Development of radiation-hard and cost-effective inorganic scintillators for calorimetric detectors based on binary glass compositions doped with cerium - SCINTIGLASS

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ABSTRACT

The project is aimed at developing industrial technology for Ce-doped glasses to match the conventional scintillators in combination of high light yield, fast response, and high radiation tolerance at a strongly competitive price and superior production scaling capabilities. The developed Ba-Gd silica glass doped with cerium possesses the largest light yield at the level of 2500 ph/MeV among heavy glasses and provides coincidence time resolution of 215 ps FWHM with SiPM readout. Glass scintillators can be promising in medical imaging devices, especially PET scanners, large-scale introscopy, certain high-energy physics applications and other applications demanding inexpensive radiation detectors.

Keywords: Scintillator; glass; ionizing radiation, detectors.

1. INTRODUCTION

The project is aimed at developing novel scintillation material.

- Scintillating materials are performance-limiting components in many ionizing radiation detectors.
- Scintillation detectors are required for medical imaging devices, introscopy, high-energy physics experiments, and other applications.
- Share of the scintillating material in the costs of a radiation detector is of major importance, together with the light yield, radiation tolerance, response time, attenuation length and chemical stability.

Currently, single-crystal-based scintillators outperform the scintillators based on ceramic or glass host materials for many scintillation properties, however, at the expense of their price. Decreasing the crystal production costs is limited by demanding technologies and expensive facilities required for growing single crystals. Application of ceramic scintillators is usually hindered by limited transparency of the ceramics. Meanwhile, glass production is inexpensive, matured, flexible and convenient for scaling in a short period of time. Light glasses enriched with ^{6}Li ions are applicable for detection of thermal neutrons, however, they can hardly be exploited for the detection of other types of ionizing radiation due to their low density. Recently, it has been shown that scintillation glasses based on barium di-silicate system BaO-2SiO_2 (DSB) are suitable for operation as scintillators in harsh irradiation environments of collider experiments [1, 2]. SCINTIGLASS project took the challenge to transfer the technology of the fabrication of DSB-based scintillating materials to industrial scale, while improving the scintillation properties of the scintillator. Provided that the developed glass scintillator exhibits scintillation properties approaching those of single-crystal-based scintillators, the glass scintillator has advantage of low price and production scalability by far not competed by single crystal scintillators.

As planned for the project, all the production of glasses prospective as scintillators has been carried out on industrial facilities of project industrial partner *Preciosa*. The production technology has been successfully developed within the year of project implementation. Ce-doped DSB glasses containing gadolinium were shown to be most prospective for further development. Optimization of the industrial production of Ce-doped DSB-Gd glasses enabled an enhancement of the light yield by a factor of two and a substantial improvement of radiation tolerance. The time resolution of the novel scintillator is superior to other scintillation glasses. Full width at half maximum (FWHM) in the coincidence time resolution (CTR) measurements combining detection of scintillation and

Cherenkov photons is found to be as short as 215 ps, close to that in single crystal scintillators.

2. STATE OF THE ART

The majority of inorganic crystalline materials are produced by the methods of pulling from the melt or sintering. For instance, lutetium silicate or garnets doped with Ce are pulled at the temperature above 1850˚C. The pulling rate of the crystal ingot from the melt does not exceed several millimetres per hour. Thus, small rate of crystallization is the general drawback of all crystal growing techniques. Glasses and glass ceramics are an alternative to the single crystals. Silica based glass melts are made by fusing silica with minerals, which contains the oxides needed to form a given composition. The molten mass is rapidly cooled to prevent crystallization and formed into glass. Glass ceramics is a polycrystalline solid obtained in controlled crystallization of the glass. Glass and glass ceramic materials can be cast in a mould of different volumes and shapes. Moreover, a large quantity of the material can be obtained in a relatively short period of time. However, most of the glasses do not exhibit scintillation properties. Despite their relatively simple and cost-effective production, heavy glasses have not been widely used in radiation detectors due to their poor radiation hardness and low light yield [3]. The main origin of the low radiation tolerance and low light yield is their amorphous structure.

In spite of the numerous attempts to make heavy lead-containing glasses scintillating, they can still be used as Cherenkov radiator only. There are ongoing but not yet successful studies to replace Pb by Bi which could trigger a new turn of the development of heavy scintillation glass for the needs in high-energy physics applications.

3. BREAKTHROUGH CHARACTER OF THE PROJECT

The technology has been transferred and optimized on industrial glass production facilities enabling production of large scintillator bulks in well-stabilized and repeatable conditions. Therefore, further production scaling will be a matter just of production volume. Within 10 months of project implementation, Ce-doped DSB scintillators produced by *Preciosa* exhibited transparency in the spectral range of scintillation peak, light yield and radiation hardness superior to those obtained in these scintillators fabricated in laboratory conditions prior to the project.

Gadolinium-containing DSB glasses activated by Ce (Ce-doped DSB-Gd) are shown to have a set of properties substantially superior to that of other glass scintillators. Moreover, this scintillator has a high density, which is especially important in medical applications.

Ce-doped DSB-Gd glasses exhibit fast scintillation response. The CTR FWHM measured by exploiting both scintillation and Cherenkov photons was found to be 215 ps. This time is only by a factor of two longer than the CTR obtained with standard measurement technique and typical LYSO crystals extensively used in PET scanners [4]. Using all photopeak events and correcting for the time walk the CTR improves from 215 ps to 163 ps FWHM. Novel method of the signal processing offers opportunities for further improvement of CTR. The key parameters of interest for two typical Ce-doped DSB-Gd glasses produced prior and after the project implementation are compared in Tab. 1.

The transfer of production technology from laboratory to industry equipment and further development of the technology resulted also in improvement of radiation tolerance of Ce-doped DSB-Gd glasses. Moreover, light-induced recovery of the initial transparency is demonstrated and might be *in situ* exploited in radiation detectors based on DSB-Gd glasses.

Tab. 1. Improvement of the key scintillation properties of Ce-doped DSB-Gd scintillation glass during the period of STINTIGLASS project implementation.

Material	before	after
Light yield within 4000 ns gate, ph/MeV	1300	2500
Coincidence time resolution, ps	>600*	215±8
Attenuation length at scintillation peak wavelength, cm	10	50

*Cherenkov photons not exploited

Summing up, substantial progress in key parameters of Ce-doped DSB-Gd glasses important for this material as scintillator has been achieved. The material parameters approach those of the conventional scintillators based on expensive single crystals. Therefore, progress by further optimization of the industrial production technology has good chances to be sufficient to push the scintillation parameters up to the level for exploiting the feature of low production costs making the glass of choice in many applications.

4. PROJECT RESULTS

After transferring from research laboratory to industrial facilities, DSB glass technology has been significantly improved and optimized. Glasses of different contents have been produced and studied, Ce-doped DSB-Gd glass has been found to be the most promising candidate for further development. In addition to its favourable scintillation properties, high gadolinium content increases the density and, consequently, the stopping power for radiation, whereas gadolinium has a large absorption cross-section for neutrons and makes the scintillator applicable for neutron detection.

In 10 months of Project implementation, colourless bulks were obtained. Technological efforts were aimed at obtaining a heavy scintillation glass combining an improved light yield, faster time response and resistance to ionizing radiation.

Fig.1 illustrates the changing colour and transparency in the course of Project implementation. The optimization has been performed by fabricating glass bulks with dimensions not less than 25x25x100 mm^3.

1th month 3th month 10th month

Fig.1. Ce-doped DSB-Gd bulks after technology development for 1, 3 and 10 months.

Doubling of the scintillation light yield was achieved. A strong correlation evidencing a negative influence of the activator in Ce^{4+} state on the light yield due to scintillation reabsorption has been established. Ce^{4+} stabilization in the glass results in a brownish coloration of the glass due to the presence of an additional broad absorption band [5]. The adjustments of the technology reducing the amount of Ce^{4+} ions have been successfully implemented. Fig. 2 presents the correlation between the optical transmission at 400 nm indicating the Ce^{4+} presence in the glass and the light yield for all samples produced in the course of the Project implementation. Increasing absorption of scintillation light by Ce ions in the state Ce^{4+} has been concluded to be the main origin of the light yield reduction.

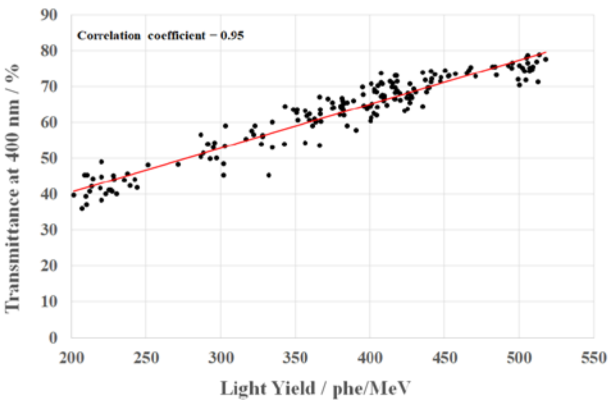

Fig. 2. Correlation between the optical transmission at 400 nm of the samples of 0.5 cm thick and the light yield measured at room temperature using a PMT with bialkali photocathode. Samples have been produced at the pre-production run with concentration of Ce_2O_3 0.76 weight %.

The electronic excitation transfer has been investigated using the transient absorption (TA) technique, as in [6], and Thermally Stimulated Luminescence (TSL). The kinetics of the TA signal probing the population of radiative state of Ce^{3+} was measured. The decay part of the kinetics contains two components. The decay time of the fast component becomes shorter for larger Ce content. Nevertheless, its fraction in the total TA signal is small relative to that of the second component with a time constant close to the time of radiative recombination, which is similar for all samples. The TA study evidenced the influence of carrier trapping. The traps have been investigated by means of TSL both below and above room temperature. Broad TSL signals related to the presence of a trap distribution are evidenced. Moreover, the signal at low temperatures can possibly be attributed to an athermal tunnelling recombination mechanism. The minimization of the influence of the traps on the scintillation properties of Ce-doped DSB-Gd glasses is a matter of forthcoming efforts.

The change in absorption coefficient induced by γ-rays of ^{60}Co source has been exploited to study radiation tolerance of the glasses. The last bulks produced by *Preciosa* exhibit low sensitivity to irradiation in the spectral range of scintillation band. The sensitivity has correlation with the light yield and has space for further decrease. Recovery of the initial transparency under irradiation in visible is observed and offers opportunity for exploitation in radiation detectors.

Timing capabilities of the scintillator were studied using CTR technique. In the best samples with dimensions 2x2x3 mm, the CTR FWHM was found to be 215 ps. Application of novel methods for data processing [7] with the time walk correction using different rise time windows between the single signal amplitude of the first and second photon detected allows to achieve the CTR FWHM as short as 163 ± 8 ps for all photo-peak events.

The samples with the light output above 300 phe/MeV have been used to assemble a prototype of a sampling calorimeter module equipped with readout electronics.

5. FUTURE PROJECT VISION

5.1. Technology Scaling

Capability of technology scaling on industrial level has been one of the key features in choosing objectives of the project already in Phase 1. The scintillation glass technology is already transferred from laboratory level to the production using industrial facilities by industrial partner having experience and large markets in production of various glass products. In Phase 2, the targeted scintillation properties will be improved and specifications to ensure quality stability will be established. Stopping power to ionizing radiation will be primarily addressed, since this property defines the application fields of radiation detectors. In view of material production, the development of the product to TRL-7 targeted in Phase 2 will be rather a matter of production volume than technology. The development of the product to higher than TRL-4 requires fabrication of detecting devices based on Ce-doped DSB-Gd glass. The first prototype of a sampling calorimeter module has already been fabricated in Phase 1. Targeted exploitation of Ce-doped DSB-Gd glass in prototype detectors dedicated for medical imaging, HEP experiments or other applications might require purposeful modification of the material, which will be ensured by a feedback with industry partner *Preciosa*.

5.2. Project Synergies and Outreach

Phase 1 evidenced a good balance of capabilities and experience of Consortium teams and efficient collaboration with industrial partner. In Phase 2, a research team with experience in device design and an industrial partner with experience in detector production are required. A team at Belarus State University is targeted as an academy partner, whereas the company *Crytur*, Czech Republic, a worldwide recognized detector solution supplier, showed already interest in joining the Consortium.

The results obtained in Phase 1 are summarized in a manuscript submitted to NIMA, and an oral report is accepted at IEEE 2020 NSS-MIC Conference. In benefit for solving problems of the Project, the academy teams are active in many research fields relevant to the Project. More than 50 peer reviewed papers and a book are published by Consortium teams within the project year. The practice to do conclusive research and publication standards will be further exploited for dissemination of the Project results. Increase in TRL during Phase 2 will enable publications in industry-targeted journals and websites.

5.3. Technology application and demonstration cases

The key advantage of the radiation detectors based on Ce-doped DSB-Gd is low production costs, therefore, units for large detecting systems are targeted as the final markets.

In the field of healthcare, the activities will be focused on developing detectors for the future market of whole-body PET scanners. Availability of such inexpensive detectors might even enable the development of devices with several layers of detectors surrounding the patient, thus, substantially increasing the diagnostic capabilities and decreasing the radiation dose experienced by patients.

The novel scintillator will enable development of introscopy devices capable of fast scanning of large volumes. The decreased scanning time will decrease the impact of homeland security facilities on traffic efficiency.

High Gd content enables developing of neutron detectors for searching explosives.

The inexpensive radiation detectors might be exploited also in autonomous systems of environment monitoring.

The Project is being accomplished by interdisciplinary Consortium covering teams with experience in material science, glass chemistry and physics, interaction of radiation with matter, and device design. Applications will require collaboration with experts in medicine and healthcare, transportation, environmental protection.

5.4. Technology commercialization

Project industrial partner *Preciosa* will serve as the first producer of the new scintillator for commercialization. It might be followed by other glass manufacturers without investments in new equipment. *Crytur* company will be included in the Consortium to develop and fabricate devices for several targeted applications and, thus, to seed the commercialization of these radiation detectors.

5.5. Envisioned risks

General risks related to timely updating of project planning, possible delays with procedures of public procurements, substantial changes in prices or personnel mobility will be mitigated using the experience of Consortium teams in accomplishing their previous projects.

The Project might encounter certain specific risks.

Aftershock of COVID-19 pandemics might retard the activities of certain teams. To mitigate the risk, Phase 2 will be planned i) in several steps with priority for production and measurements in each step and ii) to combine close collaboration and capability to work productively within a team in case of any other team being in limited capability to work.

Progress in improving certain properties might turn out to be less successful than expected, thus limiting suitability of the material for certain applications. However, several applications are in the field of the Project, thus, the risk would be mitigated by focussing activities on most promising applications.

In Phase 2, much more emphasis will be put on developing device prototypes. To mitigate the risk of having insufficient qualification, the Consortium of Phase 1 will be strengthened by two new members, one industrial, the second from academia, with experience in device design and production.

5.6. Liaison with Student Teams and Socio-Economic Study

Several students (MSc and PhD) and young researchers in the different partners have been involved in Phase 1 both in research activities and implementation of the project, which will continue in Phase 2. We will involve the young researchers in the project organisation and build a student team with the main objective to look for niche applications of radiation detectors based on glass scintillators and computer-aided design of devices of interest for the Project.

Plans for Phase 2 include an involvement of students of the international master courses of the School of Economics at UniMiB in order to consider societal challenges related to the Project.
Data for socio-economic study will be permanently accumulated both within the Project and in communications with industries and social partners.

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