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Light yield sensitization by X-ray irradiation in $BaAl_4O_7 : Eu^{2+}$ ceramic scintillator obtained by full crystallization from glass

Gaël Patton,^a Federico Moretti,^a Andrei Belsky, ^a Kholoud Al Saghir, ^b Sébastien Chenu, ^b Guy Matzen, ^b Mathieu Allix, ^b and Christophe Dujardin ^{*a}

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We report the scintillation properties of $BaAl_4O_7$: Eu^{2+} , a transparent polycrystalline ceramic prepared by full and congruent crystallization from glass. We show that a small deviation from the stoichiometric composition as well as thermal treatment duration play a crucial role regarding the charge carrier traps, leading to a strong influence on the scintillation yield. We demonstrate that when the traps are not entirely removed, X-ray irradiation allows them to be permanently filled in order to significantly enhance the scintillation output. Finally, the best sample obtained demonstrates performances able to compete with a commercially available scintillating material: CsI : Tl.

1 Introduction

Full and congruent crystallization from glass is a material preparation technique which has been recently developed for optical materials.¹⁻³ It enables production of transparent ceramics in a simple way and at low cost. Scintillating materials are able to convert ionizing radiation into visible or ultraviolet light itself detected by conventional photodetectors such as photomultiplier tubes (PMT), CMOS camera... They are widely used in many applications such as medical imaging, homeland security, oil exploration and high energy calorimetry.^{4,5} As inorganic materials, they are mainly used as single crystals. Because of their a priori lower cost and shaping potentialities, the interest in transparent ceramics as scintillators is increasing. With this in mind, doped sesquioxides, garnet, and hafnate have already been prepared using dedicated sintering techniques including high pressure.⁶⁻⁸ It appears that crystallinity as well as grain boundaries induce carrier traps, leading to afterglow, and timing performances can thus be degraded.^{9,10} In this contribution, we demonstrate that full crystallization from glass enables production of transparent ceramics exhibiting performances competing with CsI:Tl, a well known and commercially available scintillator. 11-13 Furthermore, we also noticed an extraordinary sensitivity of scintillation performances to slight deviations from stoichiometric composition, as well as to thermal treatments combined with X-ray irradiations. We show that the combination of physical

and chemical actions is able to significantly modify the energy transfer process to the emitting center and then the scintillation characteristics.

2 Transparent ceramics synthesis

Starting precursor materials of $BaCO_3$ (Alfa Aesar, > 99.8%) purity), Al_2O_3 (Alfa Aesar, > 99.997% purity) were weighed in appropriate amounts (1:2 molar ratio for the stoichiometric $BaAl_4O_7$ composition or 34:66 molar ratio for the 34BaO - $66Al_2O_3$ composition) and Eu_2O_3 (Alfa Aesar) for doping, mixed, and pressed into pellets. First, the glass beads were synthesized using an aerodynamic levitator equipped with two CO_2 lasers.^{14,15} Glass beads were obtained by melting in an argon flow a 0.05 g piece of mixed precursor at around 2100 °C followed by rapid quenching obtained by turning off the laser heating (cooling rate of approximately 300 °C/s). The glassy beads were then fully crystallized into transparent ceramics after a single heat treatment in an open-air atmosphere tubular furnace at 1100 °C for either 2h or 24h.^{1,2} Neither specific reducing treatments has been applied, as in the case of $BaAl_2O_4: Eu^{2+}$ phosphor^{16–18}, nor co-doping for charge compensation, as in $SrAl_2O_4$: Eu^{2+} phosphors¹⁹. Nevertheless, despite Eu_2O_3 has been used as precursor, most of the europium ions are obtained in the divalent form, indicating that they likely substitute Ba^{2+} . We have been investigating the scintillation properties of the four samples listed in table 1. Samples are cylinders having diameters of about 2 mm and a thickness of 0.5 mm obtained from the spheres.

To obtain the appropriate luminescence properties, the materials have been doped with europium ([Eu] = 0.5%). As a

^a Institut Lumière Matiére, UMR5306, Université Claude Bernard Lyon1-CNRS, bâtiment Kastler, 10 rue Ada Byron 69622 Villeurbanne Cedex, France. Fax: (33) 472 431 130; Tel: (33) 472 448 336; E-mail: christophe.dujardin@univ-lyon1.fr

^b CNRS, CEMHTI UPR3079, Univ. Orléans, F-45071 Orléans, France.

substitute to Ba^{2+} , europium is obtained in its divalent form. It is well known that Eu^{2+} exhibits a bright blue luminescence with a decay time in the μ s range due to the allowed electric dipole transition $4f^{6}5d \rightarrow 4f^{7}$.

Depending on the temperature treatment, $BaAl_4O_7$ ceramics can be obtained in two different phases, namely α and β .¹ While the $BaAl_4O_7$ glass gives a very weak photoluminescence signal and the α phase crystallized ceramic shows a better but still unsatisfactory luminescence intensity, the β phase ceramics give rise to intense Eu^{2+} photoluminescence and scintillation. We will thus focus our attention on this latter phase. The $BaAl_4O_7$ in β phase has a density (ρ) of 3.67 g/cm³. Such a density is a bit lower than that of $CsI : Tl (\rho = 4.5g/cm^3)$, a well known scintillator used in various applications.

In addition, glass from the $BaO - Al_2O_3$ binary system can be produced in various compositions, more precisely with a BaO content ranging from 33 to 37 mol%. A slight increase of the BaO content compared to the $BaAl_4O_7$ composition (1:2) ratio) allows easier glass synthesis and still leads to transparent polycrystalline ceramics with micrometer scale $BaAl_4O_7$ grains although a nanometer scale secondary phase $BaAl_2O_4$ which does not appear in the case of the stoichiometric composition is clearly detected by Transmission electron microscope (TEM) and X-ray diffraction (XRD) (Fig. 1). As shown in Figure 1-c, X-ray diffraction patterns of stoichiometric and overstoichiometric samples can be indexed by $BaAl_4O_7$ (CSD #424777). In the latter case, the presence of $BaAl_2O_4$ (CSD #75427) is also clearly detected as a secondary phase (see the main broad peak at 19.75°, the shoulder at 20.31° and even the weaker peak at 22.23°) which confirms the phase of the nanodomains detected in TEM (Fig. 1-b). TEM images recorded for the two tested thermal treatments (2h and 24h) do not reveal any differences. Nevertheless, XRD and TEM cannot reveal point defects and traps which have a significant impact on scintillating properties.

Table 1 List of studied samples, all of them are doped with 0.5 % of Europium.

Composition	Phase	Used name	Annealing
$33.33BaO - 66.67Al_2O_3$	β	stoichiometric	2h and 24h
$34BaO - 66Al_2O_3$	β	over-stoichiometric	2h and 24h

3 Experimental

Photo- (PL) and radio-luminescence (RL) emission spectra were obtained by using an LDLS EQ-99 lamp coupled with a Gemini180 monochromator from Jobin-Yvon or an X-ray tube with a Tungsten anode (High Voltage=30kV, dose rate 1.5mGy/s) for excitation, respectively. In both cases, emitted



Fig. 1 TEM images of (a.) $33.33BaO - 66.67Al_2O_3$ and (b.) $34BaO - 66Al_2O_3$ ceramics with thermal treatment of 2h. Arrows indicate grain boundaries. In the inset of (b), a zoom of the observed nano structures showing the crystalized secondary phase $BaAl_2O_4$. (c.) XRD patterns of the above presented compositions. The $BaAl_4O_7$ and $BaAl_2O_4$ indexating are indicated below.

light was detected by a Shamrock 500i spectrometer coupled to an EMCCD Newton camera, both from Andor.

In order to characterize the scintillation yield a Hamamatsu R-6231-100 PMT was used; data were acquired by a Lecroy LT372 digital oscilloscope and processed by homemade software. The excitation was a ^{137}Cs source which emits γ -ray with an energy of 661.7 keV. Results were corrected for the photomultiplier spectral sensitivity, and the number of photons was estimated by the single photo-electron method.²⁰ Each sample was glued on the PMT window using optical grease to ensure an appropriate optical contact and was covered by Teflon film in order to collect most of the emitted light. For each event, the signal was recorded for 10 μs and used both to build the Pulse Height Spectrum and to obtain scintillation decay time under γ -ray excitation. Luminescence time decay under UV excitation was measured by a time-correlated single photon counting (TCSPC) system from PicoQuand (PicoHarp 300) for acquisition, with a 379 nm laser (pulse duration: 15 ps) from Hamamatsu for excitation, and a PMA-C photomultiplier from PicoQuant has been used for light detection.

Thermally stimulated luminescence (TSL) measurements were performed from 90 to 650 K using a liquid nitrogen cooled stage (Linkam HFS600) with 1 K/s as heating rate. Samples were previously irradiated using the same X-ray tube as for the radio-luminescence (Hight Voltage=30 kV), and several tens of seconds are left free before starting the heater in order to avoid contribution of potential afterglow. We took care to have similar irradiation, light collection, and sample size for each measurements in order to ensure comparable glow curves. Light was collected without spectral resolution

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and then over the full emission of those ceramics using a EMI 9789 PMT in current mode.

4 Results

Emission spectra obtained under visible-UV and X-ray excitation (Fig. 2-a) are almost identical. Under x-ray excitation, a main emission centered at 488nm is dominant, as expected given the presence of Eu^{2+} , and an extremely weak Eu^{3+} emission peaking at 612nm can be observed. Under a selective excitation at $\lambda = 380nm$ corresponding to the $4f^7 \rightarrow 4f^65d$ absorption of Eu^{2+} , only the Eu^{2+} emission is observed. In addition, the weak Eu^{3+} radiative recombination is detected (not presented here) when exciting at wavelengths corresponding to the Eu^{3+} charge transfer state between 210 nm and 275 nm. Europium concentration in these ceramics can be adjusted from 0.1 to 10 %; luminescence intensity is related to the dopant concentration with a maximum observed between 0.5 % and 1 %, both for standard luminescence and scintillation yield.



Fig. 2 (a.) Room temperature luminescence of $BaAl_4O_7$ ceramics excited at 380 nm for photo-luminescence (red solid line) and with X-Ray for radio-luminescence (blue circles). (b.) decays both under pulse laser excitation at 380nm and under γ excitation (662keV from a ¹³⁷*Cs* source). For comparison CsI:Tl scintillation decay recorded under the same experimental conditions is presented.

For all samples, fluorescence decay times are identical under 380 nm and γ -ray excitation at 662 keV(Fig. 2-b). In the latter case, neither rise time nor slow components in the first 10 μ s are observed on luminescence decays. A single exponential fit procedure leads to a decay time of 670 ± 14 ns. It suggests a fast carrier transfer to the radiative recombination center without charge diffusion process.^{21–23} Moreover, the four studied samples (Table 1) exhibit identical decays indicating that neither stoichiometric deviation nor thermal treat-

ments affects the internal luminescence quantum yield. In terms of timing performance, our ceramics exhibit a decay about 3 times faster than that of CsI:Tl. They also do not exhibit a slow component in this time range, unlike CsI:Tl which shows various components over several tens of milliseconds, even when optimized.²⁴

Pulse height spectrum is a standard technique aiming to characterize the scintillation yield (also called light yield) as well as the energy resolution based on the width and the position of the photopeak.²⁵ For stoichiometric samples (Fig. 3-a), a scintillation yield of about 28000 photons/MeV is measured. A critical effect of the thermal treatment is observed when it is increase from 2 hours to 24 hours. The scintillation yield increases from 22000 to 28000 photons per MeV and the photopeak becomes much more pronounced. An energy resolution of 12 % is obtained. For the over-stoichiometric samples the opposite behavior is observed (Fig. 3-b). The best scintillation yield and energy resolution are measured for a thermal treatment of 2 hours: 42000 photons per MeV and 12 % energy resolution are calculated. Increasing the annealing treatment duration deteriorates significantly the light yield to about 25000 photons per MeV and the photopeak almost disappears. For comparison, we present the pulse height spectrum obtained with a standard CsI:Tl (crystal dimensions: $27 \times 12 \times 4mm^3$) (Fig. 3-c). Note that the lower photopeak intensity as compared to the Compton edge shoulder in the case of ceramics is partly due to their lower density but also to their smaller size.

We investigated the trap depth distribution using afterglow analysis and thermoluminescence which are the most common techniques for this purpose.²⁶ The four sample TSL glow curves are presented in figure 4. All samples show a similar glow curve shape where up to nine traps are detected between 90 K and 650 K. Peak intensities exhibit a difference of one order of magnitude when the stoichiometry and thermal treatments are modified. As reported on figure 5, the afterglow amplitude comparison among the four samples is in agreement with the glow curve intensities presented Fig.4. We also point out that for one of our ceramic, namely the over-stoichiometric annealed for 2h, the afterglow is by one order of magnitude better than CsI:TI.

5 Discussion

As mentioned previously, photo-luminescence and scintillation are similar in terms of spectral shape and kinetic decay. Nevertheless, despite all samples exhibit about the same comparative photo-luminescence yield, the analysis of pulse height spectra, reflecting the scintillation yield and the energy resolution, shows a drastic dependence on the thermal treatments and stoichiometry (Fig. 3). While luminescence process depends roughly on the local environment, the scintillation mechanism is much more complex and involves sev-







Fig. 3 Pulse Height Spectra under ${}^{137}Cs$ irradiation (662keV) of $BaAl_4O_7$ ceramics in stoichiometric composition (a.), in over-stoichiometric composition (b.) and CsI : Tl (c.) for comparison.

eral steps occurring in a larger volume. The scintillation yield (η) can be roughly described as a three step process generally written as: $\eta = \beta \cdot S \cdot Q^{27,28}$. β describes the conversion factor from the energy of the interacting photon (E_{γ}) into the relaxed electron-hole pairs. It is generally considered as:

$$\beta \approx \frac{E_{\gamma}}{(2 \sim 3) \cdot E_G} \tag{1}$$

where E_G is the energy gap of the material. This stage involves several processes such as electron-electron and electronphonon inelastic scattering, as well as Auger relaxation, and the total spatial charge spread is in the order of $10^6 nm^3$.^{29–31} S is the transfer efficiency from relaxed electron-hole pairs to the luminescent center (Eu^{2+} in this case). This is the key factor, since S is strongly affected by the presence of "killer" centers which compete with the radiative recombination ones for free carriers. These "killer" centers are related to material uncontrolled defects. Q is the luminescence efficiency, which is in the case of the four samples about identical. As described above, structural characterizations performed by XRD



Fig. 4 Left axis: TSL glow curves for different $BaAl_4O_7$ compositions and thermal treatments. Right axis: normalized Radio-luminescence intensity as a function of the temperature is plotted with black solid line.



Fig. 5 Comparison of room temperature afterglow following an irradiation of 180 s (HV=30 kV, I=20 mA). For annealing of 2 hours and 24 hours respectively, $33.33BaO - 66.67Al_2O_3$ with • and \circ , $34BaO - 66.6Al_2O_3$ with • and \Box , in solid line CsI:Tl afterglow. Each curve is normalized at Radio-luminescence intensity.

and TEM reveal that over-stoichiometric samples contain nano crystallized domains of $BaAl_2O_4$ with a radius in the order of 10nm. Because luminescence properties of all samples are similar, we suggest that these domains act as scavengers for uncontrolled defects.

Since scintillation yield is measured with a time gate of 10 μs , all traps having a significantly larger half-life at room temperature can be considered to be killing centers. In order to show this amount of non-radiative centers, traps were characterized by using the peak shape method for thermoluminescence analysis.³² For the peak at 190 K, calculated trap parameters are 0.54 eV as energy depth, and $10^{13}s^{-1}$ as frequency factor. Calculation on the trap related to the 111 K peak gives an energy of 0.27 eV and a frequency factor of $10^{11}s^{-1}$. Such traps lead to a half-life of about 100 μs and

0.1 μs at room temperature, respectively. Thus all the traps giving rise to glow peaks above 190K can be considered as killing centres. This glow curve analysis method cannot be used with accuracy for the peaks at higher temperature because of the luminescence thermal quenching and their strong peak superposition. Nevertheless this estimation is less important for this purpose because they likely have longer life times at room temperature. The influence of traps stable at room temperature is actually more pronounced than that at low temperature ones considering the evident Eu^{2+} luminescence thermal quenching above 350 K portrayed in fig. 4. In fact, traps may act in two different ways according to their thermal stability. They can be considered stable if their half-life is longer than few hours and unstable for shorter life times. In both cases trapping and luminescence recombination compete, but only unstable traps give rise to a significant afterglow. The competition between traps and luminescent centers may also lead to an increase in radio-luminescence intensity as the accumulated dose is increased. This effect is often call bright burn or radio-luminescence sensitization. 33-35 A way to characterize this effect is to measure the evolution of the light yield during X-ray irradiation. Figure 6-b presents two different measurements, both were performed after a thermal treatment (650 K) ensuring that all traps are empty. The first one (solid line) corresponds to the evolution of the radioluminescence yield under continuous X-ray irradiation. The second (red squares) is the evolution of the scintillation yield by measuring the photopeak position shift at different stages of the steady state X-ray irradiation. The detected light intensity increases up to a saturation level reflecting the filling of the traps. An increase of about 30 % is detected for the stoichiometric sample with a temperature treatment of 24 hours. The radioluminescence sensitization by steady state irradiation is affected by the filling of all traps, including those unstable at room temperature and leading to afterglow. Whereas the pulse height spectrum measurement reflects only the filling of stable traps at room temperature. Pulse height spectra were obtained after various irradiations and few minutes of delav has been kept between X-ray irradiations and pulse height spectrum measurements to read out of the afterglow. Figure 6-a presents the two pulse height spectra before and after a 600 second X-ray irradiation obtained for the stoichiometric composition with 24 hours of annealing. These data clearly fit the solid line indicating that bright burn measured under Xray is mainly due to high temperature traps. In addition, the light yield obtained after 10 minutes of irradiation with the stoichiometric sample annealed for 24h is approaching to that obtained for the over-stoichiometric sample annealed for 2h (42000 Photons/MeV). It indicates the major role of the traps in scintillation performance degradation.

Tentative explanations for the evolution of scintillation yield when composition and thermal treatments are modified



Fig. 6 (a.) Pulse height spectra before and after 600 s of X-ray irradiation. (b.) Comparison between radioluminescence sensitization by X-Rays (HV=36 kV) and the light yield under γ excitation (662 keV from a ¹³⁷*Cs* source) after different irradiation times for the stoichiometric composition with 24 hours of annealing. The radioluminescence curve has been normalized at the start of irradiation corresponding to t = 0s. The irradiation is then stopped at t = 600s. Uncertainty estimation has been deduced from a set of 5 measurements per point, including replacement of same samples.

can be drawn. Regarding the stoichiometric samples, the 2h and 24h thermal treatments show the same glow curve and the same afterglow. The scintillation yield is about the same except that the photopeak is badly defined in the case of the 2 hours thermal treatment. It suggests that inhomogeneities remain, and that a 24h thermal treatment is required to guarantee a high cristallinity degree of the ceramics. Nevertheless, this difference cannot be detected by either XRD or TEM, suggesting that only a fraction, probably at the nanoscale, of the material is badly crystallized. Regarding the over-stoichiometric ceramic, nanometre scale domains of $BaAl_2O_4$ phase have been evidenced as compared to the stoichiometric sample (figure 1). These domains could act as trap scavengers, explaining the observed difference in terms of trap concentration, which then modifies the scintillation yield and afterglow properties. When the thermal treatment is increased to 24h, one may conclude that traps are released and a slight increase of the glow curve intensity is observed. The afterglow and scintillation yield is thus degraded. In addition, the photopeak is poorly defined, suggesting inhomogeneities. Considering that traps are released from the nano domains, it is natural to conclude that they remain in the vicinity of the $BaAl_2O_4$ nano-domain leading then to inhomogeneous spatial distribution.

6 Conclusion

In this contribution, we show that Eu^{2+} doped $\beta - BaAl_4O_7$ prepared by full and congruent crystallization from glass is an efficient scintillator. The modification of the ceramic sto-

ichiometry and thermal treatments of the ceramics drastically changes the performances, pointing to the crucial role of nanodomains acting as trap scavengers. We also demonstrate that X-ray irradiation is able to fill traps acting as killing centers. This physical processes leads to a significant stable improvement of the scintillation yield and a clear shift of the photopeak position is evidenced. These significant modifications under chemical-physical treatments suggest that full optimization has not yet been reached despite the good performances already obtained. This material science oriented research is currently in progress. In addition, this ceramic sample shows very interesting performances: a density of 3.67 g/cm^3 , an emission wavelength of 450nm, which fits the silicon detectors well, a scintillation yield of about of 75% of CsI : Tl, a decay of 670 ± 14 ns and an extremely reduced afterglow. This is why this ceramic sample can be considered as a very good alternative to CsI: Tl for applications requiring a shorter decay time (in counting regime) or/and when a low afterglow and bright burn levels are particularly critical parameters.

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