

Preparation and study of polycrystalline scintillator materials

Theses of PhD Dissertation

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1. Introduction

The future of the scintillation detectors can be described as three main parts: the research on the scintillator material itself, replacement of photomultipliers with other semiconductor devices, and the modernization of processing units, developing new evaluation algorithms. Over the past decade, the development of the inorganic scintillators has undergone its renaissance. The most common scintillator materials are the various rare-earth oxyorthosilicates, from which the Ce^{3+} doped lutetium-based scintillator, the lutetium oxyorthosilicate (Lu_2SiO_5 , LSO) have the best properties in the present days. Since the cost of the growth of the LSO crystals is significantly increasing due to the high melting point (~ 2000 °C) and the costs of the starting materials, therefore, the use of the $\text{Lu}_{2-x}\text{Y}_x\text{SiO}_5$ (LYSO) crystals, partially substituted with yttrium ions, prevails. Reducing the costs, dictated by the industry, has a further possible way, namely, the use of the ceramic materials produced in polycrystalline forms. The preparation of oxyorthosilicates via conventional solid-state reactions is difficult, because of the required high synthesis temperatures. Therefore, the literature offers hydrothermal and sol-gel methods, liquid-phase sintering, and mechano-chemical processes for this purpose. In formerly published studies on YSO (yttrium oxyorthosilicate, Y_2SiO_5), LSO, and LYSO, especially fundamental research tasks were solved, but the most appropriate methods for industrial applications have not yet been developed. Accordingly, during my research, I made efforts to find a cost-effective synthesis procedure, while retaining the typical advantageous properties of these advanced materials. My research aimed at the development and study of new methods for the synthesis and characterization of suitable embedded polycrystalline phosphor scintillator, i.e., the production of Ce^{3+} -ion activated X2 phase of LYSO.

Since the market prices of the starting materials for the concerned crystals are very high, the costs can be optimized by well-selected steps of the synthesis procedure. Considering this aspects, the first step was the preparation of the X2-phase of YSO host lattice, it being meta-stable at room temperature. After the preliminary studies, my primary task was the optimization of the properly chosen synthesis method. I have investigated the suitability of various heat treatment programs, the effects of different additives (LiF , $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_2\text{O-B}_2\text{O}_3$ eutectic, NaCl and NaF) and their varying concentrations on the phase purity. As the next step, I studied the

effects of the activator additive (Ce^{3+}) concentration as a function of changes in the luminescence intensity. Finally, I examined the luminescence properties of a variety of Y^{3+} - and Ce^{3+} -containing LYSO samples.

Polycrystalline syntheses are often promoted by using melt-forming additives (mostly alkali halides) added to the starting materials and by applying high annealing temperatures (>1200 °C). The Li^+/Na^+ ion containing additives can increase the luminescence intensity by their incorporation into the host lattice. Consequently, the accurate determination of these components is of high importance for the optimization of the synthesis procedure, and to provide supporting information for crystal-physical/chemical studies. Since the YSO:Ce crystals are prepared in small amounts, the sample mass available for chemical analysis is limited to some hundred milligrams only. Liquid dosing analytical methods generally require the digestion/dissolution of the samples, and necessary sample dilutions, which operations are handicapped by the risk of sample contamination. Therefore, for the determination of additives (Li, Na) in the powdered YSO:Ce samples, highly sensitivity and selectivity solid sampling graphite furnace atomic absorption spectrometry methods were developed and applied in this research. The composition of each intermediate product was characterized during the preparation of the crystals.

2. Experimental

For determine the phase purity of the samples, Raman scattering measurements were carried out with a Renishaw 1000 Raman spectrometer attached to a Leica DM/LM microscope with a 50x objective and monochromator with a resolution of 1 cm^{-1} using the 784.5 nm line of a 27 mW diode laser as an excitation source. The phase purity of the final products was checked by X-ray powder diffraction (XRD) analysis over the scattering range of $2\theta=2-70^\circ$ with steps of 0.05° using a 1710 Phillips diffractometer equipped with a graphite monochromatized $\text{Cu}(\text{K}\alpha)$ radiation source, with fixed sample holder and theta-theta geometry. The photoluminescence (PL) spectra were measured using a Horiba Jobin Yvon Fluorolog 3-22 fluorometer. Thermogravimetric differential thermal analyses (TG-DTA) were carried out for monitoring the phase transformations and chemical reactions of samples with a PL Thermal Sciences 1500 differential scanning calorimeter system. These measurements were performed in the

temperature range from 30 °C to 1400 °C with a heating rate of 10 °C/min in air atmosphere.

For exploring the effect of the activator ions (Ce^{3+}) concentration, the photoluminescence spectra were recorded by using a Horiba Jobin Yvon Nanolog fluorometer. The emission properties were examined by exciting the Ce-doped pellet samples with a 450 W xenon lamp at a wavelength of 360 nm. The morphologic and particle size study of the synthesized samples was carried out by using a field emission scanning electron microscope Model Leo 1540XB cross-beam system consisting of a high-resolution Zeiss Gemini SEM column and using an acceleration voltage of 5 keV. The determination of Li and Na content of the powdered YSO samples were performed on an Analytik Jena Model ContrAA-700 tandem HR-CS-AAS spectrometer (Analytik Jena AG, Jena, Germany) equipped with a transversally heated graphite atomizer, Analytik Jena Model SSA-600L and MPE-60 autosamplers for solid (powder) and liquid samples, respectively. The SSA-600L has a built-in electronic microbalance (precision: $\pm 1 \mu\text{g}$), and also fitted with a liquid sample dosing accessory for dispensing solutions of additives/chemical modifiers and/or standards into the graphite boats, applied for solid sample insertion. Spectral lines of Na I 285.3013 nm, Na I 268.034 nm, and Li I 610.353 nm were selected for the analysis.

3. Theses

- 1) The solid-liquid synthesis method of polycrystalline yttrium oxyorthosilicate (YSO) was optimized for obtaining the X2-phase. On the base of XRD, Raman measurements and thermo-analytical studies, it was concluded that for any additive, the phase purity depended on the concentration of the additive and the annealing temperature. It has been found that among the studied melt-forming additives (alkaline fluorides and alkaline borates), the best photoluminescence properties for YSO were received with samples prepared with ~18 mol% LiF (at optimized, 1 mol% Ce-content), at 1400 °C.
- 2) For polycrystalline yttrium oxyorthosilicate samples prepared with the optimized procedure, a significant reduction in the particle size has been achieved, as compared to those samples of YSO and yttrium pyrosilicate reported in the literature. The particle size of the current samples was in the 200-500 nm range. Similar or better results have only been achieved with more complex and costly preparative chemical procedures, such as the sol-gel and hydrothermal methods, which required the sharp adjustment of pH, long gel formation times, flushing of the sample after the annealing process, relatively large amounts of chemicals, and/or utilization of special labware. According to my experience the reduction of particle size has greatly facilitated by using optimal amount of melt-forming LiF additive during the heat treatment. In contrast, the samples prepared with NaF additive and samples without additive possessed larger particle size and heterogeneous morphology.
- 3) The luminescence properties and the shape of the PL spectra are strongly dependent on the Ce content of polycrystalline YSO and LYSO. The maximum PL intensity was found at around 1 mol% Ce for YSO, but over this optimum the PL intensity decreased. By increasing the Ce concentration, the PL peaks shifted towards longer wavelengths and the full width at half maximum values increased, due to the enhanced number of defects in the host crystal. For low concentrations of the activator additive (0.025 to 0.5 mol%), the Ce³⁺ ions primarily located at the B1 sites, while for high concentrations (>2 mol%), they were also built in B2 sites. The same phenomenon was observed for LYSO samples. By increasing the concentration of Y in LYSO, the PL peak positions shifted towards longer wavelengths, due to the difference between ionic radii of Y³⁺ and Lu³⁺ ions. For LYSO prepared with 0.5 mol% Ce, the number of the occupied B2 sites is lower than those in YSO samples with the same Ce concentration.

- 4) Solid sampling high resolution continuum source graphite furnace atomic absorption spectrometry (SS-HR-CS-GFAAS) methods were developed and studied for the fast and sensitive quantitation of Li and Na additives in yttrium oxyorthosilicate samples. The method was optimized for solid samples by studying a set of GFAAS conditions (i.e., the dispensed sample mass, sensitivity of the analytical lines, and graphite furnace heating programs). Due to the relatively high amounts of analytes in the YSO samples, alternative, less sensitive spectral lines (Na I 285.3013 nm és Li I 610.3530 nm) were selected for the analyses. I optimized the pyrolysis and atomization temperatures of the graphite furnace heating program using Na and Li standard solutions, as well as solid oxyorthosilicate samples by recording the Welz-functions of pyrolysis and atomization curves for Li and Na. For solid oxyorthosilicate samples, the optimal T_{pyr} for Na and Li is at 1100 and 1800 °C, respectively, while the optimal T_{at} is around 2400 and 2600 °C, respectively. For calibration purposes, the method of standard addition with Li and Na solutions was applied. The correlations coefficients (R values) of the calibration graphs were not worse than 0.983. The limit of detection for oxyorthosilicate samples was 20 µg/g and 80 µg/g for Li and Na, respectively. In order to ascertain the accuracy of the calibration, CRM samples of powdered Antarctic krill and soil (laterite) was analyzed for their Na and/or Li content by means of standard addition calibration using HR-CS-GFAAS and HR-CS-FAAS methods.
- 5) On the base of the results of solid sampling HR-CS-GFAAS analysis, it was concluded that the Li^+ concentration of YSO samples greatly decreased with rising annealing temperatures (1000 °C, 1200 °C, or 1400 °C). However, this additive incorporated slightly into the host lattice, even if the annealing temperature was as high as 1400 °C.

List of own publications

Peer-reviewed journal articles on the subjects of the theses

- (1) N. Laczai, Á. Péter, L. Kovács, L. Bencs, E. Lőrincz, *Synthesis and characterization of $Y_2(SiO_4)O:Ce$ with LiF and NaF additives*, **Solid State Sciences**, 45 (2015) 23-29.
- (2) N. Laczai, L. Kovács, Á. Péter, L. Bencs, *Solid sampling determination of lithium and sodium additives in microsamples of yttrium oxyorthosilicate by high-resolution continuum source graphite furnace atomic absorption spectrometry*, **Spectrochimica Acta Part B**, 117 (2016) 8-15.
- (3) N. Laczai, G. Dravecz, I. Hajdara, Á. Péter, L. Kovács, L. Bencs, *Influence of LiF additive and cerium doping on the photoluminescence properties of polycrystalline YSO and LYSO*, **IEEE Transactions on Nuclear Science**, (2016) submitted.

Conference presentations and posters on the subjects of the thesis

- (1) N. Laczai, Á. Péter, V. Horváth, *Preparation and study of oxyorthosilicate scintillator material*, (poster), **VIII. Országos Anyagtudományi Konferencia**, Balatonkenese, 2011.
- (2) N. Laczai, Á. Péter, L. Kovács, L. Bencs, E. Lőrincz, *Synthesis and enhanced luminescence of Ce-doped oxyorthosilicates*, (poster) **Advanced Scintillator Materials**, Kharkov, 2013.
- (3) N. Laczai, Á. Péter, L. Kovács, L. Bencs, E. Lőrincz, *Polikristályos ittrium-oxi-ortoszilikát előállítás és elemanalitikai vizsgálata*, (presentation) **Magyar Kémikusok Egyesülete (MKE) 2. Nemzeti Konferencia**, 2015.
- (4) N. Laczai, G. Dravecz, L. Kovács, L. Bencs, *Determination of alkaline additives in yttrium oxyorthosilicate by solid sampling HR-CS-GFAAS*, (poster) **European Symposium on Atomic Spectroscopy- ESAS 2016**, 2016.

Peer-reviewed journal articles (not in the topic of the theses)

- (1) Zs. Ajtony, N. Laczai, N. Szoboszlai, L. Bencs, *Quantitation of toxic elements in various water samples by multi-element graphite furnace atomic absorption spectrometry*, **Atomic Spectroscopy**, 35(1) (2014) 33-42.
- (2) L. Bencs, N. Laczai, P. Mezei, T. Cserfalvi, *Detection of some industrially relevant elements in water by electrolyte cathode atmospheric glow discharge optical emission spectrometry*, **Spectrochimica Acta Part B**, 107 (2015) 139-145.
- (3) L. Bencs, N. Laczai, Zs. Ajtony, *Model calculation of the characteristic mass for convective and diffusive vapor transport in graphite furnace atomic absorption spectrometry*, **Spectrochimica Acta Part B**, 109 (2015) 52-59.
- (4) Zs. Ajtony, N. Laczai, G. Dravecz, N. Szoboszlai, Á. Marosi, B. Marlok, C. Streli, L. Bencs, *Fast and direct screening of copper in micro-volumes of distilled alcoholic beverages by high-resolution continuum source graphite furnace atomic absorption spectrometry*, **Food Chemistry**, 213 (2016) 799-805.
- (5) G. Dravecz, N. Laczai, Zs. Szaller, I. Hajdara, L. Bencs, *Solid sampling determination of magnesium in lithium niobate crystals by high-resolution continuum source graphite furnace atomic absorption spectrometry*, **Spectrochimica Acta Part B**, 2016, submitted

Poster (not in the topic of the theses)

- (1) G. Dravecz, N. Laczai, Zs. Szaller, I. Hajdara, L. Bencs, *Solid sampling determination of Mg in LiNbO₃ crystals by high resolution continuum source atomic absorption spectrometric method*, **European Symposium on Atomic Spectroscopy- ESAS 2016**, 2016.