

The amounts of Eu^{2+} and R^{3+} (Na^+) were 1 and 2 mol% of the host cation, respectively. Prior to heating the reagents were ground using a ball mill to form a homogeneous mixture. The phase and structural purity of all samples was checked by X-ray powder diffraction. Single crystals or fibers of single crystals seem to have homogeneity problems and contain easily additional impurities and/or defects and thus they were not considered in this work.

The sol–gel process is an efficient technique for the preparation of phosphors due to the good mixing of starting materials and relatively low reaction temperatures. $CaAl_2O_4:Eu^{2+}$ was prepared with a sol–gel method using aluminum isopropoxide ($Al(OC_3H_7)_3$), calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) and europium oxide (Eu_2O_3) as starting materials. The gel was first dried for 10 h at 180°C in air and then for 20 h at 850°C in a $N_2 + 12\%\ H_2$ atmosphere.

The low-resolution luminescence and afterglow spectra were measured at room temperature using a Perkin-Elmer LS-5 spectrometer. The wide band (20 nm) UV-excitation ($\lambda_{exc} = 350$ nm) was provided by a xenon lamp. Prior to the afterglow measurements the materials were exposed to radiation from a conventional (11 W) tricolor fluorescent lamp for 10 s. The delay between the initial irradiation and the afterglow measurements was 3 min. The high-resolution luminescence and excitation spectra were measured at 77 K with a SLM Aminco SPF-500C spectrofluorometer equipped with a 300 W xenon lamp.

TL is a useful method to estimate the energy levels for trapped carriers, i.e. the number and the depth of the traps. However, the TL measurements are difficult to carry out and, especially, the results are even more difficult to interpret because of e.g. overlapping peaks and retrapping. The TL glow curves were measured with a Risø TL/OSL-DA-12 system at the temperature range between 25 and 400°C employing the linear heating rates of 2, 4, 5, 6, 8 and 10°C s^{-1}. Global TL emission from UV to 600 nm was monitored. Prior to the TL measurements, the samples were exposed to irradiation from a 60 W incandescent lamp for 10 s. The delay between the exposure and TL measurements was 3 min. Although several methods can be used in the analysis of trap depths (peak shape method, heating rate method, curve fitting and preheat analysis) only the last one can seriously deal with many overlapping peaks, i.e. with traps of similar energy.

3. Results and discussion

3.1. Persistent luminescence of $MAl_2O_4:Eu^{2+}$

Together with the photostimulated luminescence [35], the persistent luminescence is based on the use of lattice defects for storing the excitation energy. However, in contrast to the phenomenon of photostimulated luminescence which has been studied exhaustively and the materials are well established and characterized, the corresponding features of the persistent luminescence are not at all well characterized. Both phenomena deal with very complicated mechanisms and involve lattice defects (vacancies, color centers) as well as the possibility to have both correlated and uncorrelated centers. These two phenomena have some common features, too, as the use of the Eu^{2+} luminescence. There remain, however, several problems in the persistent luminescence as trap identity, the energy balances, the nature of the charge carriers, in brief, the whole of the detailed mechanisms is left unknown. Some mechanisms for the persistent luminescence have been published but they are deficient and often contradictory. However, these mechanisms gave the initial idea to the present studies: the mechanisms published proposed the formation of monovalent Eu^+ and tetravalent Nd^{4+} and/or Dy^{4+} [30–34]—or, at least, the presence of their virtual counterparts as charge transfer states and excited 5*d* electron configurations. The presence of the Eu^+ or Nd^{4+} (and/or Dy^{4+}) species in ambient conditions and in oxide materials is, however, not acceptable and the suggested reduction of Eu^{2+} to Eu^+ (and oxidation of Nd^{3+}/Dy^{3+} to Nd^{4+}/Dy^{4+}) would require tremendous amounts of energy. The following examples illustrate the energies involved in the formation of the proposed species. For example, the energy of the lowest CTS band for the Eu^{3+} ion situates usually above 30,000 cm^{-1} and the corresponding CTS bands for the Eu^{2+} ion would be at a much higher energy. Although the presence of Eu^{2+} can be stabilized in the Ca^{2+} (or Sr^{2+}) site by the lattice energy there is no such energy available for the stabilization of the Eu^+ ion. Moreover, the 5*d* bands for Dy^{3+} are at 50,000 cm^{-1} [36]. The band gap E_g in oxide materials situates above or at 40,000 cm^{-1}. The mechanisms proposed so far involve thus highly dubious processes in solid state and clearly impossible under mild near UV and visible excitation available at ambient conditions. The detailed mechanisms of persistent luminescence remain thus as open questions.

3.2. Structure of MAl_2O_4 and persistent luminescence

The present studies started from the identification of the luminous center. All $MAl_2O_4:Eu^{2+}$ (M = Ca and Sr) phosphors show strong broad band emission characteristic to the Eu^{2+} ion in the blue/green visible range under UV-excitation. The Eu^{2+} luminescence which, in general, can vary from UV to red depending on the host lattice, are, in the cases of $CaAl_2O_4:Eu^{2+}$ and $SrAl_2O_4:Eu^{2+}$ centered at 440 and 520 nm, respectively (Figs. 2 and 3). It is thus pretty certain that the broad band emission, excitation and absorption of MAl_2O_4:Eu^{2+} is due to transitions between the $^8S_{7/2}$ ($4f^7$) ground state and the crystal field components of the excited $4f^65d^1$ configuration of the Eu^{2+} ion [6]. The luminescence lifetime for the persistent luminescence is very long (hours) in contrast to the ordinary Eu^{2+}-doped materials with lifetimes of 700 ns to 1.2 μs [37]. Despite the enormous difference in the time scale, both the UV-excited and persistent luminescence occur at a practically identical spectral range. The band shape and width of the UV-excited luminescence and persistent luminescence spectra were found identical too (Figs. 2–4).

The same luminescence properties point out that the luminous center in both cases is the same Eu^{2+} ion. The shape of the emission bands at room temperature suggests that there is only one luminous center. However, a survey of the crystal structures of both $CaAl_2O_4$ and $SrAl_2O_4$ reveals that these monoclinic structures [38,39] (space groups $P2_1/n$ ($Z = 12$) and $P2_1$ ($Z = 4$), respectively) offer three and two M^{2+} sites for the Eu^{2+} ion, respectively. In the monoclinic $CaAl_2O_4$ there are one M^{2+} site with CN = 9 with a distorted tricapped trigonal antiprism coordination polyhedron and two sites with CN = 6 but with distorted octahedron coordination polyhedra. The average Ca–O distances, 2.420 and 2.434 Å, for the six-coordinated Ca-sites are clearly shorter than the average distance for the nine-coordinated Ca-site (2.784 Å). With the help of the ionic radii [40] it is clear that the Eu^{2+} ions—at least at low concentrations—prefer the large nine-coordinated Ca^{2+} site in $CaAl_2O_4$ (Fig. 5). This is in agreement with the observation of only one emission band.

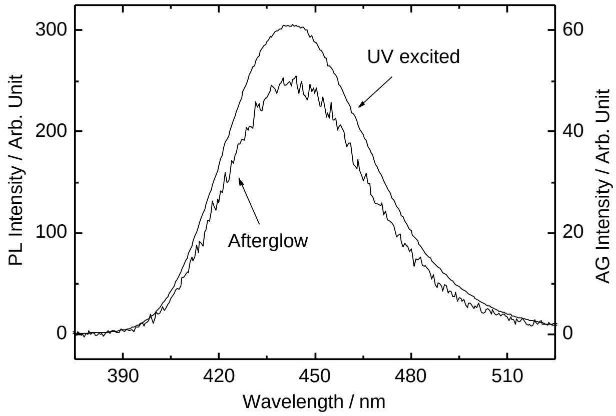

Fig. 2. UV excited (350 nm) luminescence and persistent luminescence spectra of $CaAl_2O_4$:Eu^{2+} at room temperature.

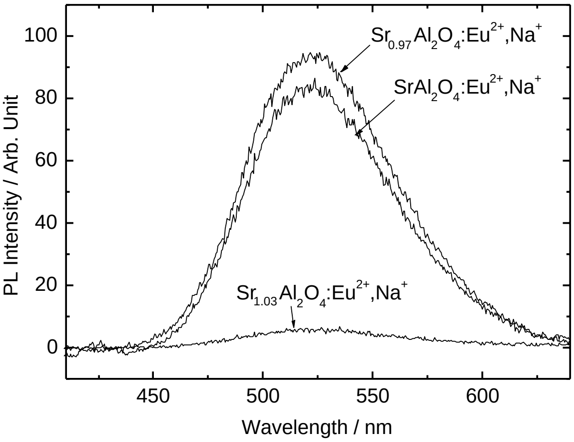

Fig. 3. Effect of stoichiometry on the UV excited (350 nm) luminescence of $SrAl_2O_4$:Eu^{2+}, Na^+ at room temperature.

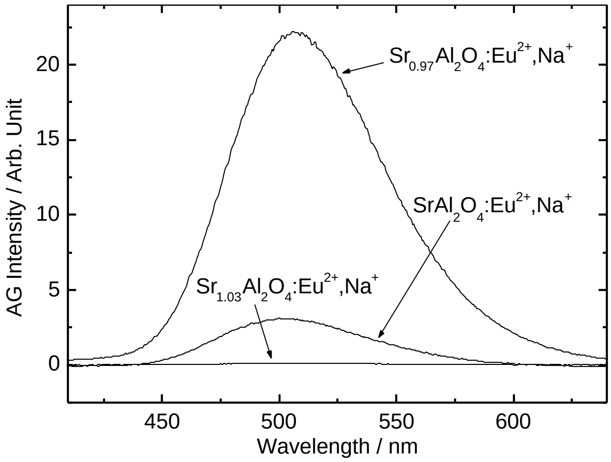

Fig. 4. Effect of stoichiometry on the persistent luminescence of $SrAl_2O_4$:Eu^{2+}, Na^+ at room temperature.

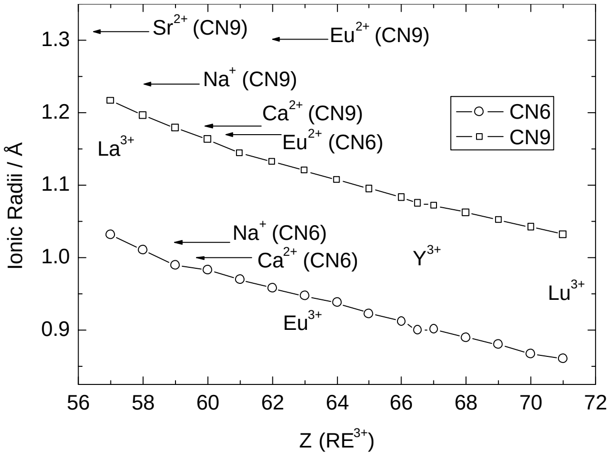

Fig. 5. Comparison of the ionic radii of the cations in MAl_2O_4:Eu^{2+}, R^{3+}, Na^+ (M = Ca, Sr) [40].

The situation is different for the $SrAl_2O_4$ host: although the crystal structures of both $CaAl_2O_4$ and $SrAl_2O_4$ belong to the same stuffed tridymite type, there are only two nine-coordinated Sr-sites with distorted tricapped trigonal antiprism coordination in the $SrAl_2O_4$ structure. The average Sr–O distances for these two sites are close to each other (2.876 and 2.838 Å) and thus no preferential site occupancy for the Eu^{2+} ions should be caused by the crystal structure. At low temperature, two band emission from $SrAl_2O_4:Eu^{2+}$ has been observed, indeed, but at room temperature there is only one band due to energy transfer between the two sites [41].

It is well known that some rare earth R^{3+} ions as Dy^{3+} and Nd^{3+} prolong and enhance considerably the persistent luminescence of $MAl_2O_4:Eu^{2+}$ [24]. Even if this effect will be treated in detail later, the sites occupied by the RE^{3+} ions in the MAl_2O_4 lattices are of interest. Comparison of the ionic radii of the M^{2+} and R^{3+} ions (Fig. 5) shows that the RE^{3+} ions fit rather well into the nine-coordinated sites in both host lattices. The smaller R^{3+} ions can, however, occupy the six-coordinated Ca-sites in $CaAl_2O_4$ too. These structural considerations show that already the starting point for the studies of the persistent luminescence in $MAl_2O_4:Eu^{2+}$ is rather complicated.

3.3. Effect of stoichiometry on persistent luminescence

An excess of barium has been shown to quench the persistent luminescence of $BaAl_2O_4:Eu^{2+},Dy^{3+}$ [28], whereas the Eu^{2+}- and Dy^{3+}-doped strontium aluminates with an Al/Sr ratio 2 have been shown to have the strongest persistent luminescence when the ratio was varied from 1 to 12 [42]. The variation of the composition in such a range may, however, lead easily to the formation of impurity phases. In this work, Eu^{2+}-doped alkaline earth aluminates with deficit, stoichiometric or excess amounts of alkaline earth were co-doped with Na^+ ions ($M_xAl_2O_4:Eu^{2+}$, Na^+; M = Ca or Sr, $x = 0.97$, 1.00 or 1.03).

Among calcium aluminates, the stoichiometric compound had the strongest UV-excited luminescence as well as persistent luminescence intensity whereas the non-stoichiometric compounds had lower intensities. The non-stoichiometry in the calcium aluminates seems thus to quench the persistent luminescence. The lattice defects formed do not favor the room temperature persistent luminescence but, instead, the traps may be too shallow or deep.

Among strontium aluminates the compounds with the deficit and stoichiometric amounts of strontium had equally strong UV-excited luminescence intensities (Fig. 3). The luminescence of the compound with excess strontium is very weak compared to those of the other two compounds. The reason for the weak luminescence intensity may be the creation of alternative relaxation paths through which the excitation energy may be lost. The persistent luminescence intensity of the compound with strontium deficit is superior to those of the others (Fig. 4). This observation supports well the importance of the cation and anion vacancies involved in the persistent luminescence processes.

3.4. Effect of sodium co-doping on persistent luminescence

The luminescence and afterglow properties of $MAl_2O_4:Eu^{2+}$, Na^+ were studied for the first time to the knowledge of the authors. The Na^+ co-doping was supposed to decrease the number of cation vacancies. The persistent luminescence intensities of calcium aluminates with and without Na^+ co-doping are equally strong. All calcium aluminates have the typical persistent luminescence time dependence where two or even three processes may be involved. The stoichiometric compound had the longest and the non-stoichiometric compounds had equal to each other but somewhat shorter persistent luminescence decay time. The results suggest that the sodium ion is not entering into the cation vacancies which idea is supported by the ionic radii of Na^+ being larger than that of Ca^{2+} (Fig. 5).

In the strontium aluminate host, the Na^+ co-doping quenched efficiently the persistent luminescence intensity (Fig. 6). Only the compound with deficit strontium had the typical persistent luminescence decay, whereas the persistent luminescence of the other two compounds is quenched logarithmically (Fig. 7). In the compound with excess strontium the lack of cation vacancies may be dominantly responsible for the quenching of persistent luminescence. Also the Na^+ co-doping and possible alternative relaxation paths of excitation energy may quench the afterglow. In the compound with strontium deficit the quenching effect of Na^+ is not so significant but this may be due to the high amount of crystal defects which enhance the persistent luminescence.

3.5. Effect of rare earth co-doping on persistent luminescence

The afterglow of the Eu^{2+} ion has been shown to be enhanced by co-activation with only some trivalent rare

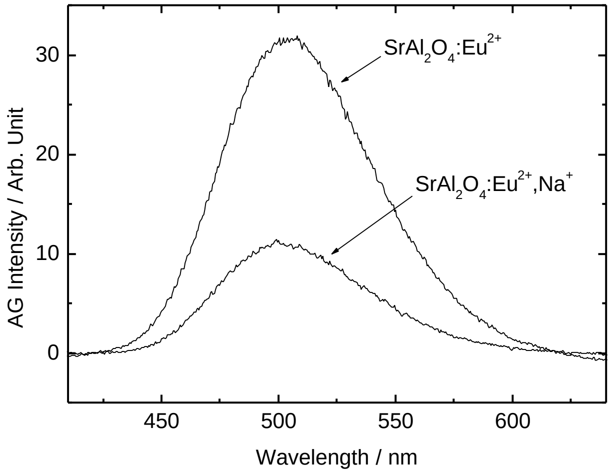

Fig. 6. Effect of sodium co-doping on the persistent luminescence of $SrAl_2O_4:Eu^{2+}$ at room temperature.

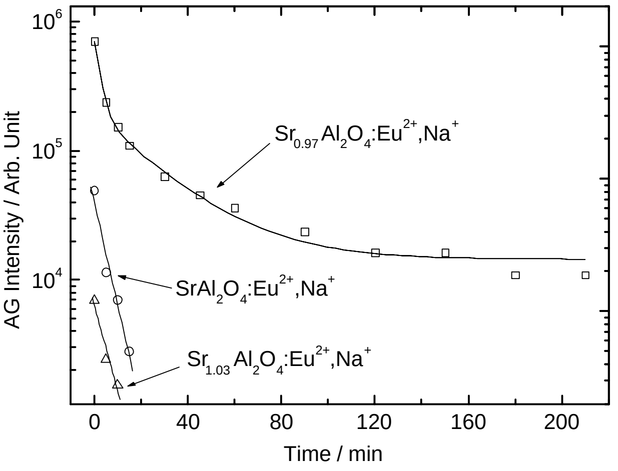

Fig. 7. Effect of the stoichiometry on the persistent luminescence lifetimes of $SrAl_2O_4:Eu^{2+}, Na^+$ at room temperature.

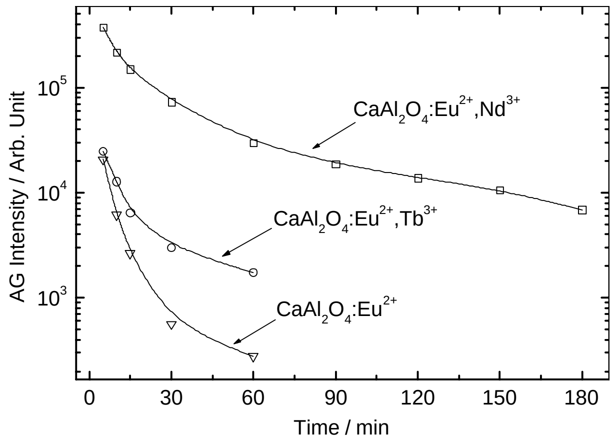

Fig. 9. Effect of rare earth co-doping on the persistent luminescence lifetimes of $CaAl_2O_4:Eu^{2+}, R^{3+}$ at room temperature.

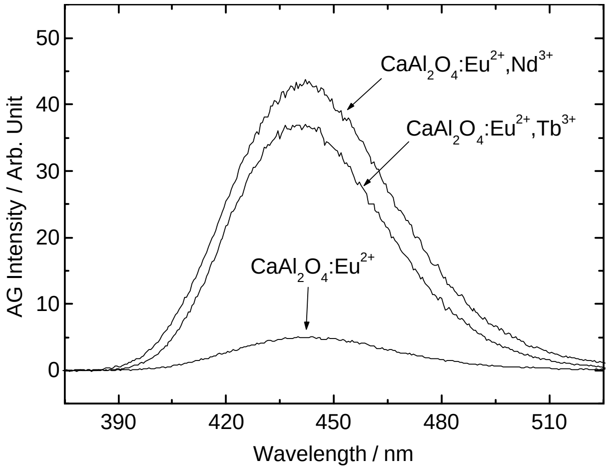

Fig. 8. Effect of rare earth co-doping on the persistent luminescence of $CaAl_2O_4:Eu^{2+}, R^{3+}$ at room temperature.

earth ions, e.g. Dy^{3+} and Nd^{3+} [30–32]. The Eu^{2+} ion acts as a luminescent center with luminescence at the blue and green regions for $CaAl_2O_4:Eu^{2+}$ and $SrAl_2O_4:Eu^{2+}$, respectively, whereas the R^{3+} ion are assumed to act as traps in these phosphors [24]. The intensity of the persistent luminescence has been found to depend strongly on the depth of these traps. The previous studies have, however, been concentrated only on the best persistent luminescence materials, i.e. $CaAl_2O_4:Eu^{2+}, Nd^{3+}$ and $SrAl_2O_4:Eu^{2+}, Dy^{3+}$. A systematic and exhaustive study of the phosphors doped only with Eu^{2+} and, on the other hand, co-doped with the whole R^{3+} series is missing, even if this kind of study is expected to reveal new facts about the persistent luminescence mechanism.

The R^{3+} ion co-doping was not found to change the persistent luminescence band position nor the shape of the spectrum (Figs. 2 and 8). The emission can thus be concluded to originate from the same Eu^{2+} center as for the non-co-doped $CaAl_2O_4:Eu^{2+}$. The luminescence from the R^{3+} or Eu^{3+} ions has not been observed which indicates that neither direct excitation of R^{3+} nor energy transfer from Eu^{2+} to R^{3+} occurs. The persistent luminescence intensity was found to depend strongly on the co-doping RE^{3+} ion: the Ce^{3+}, Pr^{3+}, Nd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+} and Tm^{3+} ions enhance—more or less—the persistent luminescence of $CaAl_2O_4:Eu^{2+}$ (Fig. 8). The most intense persistent luminescence was obtained with Nd^{3+} co-doping in agreement with previous studies. The enhancement of the persistent luminescence of $CaAl_2O_4:Eu^{2+}$ was extended not only to the intensity of persistent luminescence but the lifetime of the persistent luminescence was increased too (Fig. 9).

The La^{3+}, Gd^{3+}, Er^{3+}, Lu^{3+}, and Y^{3+} ions quenched to varying extent the persistent luminescence of $CaAl_2O_4:Eu^{2+}$, whereas the Sm^{3+} and Yb^{3+} ions caused a drastic decrease in the intensity of the persistent luminescence of $CaAl_2O_4:Eu^{2+}$. The last result was interpreted in such a way that the Sm^{3+} and Yb^{3+} ions can be reduced to the divalent state and are thus able to fill the cation vacancies involved in the persistent luminescence processes. As a proof of the presence of divalent Sm^{2+} the Nd:YAG laser excitation produced the typical luminescence spectrum of the $4f^6$ configuration (Fig. 10) with the easily recognizable $^5D_0 \rightarrow {}^7F_{0-2}$ transitions [43–45].

The typical TL glow curve of $CaAl_2O_4:Eu^{2+}$, (R^{3+}) has one prominent, broad peak at ca. 80°C followed by a tail up to 200°C (Fig. 11). The materials co-doped with the Ce^{3+}, Pr^{3+}, Tb^{3+} and Ho^{3+} ions had the same TL main peak (Fig. 11), but with increased intensity. The Nd^{3+}, Dy^{3+} and Tm^{3+} ions seemed to enhance strongly the high-temperature tail of $CaAl_2O_4:Eu^{2+}$. The glow curve of $CaAl_2O_4:Eu^{2+}, Nd^{3+}$ was very wide between 40°C and 200°C with a maximum at ca. 100°C

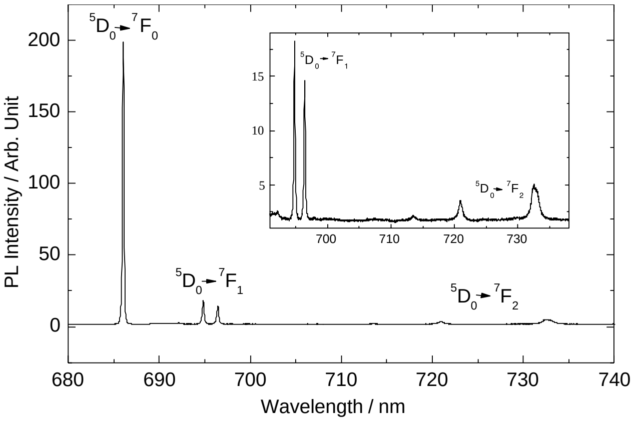

Fig. 10. Photoluminescence of Sm^{2+} in $CaAl_2O_4$:Eu^{2+}, Sm^{3+} at 77 K ($\lambda_{ex} = 532$ nm).

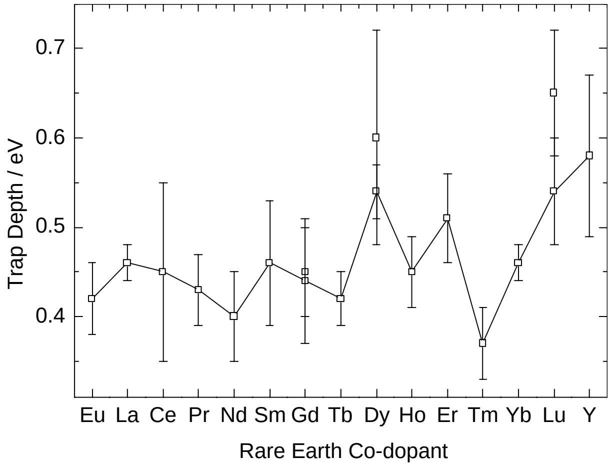

Fig. 12. Trap depths calculated by the heating rate method for $CaAl_2O_4$:Eu^{2+}, R^{3+}.

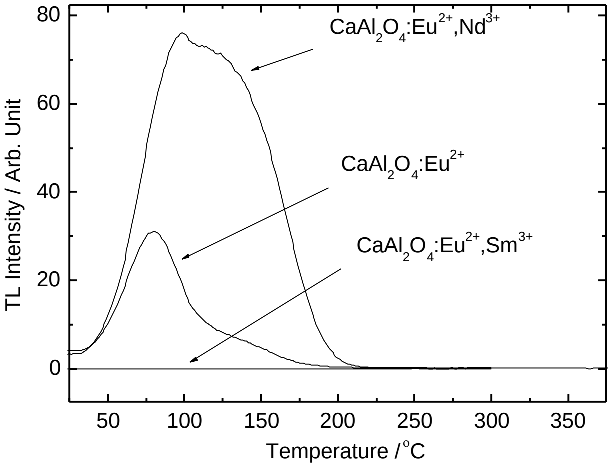

Fig. 11. Effect of rare earth co-doping on the TL glow curves of $CaAl_2O_4$:Eu^{2+}, R^{3+}.

probably consisting of several maxima close to each other. The La^{3+}, Gd^{3+}, Er^{3+} and Lu^{3+} ions suppressed strongly the TL of $CaAl_2O_4$:Eu^{2+}, whereas the Sm^{3+}, Yb^{3+} and Y^{3+} ions created also new high-temperature peaks. As a conclusion, it is quite clear that the easily reducible rare earths (Yb^{3+} and Sm^{3+}) suppressed TL intensity, whereas the easily oxidable rare earths (Ce^{3+}, Tb^{3+} and Pr^{3+}) enhanced the main TL peak intensity. The "neutral" R^{3+} ions had clearly weaker effect on the main TL peak intensity. The TL results support the observations made of the intensity of the persistent luminescence.

Using the heating rate method the trap depths of the TL main peaks of the $CaAl_2O_4$:Eu^{2+}, R^{3+} materials were estimated. The trap depths for $CaAl_2O_4$:Eu^{2+} as well as for the La^{3+}, Ce^{3+}, Pr^{3+}, Tb^{3+}, Ho^{3+} and Er^{3+} co-doped materials, which have simple glow curves with only one prominent peak, were between 0.42 and 0.51 eV (Fig. 12). For the glow curves with two overlapping peaks (Gd^{3+}, $Dy^{3+}$and Lu^{3+} co-doped aluminates), which are, however, visually separable, the first trap energy was estimated between 0.44 and 0.54 eV and the second one between 0.45 and 0.65 eV. For the Nd^{3+} and Tm^{3+} co-doped materials with one very broad TL peak the trap energies corresponding to the main TL peak were estimated as ca. 0.4 eV. For the Sm^{3+}, Yb^{3+} and Y^{3+} co-doped materials, which had new high temperature peaks in the glow curve, the first trap was between 0.5 and 0.7 eV. The R^{3+} ions had no drastic effect on the trap depths, in contrast to the TL intensities. Thus the trap densities rather than the depths seem to have importance for persistent luminescence. The estimated trap depth energies in the heating rate method have relatively large errors (between 0.02 and 0.1 eV) and thus the preheating method was used to estimate the reliability of the analysis as well as the real number of trapping levels. With the preheating technique various trapping levels for the $CaAl_2O_4$:Eu^{2+}, R^{3+} materials were observed indeed. As an example, $CaAl_2O_4$:Eu^{2+}, Dy^{3+} had at least one trap at ca. 80°C (Fig. 13), but it disappeared or was superimposed by stronger high temperature peaks already when using T_{stop} temperatures above 60°C, followed by almost linear increase above 120°C suggesting continuously distributed or closely overlapped trapping levels.

3.6. *Mechanism of persistent luminescence*

Although several studies of the persistent luminescence phenomenon have already been published, the mechanisms obtained from the MAl_2O_4:Eu^{2+}, R^{3+} materials have not been elucidated. Theories presented up to date are deficient or even contradictory. One reason of the uncertainty can be that the original afterglow of MAl_2O_4:Eu^{2+} has almost totally been

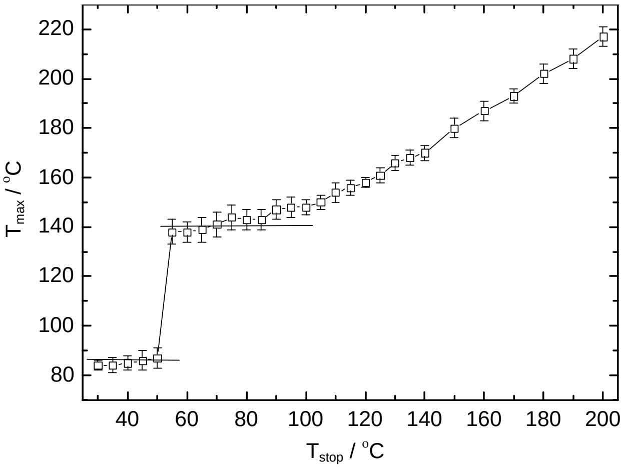

Fig. 13. Preheating curve of $CaAl_2O_4:Eu^{2+}, Dy^{3+}$.

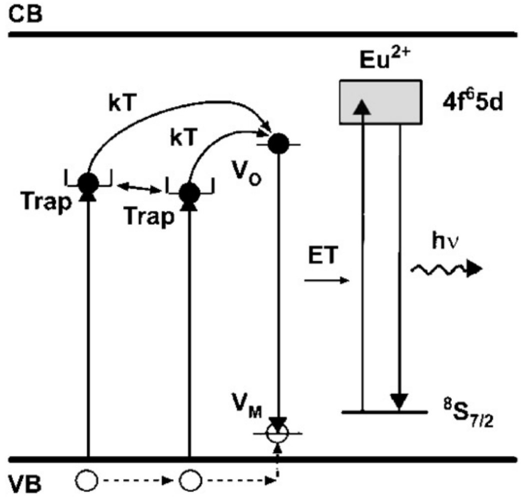

Fig. 14. Proposed mechanism of the persistent luminescence of $CaAl_2O_4:Eu^{2+}$.

forgotten although the properties of this material are very similar to the more efficient $MAl_2O_4:Eu^{2+}, R^{3+}$ ones. The rather schematic mechanisms presented involve either a direct or valence band assisted transfer of a hole from Eu^{2+} to a trap and its eventual recombination with the emitting Eu^{2+} center after thermal excitation. However, these mechanisms involve the creation of Eu^+ (and R^{4+}) ions which are highly dubious processes in solid state.

In this work, an alternative mechanism for the persistent luminescence in $MAl_2O_4:Eu^{2+}$ was searched for and is presented (Fig. 14). The excitation energy is provided either directly to the traps or via the conduction band. The electron traps are then bleached thermally at room temperature and feed electrons to the electron–hole recombination process which causes the excitation of the Eu^{2+} luminescence center by non-radiative energy transfer. The emission results from the normal de-excitation of the Eu^{2+} luminescence center. The whole process may require close contact between different defect centers (oxygen and calcium vacancies as well as the emitting Eu^{2+} ion) since the conduction band may be at too high energy to be used for electron migration. The mechanism proposed here needs no presence of monovalent Eu^+ ions. Moreover, the presence of cation (as well as oxygen) vacancies in calcium aluminates has been known already since the early 1970s [6]. The feeding of the Eu^{2+} persistent luminescence center is similar to the storage phenomena in wide band gap semiconducting materials, e.g. Si doped by Er^{3+} [46,47] and in photosimulated phosphors [35]. However, further studies utilizing different experimental spectroscopic and other techniques are needed to prove and reveal the details of the proposed mechanism.

4. Conclusions

The systematic study of other $CaAl_2O_4:Eu^{2+}$ and $SrAl_2O_4:Eu^{2+}$ with R^{3+} co-dopants other than Nd^{3+} and Dy^{3+} revealed important information so far ignored in the literature about the mechanism of persistent luminescence. It was concluded that neither reduction of Eu^{2+} to Eu^+ nor oxidation of Nd^{3+}/Dy^{3+} to Nd^{4+}/Dy^{4+} occurs in the persistent luminescence processes. However, due to reducing preparation conditions, the reduction of Sm^{3+} (and Yb^{3+}) produces Sm^{2+} (and Yb^{2+}) ions which remove the cation vacancies which act as hole traps. The R^{3+} co-doping in M^{2+} sites creates more lattice defects which enhance both the intensity and lengthen the lifetimes of persistent luminescence. It is concluded that the role of lattice defects in $MAl_2O_4:Eu^{2+}$ as traps is very important for the persistent luminescence. The $4f^N$ energy level scheme of the R^{3+} ion may also be of importance but the details of this effect are not yet clear. The energy transfer or/and cross-relaxation which feeds the emitting Eu^{2+} center underline the complicated nature of the final mechanism and emphasize the need to further studies.

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