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Modern scintillation materials. Physics, applications and perspectives

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General characteristics, principles and examples of material systems and their applications are discussed in the field of scintillation materials. Some of developments within the last decade are mentioned and current or expected trends are highlighted in research on these materials. Due to the large variety of applications, these materials have to be always tailored and have to respect specific application demands.

Key words: scintillators, luminescence, single crystals, glass, ceramic.

Introduction

Wide band-gap single crystals, glasses or ceramic scintillation materials are under development for various applications, where energetic photons (X- or gamma rays), charged particles or neutrons are to be detected. These materials have to be tailored for specific applications: while for high energy physics detectors especially high density, fast and radiation hard materials are required [1], as high as possible light yield is needed in medical applications [2]. Superfast materials with a scintillation response below 1 ns [3] would push forward the "time-of-flight"-oriented applications, in which nearly-coincidence events are to be resolved and detected. Specific requirements for material composition have to be considered in the case of neutron detection, where a high percentage of Li, B or Gd ions must be present in the material due to their enhanced cross-section for neutron capture [4]. Induced nuclear reaction with these ions in neutron capture provides an energetic output deposited in the scintillator matrix and is converted in the desired scintillation light afterwards. The variety of applications is increasing due to awareness of the public e.g. for the need of more reliable security measures due to terrorist activities, for more efficient medical tomographies to improve medical diagnostics and preventive care about the population. etc.

As said above a 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 (HE) photons into photons in the UV/VIS spectral region, which one can easily and with high sensitivity register by the above-mentioned detectors. Scintillation conversion is a relatively complicated process, which is 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 the scintillator material occurs (through the photoelectric effect, the Compton effect or by 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 radi-

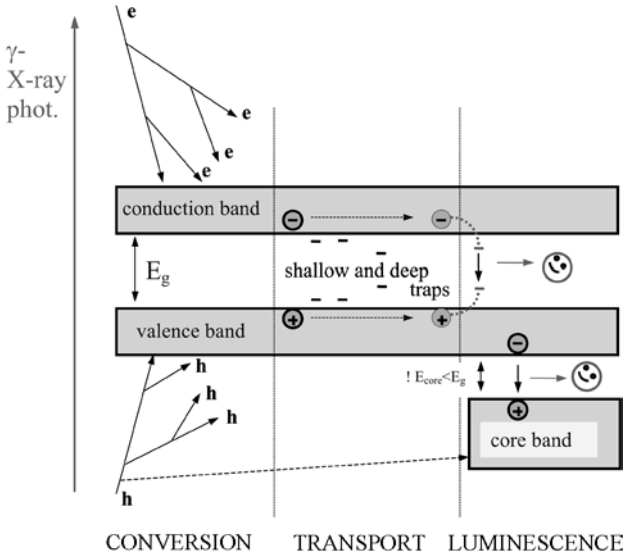

Fig. 1. Sketch of scintillator conversion in a wide band-gap single crystal materials. Crossluminescence between the valence and core band can occur only if the energetic separation of these two bands is less than E_g the band-gap.

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ative recombination. In a particular group of material the light generation occurs in radiative transition between the valence and first core bands, these are so called cross-luminescence scintillators. For a detailed description of luminescence and scintillation mechanisms and characteristics, including a description of various material systems, see [4-7].

It is the aim of this paper to review some of the important material systems, which have been under systematic attention within the last decade in research on scintillators as well as to indicate some of current trends in this research field. Furthermore, it is additional aim to draw attention to materials potentially interesting for optically transparent ceramics and applications in this field.

Bulk single crystal scintillators

To detect gamma rays especially of higher energy, quite some volume of the material is needed to obtain the complete transformation of incoming HE photon into electron-hole pairs. High density materials are mostly investigated, because the attenuation length becomes considerably shorter with increasing material density. Single crystals are the best choice due to their highly ordered lattices and minimum concentrations of harmful defects/traps, which can negatively affect mainly the above mentioned transport stage in the scintillator conversion. Two material systems can be mentioned, which were developed up to industrial production within the last decade.

At the beginning of the nineties of last century the planned new collider projects in High Energy Physics (namely Large Hadron Collider in CERN) triggered the development of new scintillator materials for calorimetric detectors. In the first stage, CeF_3 single crystals were focussed upon and broad scale international Crystal Clear Collaboration initiated this development [8]. Later on, another material of higher density – $PbWO_4$ (PWO) single crystal, was selected [1], mainly due to economic constraints. The luminescence and scintillation mechanisms appeared quite complicated in this material and the aspects of overall efficiency (light yield), scintillation decay and radiation hardness were given attention and subjected to systematic study. A breakthrough in its development was achieved by the overall positive impact of doping this material with selected trivalent ions such as La, Y, Lu and Gd [9-13]. The characteristic features of trivalent ion-doped PWO scintillator are a low light yield of the order of 100 photons/MeV, a fast scintillation decay with a dominant decay component of about 2-3 ns, no afterglow and very high radiation hardness characterised by an induced absorption coefficient lower than 1 m^{-1} [10-12]. An optimised $PbWO_4$ scintillator for High Energy Physics Applications is based on doubly doped PWO:Y, Nb and the largest production center has been set up in Bogoroditsk Technochemical Plant, Russia [14]. Later on some effort was given to increase the light yield of a PWO-based scintillator by double or multiple doping, the philosophy of which is based on including another emission center able to compete with the intrinsic nonradiative de-excitation pathway in PWO, which is based on indirect band-to-band nonradiative recombination [15]. Doping by Mo ions appears to be the technologically most feasible choice and double doped PWO:Mo,Y or PWO:Mo,La have been shown to have the highest figure-of-merit [16-19]. Research and development of PWO scintillators has been surveyed in two comprehensive review papers [7, 20].

The application of scintillators in modern medical diagnostics – tomography methods has gained considerably more attention in recent years. Essentially there are two directions under development: (i) relatively simple techniques such as X-ray Computed Tomography (CT), which allows one to obtain a fine-tuned X-ray check of different parts of the human body and reconstruct them even in 3D [2] X-CT machines are currently available even in smaller hospitals or medical units; (ii) sophisticated techniques like Positron Emission Tomography (PET), which allows the research of the human brain, the circulation and distribution of drugs in the human body in real time etc. However, qualified usage of these very expensive and complex PET machines is restricted to large medical centers at present. While in the case of X-CT classical scintillator materials like CsI:Tl or NaI:Tl can be used, the latter PET tomography technique requires a new generation of scintillation materials of high light yield, fast scintillation response and high density. From this point-of-view the present usage of $Bi_4Ge_3O_{12}$ (BGO) has the drawback namely in a slower scintillation response (300 ns decay time). Lu_2SiO_5:Ce (LSO:Ce) and recently also Gd_2SiO_5:Ce (GSO:Ce) have been studied and industrially mastered for usage in PET applications. These silicates are typical modern scintillation materials, in which the production of light is accomplished due to fast and efficient 5d-4f radiative transition of Ce^{3+} emission centres [21] and which provide also high efficiency and fast carrier transport in the conversion and transport stages sketched in Fig. 1. Also their high chemical and mechanical stability are advantages. As a disadvantage a relatively high production price can be considered due to the high melting point and tendency to cracking, which lowers the production yield. The first research reports dealing with scintillation properties of these materials are dated back to the end of the eighties and beginning of the nineties [22, 23]. A systematic comparison of the properties of samples coming from different technologies was published recently for LSO [24] and the scintillation mechanism in both compounds is well described and understood [25, 26]. The largest industrial centers dealing with the production of GSO:Ce and LSO:Ce are Hitachi Chemical Co., Ltd., Japan and CPI Crystal Photonics,

Inc., USA, respectively.

Data and quantitative parameters characterising the above mentioned and many other scintillator materials can be found in [4, 6, 27].

Thin layer material systems

Development of thin layers or nanocrystal materials seems to be in contradiction with the above statement of the need of bulk materials for HE photon detection. However, there are quite numerous applications where just X-rays with an energy below 120 KeV or accelerated electrons are to be detected: in these cases thin or thick layers can be employed especially in the case where high position sensitivity is required.

Using Physical Vacuum Evaporation technology so called "columnar growth" of CsI:Tl [28] has received increased interest due to a possibility to construct 2-dimensional large area detectors with superior sensitivity and spatial resolution. Thick films of closely packed CsI:Tl columns have been obtained (up to 2 mm thickness) with average square columns about 40×40 mm^2 [29]. Such films being directly coupled to a thin film position sensitive sensor based e.g. on amorphous Si [30] may provide an exceptionally efficient, position sensitive detector for X-ray imaging [31]. Furthermore, liquid phase epitaxy has been employed to prepare single crystal thin layers of well-know scintillators such as YAG:Ce or YAP:Ce [32]. YAG:Ce thin plates prepared by the classical cut and polish technology down to about ten micrometers thickness are currently available for accelerated electron detection with high position resolution [33].

Glass and ceramic materials

Single crystals described above offer the highest material perfection and low defect concentration. However, often the production costs are high and there is a limited possibility for their preparation and doping due to a high melting point, incongruent melting, phase transitions, very different partial pressures of the components in the case of complex compounds, low segregation coeficients for the dopants, etc. In such cases, glass or ceramic technology may offer an alternative solution.

Glass scintillators have been used in lower demand applications already for quite some time and are based on rare earth ion doped silicate-based glasses [34], in the case of neutron detection they can be prepared Li-rich [4, 35]. Within the last decade a systematic study of scintillator characteristics was performed e.g. on fluoride glasses [36] and phosphate glasses [37, 38]. In the latter case a new concept of an energy-guiding sublattice was introduced. In addition to classical technologies using glass preparation from high temperature melts, a novel approach based on sol-gel technology has been applied [39].

Ceramic phospors and scintillators have been mastered already on an industrial scale for selected material systems. In particular, Gd_2O_2S:Pr(Ce,F) offers a competitive solution in medical tomographies [40, 41] as it presently offers a light output at least about 1.8 times higher then $CdWO_4$ single crystal scintillators currently used in X-ray computed tomography. Problems of afterglow (i.e. delayed radiative recombination at Pr^{3+} emission centres due to retrapping of migrating carriers at shallow trapping states) have been successfully solved by the Ce [42] or F [43] ion codoping. Ce-codoping has resulted also in reduced radiation damage of this ceramic [44].

New trends in scintillator material research

In the field of bulk single crystals current research aims at high density, fast and high light yield materials for PET. The well-known fast and efficient $YAlO_3$:Ce (YAP:Ce) scintillator is of too low density for PET and several laboratories [45-47] have initiated an effort to increase its stopping power by replacing Y with a heavier ion, namely Lu^{3+}. A Ce-doped LuAP single crystal (density of 8.35 g/cm^3) was prepared by both the Czochralski and Bridgman [48, 49] methods. Difficulties in pure LuAP crystal growth appeared (instability of perovskite phase and frequent appearance of the garnet one) and successful attempts were reported in the preparation of the somewhat more stable mixed $Y_{1-x}Lu_xAP$:Ce crystals with the parameter x up to 0.3 and up to 0.8 by the Czochralski [50] and Bridgman [51, 52] methods, respectively. However, no industrial company can yet offer such Ce-doped Lu-rich perovskite at a competitive price and characteristics e.g. to the mentioned LSO:Ce.

New medium density materials with very high light yield exceeding the traditional CsI:Tl or NaI:Tl scintillators have been reported, namely $LaBr_3$:Ce [53] and $RbGd_2Br_7$:Ce [54]. The former one offers also a unique energy resolution of 2.9% at 662 keV, which is comparable to solid state semiconductor detectors. A disadvantage of these materials is very high hygroscopicity, which completely prevents their usage in an open air atmosphere.

Superfast scintillators with sub-nanosecond response are required for special applications, where Time-of-Flight nearly-coincidence measurements are necessary as in TOF-PET [55]. In the nineties, systematic studies were performed with superfast cross-luminescence scintillators, where radiative transition occurs between the valence and the first core band, see Fig. 1 (for review, see [6]). Recently, traditional wide band-gap materials like ZnO:Ga, PbI_2 and others were reported for their sub-nanosecond scintillation response and high efficiency at low temperatures [3]. Such materials may offer an interesting solution for the above mentioned applications under the assumption that cooled detectors

will be developed and a small Stokes shift of excitonic emission will not prevent the extraction of generated scintillation light from volume detector segments. Superfast emission from partially quenched charge transfer luminescence of Yb^{3+} in complex oxides [56] could have the potential not only for neutrino detection, but also for TOF-minded applications under the assumption that lower light yield (of the order of 10% of BGO) would be sufficient for light detectors.

Molecular beam technology has been employed to obtain thin single crystal layers of LuF_3:Ce [57], which cannot be prepared in the single crystal form easily due to phase transitions above room temperature. Such a material could be promising for X-ray detection with high spatial resolution.

New optical ceramic materials based on Lu_2O_3:Eu nanocrystallites in a SiO_2 sol-gel host and nanocrystalline cerium silicates were reported recently [58, 59], which offer intense luminescence at room temperature and in the visible spectral region. Also nanocrystalline ZnO luminescence characteristics were reported [60], which may become a perspective material due to the superfast emission mentioned above. In storage phosphors an interesting material was announced recently based on fluorobromozirconate glass-ceramic, the properties of which are significantly modified by annealing,which results in the creation of a nanocrystalline $BaBr_2$ phase in the glass matrix [61]. Such an approach may indicate the way to obtain new scintillator materials based on a partially recrystallized glass matrix with a nanocrystal luminescent phase, which could offer unusual characteristics with respect to traditional luminescent ion-doped material systems.

Conclusions

Driven by an increasing number and diversity of applications, the development of scintillator materials belongs to a rapidly proceeding area of research and the same trend is expected also in the near future. Due to the complexity of related materials research, well-organized collaboration between technology, physical characterisation and industrial/end user groups is leading the way to obtain new competitive materials.

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