

Oxide and fluoride single crystals for scintillator applications

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Abstract Luminescence and scintillation properties of PbWO_4 , XAlO_3 ($X = \text{Y, Lu, Y-Lu}$) and LiBaF_3 based scintillators are reported. The effect of present and often not understood defect states is demonstrated in different scintillator parameters and related measurements are discussed. Importance of understanding of defect states participating in the processes of energy transfer and storage in the scintillating materials is emphasised.

Key words Scintillators, PbWO_4 , $\text{YAlO}_3 : \text{Ce}$, $\text{LiBaF}_3 : \text{Ce}$, Color centres, Luminescence

1. Introduction

Selected wide band-gap insulating materials have been the subject of research for more than 100 years due to the interest of their usage in the scintillation detectors. Shortly after the X-ray discovery at the end of 19th century, CaWO_4 crystalline powder has been employed for X-ray \rightarrow visible light conversion to enhance the sensitivity of photographic film used for X-ray detection. The first true single crystal scintillator, $\text{NaI} : \text{Tl}$ has been introduced by Hofstadter in 1948 [1]. During last decade an increased interest in this research field can be noticed [2, 3, 4, 5 and ref. therein]. New coming applications namely in the High Energy Physics and medical applications demand high density, radiation hard, fast and high light yield scintillating materials. New scintillation materials for neutron detection are under study as well due to the plan to build-up new neutron facilities as e.g. European Spallation source. Finally, increasing number of applications in the industrial and related fields use typically X-ray sources below 150 keV, so that also medium density scintillator materials, which would be of advantage with respect to classical $\text{NaI} : \text{Tl}$ ($\text{CsI} : \text{Tl}$)-based detectors, are surely demanded.

Scintillation material in connection with some detection element (photomultiplier tube, semiconductor diode) ser-

ves for registration of X-rays or γ -radiation, sometimes energetic particles (electrons, protons, neutrons etc.) or ions. It is, in fact, a converter, that transforms high-energy photons into photons in UV/VIS spectral region, which one can easily and with high sensitivity register by the above-mentioned detectors. Scintillation conversion is relatively complicated process, which is usually divided into three consecutive subprocesses - *conversion, transport and luminescence* - Fig. 1. During the conversion the interaction of a high-energy photon with scintillator mate-

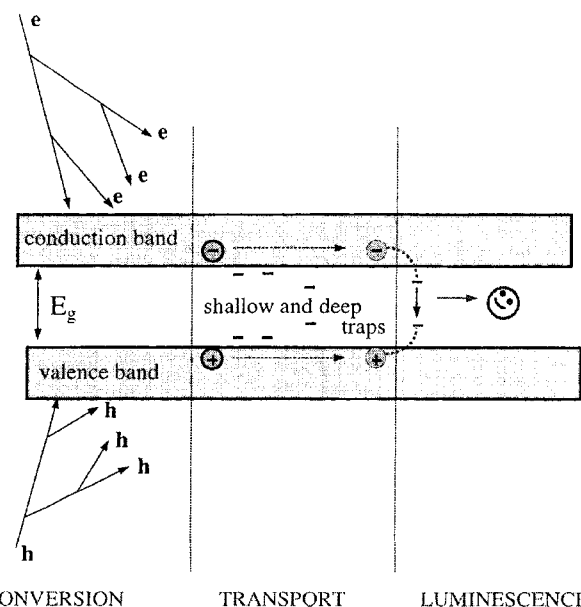


Fig. 1. The sketch of scintillator mechanism, for the details see the text.

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rial lattice occurs (through photoeffect, Compton effect or pair production), electron-hole pairs are created and thermalized. In the transport process electrons and holes (possibly also excitons) migrate through the material, possible (repeated) trapping at defects occurs, energy losses are probable due to nonradiative recombination etc. Final stage - luminescence consists in trapping of charge carriers at the luminescence centre and their radiative recombination. For the detailed description of scintillation mechanism and characteristics, namely ref. 3-5 are advised.

Crucial role of different defect states on scintillator material performance was stressed in a recent review paper dealing with CsI-based, CeF_3 , PbWO_4 and XAlO_3 :Ce ($X = \text{Y, Gd, Lu, Lu-Y}$) scintillators [5]. It will be the aim of this talk to review some experimental results related to the study of the luminescence and scintillator characteristics of the selected complex oxide and fluoride materials stressing also the role of trapping states and their influence on the material performance.

2. Experimental

All the materials described further have been prepared as single crystals using Czochralski or Bridgman techniques and the details of their preparation are outside the scope of this paper, for the details see ref. 5 and ref. therein, for complex fluorides, see e.g. [6, 7]. For scintillator purposes generally relatively high purity of starting materials is required (4 N or better), e.g. in the case of PbWO_4 , the actual impurity concentration in the crystals produced in Furukawa Ltd., Japan was around 1 ppm only.

Correlated study by several experimental techniques is required for good material understanding and characterisation. Apart from classical time-resolved emission spectroscopy, the defect properties and their role in the scintillator mechanism are worse to be studied by e.g. thermoluminescence (TSL) or electron paramagnetic resonance (EPR). Scintillator characteristics and parameters are then determined mainly at room temperature (RT) by radioluminescence, light yield, scintillation decay and induced absorption measurements.

3. Scintillator Materials

3.1. Complex oxides

In this section, PbWO_4 and Ce-doped aluminium perovskites XAlO_3 :Ce ($X = \text{Y, Y-Lu}$) will be reported in

more details. These materials have been developed for the applications in high energy physics and medical fields, respectively.

PbWO_4 was mentioned in the literature as a material interesting for scintillation detectors about ten years ago [8, 9]. Systematic investigation of its scintillation characteristics has begun somewhat later, when this material was approved for the electromagnetic calorimeter in CMS detector at Large Hadron Collider project in CERN. The development of PbWO_4 and understanding of underlying microscopical mechanism of the energy transfer and storage in this material was summarised until the end of 1999 in the review paper [5]. Due to mentioned application, the most severe requirements were put on PbWO_4 as for its radiation resistance, i.e. the stability of its scintillator parameters (mainly its light yield) under relatively high dose irradiation round tens - hundreds of Gy and typical dose rate of the order of 1~5 Gy/hour. Furthermore, high speed of scintillation response was required due to intended integration time gate of about 100~200 ns. A breakthrough improvement was achieved due to La^{3+} doping, which (in the case of optimised host matrix quality) resulted in several times increased radiation resistance and the speed of scintillation response [10, 11, 12]. Also the transmittance characteristics of such PbWO_4 :La have got improved [12], which is important especially in the application mentioned above, as large material blocks will be used (about 23 cm long). In Fig. 2 the effect of La-doping is demonstrated in the induced absorption and transmission spectra for PbWO_4 crystals grown in Furukawa Ltd. Later on, the same effect was proved for another stable trivalent ions as Y, Lu and Gd (for review see [5]) and final industrial production, which is set in Russia, is based on doubly doped PbWO_4 :Y, Nb material [13]. All these crystals

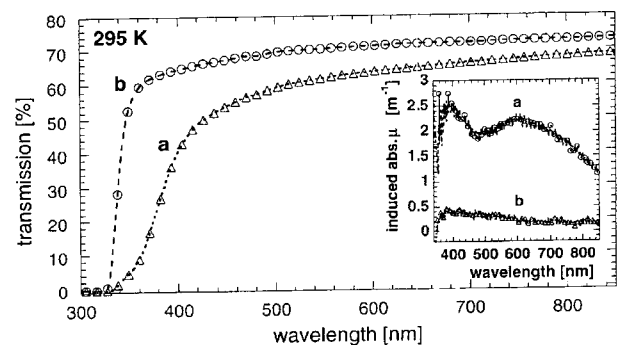


Fig. 2. Initial transmission and irradiation (^{60}Co radioisotope, 10 Gy dose) induced absorption of a couple of equivalently grown undoped (a) and La-doped (b), 80 ppm in the melt, PbWO_4 single crystals. Reprinted from Ref. 5.

are characteristic with the scintillation spectrum peaking in the blue spectral region round 410 nm (radiative de-excitation of self-trapped exciton at $(\text{WO}_4)^{2-}$ complex anion group). Their light yield is, however, (with respect to another scintillators as e.g. BGO or even NaI:Tl) very low. To apply this material in any application outside the High Energy Physics, substantial increase of its light yield would be needed. This means to create in PbWO_4 another emission centre, which (itself) will not be too slow and will be able to compete for electron and hole capture with the intrinsic nonradiative de-excitation pathways. The most prospective way seems to be based on Mo-doping as $(\text{MoO}_4)^{2-}$ group in PbWO_4 matrix is well-known emission centre emitting in the green spectral region round 500 nm and it is known as very efficient electron trap from EPR measurements [14]. However, green emitting PbWO_4 has shown a substantial amount of undesirable very slow decay components [15] and their occurrence is (among others) related to Mo-doping as well [16]. However, recent investigations of doubly doped PbWO_4 : Mo, La [17] or PbWO_4 : Mo, Y [18] did show that light yield can be enhanced 2-3 times, while keeping the slow scintillation decay components at the level typical for an undoped PbWO_4 - Fig. 3. The reason is related to efficient suppression of trapping states, which slow down the energy delivery towards the emission $(\text{MoO}_4)^{2-}$ centres due to re-trapping of migrating carriers. This trap suppression is reflected e.g. in thermoluminescence characteristics - Fig. 4. Thus

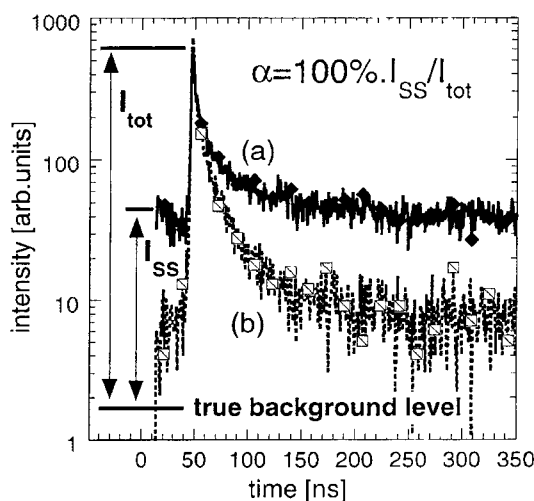


Fig. 3. Spectrally unresolved scintillation decay (^{22}Na excited) of $\text{PWO}:\text{Mo}$ (a) and $\text{PWO}:\text{Mo}, \text{Y}$ (b) at RT. Calculation of coefficient α (for the details see ref. 15) related to the presence of very slow decay component is sketched for $\text{PWO}:\text{Mo}$ decay curve. The values of $\alpha = 6.6\%$ and 0.65% are obtained for the Mo-doped and (Mo, Y)-doped samples, respectively. Reprinted from Ref. 18.

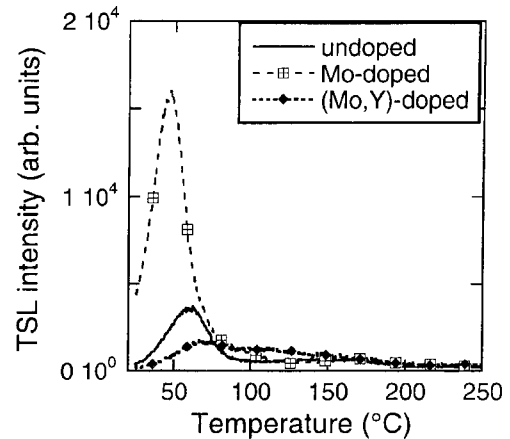


Fig. 4. Thermoluminescence glow curves of undoped, Mo- and (Mo, Y)-doped PWO samples after x-ray irradiation at RT (dose of 10^4 Gy). Heating rate = 0.1 K/s. Reprinted from Ref. 18.

doubly doped $\text{PbWO}_4:\text{Mo}, \text{A}^{3+}$ ($\text{A} = \text{La}, \text{Y}$ or possibly also Lu, Gd) might indicate an approach to increase the scintillation efficiency of PbWO_4 based scintillator keeping the slow decay components at a reasonably low level.

Only in last 2~3 years systematic studies of the processes of charge carrier localisation in PbWO_4 lattice have appeared. At first, electron self-trapping at WO_4 complex anion group was proved in EPR experiments below 50 K [19, 20]. Correlated TSL study completed the scheme of electron transfer and localisation in this temperature range [21]. Stabilisation of $(\text{WO}_4)^{3-}$ centre by nearby lying trivalent ion up to about 100 K was reported in continuing correlated experiments performed by TSL and EPR at the same samples [22]. Finally, similar study at undoped samples evidenced the existence of Pb^+ centre, which is stable up to 180 K [23]. Final goal of these studies is to arrive up to room temperature and to give a detailed interpretation for the induced absorption phenomena observed in previous papers [5, 11, 24].

Ce -doped YAIO_3 (YAP) was studied for its luminescence properties already in seventies [25] and became one of versatile scintillator materials, which could be used for different applications due to its fast response, mechanical and chemical stability and high light yield. Characteristic Ce^{3+} emission is peaking round 360 nm and photoluminescence decay is very fast (decay time 17 ns) due to partially allowed character of $5d-4f$ transition of Ce^{3+} emission centre. Even if this material is known for relatively long time, detailed understanding of energy transfer and storage processes (i.e. the nature of participating defects) is not completely known. For instance, a parasitic defect-related red emission in this material was vaguely noticed [26], but without a deeper

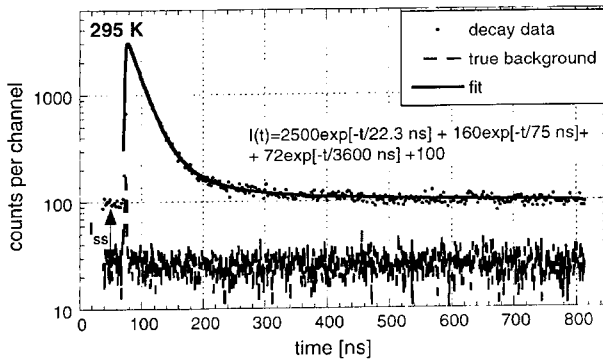


Fig. 5. Spectrally unresolved scintillation decay of $\text{YAlO}_3 : \text{Ce}^{3+}$ single crystal excited by ^{22}Na radioisotope. Slower decay components and background enhancement are related to the delayed radiative recombination of charge carriers at Ce^{3+} emission centres. The value of coefficient alpha (defined in Fig. 3) is calculated about 2.3 %. Reprinted from Ref. 5.

explanation. In the scintillation decay of $\text{YAP} : \text{Ce}$ - Fig. 5 the slower components (with respect to the mentioned 17 ns luminescence decay time) are undoubtedly present and the coefficient alpha related to the occurrence of the delayed recombination processes at Ce^{3+} ions in the time scale tens - hundreds of μs (for the definition see ref. 15) shows the value several times higher with respect to an undoped PbWO_4 . This material shows an intense TSL both below [27, 28] and above [29] RT. The former studies show clear correlation between temperature dependence of light yield, TSL glow peaks position and scintillation decay times, while the latter study above RT proposes tunneling mechanism and oxygen vacancies as electron traps to explain the observed structured TSL glow curves. Similarly to the case of PbWO_4 the correlated EPR and TSL study would be very demanding at this material to explain the nature of existing defects and their role in shaping $\text{YAP} : \text{Ce}$ scintillation characteristics.

To increase YAP matrix density of 5.36 g/cm^3 (necessary, if AP-based material is thought to be used e.g. in positron emission tomography machines, which are based on coincident detection of 511 keV photons), several laboratories have shown big effort to grow single crystals of $\text{LuAlO}_3 : \text{Ce}$ (density of 8.35 g/cm^3), but with rather problematic success due to very easy switch of the perovskite to garnet phase in the process of crystal growth (for review, see ref. [5]). One possible way in solving this problem might be the growth of mixed cation (Y-Lu) $\text{AlO}_3 : \text{Ce}$ crystals [30, 31], which would also lower the price of raw materials (Lu_2O_3 is rather expensive).

3.2. Complex fluorides

A number of studies on Ce-doped (based) fluoride

crystals appeared in the literature in the nineties with the aim to use them in the field of scintillation detection. As a most systematic example CeF_3 can be mentioned [5, 32], which was studied due to its potential usage in the above mentioned CMS detector, but in 1994 it was refused due to mainly economical and production constraints and replaced by the above mentioned PbWO_4 . Among the latest materials, the Li-containing ones are frequently studied due to their potential usage in neutron detection (Li has a big cross section in neutron capture) [33, 34]. As an example of rather interesting compound, both from application and basic physical point of view, $\text{LiBaF}_3 : \text{Ce}$ can be presented. This material is under development and characterisation in several laboratories [35-41] and its potential for neutron detection has been very seriously explored as it has shown the possibility to exclude the gamma ray-induced background in the scintillation counting using a double-discriminator-level detection system [40]. An enhanced performance was achieved in Rb-codoped material [33]. Despite this general interest, there are basic not yet explained features in $\text{LiBaF}_3 : \text{Ce}$ as e.g. anomalously big Stokes shift of Ce^{3+} emission [42] - Fig. 6. Several non-equivalent Ce^{3+} centres were evidenced in recent optical and EPR studies [43, 44], which support the idea of variety of compensation processes possible in this material, when an aliovalent ions is doped. However, this aspect needs still somewhat deeper investigation. The induced absorption features also show a rich picture with a number of peaks - Fig. 7. Actually, induced absorption of this material has been studied in several papers also with related TSL measurements [35, 36, 45] and its possible origin is discussed. Related to Fig. 7 it is worth noting that Ce-doping changes completely the observed spectrum and generally the integral intensity of the induced absorption gets lower with respect to an undoped

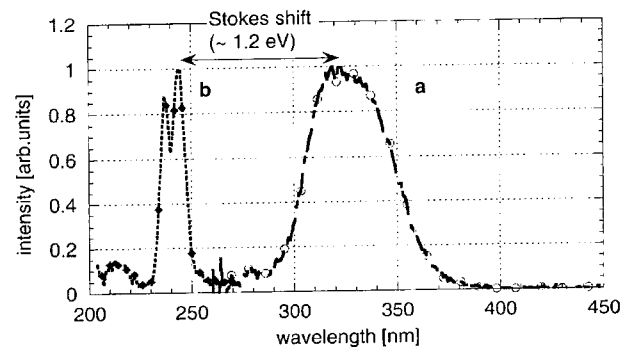


Fig. 6. Emission (a) and excitation (b) spectra related to Ce^{3+} centre in $\text{LiBaF}_3 : \text{Ce}$ at 170 K. (a) exc. = 245 nm; (b) em. = 325 nm.

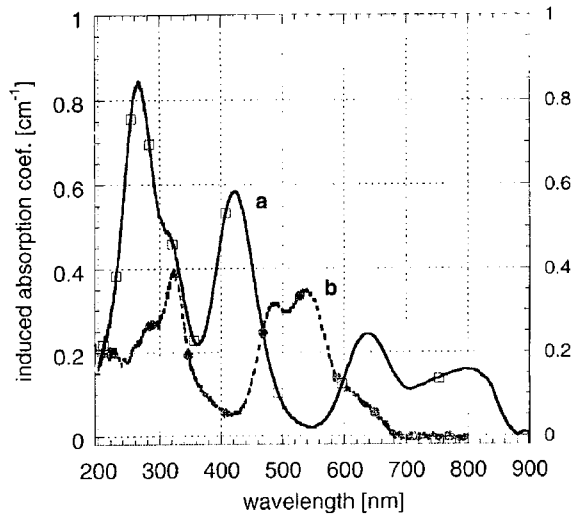


Fig. 7. Induced absorption (X-ray irradiation, Mo-tube, 25 kV, 16 mA, 10 minutes) of undoped (a) and Ce-doped (b) LiBaF_3 single crystals at RT.

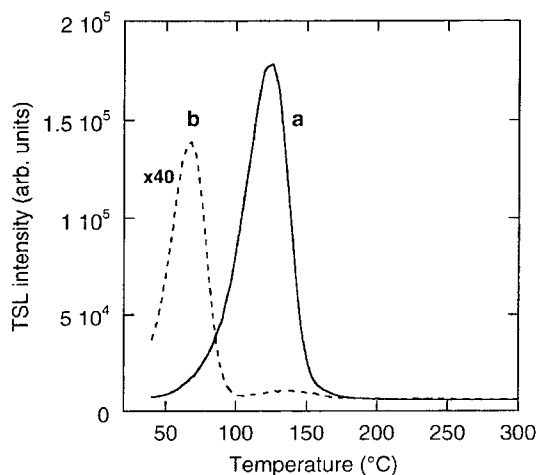


Fig. 8. TSL glow curves after X-ray irradiation at RT of undoped (a) and Ce-doped (b) LiBaF_3 single crystals.

LiBaF_3 . TSL measurements above RT at the same crystals have provided a coherent result: TSL glow curve intensity is more than 40 times lower in $\text{LiBaF}_3:\text{Ce}$, which evidences lowered concentration of traps due to Ce-doping - Fig. 8. Lower induced absorption (i.e. higher radiation resistance) is obviously of advantage, if one plan to use a material in any scintillator application. These results point to the importance of Ce^{3+} ions in the processes of defects/traps creation and compensation in LiBaF_3 lattice.

4. Conclusion

Important role of defect states and their influence on

the material scintillation performance and characteristics was discussed for the case of PbWO_4 , YAlO_3 and LiBaF_3 based scintillators. Especially in the latter two cases, quite some effort is still needed to understand the mechanism of defect creation and their nature. However, such understanding is necessary, if these materials are to be optimised towards their intrinsic limits and explored efficiently in scintillator applications.

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