Photoluminescence

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A Chemical Route Towards Single-Phase Materials with Controllable Photoluminescence

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Abstract: *A promising general approach is proposed that enables the controlled reduction of dopants to tune the photoluminescence properties of single-phase materials. The change of oxidation state of dopants in phosphor phases leads to different emission colors that can be finely tuned. This approach was illustrated with the progressive reduction of the red phosphor $SrAl_2O_4$:Eu^{3+} to green phosphor $SrAl_2O_4$:Eu^{2+} to target yellow luminescence.*

Rare-earth-metal-based photoluminescent materials are of considerable interest for their applications in solid-state lighting. To target light-emitting diodes (LEDs) with specific photoluminescence, different strategies have been proposed that usually consist in combining two or three phosphor phases.[1,2] For example, white LEDs are commonly generated by combining blue-emitting InGaN with yellow YAG:Ce^{3+} (YAG = yttrium aluminum garnet). This method suffers from a serious drawback, that is, WLEDs so produced have a low color-rendering index.[3–7] Another method consists in mixing of tricolored phosphors, such as Y_2O_3:Eu^{3+} (red), $MgAl_{11}O_{19}$:Ce^{3+}/Tb^{3+} (green), and $BaMgAl_{10}O_{17}$:Eu^{2+} (blue), in appropriate ratios and carrying out solid-state reaction at high temperatures.[8,9] However, different problems can occur, such as the interactions of the different phases during their preparation at high temperature, which could affect the emission colors or the different aging rates of the phases, leading to inappropriate ratios of colored phosphors.[10]

For the same host material, different photoluminescence properties can be obtained from dopants at different oxidation states. For example, the technologically useful Eu^{2+}-doped $SrAl_2O_4$ is a green phosphor owing to 5d–4f transitions while Eu^{3+}-doped $SrAl_2O_4$ shows red luminescence owing to 4f–4f transitions. The reduction of $SrAl_2O_4$:Eu^{3+} phase under Ar/H_2 is commonly used to obtain the long-lasting $SrAl_2O_4$:Eu^{2+} phosphorescent material.[11] However, this reduction carried out at high temperature commonly leads to almost complete reduction of the dopants. In the traditional method, the phosphors can also be synthesized in only two states: either with oxidized dopants or with reduced dopants. No control on the ratio of dopants in their oxidized states versus reduced states could be targeted so far.

In this context, we suggest a new general approach to target materials with controllable photoluminescence: the controlled reduction of dopants (CRD). An appropriate oxygen getter was used under vacuum and a temperature gradient was selected to finely control the oxidation states of the dopants. Using this soft-chemistry route, we synthesized compounds doped with rare-earth metals in a specific oxidation state. By tuning the ratio of rare-earth metals in different oxidation states, the photoemission could also be controlled in a single step. As an example, $SrAl_2O_4$:Eu^{3+} was synthesized by the Pechini process and CRD was carried out with Ti and CaH_2 as oxygen getters.

The $SrAl_2O_4$:Eu^{2+} (1%) reduced phase ($SrAl_2O_4$, space group $P2_1$, lattice parameters: $a = 8.447$ Å, $b = 8.816$ Å, $c = 5.163$ Å and $\beta = 93.42°$) is commonly synthesized by ceramic route either under Ar/H_2 or with post-treatment under Ar/H_2.[12] However, we selected the Pechini route to target the pure $SrAl_2O_4$:Eu^{3+} oxidized phase from nitrate precursors ($Sr(NO_3)_2$, $Al(NO_3)_3$, and $Eu(NO_3)_3$), and citric acid (see the Experimental Section). EDX measurements carried out on the single-phase material confirmed the chemical composition of the material. BET measurements show a specific area of 10.81 m^2g^{-1} and the crystallite size was found to be 116 nm by Rietveld refinement. As photoluminescence properties are sensitive to small modifications in the synthesis conditions, all of the post-treatments were carried out using the same $SrAl_2O_4$:Eu^{3+} batch.

The CRD was carried out using CaH_2 and Ti as reducing agents in a sealed glass tube under vacuum. These oxygen getters were not mixed with our material to avoid contamination. Instead, the phosphors were introduced with CaH_2 or Ti in separate vials, as described in the Experimental Section. The glass tubes were heated with a temperature gradient between room temperature (RT = 20 °C) to 550 °C and the products were recovered in air. The impact of the temperature of CRD on the photoluminescence properties were investigated (Figure 1).

During heating, the $SrAl_2O_4$:Eu^{3+} releases oxygen, which reacts with the oxygen getter to form the thermodynamically stable oxides TiO_2 or $CaO/Ca(OH)_2$ from Ti or CaH_2, respectively. The deintercalation of O_2 is temperature- and time-dependent process that allows the control of the amount of Eu^{3+} reduced into Eu^{2+}. Thus, for the $SrAl_2O_4$:Eu^{3+}/Eu^{2+} material, the intensity corresponding to Eu^{3+} dopant (4f–4f) decreases while that of Eu^{2+} dopant (4f–5d) increases with the reduction temperature (See the Supporting Information and Figure 2). This allows for the mixing of red and green emissions with a ratio that is directly controlled by using a different temperature of reduction. The CRD also enables the control of the photoluminescence properties of single-phase materials that is not possible using ceramic route under Ar/H_2 gas. Thus, our attempts to control the reduction under

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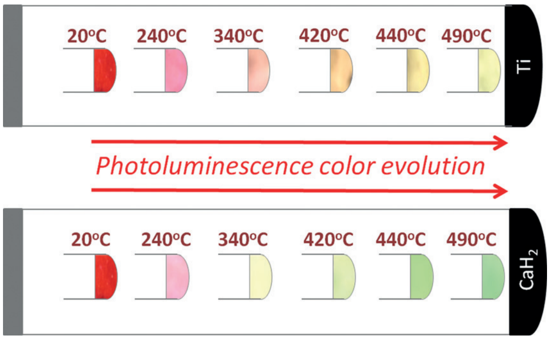

Figure 1. Evolution of emission color of $SrAl_2O_4$:$Eu^{3+/2+}$ when excited under UV light after controlled reduction of dopants with a temperature gradient using Ti and CaH_2 as getters.

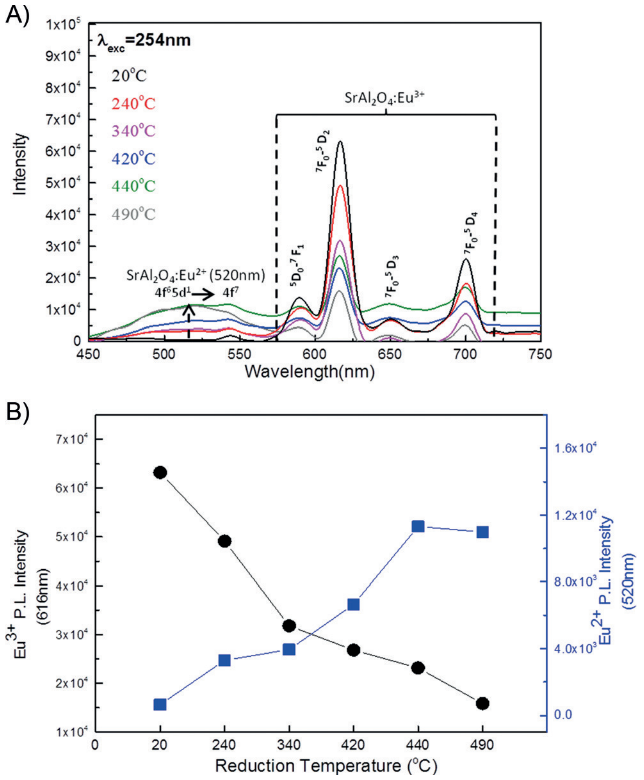

Figure 2. A) Emission spectra of $SrAl_2O_4$:$Eu^{3+/2+}$ reduced at different temperatures and B) variation of the intensity of photoemissions from Eu^{3+} and Eu^{2+} with temperature gradient using CaH_2 as getter. The characteristic peaks corresponding to Eu^{3+} at 590 nm ($^5D_0$–$^7F_1$), 616 nm ($^5D_0$–$^7F_2$), 650 nm ($^5D_0$–$^7F_3$), and 700 nm ($^5D_0$–$^7F_4$) were observed for as-synthesized $SrAl_2O_4$:Eu^{3+} sample. The broad band for the transition of $4f^65d^1 \rightarrow 4f^7$ belonging to Eu^{2+} was visible for the reduced samples. The observation of such peaks evidently show the progressive reduction of the samples.

Ar/H_2 atmosphere were unsuccessful. After a very short time, the $SrAl_2O_4$:Eu^{3+} phase was reduced to $SrAl_2O_4$:Eu^{2+}. The CRD method could, however, not lead to long persistent luminescence in the case of $SrAl_2O_4$:Eu^{3+}/Eu^{2+} material. We explain this observation by the low-temperature synthesis (Pechini method) of the $SrAl_2O_4$:Eu^{3+} phase. Thus, Kim et al. showed that the phosphorescence properties could be improved by increasing the temperature of synthesis of this phase (owing to enhanced crystallinity with the increase of temperature).[13] The presence of hydroxide groups at the surface, as evidenced by FTIR for the use of CaH_2 in CRD as getter (Supporting Information, Figure S3), was shown not to influence the luminescence by non-radiative transition (hydroxide ions might compete with the radiative transition and lead to reduced luminescence), as reduction using titanium as oxygen getter did not drastically change this result.

The controlled reduction of dopants can be compared with the topotactic reduction, which consists of using hydrides such as CaH_2, NaH, or LiH mixed with perovskite-related materials at relatively low temperature.[14–22] By creating oxygen vacancies, new materials with specific oxidation states and coordination of the elements were previously targeted. Up to now, topotactic reduction has been mainly used for magnetic materials. New phases with original oxidation states and coordination of the transition metals such as Ni^+, Co^+, and Fe^{2+} in square-planar environments were obtained. However, no soft-chemistry route was developed up to now to finely control the oxidation states of the dopants.

The impact of two getters, the metal hydride CaH_2 and the transition-metal Ti, on the photoluminescent properties of $SrAl_2O_4$:Eu^{3+} were investigated under similar conditions. We showed that the CaH_2 was more reducing than Ti. Thus, an effective and finer control on the reduction was possible using Ti as getter and this led to the tuning of the emission color. This observation is in agreement with the fact that CaH_2 is a better reductant than Ti.

The soft-chemistry route proposed herein is general owing to the number of phosphor materials it can be applied to. Of particular interest are the rare-earth metals, which present discrete f–f transition in one of its oxidation states. As the crystal lattice scarcely affects the position of the energy levels, the incorporated ion will exhibit the same emission in every material. If this element in a different oxidation state exhibit emissions which are affected by the crystal lattice, the appropriate host material and reduction conditions could be chosen to target a specific photoluminescence. For example, the 4f–4f transition of Eu^{3+} makes the materials doped with this element to be red phosphor. By choosing $SrAl_2O_4$, we are able to target phosphors in the range of "red-yellow-green" emission. Other host material such as $CsAlSi_2O_6$ could be synthesized in the future to target phosphor in the range of "red-white-blue" emission.[23] The reduction could also give the opportunity to synthesize a variety of new phosphors from one single material. Information about the emission of previously reported phosphors can also be used to know which photoluminescence could be targeted from CRD.

Henceforth, this method of reduction can be used to control very finely the oxidation state of the dopants whose effects are visual such as for photoluminescent materials. Moreover, we believe this method is not just confined to the modification of the properties of the photoluminescent materials, but could in the future lead to the control of electrical, catalytic, or optical properties of various doped materials.

Experimental Section

Synthesis of $SrAl_2O_4$: A stoichiometric amount of $Sr(NO_3)_2{\cdot}x\,H_2O$ (99%), $Al(NO_3)_3{\cdot}9\,H_2O$ (98%), and $Eu(NO_3)_3{\cdot}6\,H_2O$ (99.99%) were dissolved in a mixture of citric acid and ethylene glycol. The ratio citric acid/ethylene glycol/metal was maintained as 16:16:1. The solution was heated until a gel formed. The gel was further heated at 550 °C to facilitate the oxidation and pyrolysis of the polymer matrix and calcined at 950 °C for 2 h to lead to the formation of $SrAl_2O_4{:}Eu^{3+}$.

Controlled reduction of dopants: Impact of duration on the photoluminescence properties: In the glovebox, a glass tube was filled with 1.9×10^{-3} moles of CaH_2 and a vial of $SrAl_2O_4{:}Eu^{3+}$. This tube was then sealed under vacuum. For the reduction of $SrAl_2O_4{:}Eu^{3+}$ with CaH_2, the molar ratio of $SrAl_2O_4/Eu^{3+}/CaH_2$ was 1:4. The reductions were carried out for 96 h and 2 weeks at 550 °C (Supporting Information, Figure S1).

Impact of temperature on the photoluminescence properties: The getters Ti and CaH_2 were placed with vials containing $SrAl_2O_4{:}Eu^{3+}$ in a glass tube. The reduction was carried out for 96 h at a temperature gradient ranging from room temperature (RT = 20 °C) to 550 °C (Figure 1). Photoluminescence properties were measured for the $SrAl_2O_4{:}Eu^{3+/2+}$ samples (Figure 2; Supporting Information, Figure S2).

The IR spectra for as-synthesized and reduced $SrAl_2O_4{:}Eu^{3+/2+}$ samples were recorded in the range 400–4000 cm^{-1}. The bands corresponding to the symmetric bending of O-Al-O are observed at about 420 cm^{-1} for both samples. The antisymmetric stretching (760–900 cm^{-1} region) and antisymmetric bending (650 cm^{-1}) can also be observed in the FTIR spectra. The band at 3200–3400 cm^{-1} corresponds to the OH groups and increases from the Pechini sample to the reduced sample (reduced with CaH_2), as shown in the Supporting Information, Figure S3.

X-ray diffraction patterns were recorded at room temperature with a Bruker AXS D8 diffractometer in the Bragg–Brentano geometry with Cu K-L_3 radiation (germanium monochromator) operated at 40 mA and 40 kV. The phase identification was based on inorganic crystal structure database. The data was collected in 5–90° 2θ range with a step size of 0.013°.

Photoluminescence spectra were recorded with a Spex Fluorolog-3 spectrofluorometer (Instruments Jobin Yvon). The excitation source was a 450-W Xe light used at room temperature. The excitation spectra were corrected for the variation of the incident lamp flux, and the emission spectra were corrected for the response of the photomultiplier.

Keywords: controlled reduction · dopants · doped $SrAl_2O_4$ · europium · photoluminescence

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