

Study of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction in BaAl_2O_4 : Eu prepared in different gas atmospheres

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Abstract: The effect of different gas atmospheres such as $\text{H}_2(\text{g})$, synthetic air, carbon monoxide (CO) and nitrogen (N_2) on the $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction process during the synthesis of Eu-doped BaAl_2O_4 was studied using synchrotron radiation. The $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ reduction was monitored by analysing the XANES region when the samples are excited at the Eu L_{III} -edge. The results show that the hydrogen reducing agent is the most appropriate gas for Eu^{2+} stabilization in BaAl_2O_4 and that only some of the Eu ions can be stabilized in the divalent state. A model of Eu reduction process, based on the incorporation of charge compensation defects, is proposed.

Keywords. A. optical materials

C. XAFS (EXAFS and XANES)

D. defects

D. optical properties

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1. Introduction

Barium aluminate is one of aluminates which have been extensively studied in recent years due to its excellent properties [1, 2]. Among them we can mention the long persistence of phosphorescence [3, 4]. For these purposes, it is necessary that

barium aluminates are activated by Eu^{2+} ions. In general, Dy^{3+} ions are added as the auxiliary activators in order to improve the persistence time in this material [5, 6]. In order to obtain the Eu^{2+} -doped compound, many methods have been proposed and developed and trivalent europium oxides are the starting materials usually used to achieve this. The most commonly method is to use an atmosphere that contains a reducing agent during annealing of the phosphors [7-12]. Several gases such as N_2/H_2 , H_2 , carbon, CO and NH_3 [1] are commonly used as reducing agents. In general, the Eu reduction can occur easily using a reducing atmosphere [13, 14], but there are also cases where there is no need, for example when the Eu reduction occurs without the use of a reducing agent [15-16].

No systematic study of the efficiency of different gases for the stabilization of Eu in the 2+ valence oxidation state could be found in the literature. In most of the reported work [5, 13, 14], $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}$ phosphors have been prepared using $\text{H}_2(\text{g})$ with reduction agents. Therefore, it is also important to investigate and clarify the effects of the $\text{H}_2(\text{g})$ and other gases that could be used as reducing agent. Such studies have not been reported in the literature.

The purpose of the present study is to clarify the influence of different gas atmospheres on the reduction and stabilization of Eu^{2+} ions. In the present experiment, the XANES region of the Eu L_{III} -edge in Eu-doped $\text{BaO}:\text{Al}_2\text{O}_3$ has been measured using H_2 , synthetic air, CO, and N_2 atmospheres as reducing agents. The XANES region of the absorption spectrum was analysed as a function of temperature during the whole of the process of production of $\text{BaAl}_2\text{O}_4:\text{Eu}$ phosphor. A mechanism of Eu reduction based on Dispersive X-ray Absorption Spectroscopy (DXAS) results is proposed.

2. Experimental

$\text{Ba}_{0.97}\text{O}:\text{Al}_2\text{O}_3:\text{Eu}_{0.03}$ samples was prepared via the proteic sol-gel route[17]. Stoichiometric amount of $\text{Ba}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in coconut water (*Cocos nucifera*) and then mixed together. A gel was formed after

drying at 100 °C for 24 hours. The dried gel, named xerogel, was pre-calcined at 600 °C/1h in order to eliminate adsorbed water and part of the organic material from the coconut water present in the xerogel. The pre-calcined xerogels were fired under different reduction atmospheres (H₂, synthetic air, CO, and N₂ gases) in a furnace and the reduction of the samples was done *in situ* during the XANES measurements.

The Eu L_{III}-edge XANES data were collected on the Dispersive X-ray Absorption (DXAS) beamline of the Brazilian Synchrotron Light Laboratory (LNLS) [18] using a curved Si (111) crystal monochromator, in which a bandwidth of a few hundred of eV around 6977 eV was selected. The transmitted beam is collected continuously with increasing temperature by a CCD camera. The samples, installed inside a furnace equipped with a flux of the desired atmosphere, were submitted to a thermal treatment with a heating rate of 10 °C/min from room temperature up to 1100 °C for 1 h, which was found to be the best condition for the formation of BaAl₂O₄ as reported in a previous publication [19]. XANES spectra also were collected continuously during all thermal treatments (heating, setting and cooling). Based on a previous publication [20], four different gases were used as reducing agents during the heating treatment: (i) H₂(g), (ii) synthetic air, (iii) CO(g) and (iv) N₂(g).

3. Results

A sequence of XANES spectra measured around the Eu L_{III}-edge of the pre-calcined xerogel and standard sample of Eu₂O₃ as a function of temperature under a flow of H₂ are showed in Fig. 1. It can be seen that the signal-to-noise ratio for the Eu-doped samples is lower than for the standard sample. This fact is related to the lower concentration of Eu dopant in the sample (3 mol %), than in the reference one. At room temperature, the XANES spectrum structure is similar to the reference spectrum and exhibits only one maximum. At this point, the spectrum indicates the presence only of Eu³⁺ ions. Two different absorption edges are visible when the temperature reaches 1100°C. In this temperature, the spectrum clearly exhibits two maxima that can be identified around 6973 and 6978 eV, associated with the Eu²⁺ and Eu³⁺ species,

respectively. This is an indication that Eu^{3+} ions are reduced to Eu^{2+} during the heating treatment when H_2 gas is used as reducing agent. Upon cooling, both species also are visible but with change of the relative intensity of the absorption edges of Eu^{2+} and Eu^{3+} ions compared to the 1100°C . At the end of the heating treatment, both Eu^{2+} and Eu^{3+} ions are formed in the BaAl_2O_4 sample since two maxima are observed in the XANES spectra. This means that not all of the Eu added to the sample is actually converted to the desired divalent state upon heat treatment in a reducing atmosphere.

In a previous publication [21], where similar study was carried out for SrAl_2O_4 :Eu, different behaviour was observed. For the SrAl_2O_4 :Eu sample, the maximum is already slightly shifted to a lower energy when the temperature reaches 300°C , i.e. the Eu reduction occurs at a lower temperature than for the BaAl_2O_4 samples. This result suggests that the reduction of Eu ions is more favourable in SrAl_2O_4 than in BaAl_2O_4 . The behaviour observed can be explained based on the difference in the host structure. During heating treatment, the amount of Eu^{2+} generated is different for each host structure and this can be explained by the different energetic cost involved in the reduction process of the Eu^{3+} to Eu^{2+} . The energetic cost should also include the energy needed to create the compensation defect associated with the Eu^{3+} incorporation in the matrix. In previous publications [22, 23], computer modelling results revealed that the energetic cost involved in the incorporation of the Eu^{3+} ions in BaAl_2O_4 structure is higher than in SrAl_2O_4 structure. In both systems, the main defect is formed by two Eu^{3+} ions at the M^{2+} ($\text{M}=\text{Ba}, \text{Ca}$) site compensated by one oxygen interstitial. Therefore, since the energetic cost to incorporate Eu^{3+} defect in the SrAl_2O_4 structure is lower than in the BaAl_2O_4 structure, the cost to destroy this defect in order to reduce to Eu^{2+} ion is also lower. This can explain why the Eu reduction starts first (at a lower temperature) in the SrAl_2O_4 structure than in the BaAl_2O_4 one.

Similar annealing cycles for the Eu-doped pre-calcined xerogels using different reducing agent such as dried synthetic air, $\text{CO}(\text{g})$, and $\text{N}_2(\text{g})$ gas are showed in Figs. 2-4, respectively. In all cases, from room temperature to 800°C , the XANES curve shows only one maximum, i.e. exhibits only the trivalent Eu ions. At 1100°C , two well-resolved edges are visible, indicating two valence states for the Eu ions. In the cooling

step, the absorption peak related to Eu^{2+} decreases and the one for Eu^{3+} increases, which is consistent with the return of the Eu^{2+} to the trivalent state. Despite the intensity of both absorption edges, practically no Eu^{2+} remained when the sample was cooled down to room temperature, indicating that the process is completely reversible when dried synthetic air, $\text{CO}(\text{g})$, or $\text{N}_2(\text{g})$ gas is used as reducing agent. The results suggest that dried synthetic air, $\text{CO}(\text{g})$, and $\text{N}_2(\text{g})$ gas are not efficient in Eu reduction. This information is important, since the Eu^{2+} ions are responsible for the main long-lasting emission and were also found to be an important factor for the long phosphorescence in the model proposed by Clabau et al. [24, 25].

A summary of the results obtained from the kinetic study via Eu L_{III} XANES suggests that the presence of the different reduction agents induced different amounts of Eu^{2+} ions during the heating treatment and that the $\text{H}_2(\text{g})$ reducing agent was more effective in reducing $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ than the other gases studied. These results are inconsistent with the predictions obtained by computer simulation in a previous publication [20]. According to calculations done in previous work [20], $\text{CO}(\text{g})$ is more efficient in the process of reduction of $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$. The computer modelling results from previous work [24] showed some discrepancies concerning the efficiency of $\text{CO}(\text{g})$ in the reduction process due to the simplicity of the model proposed in the reaction schemes. The idea of the model was based on the hypothesis that oxygen donates an electron that is captured by Eu^{3+} , reducing it to Eu^{2+} , where oxygen is released by reacting with various reducing agents. In this process, it is assumed that the reduction process is irreversible, a fact that has not been proven experimentally. In the DXAS results, we see that the reduction process is reversible, and in $\text{H}_2(\text{g})$ atmosphere, some ions are stabilized in the 2+ valence state. Therefore, the reduction process reported by computer modelling in the previous work [20] is not consistent with the experimental observations presented in the present work. Thus, it is important to formulate a new mechanism of Eu reduction during the synthesis.

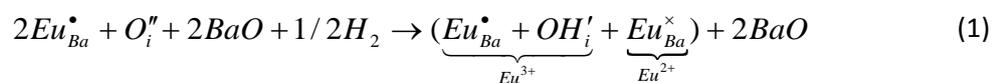
In the previous experimental work [21], a model was proposed to explain how the two valence states are actually accommodated inside the SrAl_2O_4 matrix and, in the case of the trivalent species, which are the charge-compensating defects when H_2 are used as reducing agent. However, the Eu valence state changes from 3+ to 2+ and what happens to the charge-compensating defects when the other reducing agent are

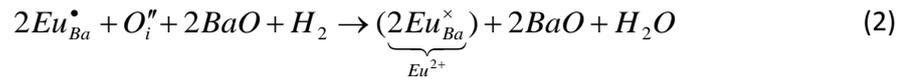
used is not mentioned. Thus, the present work proposes a model in which to explain how the two valences are actually accommodated inside the BaAl₂O₄ structure under different reducing agents.

In the previous model [21], which could be applied to BaAl₂O₄ when subjected to the H₂ reducing agent, the annealing cycles were divided into three stages: stage (i) when the XANES spectra are dominated by Eu³⁺ ions; stage (ii), when the XANES spectra are dominated by Eu²⁺ ions and stage (iii), when part of the Eu²⁺ is converted back to the trivalent state (when the H₂(g) atmosphere is used as the reduction agent) or when all of the Eu²⁺ is converted back to the trivalent state (when dried synthetic air, CO(g), or N₂(g) atmosphere is used as the reduction agent).

In Stage 1, it was suggested that the substitution of Eu³⁺ at the Sr²⁺ site, Eu_{Sr}[•], occurs, together with oxygen interstitial charge-compensating defects formed to keep the neutrality of charges throughout the sample. This defect schemes was suggested by computer simulation as the most favourable one [22]. A similar study using computer simulation of the BaAl₂O₄ structure also revealed that Eu³⁺ substitution at the Ba²⁺ site compensated by oxygen interstitials is the most favourable scheme [23]. Therefore, it can be suggested that the stage 1, proposed in the previous work [21], also could be used to explain the behaviour observed in BaAl₂O₄.

In Stage 2, the charge-compensating defects involved in the Eu reduction are different and depend on the type of gas used as the reducing atmosphere. When H₂(g) reducing agent is used, two types of defects can be proposed that may act as electron donors in the reduction to give the Eu ions. The first one is the reaction of an atomic H with the O_i^{''} already present in the sample, forming a OH_i['] defect and the second is the reaction of the two free atomic hydrogen ions with one interstitial oxygen ion, forming water vapour (H₂O), which is lost by the sample. Both proposed defect types involve the participation of the O_i^{''}, which is mainly formed due to the presence of Eu³⁺ as a charge-compensating defect. The processes that happen in this stage can be represented by the following equations:





Equations (1) and (2) describe the reactions involving the reduction of the Eu^{3+} generating as sub-products, either OH^- or water vapour, respectively. The important difference between them is that the process described by Equation (1) can be reversible and process described by Equation (2), on the other hand, cannot be reversed.

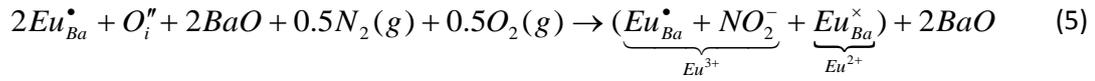
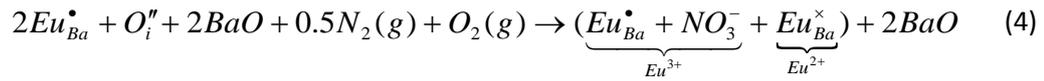
When other gases are used as reduction agents, such as $CO(g)$, dried synthetic air, or $N_2(g)$ gas atmosphere, the following mechanism can be suggested. In these cases, only one type of defect can be proposed that may act as an electron donor in the reduction to give the Eu ions.

In Stage 2, when $CO(g)$ gas is used as the reduction agent, the high temperature causes the reaction of an atomic CO with the O_i'' already present in the sample, which leads to the formation of a carbonate defect $(CO_3^{2-})_i$ in the interstitial position. The electron lost by the CO_3^{2-} in the reaction with the interstitial oxygen ion is transferred to the Eu^{3+} ion, forming the Eu^{2+} one. The processes that happen in this stage can be represented by the following equation:



As a result, some of the Eu^{3+} ions are reduced to Eu^{2+} at high temperature. The process described by Equation (3) can be reversible if the sample loses atomic CO in the cooling process.

When dried synthetic air or $N_2(g)$ gas is used as the reduction agent, the mechanism involves the reaction of an atomic N with the O_i'' already present in the sample, which leads to the formation of $(NO_2^-)_i$ or $(NO_3^-)_i$ defects in the interstitial position. The processes that happen in this stage can be represented by the following equations:



The process described by Equations (4) and (5) suggests that some of the Eu^{3+} ions are reduced to Eu^{2+} at high temperature. But the process can be reversible if the sample loses atomic N at the same time as the Eu^{2+} loses the extra electron to the O_i .

Stage 3 is basically a partially reversible process where part of the Eu returns to its original trivalent state when the H_2 atmosphere is used and a totally reversible process where all of the Eu returns to its original trivalent state when a $CO(g)$, dried synthetic air, or $N_2(g)$ atmosphere is used.

4. Conclusion

The Eu reduction process of doped barium aluminates xerogel produced by the proteic sol-gel route was investigated by DXAS measurements as a function of temperature using different reductive gases. H_2 gas was found to be the most efficient as a reducing agent, with the stabilization of Eu ions with a valence of 2+ at the end of calcination of the sample. The reduction of Eu ions is observed with other gases (synthetic air, CO , and N_2 gases), but with a reversible Eu valence. The Eu reduction processes are explained by a proposed model based on the charge compensation. When H_2 is used, the reduction of Eu ions occurs due to two charge-compensation schemes: one involves the creation of reversible OH_i' defects and the other involves the reaction of H_2 to form water vapour. The predominance of one scheme over the other is assigned to the thermal process. When the other gases are used (CO , synthetic air, and N_2), only the absorption of interstitial oxygen by carbon and nitrogen, forming carbon dioxide (CO_2) and nitric oxide (NO), respectively, is responsible for the donation of an electron.

Acknowledgments

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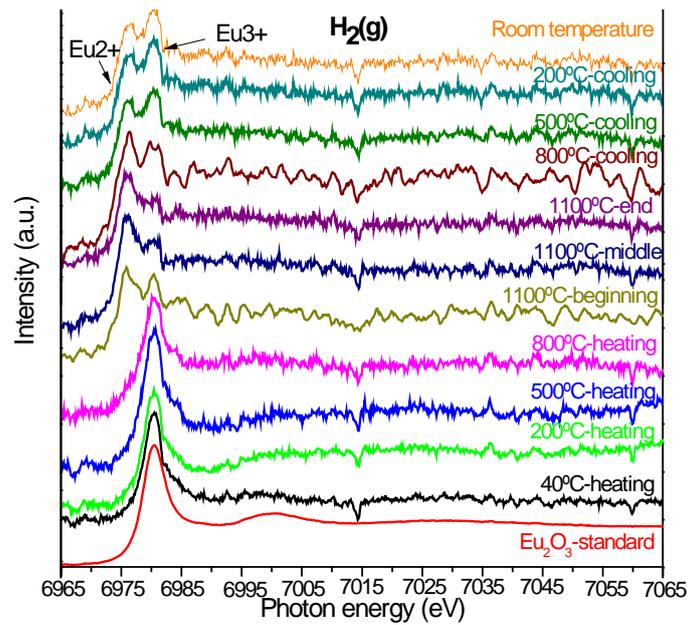


Figure 1 – Sequence of XANES spectra of barium-aluminium doped with Eu pre-calcined xerogel as a function of temperature and under a flow of H₂(g) gas.

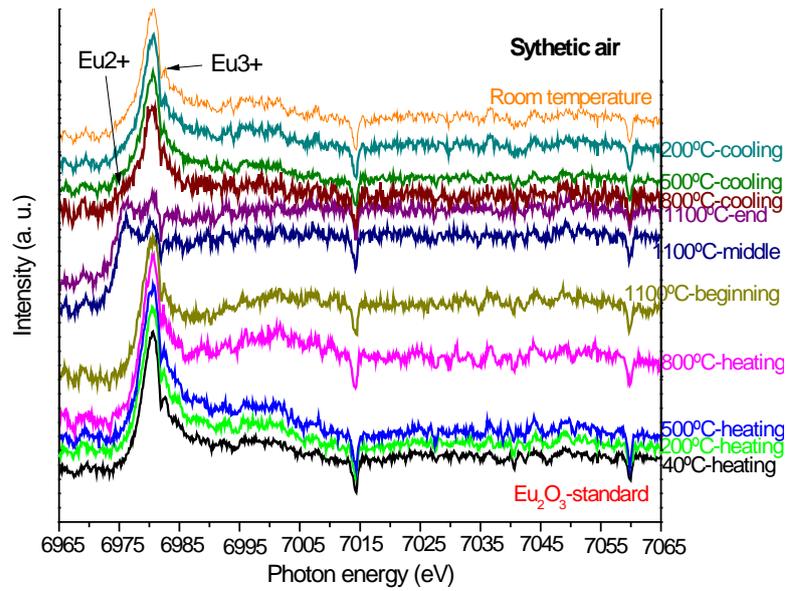


Figure 2 – DXAS spectrum of barium-aluminium nitrate xerogel doped with Eu annealing under gas mixture of Synthetic air (20%N₂+80%O₂).

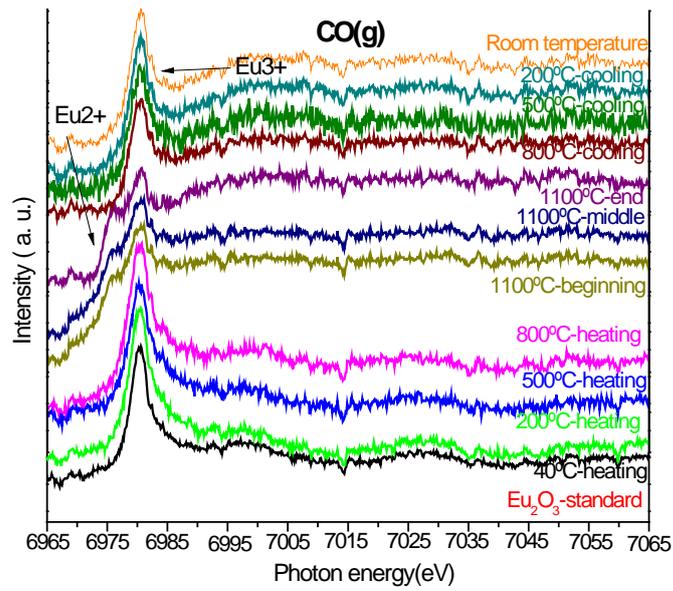


Figure 3 – DXAS spectrum of barium-aluminium nitrate xerogel doped with Eu annealing under gas mixture of CO(g) .

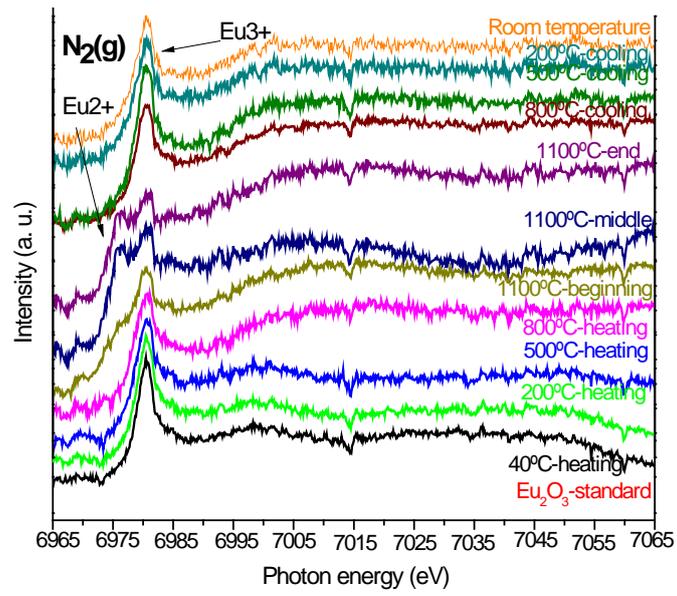


Figure 4 – DXAS spectrum of barium-aluminium nitrate xerogel doped with Eu annealing under gas mixture of $N_2(g)$.