Ceramic Processing Research

Oxide and fluoride based materials for scintillator applications

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Recent significant results in the study of scintillation properties of selected materials are given for PbWO₄, XAlO₃ (X=Y, Lu, Y-Lu) and LiBaF₃ -based single crystals and scintillation ceramics. The effect of various defect states is demonstrated in shaping scintillator parameters and achieved improvements 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: Scintillation materials, Defects, Absorption, Luminescence.

Introduction

Selected wide band-gap insulating materials have been a subject of research for more than 100 years due to the interest in their usage in the scintillation detectors. Shortly after the X-ray discovery at the end of 19th century, CaWO₄ 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, NaI: TI has been introduced by Hofstadter in 1948 [1]. During last decade an increased interest in this research field can be noticed [2-5] and ref. therein. New coming applications namely in the High Energy Physics and medicine 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 increasing interest in neutron irradiation-based applications in science, medicine and industry. Scintillation ceramics - an intermediate solution between single crystal and glass materials offer very interesting perspectives especially in the field of medical tomography methods.

Scintillation material interfaced with some detection element (photomultiplier tube, semiconductor diode) serves for registration of X-rays or γ -radiation, sometimes high-energy particles (electrons, protons, neutrons etc.) or ions. It is 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

*Corresponding author: Tel : +420-2-20318445 Fax: +420-2-3123184 E-mail: nikl@fzu.cz usually divided into three consecutive subprocesses – *conversion, transport and luminescence* – Fig. 1. During the conversion an interaction of a high-energy photon with the lattice of scintillator material occurs (through photoelectric effect, 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. The final stage, luminescence, consists in trapping the charge carriers at the luminescence centre and in their subsequent radiative recombination. For the detailed description of scintillation mechanisms and characteri-





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

stics, namely ref. 3-5 are recommended.

A crucial role of various defect states in scintillator material performance was stressed in a recent review paper dealing with CsI-based, CeF₃, PbWO₄ and XAIO₃ : Ce (X=Y, Gd, Lu, Lu-Y) scintillators [5]. The aim of this paper is to review some experimental results related to the study of luminescence and scintillator characteristics of selected scintillator materials. We focus on the role of trapping states and their effect on the material performance.

Scintillator Materials

Single crystal-based materials

In this section, $PbWO_4$, Ce-doped aluminium perovskites $XAIO_3$: Ce (X=Y, Y-Lu) and $BaLiF_3$: Ce will be reported in more details.

PbWO₄ 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 PbWO4 and understanding of underlying microscopic mechanism of the energy transfer and storage in this material was summarised until the end of 1999 in the review paper [5]. Due to the mentioned application, the most severe requirements were put on PbWO₄ with respect to its radiation resistance, *i.e.* the stability of its scintillator parameters (namely its light yield) under a relatively high dose irradiation around tens to hundreds of Gy and typical dose rate of the order of 1~5 Gy/hour. Furthermore, fast scintillation response was required due to intended integration time gate of about 100~200 ns. An essential improvement was achieved due to La³⁺ doping, which (in the case of optimised host matrix quality) resulted in the several times increased radiation resistance and speed of scintillation response [10-12]. The transmittance characteristics of such PbWO₄:La have been improved as well [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 PbWO₄ 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 PbWO₄ : Y, Nb material [13].

Recent research efforts aim to achieve a higher efficiency of $PbWO_4$ -based scintillator, which could enable its use also outside the High Energy Physics. The Mo-doping ($(MoO_4)^{2^-}$ group present in $PbWO_4$ matrix) results in an additional well-known emission centre emitting in the green spectral region around 500 nm, which is also a very efficient electron trap (deter-



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, PbWO₄ single crystals. Reprinted from Ref. 5.



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

mined by Electron Paramagnetic Resonance (EPR) measurements [14]). Unfortunately the green emitting PbWO₄ has shown a substantial amount of undesirable very slow decay components [15] and their presence is (among others) related to Mo-doping as well [16]. However, recent investigations of doubly doped PbWO₄: 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 PbWO₄ (see Fig. 3). Due to Y(La) codoping an efficient suppression of trapping states occurs, and the energy delivery towards the emission $(MoO_4)^{2-}$ centres becomes considerably less delayed due to re-trapping the migrating carriers. This trap suppression reflected is e.g. in thermoluminescence (TSL) characteristics above room temperature (RT) - Fig. 4. Thus doubly doped



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.

 $PbWO_4$: Mo, A^{3+} (A=La, 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.

Ce-doped YAlO₃ (YAP) was studied for its luminescence properties already in seventies [19] and became one of versatile scintillator materials, which could be used for various applications due to its fast response, mechanical and chemical stability and high light yield. Characteristic Ce³⁺ emission is peaking around 360 nm and a photoluminescence decay is very fast (decay time 17 ns) due to partially allowed 5d-4f transition of the Ce³⁺ emission centre. Even if this material is known for relatively long time, the energy transfer and storage processes (*i.e.* the nature of participating defects) is not yet completely understood. For instance, a parasitic defect-related red emission in this material was vaguely noticed [20], but has not been explained in detail yet. In the scintillation decay of YAP : Ce, see Fig. 5, the slower components (with respect to the mentioned 17



Fig. 5. Spectrally unresolved scintillation decay of YAIO₃ : Ce^{3+} single crystal excited by ²²Na radioisotope. Slower decay components and background enhancement are related to the delayed radiative recombination of charge carriers at Ce^{3+} emission centres. Calculated value of coefficient alpha (defined in Fig. 3) is calculated of about 2.3%. Reprinted from Ref. 5.

ns luminescence decay time) are undoubtedly present. The coefficient alpha related to the presence of the delayed recombination processes at Ce^{3+} ions in the time scale tens – hundreds of μ s (for the definition see ref. 15) shows the value several times higher with respect to an undoped PbWO₄. An intense TSL both below [21, 22] and above [23] RT was reported. The former studies show clear correlation among the temperature dependence of light yield, position of the TSL glow peaks 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.

If AP-based material is intended to be used *e.g.* in positron emission tomography detectors (based on coincident detection of 511 keV photons), it is necessary to increase the density of YAP matrix (5.36 g/cm³). Several laboratories have shown a big effort to grow single crystals of LuAlO₃ : Ce (density of 8.35 g/cm³), but with rather problematic success due to very easy switch of the perovskite to garnet phase during the crystal growth process (for a review, see Ref. [5]). One possible way to solve this problem might be the growth of the mixed cation (Y-Lu)AlO₃ : Ce crystals [24, 25], which would also reduce the cost of raw materials as Lu₂O₃ is rather expensive.

The Li-containing scintillation materials are frequently studied due to their potential usage in neutron detection (⁶Li has a big cross section in neutron capture) [26, 27]. As an example of rather interesting compound, both from application and basic physical point of view, LiBaF₃: Ce can be presented. This material is under development and characterisation in several laboratories [28-34]. Its potential for neutron detection has been very seriously explored as it shows the possibility to exclude the gamma ray-induced background in the scintillation counting using a double-discriminatorlevel detection system [33]. An enhanced performance was achieved in Rb-codoped material [26]. Despite this general interest, there are fundamental and not yet explained features of LiBaF₃: Ce as e.g. anomalously big Stokes shift of the Ce^{3+} emission [35] – Fig. 6.



Fig. 6. Emission (a) and excitation (b) spectra related to Ce^{3+} centre in LiBaF₃ : 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.

Several non-equivalent Ce³⁺ centres were evidenced in recent optical and EPR studies [36, 37], which support the idea of variety of compensation processes possible in this material, when doped with aliovalent ions. It is worth noting that Ce-doping changes completely the observed features in the X-ray induced absorption spectrum and the integral intensity of the induced absorption is reduced with respect to an undoped LiBaF₃ (see Fig. 7). TSL measurements above RT for the same crystals have provided a coherent result: TSL glow curve intensity is more than 40 times lower in LiBaF₃: Ce, which evidences reduced concentration of traps due to Ce-doping - (see Fig. 8). These results indicate the importance of Ce³⁺ ions in the processes of defects/traps creation and compensation in LiBaF₃ lattice.



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

Scintillation ceramics

The preparation of bulky single crystals of a high quality for scintillator applications is often limited by the incongruent melting of a given compound, complicated phase transitions above RT or other technological challenges, that make single crystal manufacturing either impossible or too expensive. Scintillation powders (i.e. essentially microcrystalline material prepared in a suitable chemical reaction & treatment procedure) are used in big volumes e.g. in phosphor screens, etc. but the thickness and the stopping power of such phosphor laver is very limited due to troubled light collection from a thicker powder-based film. For certain applications especially in industry and medicine so called scintillation ceramics have appeared very promising [38], because they might provide a cost effective solution yielding a material in-between a powder and single crystal. Manufacturing such translucent materials allows at least several mm thickness and still efficient light collection. Furthermore, the usage of compounds which cannot be prepared at all in the form of bulky single crystals becomes possible. Very recent review papers show a high potential of these materials in the field of diagnostic methods in modern medicine [39, 40]. Among the most promising materials there is undoubtedly Gd_2O_2S : Pr – based ceramics, which presently offers a light output at least of about 1.8 times higher with respect to CdWO4 single crystal scintillator currently used in X-ray computed tomography. Problems of afterglow (i.e. delayed radiative recombination at Pr³⁺ emission centres due to retrapping of migrating carriers at shallow trapping states) have been successfully solved by the Ce [41] or F [42] ion codoping. Cecodoping has resulted also in reduced radiation damage of this ceramics [43]. Ce ion thus apparently serves as an efficient nonradiative recombination centre at which (delayed) migrating carriers recombine nonradiatively and at the same time compensates (or competes with) certain trapping states participating in radiation damage mechanism.

Among the other materials studied in the form of ceramics for potential scintillator application one can mention classical Y₃Al₅O₁₂ garnet doped with Ce ions [44], in which the role of defect states in the energy transfer and storage processes was studied by means of scintillation decay measurements as well [45]. Furthermore, luminescence of mixed $(Y-Gd)_2O_3$: Eu ceramics was studied and namely the influence of the aliovalent dopants as Mg²⁺ and Ti⁴⁺ on the light yield and afterglow characteristics was reported [46]. Finally, also gadolinium gallium garnet doped with Cr3+, Pr3+ and Bi³⁺ was studied by correlated techniques including TSL for the occurrence of shallow and deep traps participating in the energy and transfer processes under X-ray excitation [47]. Oxygen deficiency was concluded as one possible cause of shallow trap creation in Crdoped material.

In ceramic materials, the trapping states can evolve both from bulk-like point defects (*i.e.* analogously to the single crystal systems), but also from enhanced interface/grain states inevitably present in these materials. Therefore, the study of defect-related phenomena in these materials is of crucial importance for their optimised performance in the applications.

Conclusion

Important role of defect states and their influence on the material scintillation performance and characteristics was discussed for the case of $PbWO_4$, $YAIO_3$ and $LiBaF_3$ – based scintillators and several scintillation ceramics material systems. Systematic study and understanding of defect states taking part in the processes of energy transfer and storage is necessary, if these materials are to be optimised towards their intrinsic limits and explored efficiently in scintillator applications.

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