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GLASS-CERAMIC SCINTILLATION MATERIALS FOR NEUTRON DETECTION

Abstract. In the present article we discuss a new class of scintillation materials that are prospective for application in high energy physics experiments and for detection of neutrons in a wide energy range.

Keywords: glass, glass ceramics, scintillators, Ce doping, light yield

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СТЕКЛОКЕРАМИЧЕСКИЕ МАТЕРИАЛЫ ДЛЯ РЕГИСТРАЦИИ НЕЙТРОНОВ

Аннотация. Обсуждается новый класс сцинтилляционных материалов, перспективных для применения в экспериментах в физике высоких энергий и измерении нейтронов в широком диапазоне энергий.

Ключевые слова: стекло, стеклокерамика, сцинтилляторы, легирование церием, световыход

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Introduction. Glass is an inorganic product of fusion which is cooled to a rigid condition without crystallizing. There is a family of materials called glass ceramics. It has an intermediate position between single crystals and glasses. Glass ceramics [1] is polycrystalline solid obtained due to controlled crystallization of the glass. In general, glass ceramics can be obtained by several methods. One of the methods is based on the synthesis of microcrystallites inside the glass. In this case, the glass is made from a raw glass material with a chemical composition that is close to the chemical composition of the desired microcrystals. After melting, the glass is exposed to a temperature close to the crystallization temperature for an extended period of time. The main goal of this step is to form the seeds of the desired microcrystals. After this, the glass is exposed to gradually increasing temperature. The main goal of this step is to promote the growth of nano- or micro-crystals inside the glass matrix. In general, crystallites at their formation in the glass can capture activating ions like Ce^{3+} and form scintillators. This requires a high concentration of Ce^{3+} in the precursor (mother) glass and crystallographic availability for cerium to be stabilized in the crystallite in the trivalent state. Glass and glass ceramics materials can be worked in the mold, moreover, a large quantities of the material can be obtained in a relatively short period of time. However, most of the glasses do not possess scintillation properties. Among different scintillating materials, scintillating glasses, despite their relatively simple and cost-effective production, have not been widely used in nuclear instrumentation up to now due to their poor radiation hardness and low light yield. The main cause of the low radiation tolerance and low light yield of usual scintillating glasses is their amorphous structure. The "non-organized" structure of the atoms allows the presence of structural defects, which favor the creation of colors centers under irradiation.

Lithium Silicate Glass Ceramics. The exception is a family of lithium silicate glasses doped with Ce ions that show high light yield under thermal neutrons [2–4]. There are several lithium containing scintillation glasses doped with Ce [5] and Tb [6] which are available on the market. The most widely applied scintillation glass is GS20 type glass which has a complex Si–Al–Li–Mg–Ce composition. This composition is hardly used to obtain glass ceramics which has obvious advantages over the amorphous

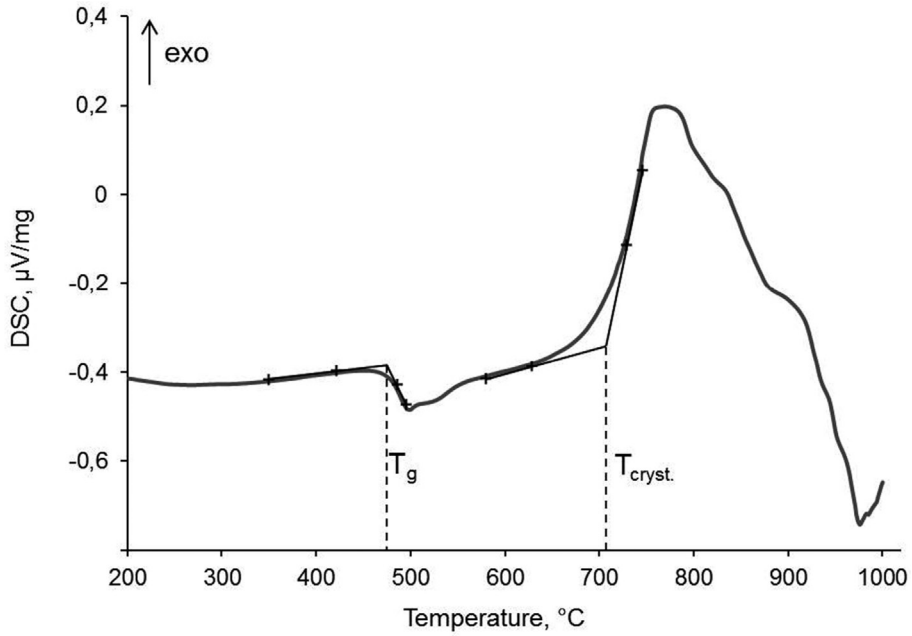

Fig. 1. Differential Scanning Calorimetry Thermogram of the glass obtained from stoichiometric mixture of $Li_2O*2SiO_2$

glass. Glass-ceramics combines the luminescent properties of rare-earth ions in crystallites and remaining mother glass. Moreover, it possesses better thermal conductivity, chemical stability, and mechanical strength.

The use of simple stoichiometric compositions allows the crystallization of one sort of crystallites inside the mother glass. The glass composition corresponding to the stoichiometric ratio $Li_2O*2SiO_2$ allows the formation of homogeneous glass-ceramics [7]. The formation of crystal nucleation occurs homogeneously throughout the volume of the glass [8]. Such glass-ceramics has been widely used in engineering and medical prostheses; It comprises lithium disilicate crystalline inclusions with sizes more than 1 micron and is opaque. Fig. 1 shows the Differential Scanning Calorimetry (DSC) thermogram of the glass obtained from stoichiometric mixture of $Li_2O*2SiO_2$. The point 475 °C corresponds to the glass transition temperature (Tg). The crystallization effect starts after 550 °C and reaches its maximum near 770 °C, which corresponds to crystallization of the lithium di-silicate $Li_2Si_2O_5$. The addition of Ce ions shifts the crystallization peak to higher temperatures.

The glass made of a stoichiometric composition of $Li_2O*2SiO_2$ allows keeping a high content of Li ions in the mother glass at heavy doping with Ce oxide up to 10 wt.%. Fig. 2, 3 show the room temperature photo-luminescence spectra and its excitation, depending on the annealing temperature for the same annealing time. The characteristic luminescence of Ce^{3+} ions, which has the band maximum near 400 nm, is observed in the mother glass sample before annealing. Annealing at 650 °C for 1 hour leads to a shift of the photo-excitation and luminescence maxima to a long wavelength range for 12 nm and 25 nm, respectively. The changes in the shape and the structure of the excitation bands indicate that Ce^{3+} ions are localized in $Li_2Si_2O_5$ crystallites, whose presence is confirmed by the XRD method.

The size of $Li_2Si_2O_5$ crystallites in the glass is determined by the annealing temperature and duration. The thermal glass processing is performed under the conditions that prevent the emergence of crystallites with dimensions greater than 100 nm. When the particle size is greater, the particles scatter light themselves, which results in a decrease of the light output. If the crystallite size is less than 100 nm, the scintillation of Ce^{3+} ions in the glass and the crystallites is combined, thereby increasing the total yield.

Partially crystallized $Li_2O*2SiO_2$ glass containing nano-crystallites of $Li_2Si_2O_5$ has a light yield of more than 7000 ph/neutron and provides an energy resolution at the registration of thermal neutrons better than 8.5 %. The average decay time of the scintillation is 70 ns, so the considered glass ceramics can be a reasonable substitution of ^3He counters when a high counting rate or a large area of the detector is required.

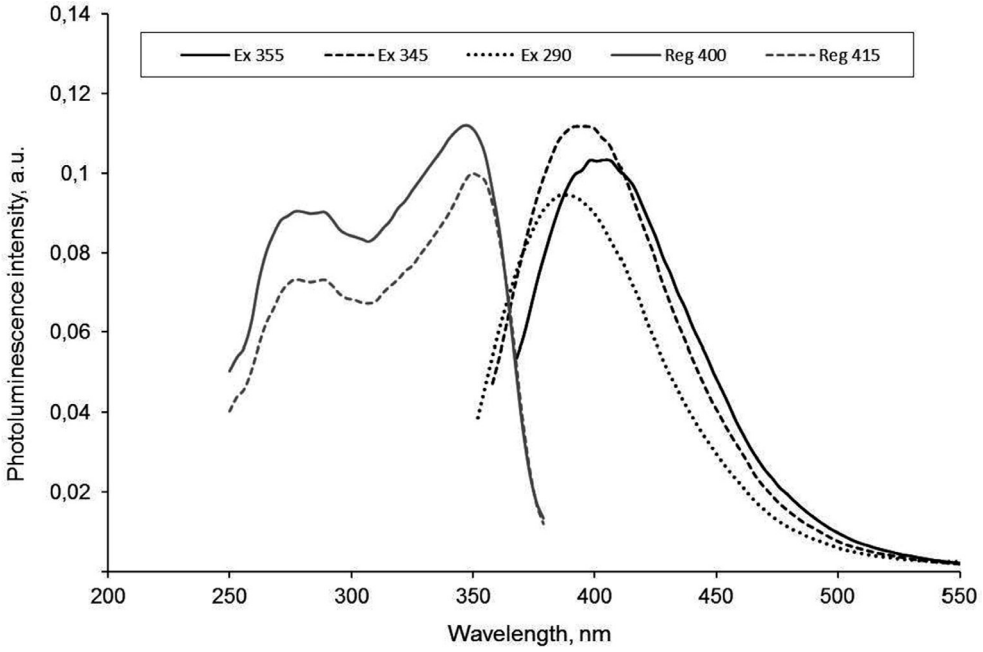

Fig. 2. Luminescence at different excitations (Ex) and luminescence excitation spectra at different registration (Reg) of $Li_2O*2SiO_2$ mother glass

Barium Silicate Glass Ceramics. Heavy Loaded with Gd Glasses with barium (Ba) have a higher density; however, they have the smallest LY in the series of silicate glasses [9]. Colorless, cerium- and phosphorus-containing barium silicate glasses with a density of 3.3–4.13 g/cm^3, a radiation length < 43.5 mm, and a fluorescence spectrum at 415–430 nm have been described in (US patent 4 566 987, January 28, 1986). The maximum density of the glass is achieved with a composition containing 10 different elements where the content of BaO is 55.6 wt.%. Further increase of the glass density by increasing the BaO content in the initial mixture leads to an increase in the temperature of glass working. The density of the glass obtained from the composition $BaO*2SiO_2$:Ce does not exceed 3.7 g/cm^3.

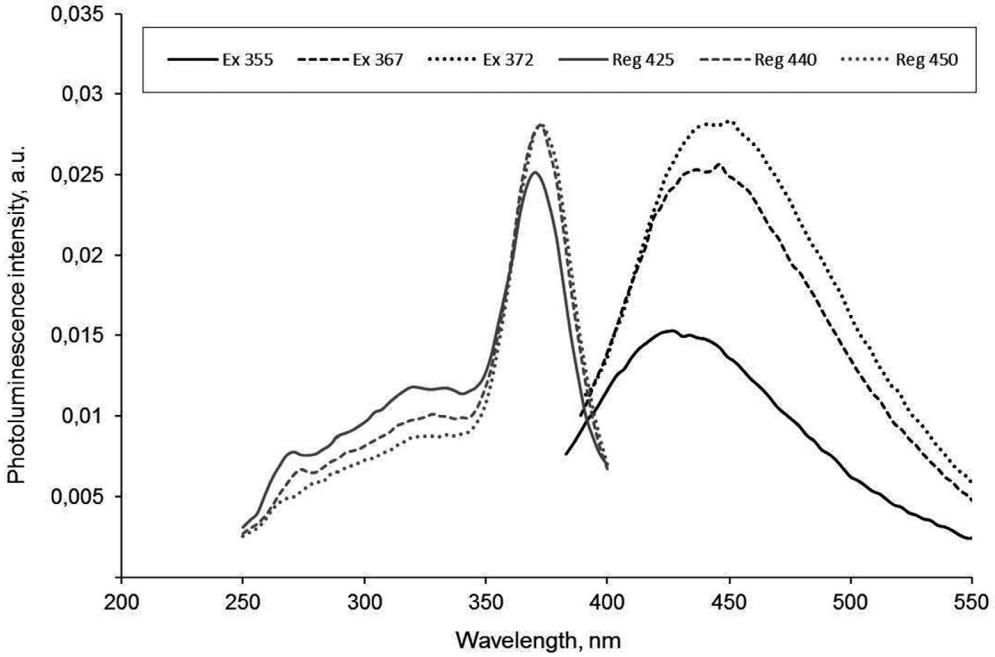

Fig. 3. Luminescence at different excitations (Ex) and luminescence excitation spectra at different registration (Reg) of $Li_2O*2SiO_2$ mother glass annealed at 650 °C during 60 min

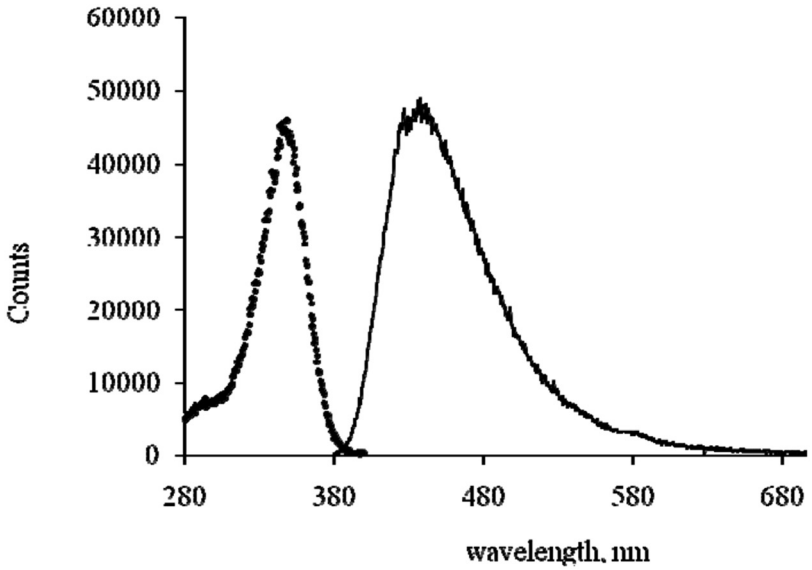

Fig. 4. Room temperature luminescence (solid) at 350 nm excitation and luminescence excitation spectrum (dots) at 435 nm registration of the oxy-fluoride glass worked from Ba–Gd–Si–Ce composition

Further increase of the glass density, the effective atomic charge, and the light yield is achieved by admixture of the stoichiometric composition of Gd_2O_3 and SiO_2 with 1:1 mol. ratio to the composition 2:3 mol. ratio of chemicals BaO and SiO_2 in and additive of CeO_2. The glasses obtained from these compositions have a density higher than 4.5 g/cm^3. A further increase in the resulted density and the decrease in the temperature of glass working are achieved by using the composition of oxides and fluorides. The resulted glass is the oxy-fluoride glass. Oxide and oxy-fluoride glass ceramics have been studied for high energy physics applications [10–12].

Fig. 4 shows the luminescence (right) and the luminescence excitation spectrum (left) of the oxy-fluoride glass. The luminescence band with the maximum near 435 nm dominates in the spectrum.

The scintillation kinetics is well approximated using a sum of three exponentials. The pulse shape contains a 6-ns component (~10 % of total weight) and is dominated by a fast 30-ns decay (~40 % of total weight) and a slightly slower component (~50 % of total weight) around 180 ns. The presence of this slower component in the scintillation depends on both Ce concentration and Ba/Si ratio in the final composition. It is noteworthy that ~74 % of the light is contained in the first 100-ns. The light output is around 100 pe/MeV, being five times larger than that of a PWO crystal at room temperature [3]. The temperature dependence of light output at the temperatures from –25 to +25 °C is very low. The temperature coefficient was found to be less that 0.04%/°C [3], which makes this material very convenient to construct large-volume detectors.

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