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Persistent luminescence of Eu^{2+} doped alkaline earth aluminates, MAl_2O_4:Eu^{2+}

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Abstract

The polycrystalline Eu^{2+} and RE^{3+} (rare earth) doped alkaline earth aluminates MAl_2O_4:Eu^{2+},RE^{3+} (M=Ca and Sr) were prepared by a solid state reaction starting from the corresponding oxides (Al, RE) and carbonates (Ca, Sr). The UV-excited photoluminescence, persistent luminescence (afterglow) and thermoluminescence of these materials was studied and compared. The two spectra (band position and width) were very similar indicating that the luminescent centre is an Eu^{2+} ion in both cases. A slight blue shift was observed in the afterglow emission in some cases. The RE^{3+} co-doping had no effect on the position and shape of the persistent luminescence band but the Nd^{3+} and Dy^{3+} ions enhanced the most the afterglow and thermoluminescence of the $CaAl_2O_4$:Eu^{2+} and $SrAl_2O_4$:Eu^{2+} materials, respectively. Easily reducible rare earth ions such as Sm^{3+} and Yb^{3+} suppressed both the afterglow and thermoluminescence of MAl_2O_4:Eu^{2+}. Based on these observations, the mechanism of RE^{3+} co-doping is discussed.

Keywords: Phosphors; Recombination and trapping; Luminescence

1. Introduction

The Eu^{2+} doped solid state materials usually show strong broad band luminescence with a short decay time — of the order of some tens of nanoseconds [1]. The characteristic broad band luminescence originates from transitions between the $^8S_{7/2}$ ($4f^7$) ground state and the crystal field components of the $4f^6 5d^1$ excited state configuration (Fig. 1). The luminescence is very strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electromagnetic spectrum. The very short decay time and strong intensity of the luminescence is due to the allowed nature of the electronic interconfigurational transitions — both in the excitation and emission. The Eu^{2+} emission is intense enough to find important industrial applications in, for example, the tricolor low pressure mercury fluorescence lamps.

In addition to the initial very short decay time, the photoluminescence of Eu^{2+} doped alkaline earth aluminates, MAl_2O_4:Eu^{2+} (M=Ca, Sr, Ba), also show luminescence with very long lifetime at the same characteristic blue/green visible range as the photoluminescence itself [2–5]. This long decay is detrimental to the use of these materials as ordinary luminophors. However, since the lifetime greatly exceeds that of any other material known to date [6], this offers an unexpectedly large field of applications for the use of these aluminates.

The long afterglow exhibited by some materials is

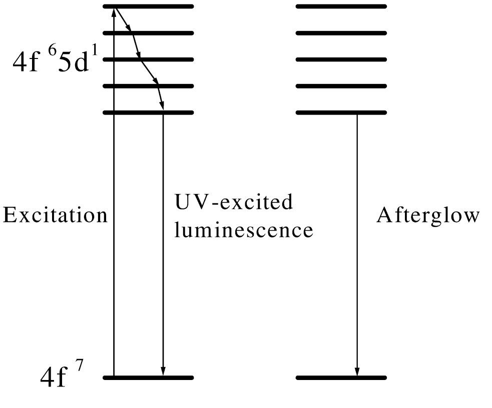

Fig. 1. Energy level scheme of the Eu^{2+} ions involved in the UV-excited and persistent luminescence processes in MAl_2O_4:Eu^{2+},RE^{3+}.

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usually considered as a disadvantageous feature among the properties of the phosphor when applications are concerned. Despite the initially unwanted nature of the strong afterglow, there has been a constantly growing market for persistent luminescence materials for several tens of years. The material mainly used so far, ZnS doped with copper is, however, extremely sensitive to moisture and thus is chemically unstable [6]. Moreover, the duration of the visible afterglow is unsatisfactory being of the order of a few hours only.

The origin of the extremely long persistent luminescence of $MAl_2O_4:Eu^{2+}$ is probably due to alkaline earth vacancies [6]. The effective mechanism of the persistent luminescence is not known but it is supposed to involve the formation of both electron and hole trapping and subsequent slow thermal bleaching of the traps followed by emission from Eu^{2+} ions [7–11]. The main charge carriers in similar systems (e.g. photostimulated materials [12]) were identified as electrons and ions but the importance of holes has gained more ground in the persistent luminescence materials, however. The persistent luminescence lifetime and intensity can be enhanced even more with the addition of some trivalent RE^{3+} ions [9]. As for the practical applications, even the alkaline earth aluminates have been found too sensitive to moisture despite their luminescence properties being much superior to the conventional ZnS:Cu materials.

There is thus a demand for better and more stable materials. The search for persistent luminescence materials would be greatly facilitated if the underlying mechanisms were known. In the present work, a systematic investigation was carried out on the Eu^{2+} doped alkaline earth aluminates $MAl_2O_4:Eu^{2+}$. Especially, the role of the co-doping with different RE^{3+} ions in the enhancement of the afterglow from $MAl_2O_4:Eu^{2+},RE^{3+}$ was studied by several spectroscopic means, i.e. the photoluminescence, persistent luminescence, and thermoluminescence of these materials were examined in detail.

2. Experimental

2.1. Sample preparation

The polycrystalline Eu^{2+} and RE^{3+} doped alkaline earth aluminates $MAl_2O_4:Eu^{2+},RE^{3+}$ (M=Ca and Sr; RE^{3+}= La^{3+}–Lu^{3+}, Y^{3+}; excluding Pm^{3+} and Eu^{3+}) were prepared by a high temperature solid state reaction between the stoichiometric mixtures of the alkaline earth carbonates (MCO_3), aluminum oxide (Al_2O_3), europium oxide (Eu_2O_3) and rare earth oxide (usually RE_2O_3), in a reducing (N_2+12% H_2) gas sphere at 1250–1300°C for 4–6 h with boron oxide (B_2O_3, 1 mol %) used as a flux. Prior to heating the reagents were intimately ground to a homogeneous mixture in a mortar or by a ball mill. The heating was carried out in an alumina boat in order to reduce the contamination of the sample. The nominal concentration of the Eu^{2+} dopant and the RE^{3+} co-dopants were 0.5 and 1 mol %, respectively. The purity of the starting materials ranged from the luminescent material grade (at least 4 N) for the RE oxides to the standard analytical grade for the other materials. The phase and structural purity of all samples were routinely checked by X-ray powder diffraction methods — followed in some cases by the Rietveld profile refinement analysis, but no presence of additional phases or impurities was observed.

2.2. Instrumental methods

The conventional UV-excited photoluminescence and afterglow spectra were obtained at room temperature with a Perkin-Elmer LS-5 spectrometer with the narrow band excitation at 350 nm from a 8.3 W xenon lamp. Prior to the afterglow measurements, the samples were exposed to irradiation from a normal 11 W tricolor luminescent lamp for 10 s. The delay time between the initial irradiation and afterglow measurements was 3 min.

The thermoluminescence glow curves were measured with a Risø TL/OSL-DA-12 system in the temperature range between 25 and 500°C using heating rates of 2, 4, 6, 8 and 10°C s^{-1}. The global TL emission from UV to 600 nm was monitored. Prior to the thermoluminescence measurements, the samples were exposed for 10 s to the irradiation from a normal 60 W incandescent lamp. The delay time between the initial irradiation and thermoluminescence measurements was 3 min. The irradiation was chosen to correspond to the actual application conditions of the materials studied.

3. Results and discussion

3.1. UV-excited photoluminescence

Under UV-excitation $CaAl_2O_4:Eu^{2+}$ yielded at room temperature blue (λ_{max}=440 nm; Fig. 2) and $SrAl_2O_4:Eu^{2+}$ green luminescence (λ_{max}=520 nm). Both emission bands could be fitted to a single Gaussian profile indicating emission from one site only. This seems to be in contrast to the crystallographic data which yields for these two tridymite type monoclinic structures (with space groups $P2_1/n$ and $P2_1$, respectively) three and two M^{2+} sites of very low symmetry, respectively [13,14]. In $CaAl_2O_4$, the Eu^{2+} ion seems to have a pronounced tendency to occupy the nine coordinated site with most space while at low temperature, two emission bands have been observed from the two sites in $SrAl_2O_4:Eu^{2+}$ [5]. The intraconfigurational 4f–4f transitions of the Eu^{2+} ion are too weak to be observed with the sensitivity scale of the measurements since they are not allowed by the parity rule (as well as by any other selection rule either).

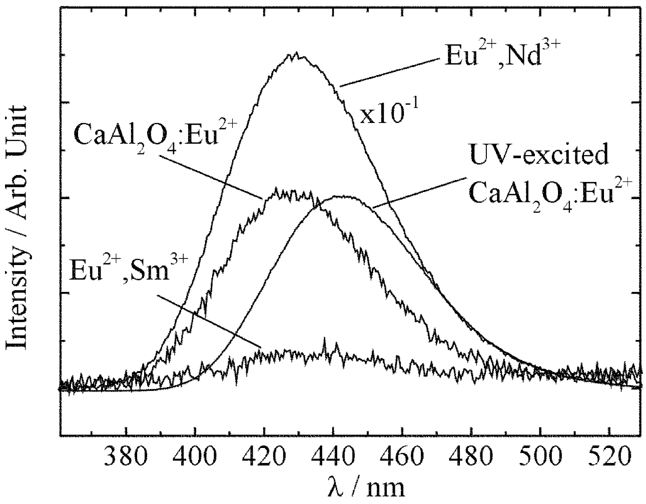

Fig. 2. UV-excited and afterglow spectra of selected $CaAl_2O_4:Eu^{2+},RE^{3+}$ materials.

3.2. Persistent luminescence

The shape and bandwidth of the UV-excited luminescence and afterglow spectra are, however, close to identical indicating that the emitting centre in both cases is still an Eu^{2+} ion (Fig. 2). The slight blue shift in the afterglow band may be explained by the perturbing effect of neighboring defects. Since the excited $4f^6 5d$ configuration of the Eu^{2+} ion is extremely sensitive to the changes in the environment in contrast to the well shielded $4f^7$ ground configuration the afterglow emission wavelength may be modified, too. It has generally been agreed that the persistent luminescence is due to the trapping of energy in the defects followed by a slow thermal bleaching of the traps and transport of the charge carriers to the recombination centre — the Eu^{2+} ion. Originally, the defects in the alkaline earth aluminates were identified as alkaline earth vacancies V_M since it was observed that only the barium aluminate materials with stoichiometric amount or excess of aluminum oxide exhibited strong afterglow while materials with excess of alkaline earth showed very poor persistent luminescence [15]. The fast decay emission from the $MAl_2O_4:Eu^{2+}$ materials originates from the Eu^{2+} ions in the normal M^{2+} sites while the afterglow emission with long decay originates from the Eu^{2+} ion sites fed by the neighboring defects. In order to have this process efficient — as it was experimentally observed — the distance between trap and the recombination centre should be short. The lattice defects also have a tendency to group together in a material which should facilitate this process.

3.3. Effect of the addition of RE^{3+} ions

The addition of only a few RE^{3+} ions (Nd^{3+} and Dy^{3+}) as co-doping ions to the $MAl_2O_4:Eu^{2+}$ systems ($CaAl_2O_4:Eu^{2+}$ and $SrAl_2O_4:Eu^{2+}$, respectively [7]) has been shown to enhance significantly the persistent luminescence of the Eu^{2+} ion. In our experiments, similar results were obtained. Despite the fact that the $CaAl_2O_4:Eu^{2+},Nd^{3+}$ and $SrAl_2O_4:Eu^{2+},Dy^{3+}$ systems have been rather extensively studied by several research groups, the underlying mechanisms for the persistent luminescence from the aluminate materials are not known at all. Even the nature of the charge carriers is contested, even though most support the dominating role of the holes. One of the reasons for the disagreement might be that the investigations have been limited to the clarification of the effect of the best RE^{3+} co-dopants while the study of the other co-dopants might well throw a lot of new light into the mechanisms. Accordingly, in this work the effect of all the RE^{3+} co-dopants was studied in detail.

As the first result, the addition of any of the RE^{3+} co-dopants did not change the wavelength position or the bandwidth of the afterglow or photoluminescence spectra. On the other hand, RE^{3+} ions such as Sm^{3+} and Yb^{3+} suppressed severely both the afterglow and the UV-excited luminescence of $MAl_2O_4:Eu^{2+}$. The common feature of these quenching ions is their easy reduction to the divalent state. The suppression of the afterglow can be due to the charge transfer from the Eu^{2+} ion to the Sm^{3+}/Yb^{3+} ion which is a well known phenomenon to occur as a result of an interaction between the dopant and the host matrix [1]. After this redox process a substantial number of the europium ions would be in the trivalent state. However, the luminescence of the Eu^{3+} or Sm^{2+}/Yb^{2+} ions was not observed as can be expected due to the weak luminescence of those ions compared with the Eu^{2+} ion, the UV-excited emission of which still dominates the emission despite partial quenching. On the other hand, the Sm^{2+} and Yb^{2+} ions can easily occupy the M^{2+} vacancies thus depriving the persistent luminescence of its excitation source.

3.4. Thermoluminescence

In order to investigate further the significant effect of the RE^{3+} co-doping on the intensity of the persistent luminescence from the $MAl_2O_4:Eu^{2+}$ materials, the measurement of the thermoluminescence glow curves of these materials was carried out. The thermoluminescence of the monoclinic $CaAl_2O_4:Eu^{2+}$ was observed at temperatures between 40 and 190°C (Fig. 3). The maximum of the glow curve was at 90°C beyond which the TL intensity decreased rapidly until the second weaker maximum at 160°C. With RE^{3+} co-doping, a strong and wide glow peak of the $CaAl_2O_4:Eu^{2+},Nd^{3+}$ was found between 40 and 240°C with the maximum at 135°C. The curve consists of several maxima next to each other and thus the formation of several new traps was confirmed. Trapping levels are probably very close to each other which should be expected since the charge compensation effects between the RE^{3+} ions and the M^{2+} ions in which site the RE^{3+} ions are expected to reside can be of several types and of

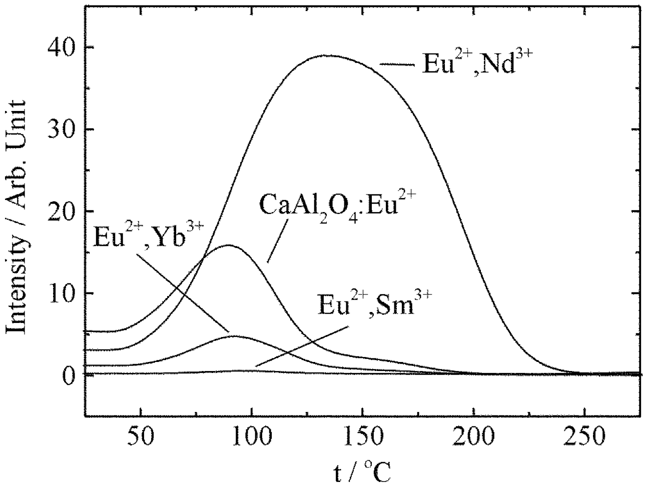

Fig. 3. Thermoluminescence glow curves of selected $CaAl_2O_4:Eu^{2+},RE^{3+}$ materials.

different crystallographic orientations. The most probable defect created by the charge compensation is again the M^{2+} ion vacancy since two RE^{3+} ions may replace three M^{2+} ions. The other possibility of the charge compensation, the introduction of interstitial oxide ions, is much less probable because of the reducing gas sphere used in the preparation and the tendency of the material itself to form M^{2+} ion vacancies.

Because the thermoluminescence of the $CaAl_2O_4:Eu^{2+},Nd^{3+}$ was observed near room temperature, the depth of the traps was appropriate to produce an intense and persistent luminescence. The exact mechanism of the RE^{3+} co-doping, however, is far from clear. As pointed out by several authors (e.g. Ref. [11]), the mechanism(s) may be much more complicated than the direct feeding of the emitting Eu^{2+} centre. In fact, several facts contradict this simple effect: first, neither the afterglow emission band position nor the shape were affected by the RE^{3+} co-doping. Moreover, the Gaussian profile of the thermoluminescence glow peaks suggests a 2nd order kinetic mechanism, in other words, the retrapping of the energy released from the RE^{3+} traps would occur. In conclusion, the Nd^{3+} co-doping may have two different effects pointing out to the same direction, i.e. to the enhancement of the afterglow from $CaAl_2O_4:Eu^{2+},Nd^{3+}$: first, the creation and possibly at the same time the stabilization of the M^{2+} vacancies, and secondly, the feeding of the energy trapped to the RE^{3+} sites to the M^{2+} vacancies and finally to the emitting Eu^{2+} centre. Similar results were obtained for $SrAl_2O_4:Eu^{2+},Dy^{3+}$.

The thermoluminescence maximum at 90°C in $CaAl_2O_4:Eu^{2+}$ was strongly suppressed by the Yb^{3+} and Sm^{3+} ions which agrees well with the fact that these ions also suppressed the afterglow of $CaAl_2O_4:Eu^{2+}$. This may indicate that the quenching of the persistent luminescence might not be due to a direct charge transfer from the Yb^{3+} and Sm^{3+} ions to the Eu^{2+} ion but a perturbation or even a destruction of the traps directly feeding the emitting Eu^{2+} centre. Once again, some kind of charge transfer may be involved but this requires more detailed studies.

3.5. Mechanism of persistent luminescence

The persistent luminescence as well as thermoluminescence result from the thermally stimulated recombination of trapped charge carriers (Fig. 4). In the case of the persistent luminescence, the electrons/holes can be released from the traps at near room temperature. In the simplest model, electrons and holes are distributed evenly in the matrix and the distance between the different charge carriers is rather long. In the case of the hole trapping, the thermal excitation from the trapping level to the recombination centre takes place via the valence band. Some results of this work may suggest that the traps and emitting centres are located very close to each other. Accordingly, an alternative model of localized transitions should be considered, According to this model, the trapped electrons and holes are located as pairs and luminescence can result from indirect centre-to-centre transitions. In the $MAl_2O_4:Eu^{2+},RE^{3+}$ materials, the persistent luminescence is very strong and thus the mechanism has to be very effective or/and the distances short between the species participating in the process. In the case of localized transitions, thermoluminescence will not be accompanied

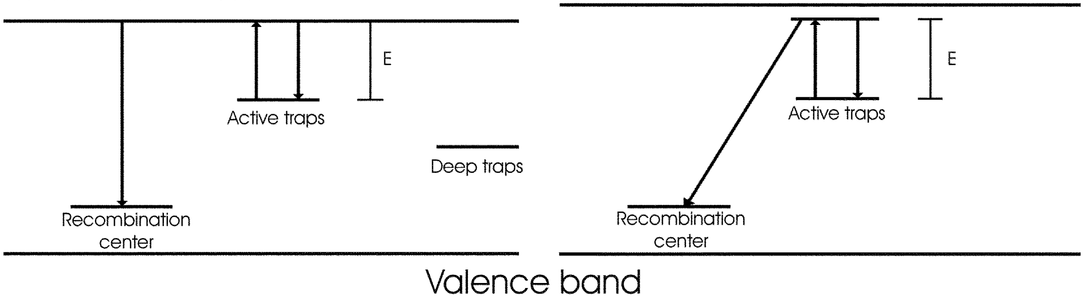

Fig. 4. Thermoluminescence models.

by thermally stimulated conductivity. Although the photoconductivity of the Eu^{2+} doped alkaline earth aluminates has been reported [7], taking into account the experimental difficulties and the difficult quantification of the results, the persistent luminescence mechanism may well also involve localized transitions.

4. Conclusions

The shape and bandwidth of the UV-excited photoluminescence and persistent luminescence spectra are similar indicating the same emitting Eu^{2+} ion centre. A slight blue shift was sometimes observed in the afterglow band of MAl_2O_4:Eu^{2+}. The alkaline earth vacancy perturbing the electrostatic field around the Eu^{2+} ion in MAl_2O_4 may be the reason for this shift but verification needs some additional work.

The RE^{3+} co-doping drastically affected the intensity of both the afterglow and the thermoluminescence of MAl_2O_4:Eu^{2+},RE^{3+}. The co-doping of $CaAl_2O_4$ and $SrAl_2O_4$ by Nd^{3+} and Dy^{3+}, respectively, intensifies the luminescence of MAl_2O_4:Eu^{2+} by an order of magnitude. However, the easily reducible rare earths like Sm^{3+} and Yb^{3+} suppressed both the afterglow and the thermoluminescence. This can be due to charge transfer from the Eu^{2+} ion to the RE^{3+} ion or to the partial suppression of the initial traps, presumably the M^{2+} vacancies. In the opposite manner, the enhancement of the persistent luminescence may be due to the increase in the number and/or the efficient feeding of the trapped energy to the M^{2+} vacancies.

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