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Persistent luminescence behavior of materials doped with Eu$^{2+}$ and Tb$^{3+}$

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Abstract: In this work, the persistent luminescence mechanisms of Tb$^{3+}$ (in CdSiO$_3$) and Eu$^{2+}$ (in BaAl$_2$O$_4$) based on solid experimental data are compared. The photoluminescence spectroscopy shows the different nature of the inter- and intraconfigurational transitions for Eu$^{2+}$ and Tb$^{3+}$, respectively. The electron is the charge carrier in both mechanisms, implying the presence of electron acceptor defects. The preliminary structural analysis shows a free space in CdSiO$_3$ able to accommodate interstitial oxide ions needed by charge compensation during the initial preparation. The subsequent annealing removes this oxide leaving behind an electron trap. Despite the low band gap energy for CdSiO$_3$, determined with synchrotron radiation UV-VUV excitation spectroscopy of Tb$^{3+}$, the persistent luminescence from Tb$^{3+}$ is observed only with UV irradiation. The need of high excitation energy is due to the position of $^7F_6$ level deep below the bottom of the conduction band, as determined with the $^4I_9^1\rightarrow^4I_{5^1}$ and the ligand-to-metal charge-transfer transitions. Finally, the persistent luminescence mechanisms are constructed and, despite the differences, the mechanisms for Tb$^{3+}$ and Eu$^{2+}$ proved to be rather similar. This similarity confirms the solidity of the interpretation of experimental data for the Eu$^{2+}$ doped persistent luminescence materials and encourages the use of similar models for other persistent luminescence materials.

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References and links


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1. Introduction

Persistent luminescence materials can emit light for several hours after the removal of the irradiation source. These materials have received special attention lately due to their significant applications in emergency signalization, micro defect sensing, optoelectronics for image storage, detectors of high energy radiation and thermal sensors [1,2]. The persistent luminescence phenomenon is considered a special case of thermally stimulated luminescence, where the excitation energy is stored to traps and then released, induced by thermal energy available at room temperature [1]. The advance in the persistent luminescence materials research arose with the discovery of the phosphor Sr\(_2\)Al\(_2\)O\(_4\)-Eu\(^{2+}\),Dy\(^{3+}\) [2] in 1996. This breakthrough was followed by the finding of new efficient persistent luminescence materials based on different stable aluminates CaAl\(_2\)O\(_4\)-Eu\(^{2+}\),Nd\(^{3+}\) [1], Sr\(_2\)Al\(_2\)O\(_4\)-Eu\(^{2+}\),Dy\(^{3+}\) [3] and
silicate materials like \( \text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+} \) [4]. Presently, the best materials can continue emitting light in excess of 24 \( \text{h} \) in the dark.

One may observe that the majority of published works are about \( \text{Eu}^{2+} \) doped materials. Despite this majority, other materials containing different dopants, such as \( \text{Tb}^{3+} \) [5–8], \( \text{Eu}^{3+} \) [9,10], \( \text{Mn}^{2+} \) [11,12] or \( \text{Ti} \) [13,14] also show efficient persistent luminescence. Among these materials, those doped with \( \text{Tb}^{3+} \) ions perform the best though only very recently the first persistent luminescence mechanism based on solid experimental data for a \( \text{Tb}^{3+} \) doped material was developed [5].

In order to improve the luminescence intensity and duration of the persistent phosphors it is important to know profoundly the mechanism of the phenomenon. The mechanism of \( \text{Eu}^{2+} \) persistent luminescence has attracted much attention lately [1,2,15] and is close to achieving general acceptance though some minor details are still contested [1]. Comparing the \( \text{Eu}^{2+} \) persistent luminescence materials with those doped with different dopants e.g. \( \text{Tb}^{3+} \) may still contribute significantly to the understanding of the persistent luminescence mechanisms.

In this work, the persistent luminescence mechanisms for \( \text{Eu}^{2+} \) (in \( \text{BaAl}_2\text{O}_4 \)) [1,16] and \( \text{Tb}^{3+} \) (in \( \text{CdSiO}_3 \)) [5] are discussed. Both mechanisms were developed based on the experimental results derived from photoluminescence, synchrotron radiation (SR) UV-VUV spectroscopy and thermoluminescence measurements. The positions of the ground state of the \( \text{R}^{2+} \) and \( \text{R}^{3+} \) ions (\( \text{R}: \text{La-Nd}, \text{Sm-Lu} \)) in the hosts’ band structure were determined using the \( 4f \to 5d \) and the ligand-to-metal charge-transfer (LMCT) transitions following the ideas of the previous empirical model [17].

### 2. Experimental

#### 2.1 Materials preparation

The \( \text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+} \) materials were prepared via combustion synthesis, where the metal nitrates and urea were used as reactants and fuel, respectively. The precursors were dissolved into the smallest possible amount of distilled water. A silica capsule filled with the homogeneous solution was inserted into a furnace pre-heated at 500 °C [16,18–20]. The reaction began after ca. 5 minutes after the introduction of the capsule into the furnace. The mixture was then self-ignited with a white flame and produced a white powder. After the completion of the reaction, the furnace was turned off and was allowed to cool freely. The products were removed from the oven when the temperature had decreased to ca. 25 °C. The nominal concentrations of \( \text{Eu}^{2+} \) and \( \text{Dy}^{3+} \) were 1 and 2 mole-% (of the \( \text{Ba}^{2+} \) amount), respectively.

The polycrystalline \( \text{CdSiO}_3:R^{3+} \) (\( \text{R}: \text{Eu} \) and \( \text{Tb} \)) materials were prepared with a conventional solid state reaction. Cadmium acetate (\( \text{Cd(CH}_3\text{COO})_2\cdot2\text{H}_2\text{O} \)), fumed silica (\( \text{SiO}_2 \)) and rare earth nitrates (\( \text{R(NO}_3)_3\cdot6\text{H}_2\text{O} \)) in stoichiometric amounts were ground intimately. The mixtures were then heated in air at 950 °C for seven hours in aluminosilicate crucibles. The nominal concentration of \( \text{R}^{3+} \) (of the \( \text{Cd}^{2+} \) amount) was 1 mole-%.

For both materials, the europium, terbium and dysprosium nitrates used for doping were obtained from the respective oxides with a reaction with concentrated nitric acid.

#### 2.2 Apparatus

The photoluminescence measurements on the \( \text{CdSiO}_3:\text{Tb}^{3+} \) and \( \text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+} \) materials were carried out at room temperature with a SPEX-Fluorolog-2 spectrofluorometer equipped with two 0.22 m SPEX 1680 double grating monochromators. A 450 W Xenon lamp was used as the excitation source. The excitation, emission and persistent luminescence spectra were collected at an angle of 22.5 ° (front face). All spectra were recorded using automatic detector mode correction.

The time-resolved excitation spectra of the \( \text{BaAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+} \) material were recorded with a SPEX 1934D phosphorimeter accessory coupled to the SPEX-Fluorolog-2 spectrofluorometer. A 50 W pulsed Xenon lamp was used as the excitation source and the spectra were recorded with a 1 ms delay.
The UV-VUV excitation spectra of the CdSiO$_3$:R$^{3+}$ (R: Eu, Tb) and BaAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ materials were recorded between 80 and 330 nm by using the UV-VUV synchrotron radiation facility at the SUPERLUMI beamline I of HASYLAB (Hamburger Synchrotronstrahlungslabor) at DESY (Deutsches Elektronen-Synchrotron, Hamburg, Germany) [21]. The polycrystalline materials were mounted on the cold finger of a liquid He flow cryostat and the spectra were recorded at selected temperatures between 10 and 298 K. The setup consisted of a 2-m McPherson type primary (excitation) monochromator with a resolution up to 0.02 nm. The UV-VUV excitation spectra were corrected for the variation in the incident flux of the excitation beam using the excitation spectrum of sodium salicylate as a standard.

3. Results and discussion

3.1 Photoluminescent properties

The emission spectrum of CdSiO$_3$:Tb$^{3+}$ was obtained under excitation in the host at 247 nm at room temperature (Fig. 1, left). The spectrum is composed almost exclusively of the line emission due to the intraconfigurational 4f$^8$ transitions of Tb$^{3+}$, $^5$D$_{3/2}$$\rightarrow$$^7$F$_{J}$ and $^5$D$_{5/2}$$\rightarrow$$^7$F$_{J}$. The most intense transition of Tb$^{3+}$, $^5$D$_{4}$$\rightarrow$$^7$F$_{5}$, peaks at ca. 545 nm and yields the green emission color. For practical applications, this is close to the optimal sensitivity range of the human eye though at low illumination conditions blue emission might be even better. Due to the low site symmetry (C$_1$) of the three Cd$^{2+}$ sites occupied by Tb$^{3+}$ in CdSiO$_3$ (and to the charge compensation defects), the appearance of the Tb$^{3+}$ emission is more or less band-like due to many superimposed Tb$^{3+}$ emission lines. It has been reported [22] that the CdSiO$_3$:Tb$^{3+}$ emission, as many of CdSiO$_3$ doped with the R$^{3+}$ ions with less strong luminescence in visible (e.g. Nd$^{3+}$ and Gd$^{3+}$ just to mention a few), contains also a broad band centered at ca. 400 nm. In the present investigation, this band emission is either very weak or entirely absent, indicating that the energy transfer process from the host to Tb$^{3+}$ is effective. Furthermore, the almost total absence of the $^5$D$_{3/2}$$\rightarrow$$^7$F$_{J}$ transitions from CdSiO$_3$:Tb$^{3+}$ in the blue (and near UV) range is rather unusual taken into account the low dopant concentration, only 1 mole-%. This may be interpreted in a way that the emission from the $^5$D$_{3/2}$ level(s) is quenched and the excitation energy ends to the $^5$D$_{5/2}$ level(s) instead. The absence of the $^5$D$_{3/2}$ emission indicates that the $^5$D$_{3/2}$ levels are located in the conduction band (CB) of CdSiO$_3$ and the $^5$D$_{3/2}$ emission is quenched to the lowest emitting levels, $^5$D$_{5/2}$ via the host’s CB. The 77 K emission spectrum shows that the $^5$D$_{3/2}$ emission is completely quenched at low temperatures, in agreement with the position of $^5$D$_{3/2}$ close to the CB bottom.

The emission spectrum of BaAl$_2$O$_4$:Eu$^{2+}$,Dy$^{3+}$ (Fig. 1, right) presents a broad band assigned to the interconfigurational 4f$^6$5d$^1$$\rightarrow$$^7$F transition of Eu$^{2+}$. Two maxima, peaking at 435 and 500 nm, were observed due to the transitions from the lowest $^4$D level of the excited 4f$^6$5d$^1$ configuration to the ground $^8$S$_{7/2}$ level of the 4f$^6$ configuration of Eu$^{2+}$. The existence of two bands can be due to the presence of two Ba$^{2+}$ sites in the BaAl$_2$O$_4$ structure or to the creation of a new Ba$^{2+}$ site due to the effect of water exposure on BaAl$_2$O$_4$:Eu$^{2+}$ [23].

The persistent emission spectra, measured 120 s after ceasing the irradiation, are very similar to the conventional ones. For the Tb$^{3+}$ material, the $^5$D$_{3/2}$ persistent emission is even less intense than the conventional one (when compared to the $^5$D$_{5/2}$ one) but the differences are too small to justify a different quenching mechanism. The Tb$^{3+}$ persistent luminescence is also observed under excitation on the $^5$D$_{3/2}$ level (378 nm), indicating that this level is indeed located in host’s CB. In the case of the Eu$^{2+}$ doped material, the only difference is the absence of the 435 nm band in the persistent luminescence spectrum, indicating that probably one of the Ba$^{2+}$ sites does not participate on the persistent luminescence process.
One of the most critical points in the proposed mechanisms of persistent luminescence for Eu$^{2+}$ [1] is the transfer of the charge (electron) from the 4f$^6$5d$^1$ levels to the host’s conduction band: both the energetics (position of the 4f$^6$5d$^1$ levels vis-à-vis CB) and the time of transfer (transition probability) seem to matter. The lifetime of the Laporte allowed though spin-forbidden 4f$^6$5d$^1$ $\rightarrow$ 4f emission of Eu$^{2+}$ is ca. 1 µs, which seems to be largely sufficient to allow efficient electron transfer to CB. The case with the Tb$^{3+}$ doped materials is somewhat similar to the Eu$^{2+}$ doped ones: the excitation occurs to the 4f$^7$5d$^1$ levels which are located, at least partially, in host’s CB. This requires a host with low band gap energy, however, because the 7F$_6$ ground level of Tb$^{3+}$ is considerably farther away from the host’s CB than the 8S$_{7/2}$ ground level of Eu$^{2+}$. To perhaps balance this disadvantage, the lifetime of the Laporte forbidden 5D$_4$ $\rightarrow$ 7F$_J$ transitions is much longer, in the range of several ms, thus enabling the capture of electrons to CB in a manner even more efficient than for the Eu$^{2+}$ ion.

3.2 Trap nature and structure

The persistent luminescence phenomenon occurs due to the presence of charge carriers (electrons or holes) trapped in defects in the host structure. In the mechanisms studied, it is suggested that the electron (e$^-$) is the charge carrier, implying the presence of electron acceptor defects (e.g. oxygen vacancy V$_{O^2-}$) [1]. The creation of the oxide vacancies can occur in both cases studied by the evaporation of metal oxides (MO, M: Cd, Ba) at the high preparation temperatures together with a cation vacancy (V$_{M^+}$). Furthermore, the lattice defects are created by the charge compensation necessary when a R$^{3+}$ ion replaces a M$^{2+}$ host cation (R$_M^+$), either creating a metal vacancy V$_{M^+}$ or an interstitial oxide ion O$_{iO^-}$. All symbols are according to the Kröger-Vink notation [24]. In the Eu$^{2+}$ doped materials, R$^{3+}$ co-doping frequently increases the persistent luminescence efficiency, since R$^{3+}$ may also act as traps. However, in the Tb$^{3+}$ doped CdSiO$_3$, there is no need for co-doping because Tb$^{3+}$ acts both as a luminescence center and a creator of the energy storing defects.

When studying more closely the CdSiO$_3$ structure [25] as presented in the DIAMOND [26] view (Fig. 2), it is observed that the Cd-Cd distance between the terminal Cd ions belonging to different three-membered ribbons (only two shown) is ca. 5.2 Å whilst within the ribbons composed of three CdO$_6$ octahedra the distances are rather short, ca. 3.4 Å. There is thus a considerable free space that may accommodate an interstitial oxide ion needed to compensate the charge (Tb$^{3+}$ vs. Cd$^{2+}$) mismatch. In fact, the distance of 5.2 Å is just sufficient to form two Tb-O bonds of the length 2.5-2.6 Å. The position of the charge compensation defect immediately adjacent to the two Tb$^{3+}$ ions (Tb$_{Cd}^+$) gives a rather infrequent clear possibility for clustering of the defects as follows: Tb$_{Cd}^+$ - O$_{iO^-}$ - Tb$_{Cd}^+$. This should be studied further with e.g. synchrotron radiation EXAFS methods.
The interstitial oxide may well be accommodated in the regular 2b (½, ½, ½) site in the space group P2₁/c, yet to be studied by DFT (Density Functional Theory) calculations, giving the Tb-O distances of 2.54 Å. This value is few tenths of Å longer than the optimal bond distance of Tb-O but well within the bond range found for the Tb-O bond. However, this yields one short (2.1 Å) O-O distance between O' and one oxygen in the SiO₄ groups, much shorter than the O-O distances in the SiO₄ group (2.56 – 2.80 Å) in e.g. CdSiO₃. Because of this increased oxygen-oxygen repulsion the interstitial oxide may have reduced stability, and may be replaced by trapped electrons and thus may have an important role to play in the energy storing in the persistent luminescence. An analogous situation has been reported [27] to arise in the cuprate superconducting phases. Taken into account that the crystallographic position of the interstitial oxide is only an approximate one, the Tb-O and O-O distances may well be modified with the optimization of the atomic positions. This optimization is being carried out with the DFT calculations but is out of the scope of the present work.

Similar free spaces may probably exist in other hosts as MAI₂O₄ accepting interstitial oxygens when co-doped with R³⁺. The analysis of their structure can help the understanding of the effect of the co-dopants in the persistent luminescence of Eu³⁺ doped materials, too. Furthermore, the reduction mechanism of Eu³⁺ to Eu²⁺ without the use of reducing atmosphere proposed for the BaAl₂O₄ material [16] involves the release of O'. Therefore, the reduced stability of O' may be related to this spontaneous reduction, and further studies with other hosts should be carried out.

3.3 Band gap structure

The Synchrotron Radiation (SR) excitation spectra of the materials (Fig. 3) were measured at 10 K in order to avoid the persistent luminescence which may smudge the excitation spectrum, at least at room temperature. A sharp edge is observed at ca. 235 nm (5.28 eV) in the excitation spectra of the Tb³⁺ doped CdSiO₃. The edge is the excitation from the top of the valence (VB) to the bottom of the conduction band, i.e. the band gap energy (Eg). In the excitation spectra of the Eu³⁺ doped BaAl₂O₄, the corresponding edge is at a much higher energy, at ca. 190 nm (6.5 eV). As assumed above, the band gap should be smaller for the Tb³⁺ doped materials to enable persistent luminescence at all or, at least, to let the persistence to be excited with low energy UV radiation (or blue light) and thus improve the efficiency. However, despite the low band gap energy, the persistent luminescence from Tb³⁺ in CdSiO₃ is observed only with UV irradiation.

One may observe in the UV-VUV excitation spectrum of CdSiO₃:Tb³⁺ (Fig. 3) the weakness of the Tb³⁺ 4f⁶→4f⁴5d¹ transition bands even at 10 K indicating the easy
delocalization of electrons to the conduction band of CdSiO₃. This was originally shown for the Ce³⁺ doped Y₃Al₅O₁₂ (YAG) single crystals [28]. The 4fⁿ→4fⁿ⁻¹5d¹ transitions can thus lose their superior intensity relative to the 4f-4f transitions when they are within the host’s CB. The 4f⁵5d¹ levels of Tb³⁺ are thus probably entirely inside CB, whilst the 4f⁶5d¹ levels of Eu²⁺ are only partially inside the CB since some Eu²⁺ 4f→4f⁵5d¹ transition bands have rather high intensity.

![Diagram](image)

Fig. 3. The SR UV-VUV excitation spectra of CdSiO₃:Tb³⁺ and BaAl₂O₄:Eu³⁺,Dy³⁺ at 10 K.

In order to determine the R²⁺/³⁺ (R: La-Nd, Sm-Lu) 4f ground state positions in the hosts’ band structure, it is important to start with their LMCT transitions [17]. The most accessible CT transition in the whole Rⁿ⁺ doped CdSiO₃ system is for CdSiO₃:Eu³⁺. This information is obtained by the SR UV-VUV excitation spectrum of Eu³⁺ (Fig. 4, left), where a broad band is observed between 230 to 270 nm (5.4 to 4.7 eV, respectively). The band was assigned to the LMCT O²⁻(2p)→Eu³⁺ transition. The CT energy gives the position of the Eu²⁺ ground state in the band gap (4.7 eV above the top of the host’s VB). The energy difference between the ground levels of the same rare earth but in a different oxidation state, i.e. Eu²⁺ and Eu³⁺, depends on the host. This difference is quite high for a free ion (18 eV) but is lowered in solid state, e.g. in fluorides, oxides and sulfides down to >7, 6-7 and <6 eV, respectively [29]. For the Eu²⁺/Eu³⁺ pair in CdSiO₃, a value of 6.1 eV was used for this energy difference due to the softness of the CdSiO₃ host. Once the position of the ground level of Eu³⁺ is known, following the host independent evolution of the R³⁺ energy levels [30], it is possible to determine the position of the ground levels of all other R³⁺’s. For example, the energy of the Tb³⁺ ground level (⁷F₉) is at 3.5 eV above that of Eu³⁺ (⁷F₉). The Tb³⁺ (⁷F₉) ground level position in CdSiO₃ was thus found at ca. 2.1 eV above the VB top. The position of the ⁷F₉ ground level deep in the band gap explains the presence of persistent luminescence only with UV irradiation.

For the BaAl₂O₄ system, the trivalent Eu³⁺ doped material is not easily obtained, since the spontaneous reduction from Eu³⁺ to Eu²⁺ occurs even in non-reducing atmospheres [16,31]. Furthermore, the 4f-4f transitions of Eu³⁺ are absent in the steady-state spectra due to non-radiative processes (quenching) by Eu²⁺, whose 4f⁶5d¹→4f⁶ transitions are allowed, having a much shorter lifetime (ca. 1 μs) than the 4f→4f transitions of Eu³⁺ (several ms) and thus larger transition probability. Consequently, in order to determine the Eu³⁺ LMCT in BaAl₂O₄, the time-resolved excitation spectra of BaAl₂O₄:Eu³⁺,Dy³⁺ were measured at 77 K with a delay of 1 ms to avoid both the persistent luminescence and the Eu²⁺ emission (Fig. 4, right). A broad band is observed between 220 to 300 nm (5.6 to 4.1 eV) readily assigned to the Eu²⁺ O²⁻(2p)→Eu³⁺ LMCT transition, though overlapped by several Eu³⁺ ⁷F₉→⁵D_j bands. The higher energy position of the Eu²⁺ ground state in the BaAl₂O₄ band gap, as in the majority of the hosts [17] allows the excitation of persistent luminescence with blue light even in wide band gap hosts.
3.4 The mechanisms of persistent luminescence

Once the collection of vital information about the energy level systems in both the Tb$^{3+}$ doped CdSiO$_3$ and the Eu$^{2+}$ doped BaAl$_2$O$_4$ was completed, the mechanisms of the persistent luminescence could be constructed. As a first observation, despite some differences in the photoluminescence processes, band gap energy and ground state positions of the luminescence centers, the mechanisms for Tb$^{3+}$ and Eu$^{2+}$ are quite similar. The duration of the persistent luminescence is comparable in both cases, longer than 1 h.

In general, the charging mechanisms for both the Eu$^{2+}$ and Tb$^{3+}$ doped materials consider that (Fig. 5): i) under irradiation of the material, in addition to conventional luminescence, some electrons escape to the host’s conduction band, along with a simultaneous formation of the pairs Eu$^{2+}-h^+$ or Tb$^{3+}-h^+$; ii) some of these electrons are trapped from CB to the defects created by charge compensation and the release of the unstable interstitial oxide, thus storing part of the excitation energy. The reverse decharging process of freeing the electrons from the traps to the excited states via CB precedes the radiative relaxation of the system back to the ground states of Eu$^{2+}$ or Tb$^{3+}$ via the excited states $4f^55d^1$ (Eu$^{2+}$) or $3D_{3,4}$ (Tb$^{3+}$) – thus creating the persistent luminescence.

4. Conclusions

In closing the present work, plausible mechanisms coherent with experimental evidence could be constructed for the persistent luminescence from both Eu$^{2+}$ and Tb$^{3+}$. The mechanisms were found rather similar, despite many seemingly different basic properties of the systems,
including the nature of the inter- and intraconfigurational transitions. In both systems, the electrons were found as the charge carriers and the nature of the traps is thus similar (electron traps). Nevertheless, the R$^+$ co-dopants may act in different ways in the two systems. For CdSiO$_3$, the structural analysis showed that the interstitial oxide ions created by charge compensation can be accommodated in the free space. The low stability of these interstitial oxide ions can cause their substitution by trapped electrons thus acting as electron traps creators. More profound structural analyses should be carried out to find if the possible free space for O$^-$ exists in other hosts as MAI$_2$O$_4$. Only sparse data is available about the general properties for the Tb$^{3+}$ doped persistent luminescence materials, thus more detailed studies are needed on these systems, too.

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