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Temperature dependence of Ce-emission kinetics in YAG:Ce optical ceramic

E. Zych[a,b,*], C. Brecher[b]

[a]Faculty of Chemistry, Wroclaw Univ., 14 F. Joliot-Curie St., 50-383 Wroclaw, Poland
[b]Chemistry Dept., Boston Univ., 590 Commonwealth Ave., Boston, MA 02215, USA

Abstract

We have measured the scintillation decay kinetics of the Ce-emission from a YAG:Ce optical ceramic material over a temperature range between 110 and 450 K. Above room temperature the decay can be well described by the sum of two exponential terms, but below room temperature a third term is needed. This new component has a characteristic time shorter than the radiative lifetime of the Ce ion, varying from 33 ns at 110 K to 18 ns at 300 K. The presence of the short component can be explained in terms of the distortion of the YAG host band structure and the introduction of surface-boundary states into the otherwise forbidden energy region, which drains the emitting 5d levels of Ce ions located in the vicinity of the grain-boundaries. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: YAG:Ce; Scintillator; Transparent ceramic; Recombination and trapping; Grain boundaries

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1. Introduction

The past decade has seen extensive research on scintillator materials, in response to the need for high-performance detectors for use in high-energy physics, medicine and industry. Despite enormous effort [1–3], however, very few efficient new detector materials were actually discovered. One of these few was Ce-doped yttrium aluminum garnet ($Y_3Al_5O_{12}$:Ce, or YAG:Ce), single crystals of which showed a light output under gamma excitation of some 17 500 photons per MeV of absorbed gamma-ray energy [4,5]. This is more than double the 8200 ph/MeV output of the broadly utilized bismuth germanate ($Bi_4Ge_3O_{12}$, or BGO) [6]. Unfortunately, YAG itself is deficient in stopping power for many applications, due to its low density ($\approx$5 g/cm^3). However, this deficiency can be readily overcome by replacing the Y^{3+}-ion with Lu^{3+}, raising the density by more than 50%. The analogous lutetium compound ($Lu_3Al_5O_{12}$:Ce, or LuAG:Ce) has the same crystal structure and shows very similar spectroscopic properties [7], so that its increased stopping power makes it quite attractive for a number of practical applications, such as tomographic diagnostic techniques.

In recent years a new type of material, transparent optical ceramics, has emerged as an alternative to single crystals for a number of optical applications. Optical ceramics are formed in a solid phase from properly processed isotropic powder materials. Such powders are cold-pressed to some 50% of the theoretical crystalline density, after which they are densified at elevated temperatures to very nearly 100% by sintering, mechanical hot-pressing, or hot-isostatic-pressing (HIPing). The choice of technique depends on specific material/device requirements, but each approach can reproducibly and cost-effectively produce transparent bulk components even in sizes and shapes required for a specific application, which significantly reduces the after-preparation material wastage. Further, such materials do not exhibit any concentration gradient of dopants within their whole volume, which is in practice not achievable with single crystals. These properties make optical ceramics very attractive alternatives to single crystals. Indeed, it has already been demonstrated that such materials can successfully compete with, and sometimes outperform, their single crystal counterparts [8–13].

Until now the most successful application of optical ceramics has been as passive elements, such as optical windows. They have also found use as laser materials, where excitation of the emitting center does not involve energy transfer from the excited host to the luminescent ions. The last process is the crucial step for efficient

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*Corresponding author. Tel.: +48-71-3204-304; fax: +48-71-3282-348.

E-mail address: zych@wchuwr.chem.uni.wroc.pl (E. Zych)

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emission under excitation by ionizing radiation [7,14,15], typically gamma-, cathode- or X-rays: Excitation absorbed in the host material must be effectively passed to the emitting center.

In recent years we have conducted an extensive research program on the scintillation properties of YAG:Ce transparent ceramics [4,5,16–18]. During the course of the work, we discovered a number of interesting properties specific to the YAG ceramic phase, showing that the microstructure of the host influences the spectroscopic behavior of the material. Upon comparison with results obtained from single crystal material we were able to elicit the ceramic-specific effects from the overall picture observed. One of the most unusual and puzzling effects that we discovered was the presence of a short component, having a time constant of about 20 ns, in the Ce-scintillation decay of the ceramic material. This short component under gamma excitation is not present in the single crystal, whose decay we [4,16] and others [19] find to require only two exponential components, having time constants in the neighborhood of 65–85 ns and 300–400 ns. The amount of light contained in the short component at room temperature was about 5% of the total [4], varying slightly depending on the specimen. This new short component of the decay kinetic, however, was present exclusively under gamma excitation, and was not observed for any of the other (optical) excitation energies: 460, 340, 230 nm, which represent direct Ce excitation, or 178 nm, corresponding to the host valence-to-conduction band electron elevation. This was especially surprising for 178 nm or shorter wavelengths (e. g., the 150 nm deuterium line), since such light simulates what happens under gamma-rays, exciting the host material and requiring transfer of energy from the host lattice to the Ce ions. Evidently, excitation at energies greater than the band gap is a necessary but not sufficient condition for the anomalous behavior. In order to achieve a better understanding of the unusual kinetics of gamma-excited Ce-emission in the ceramic, we explored the subject further and recorded decay traces of the Ce-luminescence in the YAG host over a broad range of temperatures. This paper reports on the results of this study.

2. Materials and experiments

The ceramic sample investigated was prepared by hot-pressing appropriate YAG:Ce powder at 1750 C under the pressure of about 300 atm. The details of the preparation procedure are given elsewhere [4,16,18]. The average grain size of the specimen was about 40 μm, making it comparable to the specimen on which we reported previously and systematically referred to as ‘‘ceramic #1’’ [4,16,18]. The decay of Ce-emission was recorded using a ^{137}Cs excitation source and the emission was observed directly with a Hamamatsu photomultiplier. The emitted light was passed through with a filter that blocked light of wavelength shorter than about 470 nm, to reject any vestige of host-related emission arising around 200–450 nm region [17]. The spectral distribution of the emission was recorded with a simple 0.25 m Jarrell–Ash monochromator. The measurements were performed over the 110–450 K temperature range, below which the signal was already too weak for reliable measurement in our experimental setup. For all the results analytical fits with two or, where necessary, three exponential terms were performed.

3. Results and discussion

Stimulation of the transparent ceramic Ce-doped YAG with gamma radiation results in the well-known emission of the Ce-ion in the host, peaking around 530 nm and extending over some 480–650 nm spectral region. Its intensity rises with temperature up to some 300–350 K, above which it remains essentially constant. A low-intensity luminescence in the UV region, comprising not more than 1–3% of the total emitted light, accompanies the emission from Ce ions. Its part in the total light emitted decreases as the temperature rises. A thorough characterization of the UV emission in transparent ceramic YAG can be found elsewhere [17].

Our earlier work showed that the Ce-scintillation is partially quenched [4,16] and we anticipated that the magnitude of this effect would decrease as the temperature was lowered. The concrete results, however, turned out not to be as straightforward as we expected. In Fig. 1 we present the traces of the Ce-emission decays at two different temperatures, 110 and 450 K. The differences

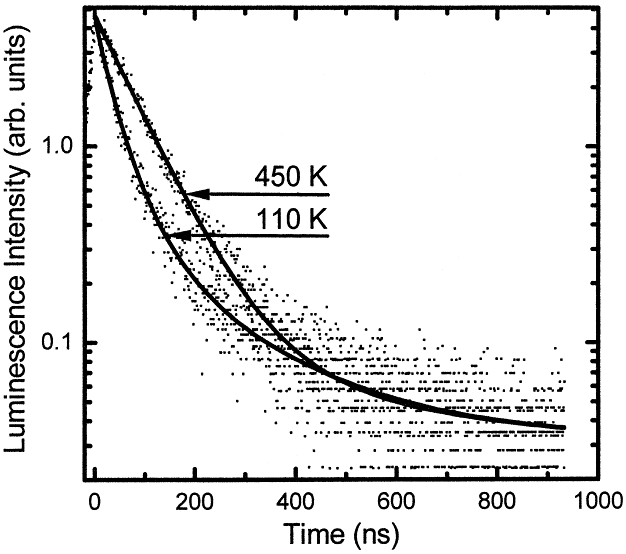

Fig. 1. Scintillation decays of the cerium emission from YAG:Ce ceramic material at high and low temperatures.

between the two traces are readily seen, beginning at time zero and extending for about 400 ns. The 450 K decay trace, which closely resembles the analogous result recorded for the single crystal, indicates that at this higher temperature the early stage of Ce-emission is significantly slower than at 110 K. Analytical fits of the two traces reveal that the 450 K trace can be accurately simulated with a two-exponential sum with time-constants $\tau_1=77$ ns and $\tau_2=350$ ns. These values are in good agreement with those found for a single crystal doped with Ce at the same level [20]. However, the rapid initial drop-off in the 110 K trace could be adequately reproduced only by adding a third component to the fitting function. In this case the three resultant time-constants were $\tau_1=33$ ns, $\tau_2=67$ ns and $\tau_3=320$ ns. The τ_2 and τ_3 values are again in very good agreement with those found for the single crystal at the same temperature [20]. However, since the radiative decay time of the Ce ion at 110 K is about 63 ns, the presence of a component almost twice as fast indicates that, despite the low temperature, the cerium-scintillation is partially quenched.

We performed similar measurements and analogous fitting procedures for each recorded trace in the whole range of investigated temperatures. The results divide the cerium scintillation decay traces into two groups. The first one consists of results for temperatures 350–450 K, all of whose decay traces could be easily fitted by a sum of two exponential terms. In each of these cases, the fits produced a pair of time-constants, whose values were close to those found for the 450 K trace as presented above. For all temperatures in the range of 110–300 K, however, the experimental traces could be fitted only with the aid of a third term. This presents us with a picture in which a quenching mechanism apparently *increases* as the temperature is lowered, a paradoxical situation to say the least.

The results presented in Fig. 2a, however, shed some light on this problem. A detailed analysis of the changes of the short component time-constant (τ_1) over the temperature range of its existence (110–300 K) reveals that the value of this parameter varies with temperature in a systematic manner, increasing steadily from some 18 ns at room temperature to about 33 ns at 110 K. In Ref. [4], where the existence of the anomalous short component (at room temperature) was first reported, its existence was attributed to the Ce ions in the vicinity of the grain boundaries. It was hypothesized that the distortion of the band structure of the host material in this region introduced a quenching process that operated only on the small fraction of Ce ions in the interfacial vicinity. At the same time, the interfacial effects tended to draw into the vicinity more of the free carriers formed by the gamma radiation in the host, thereby channeling more excitation to the very same ions subject to the quenching process. Now, the lack of the short component at temperatures above 300 K is no longer so peculiar. Indeed, the results presented in Fig. 2a imply that the emission from these ions is progressively *less* quenched as the temperature drops from 300 K, allowing the τ_1 value to increase with cooling, a far more reasonable situation. Moreover, the lack of the short component above some 300 K would indicate not the *lack* of quenching at higher temperatures, but rather that all the Ce-ions *susceptible* to quenching (those residing in the grain boundary region of the ceramic host) do not emit at such temperatures at all. In other words, at temperatures above 300 K the quenching of the emission from such ions is complete and their faster decay is no longer detectable.

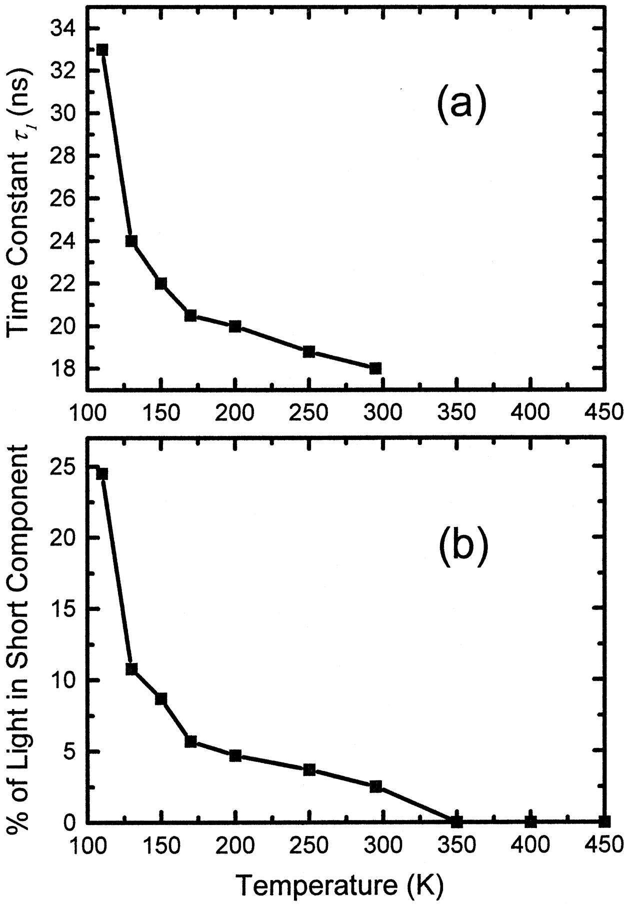

Fig. 2. Temperature dependence of the time-constant of the short component and its contribution to the total emission.

Using the parameters derived from the analytical fits we also calculated the relative amount of light emitted by the quenched Ce-ions (as a percent of the total light emitted), giving the results graphically presented in Fig. 2b. It is immediately evident that the temperature pattern of this parameter is quite similar to that of the parameter τ_1. However, the magnitude of the change is much greater: While the time constant of the short component just about doubles upon cooling from room temperature to 110 K, the relative contribution of this term to the total light rises from some 3% to almost 25%, nearly an order of magnitude, and far too great to be explained by the decay time increase alone. Another effect must also be operating here.

There are two ways in which a lowering of the temperature can enhance the population ratio of ‘‘partially quenched’’ to ‘‘normal’’ Ce ions: an increase in the former, *or* a decrease in the latter. We already know that the emission intensity from single crystal material drops by a factor of four upon cooling from room temperature to about 100 K [20], an effect that can be readily explained by the trapping of free carriers at point defects in the lattice. Since most of the Ce ions in the ceramic reside in the interior of the grains, far from the interfaces, we would certainly expect their emission to show similar behavior. The grain boundary region, however, is conceptually already a trap [4,21], although one that extends along a line rather than a single point, and with a bottom energetically deep enough to reach the emitting level of Ce ions in the vicinity, as depicted in Fig. 3. While this trench is too deep for the escape of any free carriers that have fallen in, there is only minimal barrier to motion along the length. Consequently these carriers can migrate to the ‘‘partially quenched’’ Ce ions in the immediate vicinity even at low temperatures, while remaining unavailable to those in the interior of the grains. Thus the emission from the ‘‘partially quenched’’ ions should decrease less as the temperature drops, increasing their relative contribution to the total.

On the other side of the population ratio, the absolute number of ‘‘partially quenched’’ Ce ions that participate in the total emission can actually increase as the temperature is lowered. Here we must remember that there is not merely a single type of affected ions but rather a broad range, depending on their distance from the interfacial lattice discontinuity. This implies an equally broad range of quenching. At the high end of the temperature range, we see emission only from Ce ions well within the interior of the grain, far from its boundaries. At lower temperatures, some of the formerly dark ions closer to the grain boundaries begin to participate in the emission, introducing a previously undetectable anomalously fast component. As the cooling proceeds, more and more grain boundary ions begin to participate, even while the behavior of the earlier ones begins to approach that of the bulk ions. This would tend to suppress the observable effect somewhat, and could account for the shallow slope of the temperature dependence of both the decay time and relative magnitude of the anomalous decay component, as seen in Fig. 2. Only when the temperature has dropped below about 170 K do we begin to see a sharp increase in the temperature dependence of these two parameters.

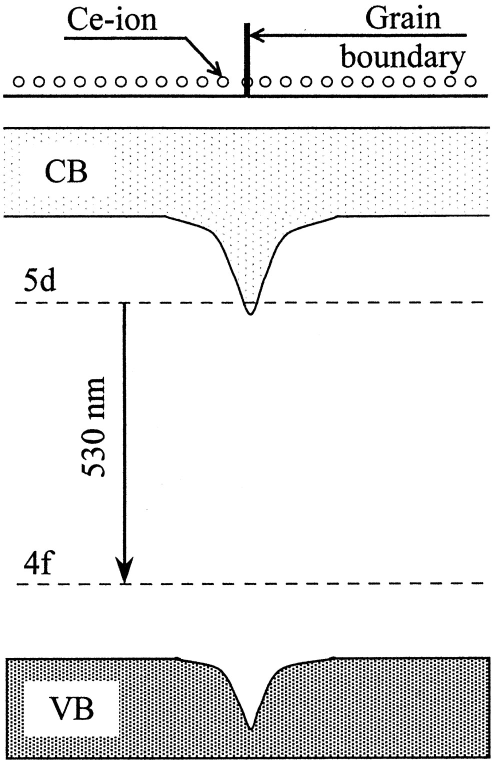

Fig. 3. Depiction of the distortion of the band structure by the grain boundary and the resultant quenching of the Ce-emission.

Ending our considerations we wish to warn against the all too common tendency to impart an unwarranted physical significance to the parameters derived from the decay trace fits. In fact, these parameters (time constant and amplitude) have an unambiguous physical meaning only for a decay that can be described with a single exponential term. While the necessity to involve a second or, even worse, a third exponential term may lead us to a good mathematical description, that does not mean the process itself consist of similarly independent steps. More often than not, and certainly here, the decay constants are describing some unspecified average, preventing a direct translation of the mathematical portrayal of the process into a perception of its physics.

On the other hand, however, the necessity to use two- or three-exponential expression to properly reconstruct a decay does indicate the complexity of the emission mechanism. The departure of the kinetics from single-exponential behavior can be then seen as a measure of the perturbing influences. As we have seen, the influence of ceramic-specific effects on the Ce-scintillation kinetics can be substantial indeed.

4. Summary and conclusions

In this paper we have presented the results of decay kinetic measurements of the Ce-emission from an optical ceramic YAG host excited with gamma-radiation. These measurements reveal that a significant fraction of the excited Ce ions decay more rapidly than the radiative rate, and that this fraction increases and the rate decreases as the temperature is lowered. The average time constant of this decay increases from some 18 ns at 300 K to about 33 ns at 110 K. The existence of this anomalously fast decay component, and its temperature-dependent behavior, can be explained by a model involving the one-dimensional trapping of free carriers in a potential trench defined by the grain boundaries. The results complement the room temperature measurements presented previously [4], and support the phenomenological model derived to explain them. The results shed a small degree of light onto the role of the abnormal surface (boundary-region) states on the kinetics of the scintillation process in Ce-doped YAG ceramic, and may help to define the potential of such materials for practical detector applications.

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