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Katedra dozimetrie a aplikace ionizujícího záření

Multicomponent Oxide Scintillators: Physical Mechanisms, Defects, Material Optimization and persistent Bottlenecks

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v oboru Aplikovaná fyzika

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Souhrn

Scintilační materiály se používají k detekci a monitorování ionizujícího záření (typicky rtg. či gama paprsky) nebo svazků urychlených nabitých částic v mnoha různých aplikacích. Autor této přednášky pracuje na jejich výzkumu a vývoji již více než třicet let v cílených národních i mezinárodních konsorciích, která zahrnují i průmyslové partnery, a shrnuje zde nejvýznamnější dosažené výsledky za posledních 10-15 let ve skupině multikomponentních kyslíkatých materiálů. Pro scintilátory na bázi tzv. granátů je stručně popsán objev materiálu GGAG:Ce, který znamenal průlom v kyslíkatých objemových monokrystalech a začal být okamžitě používán v praktických aplikacích. Kombinatorický výzkum a inženýrství elektronové struktury a defektních stavů materiálu jsou klíčové techniky a vybrané aspekty jejich použití při jeho vývoji jsou zde stručně popsány. Scintilátory na bázi hliníkových perovskitů, jejichž základem je klasický YAP:Ce, jsou opačným příkladem: navzdory více než dvě dekády trvajícímu úsilí mezinárodní komunity nebyl zatím vyvinut jeho analog s výrazně vyšší hustotou. Popisujeme několik slepých cest a přetrvávajících překážek při jeho vývoji. Zahrnujeme také popis několika aspektů vývoje a optimalizace scintilátorů na bázi křemičitanů, kde jsme přispěli k pochopení fyzikálního mechanismu scintilace, podstaty defektů a nábojových pastí a k materiálové optimalizaci. Ve všech uvedených případech ukazujeme komplexnost vývoje a výzkumu scintilačních materiálů a potřebu použití širokého spektra metod technologie přípravy, charakterizačních experimentů, ale také expertízy a *know-how* členů výzkumného týmu napříč několika obory. To vše vysvětluje, proč se při výzkumu a vývoji scintilačních materiálů vytvářejí rozvětvené spolupráce mezi mnoha týmy, které probíhají i přes několik kontinentů. Závěrem nastiňujeme perspektivy, potřeby a koncepce dalšího výzkumu a vývoje v této oblasti, a to jak z hlediska vědy samotné, tak souvisejících pedagogických aktivit, které budeme rozvíjet v České republice i ve spolupráci se zahraničními institucemi.

Summary

Scintillation materials are used in applications where ionising radiation or accelerated particles are to be detected or monitored. The author of this lecture has been working in their R&D for about three decades in focused national and international consortia incl. industrial partners. Herein he provides an overview of the most important achievements in last 10-15 years in the group of multicomponent oxide materials. In the case of garnet scintillators, the discovery of the so-called GGAG:Ce single crystal scintillator is briefly described which can be classified as a breakthrough in oxide scintillators with immediate practical applications. Combinatorial research, band-gap engineering and defect engineering strategies were used in its development and optimization and their particular aspects are noted. Perovskite scintillator group based on the classical YAP:Ce scintillator is an opposite case: despite more than two-decade lasting effort of the community, its efficient high density analog has not been realized yet. A few blind ways and persistent bottlenecks met in its R&D are described. Particular aspects of silicate scintillators development, with which we have contributed to their understanding, physical description and optimization, are briefly surveyed as well. In all the cases, the complexity of scintillator R&D, the need to use a broad portfolio of manufacturing, experimental and also modeling/theoretical methods and approaches and necessity of involvement of extended expertize and know-how in the research team is illustrated. It justifies and explains the fact of broad scale collaboration among many teams in this field over the globe. Finally, brief scientific and pedagogical perspectives and concepts for future work are provided.

Klíčová slova

Scintilátor, luminiscence, bodový defekt, nábojová past, přenos energie, spektroskopie

Keywords

Scintillator, luminescence, point defect, charge trap, energy transfer, spectroscopy

Content

1. Introduction [1]

Scintillating material works as a spectral and energy transformer: it converts the energy from an X- or gamma-ray photon or accelerated charged particle into a bunch of ultraviolet-visible (UV/VIS) photons, i.e. to the flash of light. Alternatively, the accelerated charged particles (electrons, protons or more heavy ions) or even neutrons can be detected via their energy deposit in the interaction with the scintillator host which is again converted into the flash of light. In practice, the scintillation detector consists of two parts, namely (i) scintillating material itself and (ii) photodetector which converts the mentioned UV/VIS photons into an electrical signal I(t), see **Figure 1**.

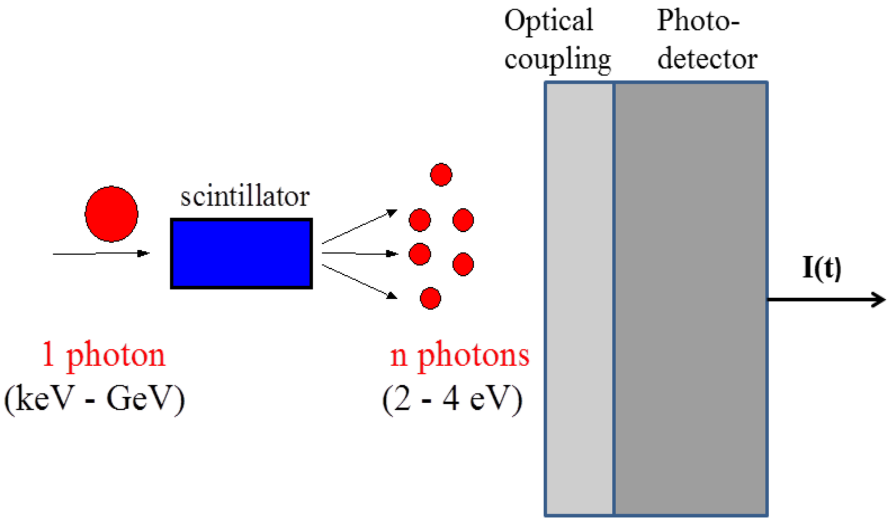


Figure 1. Principle of scintillator material and set-up of scintillation detector.

Scintillation mechanism can be divided into three consecutive sub-processes: *conversion, transport and luminescence,* see **Figure 2.** During the initial conversion a multi-step interaction of a high-energy (here considered below ~1 MeV) photon with the lattice of the scintillating material occurs through the photoelectric effect and Compton scattering effect; below the photon energy of 100 keV the former is of major importance. Many electron–hole pairs are created and thermalized in the conduction and valence bands, respectively. This first stage is concluded within less than 1 ps. In the transport process, electrons and holes (eventually created excitons) migrate through the material, repeated trapping at defects may occur, energy losses are probable due to nonradiative recombination, etc. Considerable delay in the migration can be introduced due to the mentioned charge carrier recapture at trapping levels in the material forbidden gap. This stage is the least predictable as the material point defects, flaws, surfaces and interfaces can introduce energy levels into the forbidden gap and strongly modify/degrade otherwise high intrinsic scintillation performance. Apparently, these phenomena are strongly dependent on manufacturing technology. The final stage, luminescence, consists in consecutive trapping of the electron and hole at the luminescence centre and their radiative recombination. In a particular group of materials the light generation occurs as a result of radiative transitions between the valence and first core bands as sketched in **Figure 2**; these are so-called cross-luminescence scintillators.

Each stage of scintillation process has thus a specific impact on both the basic physical processes and practical performance parameters. Chemical composition of material, its structural and atomistic quality and also its morphology (single crystal, ceramics, nanomaterial, composites) are of the key importance and must be considered in practical material optimization.

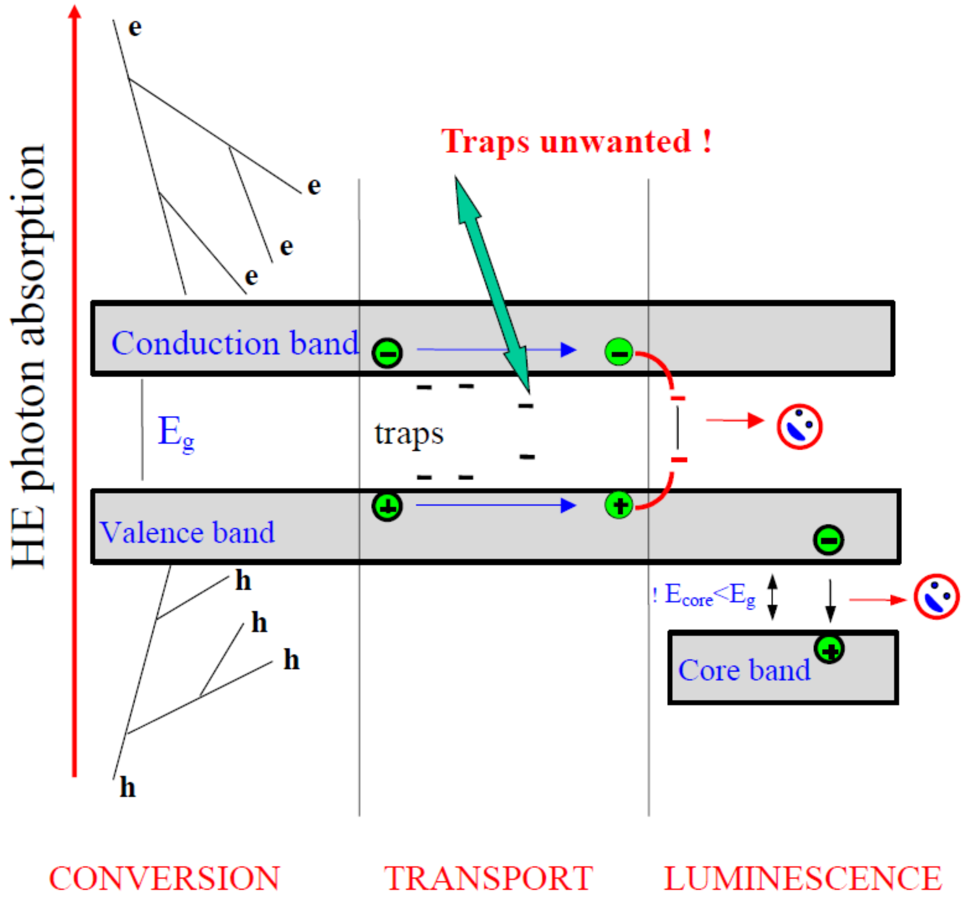


Figure 2. Sketch of scintillator mechanism in a solid state crystalline material.

This short commented review of selected publications, cited throughout the text, dealing with the advanced scintillation materials based on multicomponent oxides follows the direction of R&D outlined in my Habilitation Thesis in 2015. Another five years of intense research work brought deeper understanding of atomistic aspects of the proceseses of energy transfer and storage in their scintillation mechanism, several novel ways of materials optimization, but has also pointed out to persistent bottlenecks and challenges which are still limiting the performance in some material groups and have not been overcome yet. Given the multidisciplinary nature of this research, need of several different advanced manufacturing technologies, and broad portfolio of characterization techniques, the studies described below were accomplished in broad national and international collaborations.

2. Multicomponent oxide scintillators: Main achievements

Multicomponent oxides are defined by the presence of typically three-to-four cations in the chemical formula. They are solid solutions of the limit compositions with the ability to form crystalline material at (nearly) any intermediate chemical composition which allows fine tuning of their electronic band structure. It is usually called band-gap engineering. In case of the Ce- or Pr-doped scintillating materials we are focused mainly on the bottom part of the conduction band due to negatively acting electron traps. These materials are prepared as the bulk single crystals using the Czochralski or Bridgman growth from the melt, single crystalline films using the liquid phase epitaxy, or optical ceramics using the vacuum sintering and hot isostatic pressing. Quite several technologies are also readily used to produce crystalline (nano)powders. Targeted acting on the defects and traps themselves is usually achieved by codoping in the manufacturing process or annealing of as grown material. Usually, we call this approach the defect engineering. Both strategies have been used in the R&D of scintillating materials described below.

2.1 Garnet structures

The most systematic and extended studies we performed on the so-called garnet structures where the well-known $Y_3Al_5O_{12}$ (YAG) and $Lu_3Al_5O_{12}$ (LuAG) compositions are further admixed with Gd and Ga ions. We reviewed these studies in [2] until 2015. The key results include the combinatorial composition&property mapping [3,4] resulting in the discovery of the so called GGAG garnet (Ce-doped $Gd_3Ga_xAl_{5-x}O_{12}$, x = 2-3) which is the most efficient scintillator among bulk oxides currently existing [3] and has been immediately commercialized. Its high light yield approaching 60 000 phot/MeV, close to the theoretical limit, has been achieved by immersion of shallow electron traps in the conduction band. This is due to decreased conduction band edge (with respect to that of YAG and LuAG) constituted from the Gd^{3+} and mainly Ga^{3+} energy levels. Therefore, trapping of electrons migrating in the conduction band, which results in the delayed radiative recombination at Ce^{3+} centers, has been substantially diminished. In addition, Gd^{3+} cation ensures stronger crystal field around the Ce^{3+} ion. Consequently, sufficiently high ionization barrier of $5d^1$ excited state of Ce^{3+} prevents ionization losses at the emission center around room temperature (RT). The energy level sketch and dependence of the light yield on host chemical composition are provided in **Figure 3**.

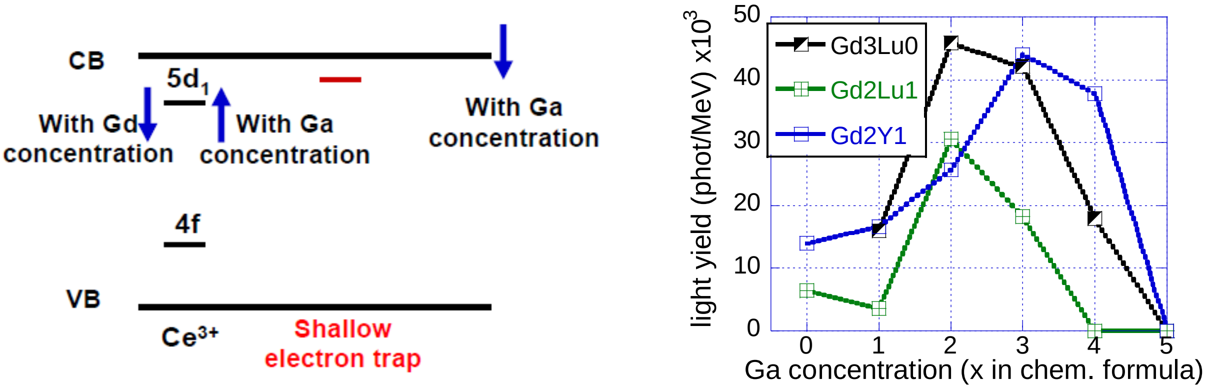


Figure 3 Trends in energy level positioning (left) and light yield values (right): dependence on the host chemical composition in $(Gd,Lu,Y)_3Al_{5-x}Ga_xO_{12}$*:Ce garnet single crystals [3].*

The biggest commercially manufactured crystals are of 3-inch diameter, see **Figure 4**, produced by the Czochralski technique in C&A Corp. in Sendai, Japan.

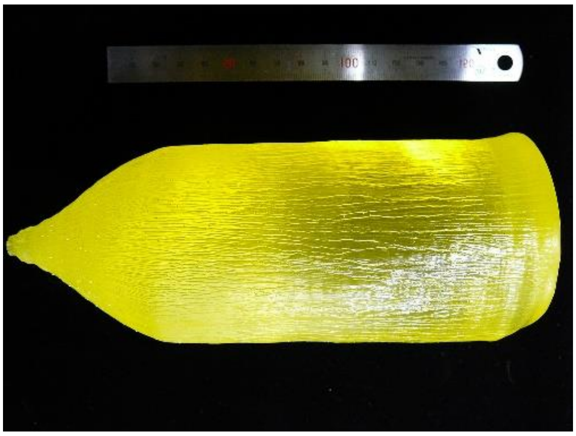


Figure 4 Czochralski technique grown 3 -inch diameter GGAG:Ce single crystal. Courtesy of A. Yoshikawa.

Further research revealed interesting compositional dependence of the light yield and energy resolution in GGAG:Ce within the formula above which improved the energy resolution down to 4.2%@662 keV [5]. It is worth mentioning that the forerunner of this discovery was our study of the influence of gallium admixture into LuAG [6] indicating the possibility of efficient band-gap engineering in these solid solution garnets. We have also studied the peculiarities of gallium embedding in solid solutions of $Gd_3(Ga,Al)_5O_{12}$ crystals [7] where, unexpectedly, gallium preferentially occupies the smaller aluminum tetrahedral site. The main reason for this peculiar cation distribution consists in the stronger covalency of the Ga−O bond compared with the Al−O bond. Furthermore, there is also the need for decreasing the cation−cation repulsive force which has been suggested in earlier literature as well (see ref.13 in [7]).

We have also addressed the stability of garnet phase in $Gd_3(Ga,Al)_5O_{12}$:Ce [8]. It is well known that with increasing size of the rare earth (RE) cation in $RE_3Al_5O_{12}$ the stability of the garnet structure decreases and $Gd_3Al_5O_{12}$ crystals cannot be prepared from the melt as the resulting material is a mixture of garnet and $GdAlO_3$ perovskite phases. The secondary perovskite phase nanoinclusions have already been detected in $Gd_3Ga_xAl_{5-x}O_{12}$:Ce ($x<2.25$) crystals by sensitive and selective photoluminescence (PL) spectroscopy, see **Figure 5**. Only the $Gd_3Ga_{2.5}Al_{2.5}O_{12}$:Ce compositions ($x\geq2.5$) showed pure garnet phase.

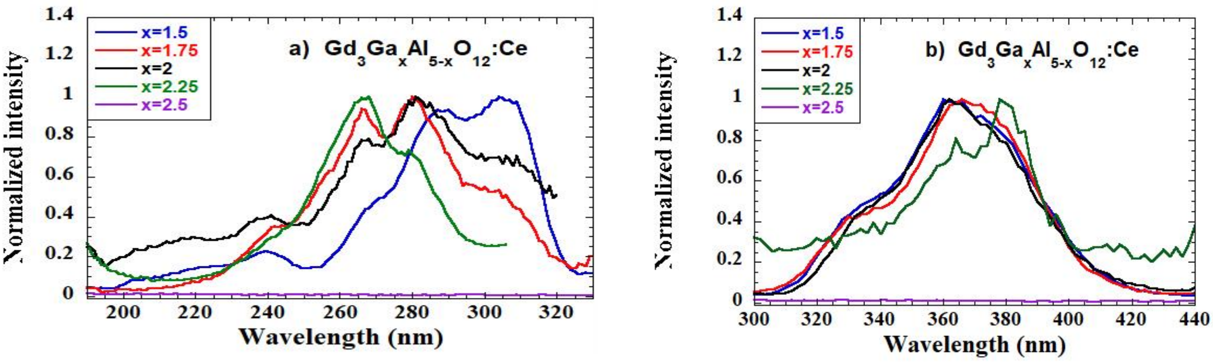


Figure 5 Selective photoluminescence spectroscopy of perovskite nanoinclusions in $Gd_3Ga_xAl_{5-x}O_{12}$*:Ce crystals: Normalized RT PL excitation spectra for the emission at 360 nm (left); Normalized RT PL emission spectra under excitation at 290 nm (right) [8].*

Another important milestone in optimization of cerium doped garnet scintillators was achieved by us applying the stable divalent ion codoping which stabilizes the Ce^{4+} center. This center provides an additional fast radiative recombination pathway in scintillation mechanism and thus accelerates the scintillation response. We have shown it for the first time in the Mg-codoped LuAG:Ce [9] and soon after also in GGAG:Ce where the Mg and Ca codoping was compared showing better performance for the former [10]. Positive effect of Mg-codoping was shown also in the LuAG:Ce [11] and (Gd,Lu)GAG:Ce [12] thin films prepared by the liquid phase epitaxy and in LuAG:Ce optical ceramics [13]. Explanation of the positive role of stable Ce^{4+} in scintillation mechanism is provided in **Figure 6**: The Ce^{4+} center can directly compete with any electron trap for an electron capture in the very first instants of the scintillation mechanism so that it will directly convert a fraction of slow part of scintillation response (coming from the delayed radiative recombination due to trapped electrons) to the fast one. Ce^{3+} is less efficient in this respect as it must first capture the hole. Meanwhile, the electrons available in the conduction band can get localized in traps in the forbidden gap. It is worth noting that Ce^{4+} works in parallel with the Ce^{3+} center, they are not competing, even if their relative concentration must be optimized for the best figure of merit based on the scintillation light yield and timing characteristics. It has been noticed that in the case of heavy Mg^{2+} codoping in LuAG:Ce,Mg [9] the scintillation decay is dominated by the decay times of 14-20 ns which are much faster in comparison with Ce^{3+} photoluminescence decay times of about 58 ns. We provided an explanation in our later study [14]: Both the speed up of the Ce^{3+} - related PL decay and the reduction of the respective light yield with the increasing Mg content observed under excitation in the 4f - $5d^1$ absorption band of Ce^{3+} at low temperatures occurs due to the luminescence quenching in the $5d^1$ excited state of the $\{Ce^{3+} - Mg^{2+}\}$ centers.

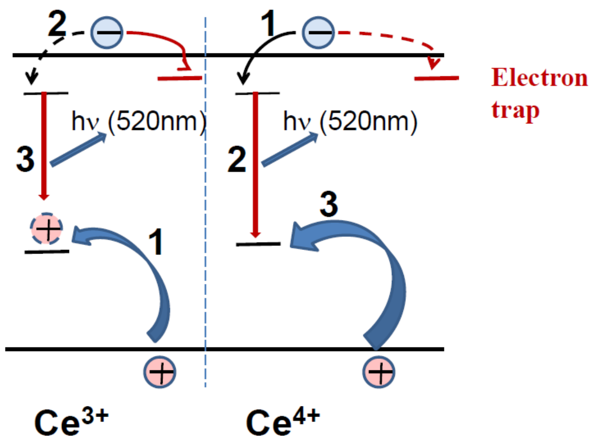


Figure 6. The individual steps of charge carrier capture at cerium centers in the scintillation mechanism of cerium doped garnet scintillators [2].

Interestingly, the mentioned Mg^{2+} and Ca^{2+} codoping in GGAG:Ce did not improve the light yield further [10], but it did improve its timing characteristics. Especially, it accelerates the rising edge of scintillation decay, see **Figure 7**, which is an important factor in improvement of the so called coincidence time resolution (CTR). CTR is the parameter of critical importance in applications where the time-of flight (TOF) technique is used, such as medical imaging (TOF-PET, TOF-CT) or high energy physics calorimetric detectors, see the review [15]. CTR below 200 ps was achieved in GGAG:Ce,Mg which is comparable with commercial LYSO:Ce,Ca used in TOF-PET devices. Similar performance and mutual comparison between GGAG:Ce,Mg and commercial LYSO:Ce,Ca we also reported in case of high energy physics applications [16].

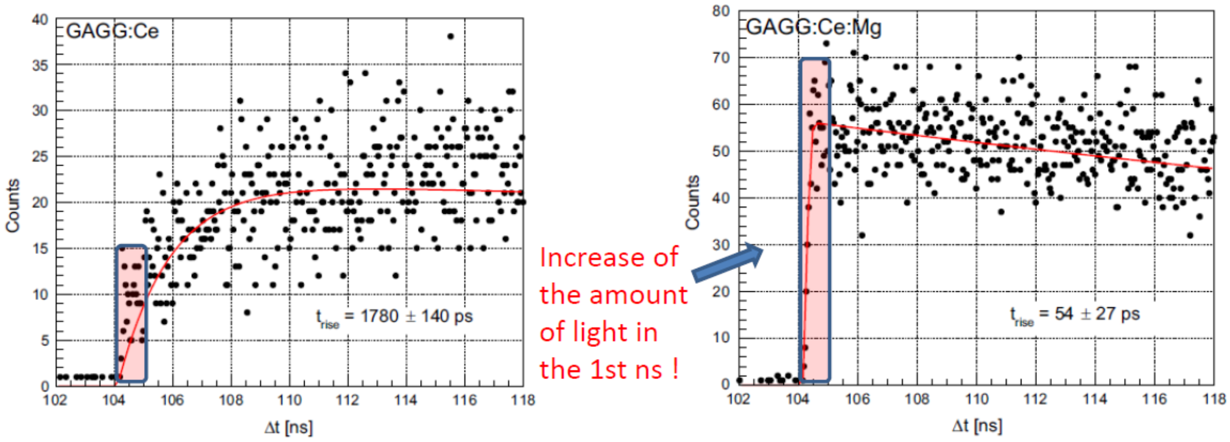


Figure 7. Decrease of rising time in the scintillation response of GGAG:Ce due to Mg codoping is demonstrated.

Furthermore, we have also studied the effect of the post-growth air annealing in the Ce-doped garnet and perovskite single crystal scintillators which contribute to stabilization of Ce^{4+} as well [17]. The study did further confirm the positive role of the stable Ce^{4+} center in the scintillation mechanism in garnets which is even enhanced by reduction of deep trap concentration based on oxygen vacancies. All the above mentioned studies prove the positive effect of the Ce^{4+} center in the scintillation mechanism of garnet scintillators which has been already incorporated in commercial production. On the contrary, given the positioning of the ground state of Pr^{3+} in the forbidden gap of garnets, it appeared impossible to use this strategy for optimization of Pr-doped LuAG (or any other Pr-doped garnet) due to large overlap of the charge transfer (CT) absorption of Pr^{4+} and fast 5d-4f luminescence of Pr^{3+} [18], **Figure 8**. Such an overlap causes both the reabsorption of Pr^{3+} fast scintillation component and nonradiative energy transfer loss.

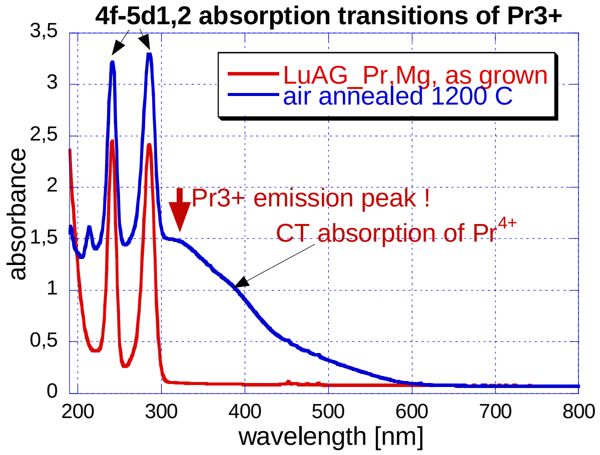


Figure 8. Absorption spectra of as grown and air annealed LuAG:Pr,Mg. Position of fast 5d-4f emission of Pr^{3+} is marked by an arrow.

2.2 Perovskite structures

Talking about the bulk single crystal perovskite scintillators, we have to remind the founder of this family, namely the $YAlO_3$:Ce (YAP:Ce) reported in literature already in the 1980s, see reviews [1,2]. Fast and efficient luminescence and scintillation is achieved due to the parity and spin allowed 5d-4f transition of Ce^{3+} giving rise to the emission band at 360-370 nm with the photoluminescence decay time of 18 ns, which is free from thermally induced nonradiative quenching at least up to 600 K. Fast scintillation decay dominated by the 25-35 ns decay time, light yield above 20 000 phot/MeV and excellent energy resolution around 4%@662keV together with the solid mechanical and chemical stability are other practical advantages of this scintillator. It is used in applications in various fields and the CRYTUR spol. s r.o. is one of leading industrial manufacturers of YAP:Ce, **Figure 9**. Given the low effective atomic number Z_{eff}=32 of YAP host, a concerted international effort appeared in the mid 1990s to grow a single crystal of its heavy $LuAlO_3$ (LuAP) analog the Z_{eff} of which is 64.9 approaching that of LSO:Ce (Z_{eff} = 66). The growth of LuAP-based crystals is, however, very challenging due to the instability of perovskite phase becase of small ionic radius of Lu. Thus, attempts were made to grow mixed $Y_{1-x}Lu_x$AP:Ce crystals. Mixed (Y-Lu)AP:Ce crystal growths, x = 0.6-0.7, using the Czochralski method, have been mastered by a few industrial producers. However, high price of this material and much lower light yield of about 10 000 – 12 000 phot/MeV compared to those of YAP:Ce and LYSO:Ce resulted in its commercial failure and R&D of these materials practically stopped. The latest review which includes all the details in the R&D history of these perovskite scintillators we published in 2010 [19].

Figure 9 Photo of the Zr-codoped YAP:Ce single crystal (45 mm in diameter and 125 mm in length). Courtesy of the CRYTUR company.

Several attempts have been reported in recent literature to prepare the stable perovskite structure with a large rare earth cation based on $LaAlO_3$ which is easier to grow in the bulk single crystal form. The Ce-doped $LaAlO_3$, however, shows no luminescence due to immersion of all the excited 5d states of Ce^{3+} in the host conduction band. Our recent attempts to grow $(La,Ce)AlO_3$ solid solution [20] have not provided a desired brighter scintillator due to an unclear perturbation and possible clustering of Ce^{3+} centers into another Ce-rich phase. Low energy shifted luminescence around 480 nm and very weak scintillation was obtained due to some essential bottleneck in scintillation mechanism. The Gd-admixed YAP host we found also unsuitable due to the reverse energy transfer $Ce^{3+} \rightarrow Gd^{3+}$ which is responsible for intense slower decay component, see **Figure 10**, and consequently lower light yield [21].

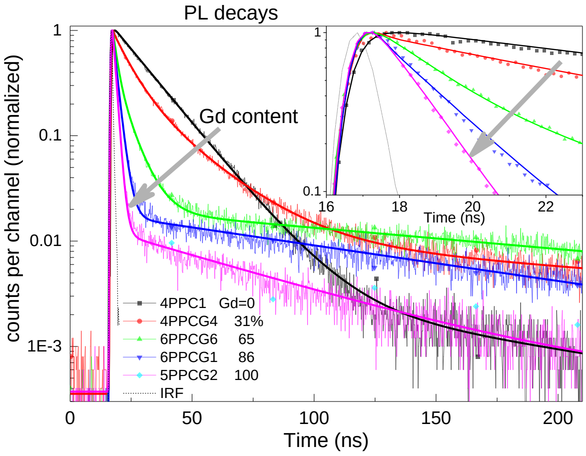


Figure 10 Photoluminescence decays of Ce^{3+}in $(GdY)AlO_3$:Ce epitaxial films at ex=300 nm, em=365 nm. The thick solid lines are convolutions of the (multi-) exponential fitting curve with the instrumental response function, IRF. In the inset the decays at a short time after excitation are shown, the gray arrows show increasing Gd content [21].

2.3 Ortho- and pyro-silicate structures

Scintillation characteristics of the Ce-doped rare-earth (RE) orthosilicates were reported for the first time in 1980s, namely for Gd_2SiO_5:Ce (GSO:Ce). Following investigations were devoted also to several other compounds of this material family, e.g.: Lu_2SiO_5:Ce (LSO), Y_2SiO_5:Ce (YSO), (Y_2)-$Lu_2Si_2O_7$:Ce (YPS and LPS) and several mixed compounds as well (most notably $(Gd)_{2-x}$ - or $Lu_{2-x}Y_xSiO_5$:Ce – GYSO and LYSO respectively), see the review in [19]. Single crystals were grown by the Czochralski technique using an iridium crucible, which is necessary due to very high melting point of these compounds (ranging between ~1950-2150 ^{0}C). In LYSO:Ce orthosilicates we contributed to the description of physical mechanism of luminescence and scintillation and also to the energy transfer and storage process by revealing tunneling processes in the thermoluminescence above RT [22]. We separated luminescence contributions from two Ce^{3+} centers substituting for Lu1 and Lu2 cations at different sites, see **Figure 11**, and determined their temperature stability and the mechanism of quenching [23].

Interestingly, based on large sample set of Ce-doped LSO and YSO single crystals with broad range of Ce^{3+} concentration, we have recently proposed another intepretation of the dominant violet (~400nm) and weak long-wavelength shifted blue-green (~480 nm) emission which were ascribed at the beginning of 1990s to the Ce1 and Ce2 centers, respectively. We suggest that the dominating violet doublet emission band of these materials arises from the Ce^{3+} ions, substituting for lutetium/yttrium ions in both crystal lattice sites (Lu1/Y1 and Lu2/Y2), i.e. the intense Ce1 and weak Ce2 emission bands are closely spaced and strongly overlapped. The weaker lower-energy (blue-green) broad emission band of these materials, showing the superlinear dependence of its intensity on the Ce^{3+} concentration, arises from the dimer $\{Ce^{3+} - Ce^{3+}\}$ centers the existence of which is confirmed by the EPR experiment.

We have also studied the mechanism of stabilization of Ce^{4+} in orthosilicate thin films or bulk crystals due to Pb^{2+} impurity [25] and Ca^{2+} codopant [26], respectively, which paved the way to the Ce^{4+} application in scintillation mechanism of garnets described in Section 2.1.

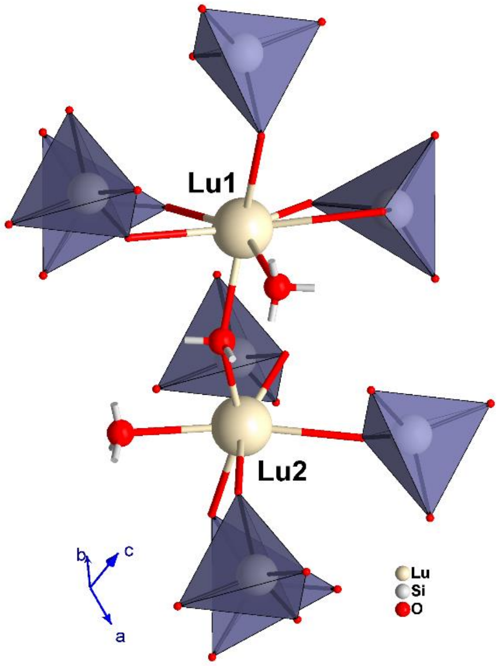


Figure 11 The structure of LSO with two Lu sites displayed and surrounding SiO4 tetrahedra [19]. Ce^{3+} occupies mainly (90-95%) the larger Lu1 site, while only 5-10% of it resides at smaller Lu2 site. Three oxygen ions with cut bonds form OLu_4 tetrahedra and do not participate in Si-O bonds.

In pyrosilicates we concentrated on recently discovered La-stabilized pyrosilicate structure of general formula $(La,Gd)_2Si_2O_7$ which allows, due to congruent crystal growth from the melt, preparation of large high-quality single crystals. We described in detail the Ce^{3+} luminescence mechanism in such a host incl. temperature stability of Ce^{3+} center [27]. Given the high energy barrier for thermal quenching this high light yield scintillator (above 30 000 phot/MeV) can be used up to temperatures extending 200 ^{0}C, e.g. in well-logging or other geo-physical applications.

3. Materials optimization: defects, charge traps and bottlenecks

To diminish the negative role of charge carrier interactions in the conversion stage and charge carrier trapping in the transfer stage of the scintillation mechanism in oxide materials their nature must be understood. We have proven in several studies that in the latter case the electron paramagnetic resonance (EPR) experiment is the most powerful tool for such a purpose. The correlated EPR and thermally stimulated luminescence (TSL) experiments provide an important information on how such traps influence the timing characteristics of scintillation response. We accomplished such studies in the last decade in garnets [28,29] and silicates [30,31]. EPR experiments can also provide interesting hints about the embedding of the emission center itself in the host structure which we studied especially in perovskites [32] where pairing of Ce^{3+} ions was revealed in the $YAlO_3$ (YAP) structure and above-mentioned silicates [24].

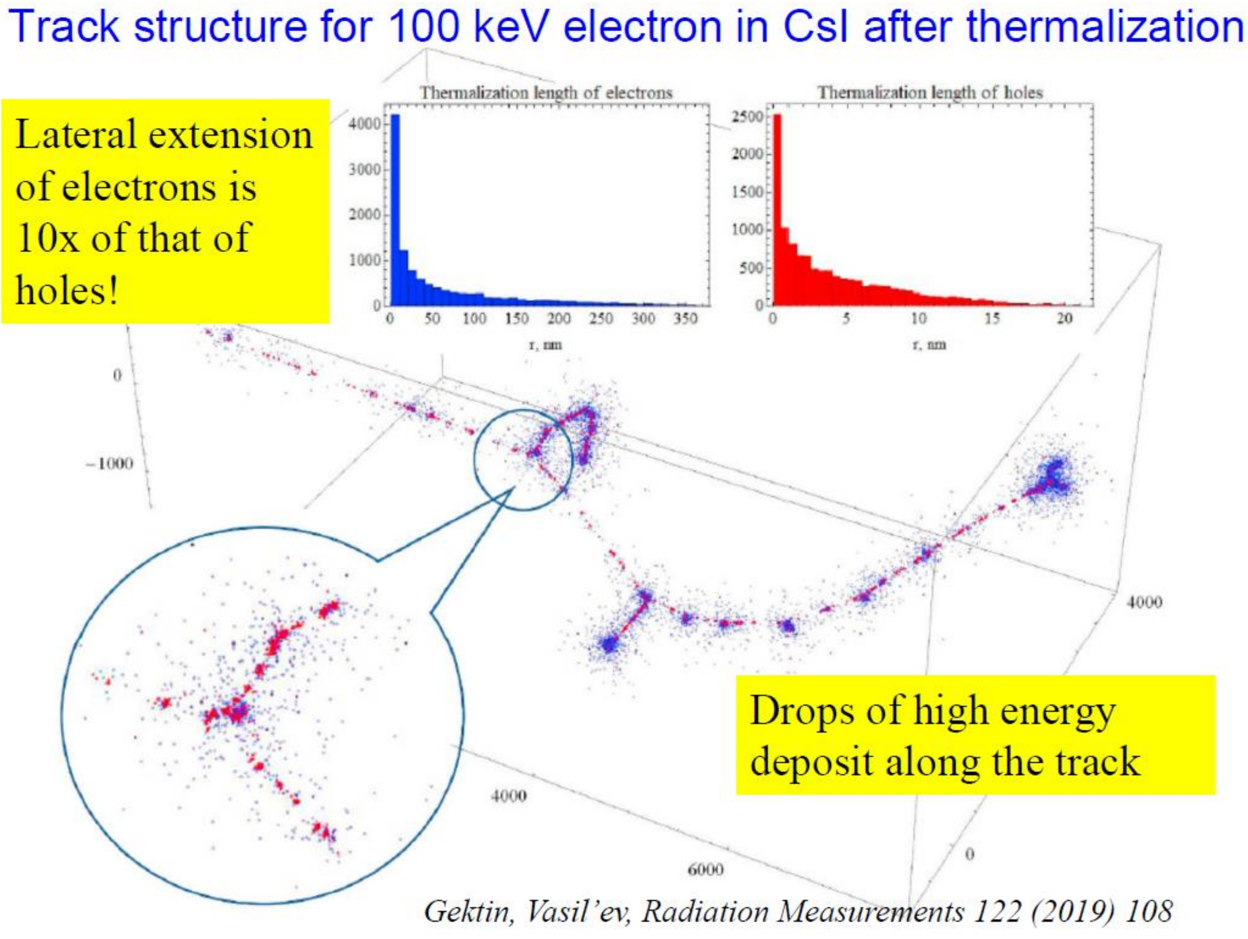
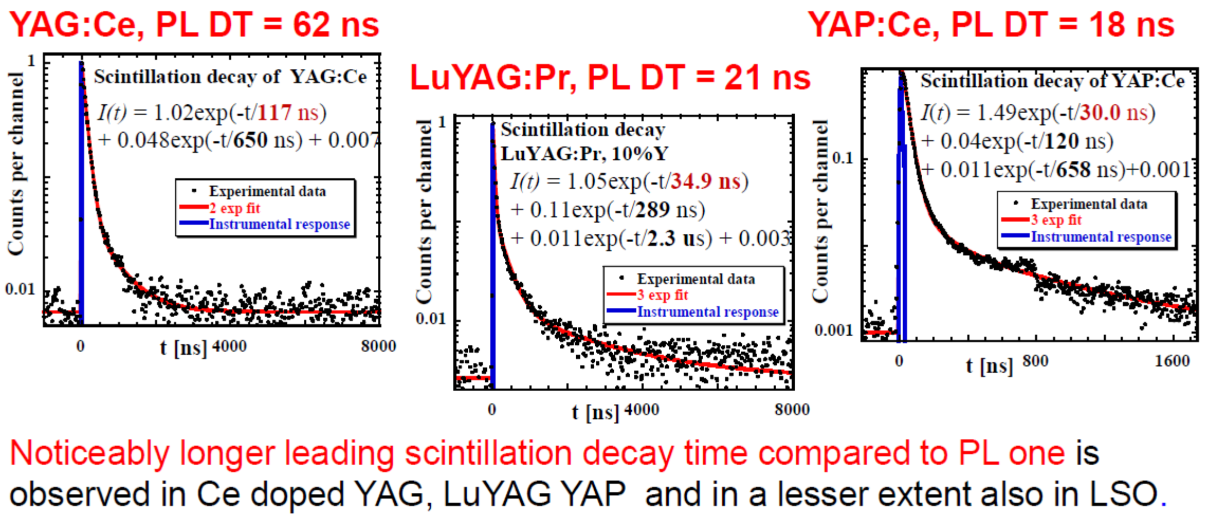


Figure 12 Ionization track model in CsI after 100 keV electron excitation (reprinted from Gektin et al, Radiation Measurements 122 (2019) 108.

The charge carrier interactions in conversion stage are difficult to study experimentally as they occur in the subpicosecond time scale and high intensity pulsed excitation sources are necessary to achieve high excited charge carrier density comparable with that in nano-spaced regions along the ionization track, see **Figure 12**. Understanding the conversion stage appears more and more demanding due to the need to improve energy resolution in scintillating materials which is a critical parameter e.g. in the homeland security applications. As summarized in [2,15,34] it is highly compound-specific approach, because nonlinearity of a scintillator is up to a great extent influenced by the second and third order interactions of charge carriers and excitons in the conversion stage. Thus, an improvement of energy resolution was achieved in $LaBr_3$:Ce by the alkali earth ion codoping, while in GGAG:Ce by the host composition tuning or in LuAG:Ce by diminishing the antisite defect concentration in the liquid phase epitaxy grown single crystalline films. So, apparently, specific defects play the role even in the conversion stage and subpicosecond time scale in shaping processes related to the charge carrier and exciton interactions.

Nowadays, the practically aimed and success-oriented world does not accept well the negative results, i.e. those which show the blind ways in a material development or persistent challenges and bottlenecks which have not been overcome yet. In our research discussed here it is especially the case of the perovskite scintillators described in Section 2.2. Given the unique combination of scintillation characteristics in the YAP-based materials, a great effort was paid from the mid-1990s to develop their high-density analogs. However, no breakthrough has happened so far. We can mention yet another persistent bottlenecks challenging the practical usage of several oxide materials [33, 34]: (i) very intense slow component responsible for low light yield and strong afterglow in the Pr-doped YAP; (ii) systematically slower scintillation decays in the case of Ce-doped YAG, LuAG or LuYAG single crystals the dominating decay time of which is almost two times longer compared to the photoluminescence decay time, see examples in **Figure 13**; (iii) high nonproportionality of ortho and pyrosilicate scintillators which especially degrades the energy resolution of these high light yield and fast scintillators. Low energy resolution degrades the figure of merit of LSO:Ce and LYSO:Ce for their use in PET and TOF-PET applications as it limits the possibility to remove coincidence events which include the Compton scattering process.


YAG:Ce, PL DT = 62 ns

LuYAG:Pr, PL DT = 21 ns

YAP:Ce, PL DT = 18 ns

Noticeably longer leading scintillation decay time compared to PL one is observed in Ce doped YAG, LuYAG YAP and in a lesser extent also in LSO.

Figure 13 Demonstration of the difference in the leading decay times (DT) in the luminescence and scintillation decays in the Ce^{3+} *doped YAG and YAP and* Pr^{3+} *doped LuYAG single crystals. Fit of the decay (solid red line) is a convolution of instrumental response and multiexponential function I(t) displayed in graphs.*

4. Conclusions, scientific and pedagogical perspectives in the field

Application of modern strategies of the band-gap and defect engineering by means of tailored solid solutions and aliovalent doping, respectively, have proved useful in ultimate optimization of several groups of scintillating materials (here demonstrated for garnets). At the same time, there are persistent bottlenecks and challenges in the scintillation mechanism which trouble material optimization and practical exploitation (here demonstrated for heavy perovskites) and ask for R&D continuation and novel breakthrough ideas. Due to complexity of scintillation mechanism, its sensitivity to atomistic irregularities in the material structure as well as demanding and expensive manufacturing technologies the search for material optimization strategies is certainly both exciting and frustrating research.

Scientific perspectives of R&D in scintillator field in the next one-to-two decades at least are bright due to ever increasing usage of X-ray, gamma-ray and accelerated charged particle and neutron beams in many important fields incl. medical imaging, homeland security, military, high-tech industry, raw materials mining, environment monitoring and others. In all these activities scintillating materials are of major importance in the detection and monitoring devices. Moreover, the study of point and extended defects mentioned in some examples in Section 2 and 3 is of critical importance also in other optical materials, e.g. those used in the solid-state lasers, power luminophores and nonlinear optics (e.g. for frequency doubling) as such defects are often degrading the material performance. It is worth noting that in the Czech Republic we have several important industrial enterprises working in the field, e.g. the CRYTUR spol. s r.o. in Turnov and TESCAN ORSAY Holding in Brno to mention a few, and other R&D laboratories in institutes of the Czech Academy of Sciences and Czech universities which have activities in the field of optical, luminescence and scintillation materials. Apparent need for university and doctoral education in this direction is at present secured by two specific lecture courses for master and doctoral students provided by myself at FNSPE, CTU and by other courses at several universities providing knowledge in the field of luminescence and optical solid-state materials and optics in general. I have been continuously developing the mentioned lecture courses to update their content with new knowledge and trends in current R&D worldwide taking advantage of our front position in international community in this field and I will continue this practice in the future. Furthermore, I will advertise new topics for doctoral students. The center of gravity of this focused education in the field of luminescence and scintillation materials will be kept at FNSPE, CTU, but it is worth noticing that doctoral students in this field are also educated at FMP CU in Prague and increasing interest in the last decade has also appeared in the Technical university of Liberec so that there is a broad base to further develop the highest education of young generation in the field of luminescence and scintillation materials and their practical applications.

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