

Scintillation mechanisms in Ce³⁺ doped halide scintillators

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Last couple of years witnessed the development of various new Ce³⁺ doped halide scintillators (LaCl₃, LaBr₃, LuI₃, Cs₂LiYCl₆, Cs₂LiYBr₆) that possess excellent gamma ray or thermal neutron detection properties. The scintillation pulse in LaBr₃:Ce³⁺ is 20 times faster than in the most commonly used scintillator NaI:Tl. This, combined with a more than two times better energy resolution and higher gamma ray stopping power, makes it ideally suited for many different applications. In this work the scintillation properties and mechanisms of Ce³⁺ doped inorganic halide (Cl, Br, I) compounds are reviewed; especially the role of V_k centers and self trapped excitons (STEs) in the energy transfer from the ionization track to Ce³⁺ is treated. Aspects of the lifetime and thermal stability of the self trapped exciton, the migration speed of V_k centers and STEs, spectral overlap between STE emission and Ce³⁺ absorption, and the influence of the type of anion (Cl, Br, I) are addressed.

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1 Introduction

Despite a long history on the research and development of scintillator crystals still new ones are developed especially in the field of Ce³⁺ doped rare earth trihalide compounds. LaCl₃:Ce³⁺ and LaBr₃:Ce³⁺, discovered 3–4 years ago, are excellent scintillators [1–3]. Energy resolution, proportionality of response, decay time, and density are better than that of the hitherto most widely used scintillator NaI:Tl. On the other hand Ce³⁺ doped LaI₃ is a very poor scintillator where as LuI₃:Ce³⁺ is again very efficient [4, 5]. Ce³⁺ doped Cs₂LiYCl₆ and Cs₂LiYBr₆ are efficient and fast, and can be used to detect thermal neutrons via a capture reaction on ⁶Li isotopes [6]. Scintillator properties vary widely with the type of compound and in order to understand this, information is needed on the mechanism of scintillation and the physical processes determining that properties.

LaCl₃:Ce³⁺ and LaBr₃:Ce³⁺ show almost maximum possible light output, however most scintillators and phosphors do not reach that maximum due to electron–hole losses. There are many reasons. Free electrons and holes may recombine radiationless already inside the ionization track or defect sites can trap them. Even if they reach Ce³⁺ it does not necessarily lead to photon emission. Concentration quenching, thermal quenching, or quenching via auto-ionization all lead to scintillation light losses.

In this work the mechanisms of excitation of Ce³⁺ that we think are present in halide scintillators are reviewed. Often the migration of trapped hole centers (V_k) centers and self-trapped excitons (STE) play an important role in the transport of excitation energy from the ionization track to Ce³⁺. Migration speed and efficiency and therewith also the scintillation decay and scintillation light yield depend critically on the type of compound, the Ce concentration, and the temperature. Despite the large variation in type and complexity of scintillation processes, there appear clear trends in scintillation behavior. For example in the sequence chloride, bromide, and iodide compounds, the transfer speed and efficiency generally tends to increase.

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2 Main scintillation mechanisms

The preferred scintillation mechanism is the prompt transfer (faster than 1 ns) of a free electron and free hole from the ionization track to Ce³⁺ leading to 4f–5d excitation and followed by 5d–4f emission with 100% efficiency. However, there are always competing processes. Two types of mobile defects often play an important role in the scintillation mechanism. A hole at the top of the valence band is not stable and will be bound between two anions to form an X₂⁻-like molecular complex (X = F, Cl, Br, I) accompanied by strong lattice relaxation [7]. The complex is better known as a V_k center that may jump from one site to an adjacent site by thermal activation. It also carries a positive charge and tends to trap an electron from the conduction band. When this happens, a self-trapped exciton (STE) is created which is a neutral defect that also may migrate by thermal activation. Because it is neutral, the migration speed is usually faster than that of a V_k center [7].

The role played by V_k and STE centers in the scintillation mechanism is illustrated in Fig. 1. Figure 1a shows the self-trapping of a hole into a V_k center (arrow 1), next the V_k center migrates by a thermally activated hopping motion to the Ce³⁺ ion where it is trapped to form Ce⁴⁺ or an Ce³⁺–V_k associated complex. Finally the electron is trapped in this center (arrow 2) leading to excitation of Ce³⁺ followed by 5d–4f photon emission (arrow 3). We will refer to this type of mechanism as the mechanism of binary V_k and electron diffusion. When such mechanism takes place, the scintillation decay time τ_s is determined not only by the lifetime τ_v of the 5d-state of Ce³⁺ but also by the transfer speed of V_k centers to Ce³⁺ and electrons to Ce⁴⁺ or Ce³⁺–V_k.

The situation is more complex when the V_k center, before being trapped by Ce, traps an electron to form an STE, see Fig. 1b. The STE is a luminescent defect by itself with typical decay time of several microseconds (arrow 1). The STE is also a mobile defect that, when in the neighborhood of Ce³⁺, may transfer its energy to Ce³⁺ (arrow 2) leading to delayed Ce³⁺ emission (arrow 3). In some compounds the STE emission is quenched at low temperature, and when the lifetime of the STE is shorter than the time needed to transfer energy this can be an important scintillation loss factor. Depending on the spectral overlap between STE emission and Ce³⁺ absorption, radiative transfer is also possible.

The above schemes show that there are many different routes of energy transfer from the ionization track to Ce³⁺, and often different processes are active simultaneously in mutual competition with each other leading to complicated scintillation mechanisms. The dominance of one route over the other depends on temperature, concentration, and type of compound.

2.1 Chloride scintillators

Figure 2a shows the X-ray excited emission spectra of LaCl₃:0.6% Ce³⁺ [8]. At 135 K, Ce³⁺ emission is observed as the double peaked structure at 337 nm and 358 nm. In addition a 0.70 eV broad band emission is observed peaking at 400 nm. This emission is caused by STEs. Upon heating to 400 K, the STE emission disappears and the Ce³⁺ emission gains intensity leaving the integral intensity almost invariant. The explanation is as follows. At low temperature the free holes have two options: 1) they self-trap to form a V_k center or 2) they are trapped by Ce³⁺ to form Ce⁴⁺. This all happens on the sub-nanosecond

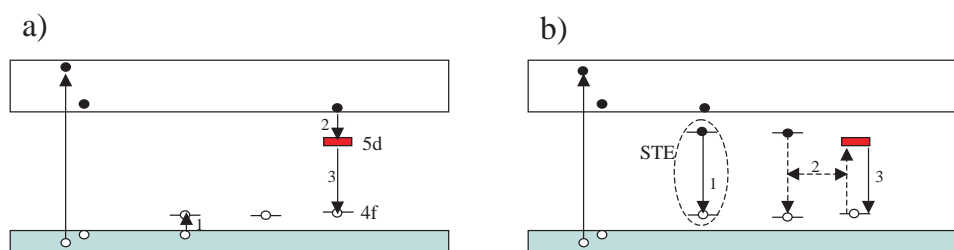


Fig. 1 (online colour at: www.pss-a.com) a) Binary V_k and electron diffusion, and b) STE migration in the scintillation process.

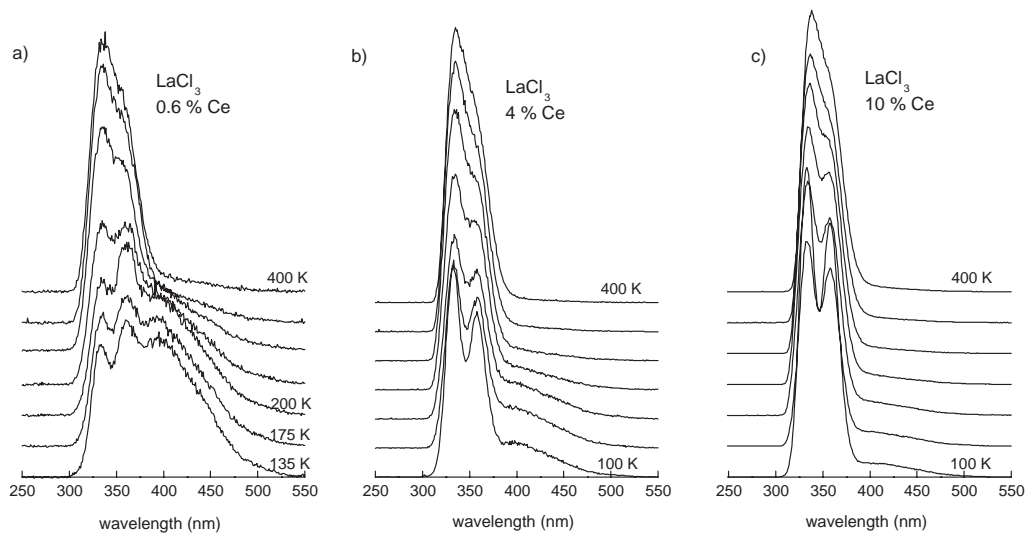


Fig. 2 X-ray excited emission in $\text{LaCl}_3:\text{Ce}^{3+}$ as function of temperature and concentration. Unless indicated otherwise spectra are separated by 50 K temperature intervals.

time scale. At 135 K, the V_k mobility is low and eventually it traps an electron to form an STE that provides the broad band emission with about 2.2 μs decay time. Electrons trapped by Ce^{4+} give the characteristic Ce^{3+} emission doublet due to 5d–4f emission with decay time of about 30 ns. Upon heating, a thermally activated transfer of energy from the STE to Ce^{3+} takes place. Whether elevated temperature is needed to overcome barriers in the migration stage or in the transfer stage or a combination of both is not yet clear. Anyway, 5d–4f emission with an effective lifetime dictated by the transfer rate from the STE is observed. In the scintillation decay spectrum at room temperature two decay components are observed. There is a fast non-exponentially decaying component in the first few 100 ns and a slow one with 2.2 μs decay. The slow component dominates and accounts for 70% of the total emission [8]. It is caused by a combination of STE emission and 5d–4f emission due to the delayed transfer from STEs to Ce^{3+} .

The delayed transfer from STE to Ce^{3+} makes $\text{LaCl}_3:0.6\% \text{Ce}^{3+}$ a scintillator too slow for many applications. The situation improves much when the Ce concentration is increased to 10% [1]. STE emission disappears from the X-ray emission spectra, see Fig. 2a and b. Figure 3 shows the scintillation decay curves as function of the Ce concentration. The direct capture probability of electrons and holes by Ce^{3+} increases with concentration leading to a more intense fast component. The lifetime of the exciton decreases due to the increasingly faster transfer from STEs to Ce^{3+} . Figure 2c shows that STE emission is not observed anymore for 10% Ce^{3+} at room temperature. A fast Ce^{3+} 5d–4f emission of 26 ns decay time accounts for 40% of the total light output, see Fig. 3e. 30% of the emission has 210 ns decay. The rest is due to delayed 5d–4f Ce emission caused by transfer from STEs with about 800 ns decay time [9].

The results for LaCl_3 demonstrate the role of the STE in the scintillation process and how the STE influences the properties as function of concentration, temperature, and time. The proposed mechanism is supported by magnetic resonance investigation [10].

In elpasolite chlorides the scintillation processes are much different. This is immediately clear from the X-ray emission spectrum of $\text{Cs}_2\text{LiYCl}_6:0.5\% \text{Ce}^{3+}$ in Fig. 4 [11]. In pure $\text{Cs}_2\text{LiYCl}_6$, a broad emission band around 310 nm is due to STEs. In the Ce^{3+} doped elpasolite, one observes the characteristic Ce^{3+} emission doublet and a remnant of STE emission. The dip in emission around 350 nm is due to re-absorption of STE emission by Ce^{3+} . This means that contrary to the situation in $\text{LaCl}_3:\text{Ce}^{3+}$ radiative transfer is an important process. Similar features were observed in other elpasolite systems like $\text{Cs}_2\text{LiLaCl}_6$ and also in Li_3YCl_6 which has different crystal structure [11]. Besides radiative transfer, also evidence for transfer by means of capture of migrating STE centers was found; quite similar as for $\text{LaCl}_3:\text{Ce}$. In addition the mechanism of binary V_k and electron diffusion was suggested [11, 12].

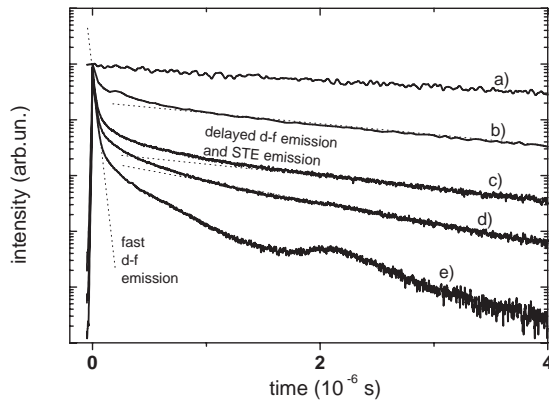


Fig. 3 Scintillation decay curves at room temperature of $\text{LaCl}_3:x\% \text{Ce}^{3+}$. a) $x = 0$, b) $x = 0.6$, c) $x = 2$, d) $x = 4$, e) $x = 10$, the bump at $2 \mu\text{s}$ is caused by after pulsing in the photomultiplier tube (from Ref. [9]).

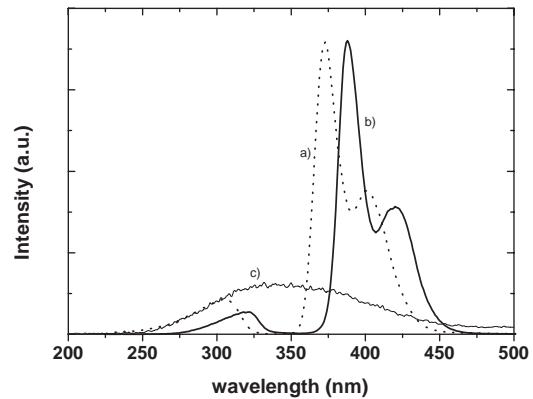


Fig. 4 X-ray excited emission spectrum of elpasolite halide scintillators. a) $\text{Cs}_2\text{LiYCl}_6:\text{Ce}^{3+}$, b) $\text{Cs}_2\text{LiYBr}_6:\text{Ce}^{3+}$, c) pure $\text{Cs}_2\text{LiYCl}_6$.

2.2 Bromide and iodide scintillators

Contrary to $\text{LaCl}_3:0.6\% \text{Ce}^{3+}$, LaBr_3 is already a very efficient and fast scintillator at 0.5% doping level. The emission is entirely due to Ce^{3+} , and STE emission is not observed. A decay time of 30 ns is obtained, but the decay spectrum also reveals a rise time signifying that some delay does occur due to transfer processes. The rise time is much shorter for concentration larger than 4% and the decay time decreases to 15 ns [3, 13]. In this situation all free electron and holes are trapped promptly without the intermediary role of migration processes, and an ideal scintillator mechanism is active. When we compare the X-ray emission, see Fig. 4 of $\text{Cs}_2\text{LiYBr}_6:1\% \text{Ce}^{3+}$ with that of $\text{Cs}_2\text{LiYCl}_6:0.5\% \text{Ce}^{3+}$ they are quite similar. Again the radiative transfer from the STE to Ce^{3+} is an important mechanism.

Triggered by the good scintillation properties of $\text{LaBr}_3:\text{Ce}$ and $\text{LaCl}_3:\text{Ce}$, Ce^{3+} doped LaI_3 and LuI_3 compounds were studied [4, 5]. With smaller values (3.5–4.5 eV) for the band gap, in principal higher-light yields are possible. However, we observed that at room temperature Ce^{3+} does not emit in LaI_3 . Decay time and luminescence intensity studies as a function of temperature revealed an activation energy of 0.1–0.2 eV [4]. We interpret this as the energy difference between the emitting 5d state of Ce^{3+} and the bottom of the conduction band of LaI_3 . At temperatures above 120 K the 5d electron can be thermally activated to the conduction band leading to luminescence quenching at room temperature. The situation improves much for $\text{LuI}_3:\text{Ce}^{3+}$. The slightly larger band gap and longer wavelength of emission lead to larger activation energy, and room temperature stable emission is observed with fast decay. The scintillation mechanism is still under study, but it appears already that STEs do not play an important role in the scintillation mechanism. At 0.5% Ce^{3+} concentration all emission is fast 5d–4f emission [5]. This resembles the situation in $\text{LaBr}_3:0.5\% \text{Ce}^{3+}$.

2.3 Influence of the type of anion

The previous sections showed the various pathways for the free charge carriers to be transferred to Ce^{3+} . From a fundamental and applied physics point of view it is important to know the reasons why some processes are dominant over others and how this depends on type of compound. Particularly interesting questions are: i) what determinates the branching ratio between charge trapping by Ce and charge trapping by the host lattice to form V_k or STE centers, ii) what controls the emission wavelength and thermal quenching rate of STEs, and iii) what parameters are important for the migration rate of STEs and V_k centers? In a first attempt to answer some of these questions we undertook a study on Ce^{3+} doped

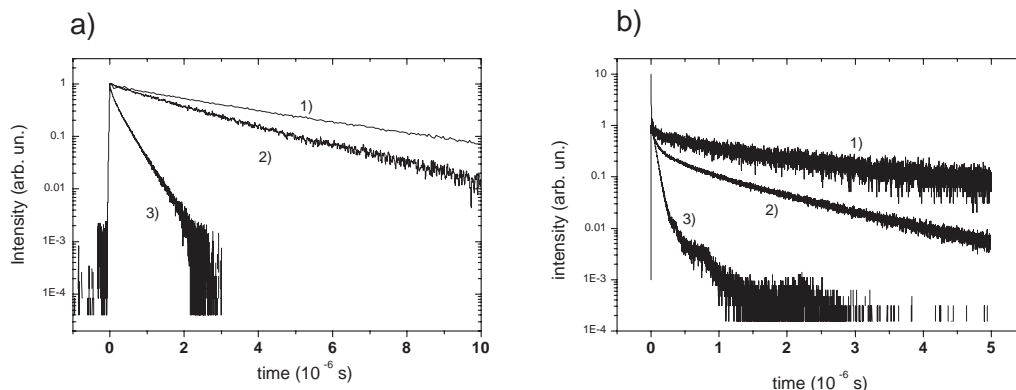


Fig. 5 a) Gamma-ray excited scintillation decay spectrum of 1) pure K_2LaCl_5 , 2) K_2LaBr_5 , and 3) K_2LaI_5 at room temperature. b) Gamma-ray excited scintillation decay spectrum of 1) $\text{K}_2\text{LaCl}_5:0.1\% \text{ Ce}$, 2) $\text{K}_2\text{LaBr}_5:0.7\% \text{ Ce}$, and 3) $\text{K}_2\text{LaI}_5:0.7\% \text{ Ce}$ at room temperature.

K_2LaCl_5 , K_2LaBr_5 , and K_2LaI_5 [14]. Because the crystal structure is in each case the same, the effect of the type of anion can be studied.

X-ray excited emission spectra of these compounds doped with a relatively small concentration of Ce^{3+} show like for $\text{LaCl}_3:\text{Ce}^{3+}$, the Ce^{3+} emission doublet together with a broad STE emission [14, 15]. Figure 5a shows gamma ray excited scintillation decay time spectra of the STE emission in the pure compounds. The decay time of the STE emission shortens from $3.7 \mu\text{s}$ in K_2LaCl_5 , to $2.2 \mu\text{s}$ in K_2LaBr_5 , to 350 ns in K_2LaI_5 . STE lifetime shortening is also observed in the alkali-halides in the sequence Cl, Br, I. It is attributed to increase of spin-orbit interaction leading to admixture of singlet spin states into the emitting triplet state of the STE [7].

The scintillation emission of $\text{K}_2\text{LaCl}_5:0.1\% \text{ Ce}^{3+}$ is almost entirely composed of $\text{Ce}^{3+} 5d-4f$ emission [14, 15], but the decay spectrum resembles that of the pure compound and is governed by the life time of the STE, see Fig. 5b. The same applies to $\text{K}_2\text{LaBr}_5:\text{Ce}^{3+}$ but in addition a fast decay component is present in the first few 100 ns. Finally for $\text{K}_2\text{LaI}_5:\text{Ce}^{3+}$ the emission is predominantly very fast Ce^{3+} emission with 24 ns decay time. The increasingly faster response in the sequence Cl, Br, I and diminishing importance of STE mediated transfer is much like what is observed for $\text{LaCl}_3:\text{Ce}$, $\text{LaBr}_3:\text{Ce}$ and $\text{LuI}_3:\text{Ce}$.

Studies on the alkali-halides have revealed that the migration rates of STEs and V_k centers tend to increase with larger size of the anion and with smaller size of the cation [7, 14]. It now seems that similar features reappear in the scintillation mechanism in the more complicated trihalide compounds. One may also speculate that in the elpasolite crystals with the large Cs atoms the STE mobility is too low for efficient transport to Ce and radiative transfer from STEs is then a dominant mechanism. The short STE lifetime, the high migration rate for both V_k and STE centers, and the small band gap of iodine compounds are very favorable properties required for developing scintillators with even better performance than $\text{LaBr}_3:\text{Ce}^{3+}$.

3 Summary and conclusions

Over the years we have studied the scintillation mechanisms of many Ce^{3+} activated halide compounds. Although the mechanisms can be very complicated, it appears that often similar processes of energy transfer from the ionization track to Ce^{3+} can be distinguished. The preferred one is the prompt trapping of holes and electrons by Ce^{3+} leading to a scintillation decay determined by the lifetime of the excited $5d$ state. However, often the scintillation emission is delayed due to the energy transfer by means of thermally activated migration of STEs or V_k centers. In this work several examples were given to demonstrate how these transfer processes influence the scintillation response. A mayor conclusion is that when the anion changes from Cl, Br, to I the lifetime of the STE shortens and the transfer speed of the STE and V_k centers tends to increase. Generally this leads to a faster scintillation response.

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