Proc. Estonian Acad. Sci. Phys. Math., 2004, **53**, 4, 237–251 https://doi.org/10.3176/phys.math.2004.4.04

# New scintillation materials for scientific, medical, and industrial applications

# Svetlana Zazubovich

Institute of Physics, University of Tartu, Riia 142, 51014 Tartu, Estonia; svet@fi.tartu.ee

Received 2 December 2003, in revised form 28 April 2004

**Abstract.** Information is presented on the terminated NATO Science for Peace project devoted to the search and study of some new and/or improved scintillation materials. In the framework of this project, in 2000–2003 various undoped, Mo<sup>6+</sup>-, Cr<sup>3+</sup>-, Cd<sup>2+</sup>-, Ba<sup>2+</sup>-doped and double Mo<sup>6+</sup>, Y<sup>3+</sup>- and Mo<sup>6+</sup>, Nb<sup>5+</sup>-doped lead tungstate crystals, undoped and Ce<sup>3+</sup>-doped yttrium aluminium and lutetium aluminium perovskite and garnet crystals, and Ce<sup>3+</sup>-, Tb<sup>3+</sup>-, Mn<sup>2+</sup>-doped Gd-rich phosphate glasses were studied in the Institute of Physics, University of Tartu. The most important results of these investigations obtained in collaboration with the colleagues from Italy and Czech Republic are briefly reported.

Key words: scintillators, lead tungstates, perovskites, garnets, phosphate glasses.

# 1. INTRODUCTION

The NATO Science for Peace Project No. 973510 "SfP-Scintillators" was devoted to the search and study of some new or improved scintillation materials for scientific, medical, and industrial applications. The work was carried out in 2000–2003 in the Institute of Applied Physics "Nello Carrara", Florence, Italy (the NATO country project Co-Director Dr. Gian Paolo Pazzi), in the University of Milan-Bicocca, Milan, Italy (Co-Director Dr. Anna Vedda), in the Institute of Physics, Academy of Sciences of Czech Republic, Prague (Co-Director Dr. Martin Nikl), in the CRYTUR Ltd. company (end-user), Turnov, Czech Republic (Co-Director Dr. Karel Blazek), and in the Institute of Physics, University of Tartu, Estonia (Co-Director Dr. Svetlana Zazubovich). In the Institute of Physics, University of Tartu, scientists of two laboratories were involved in the project: of the Laboratory of Physics of Ionic Crystals headed by Prof. Aleksandr Lushchik (Dr. S. Zazubovich, Dr. Tatjana Savikhina, and students/young scientists Dr. Vladimir Babin and MSc. Aleksei Krasnikov), and

of the Laboratory of Low Temperatures headed by Dr. Rein Kink (Dr. Andres Stolovits and Dr. Kaido Kalder).

Several topical problems in this field can be solved by applying the available technology. In the area of medical imaging, the sensitivity and further development of the positron emission tomography (PET) technique are strongly limited by a rather low response of the currently used Bi<sub>4</sub>Ge<sub>3</sub>O<sub>12</sub> (BGO) scintillator (decay time 300 ns). The project called for the use of faster, denser, and higher light yield scintillators in order to increase the sensitivity and space resolution of PET machines. Such material would also enable application of lower isotope doses (i.e., a lower patient radiation load). Industrial applications do not allow the usage of BGO at high temperatures (above 60–70 °C) due to rapid scintillation quenching. The usage of NaI:Tl is often limited by low resistance of the material due to its high hygroscopicity.

The systems, which were chosen for the study and technology transfer towards industrial production, can provide a solution to the application problems mentioned above. The developed systems can replace the materials currently used and improve considerably the performance of scintillation detectors in different applications. The improved characteristics of detectors result in a better performance of a number of processes in the industries and medicine, where such detectors are used. The field of medical imaging was of particular interest for us, because new tomographical methods have crucial importance in routine medical checks (e.g., scintimammography), cancer treatment, brain mapping, research of optimum drug dosage and circulation, etc. Better medical diagnostics is immediately reflected in a higher quality of medical care and an improved general health of people.

The main goal of the project was detailed study of new and/or improved scintillation materials, which could significantly increase scintillation detector performances in several fields of applications. On the basis of the results obtained, we aimed at elaboration of the methods for the improvement and optimization of the characteristics of these materials and searching for new systems for the scintillation applications.

The more specific objectives were:

- 1. establishment of the origin and the structure of the luminescence centres and of their relaxed excited states responsible for the luminescence processes;
- 2. study of the mechanisms of various processes (e.g., radiative and non-radiative decay of the exciton and impurity-induced states, creation of defects, energy migration, energy transfer, charge transfer) taking place in these materials;
- 3. study of the scintillation mechanism for the investigated systems;
- 4. determination of the conditions (e.g., the procedure of preparation and subsequent treatment, doping ion type and optimum concentration, host material composition, co-doping ion type and concentration) to achieve the needed scintillation characteristics (e.g., the maximum light yield, fast luminescence decay, high radiation stability).

The project was especially important for the Tartu team for the following reasons. The development of new scintillation materials requires preparation of a large number of various samples, operative change (also in the course of investigations) of their preparation conditions and of the type and concentration of impurities, and application of various methods for the investigation of the samples. The research is often limited by a very high cost of the raw materials needed or complicated crystal growth procedures. To achieve progress in this field, collaboration between physicists, chemists, crystal growers, industries, and end-users is strongly required. Substantial financial support from different sources is also needed to buy expensive raw materials and equipment and to support the students.

Since 1993, our group has been working in close cooperation with the Institute of Physics, Prague, and the Institute of Research on Electromagnetic Waves (from 2002 – the Institute of Applied Physics "Nello Carrara"), Florence. In 1994–1999 our joint work was carried out in the framework of NATO Linkage projects. Through the collaboration with the above-mentioned laboratories and also with the Department of the Material Science of the University of Milan-Bicocca, Milan, and the CRYTUR Ltd. company, Turnov, in the framework of the NATO Science for Peace project we could obtain all the necessary samples, use the experimental facilities in other laboratories, buy the expensive equipment, send the students to partner laboratories for a long-term training, participate in conferences and coordination meetings. The samples for our research were produced by CRYTUR Ltd. in Turnov and in the technological laboratories of the Department of Chemistry and Department of Optical Crystals of the Institute of Physics in Prague and prepared (cut, shaped, polished, and oriented) in the Optical Workshop of the Institute of Physics, Prague, and in CRYTUR Ltd.

The results obtained have been presented in 11 reports at international conferences and published in papers  $[^{1-13}]$ . Two articles concerning the project were published in *NATO Science and Society Newsletter* (No. 54, July 2000 and No. 62, March 2003).

# 2. MATERIALS

The following systems were studied in Tartu in the framework of the project.

1. Single crystals of  $Ce^{3+}$ -doped lutetium yttrium aluminium perovskites  $Lu_xY_{1-x}AP:Ce^{3+}$  (x=0.3) (LuYAP:Ce crystals). To find an optimal codoping for LuYAP:Ce, the doubly doped ( $Ce^{3+}$ ,  $Th^{4+}$  or  $Ce^{3+}$ ,  $Zr^{4+}$ ) yttrium aluminium perovskite YAlO<sub>3</sub>(YAP) single crystals were studied instead of LuYAP due to the equal characteristics of both matrices but much lower production costs of YAP single crystals compared to LuYAP. The optimal co-doping developed at YAP:Ce matrix was transferred to LuYAP:Ce matrix. The as-grown and/or annealed samples with different contents of  $Ce^{3+}$  ions and co-doping ions were studied.

- 2. Single crystals of undoped and  $Ce^{3+}$ -doped yttrium aluminium garnets  $Y_3Al_5O_{12}$  (YAG) and lutetium aluminium garnets  $Lu_3Al_5O_{12}$  (LuAG).
- 3. PbWO<sub>4</sub> single crystals, having the scheelite crystal structure, undoped or doped with Mo<sup>6+</sup>, Cd<sup>2+</sup>, Cr<sup>3+</sup> or Ba<sup>2+</sup> ions, without co-dopings and co-doped with Y<sup>3+</sup> or Nb<sup>5+</sup> ions, grown by Czochralski or Bridgman methods, nonannealed or annealed at different conditions, containing different concentrations of impurity ions or crystal structure defects. For comparison, the single crystals of ZnWO<sub>4</sub> and CdWO<sub>4</sub>, having the wolframite crystal structure, and PbMoO<sub>4</sub> crystals, having the scheelite crystal structure, were examined.
- 4. Gadolinium-rich alkali metal Gd phosphate glasses doped with Ce<sup>3+</sup>, Tb<sup>3+</sup>, or Mn<sup>2+</sup> ions (glasses of the Na(K)GdCe, NaGdTb, and NaGdMn types) with different glass compositions and impurity concentrations. For comparison, the same but undoped glasses and Gd-free glasses were studied.

Co-doping by aliovalent ions (e.g., by  $Zr^{4+}$  or  $Th^{4+}$  in the first case, by  $Y^{3+}$  or  $Nb^{5+}$  in the third case) was used for the final optimization of scintillation characteristics (to maximize the light yield, to minimize slow decay components, to keep high radiation hardness, etc.).

These systems were chosen for the following reasons.

The most important characteristics of scintillators are the emission energy suitable for registration by the most sensitive detectors available; high luminescence efficiency and short decay time; high density of the material; a high effective atomic number; radiation, thermal, and mechanical stability. The low cost and simple preparation procedure are also very important.

A Ce<sup>3+</sup>-doped Lu<sub>x</sub>Y<sub>1-x</sub>AlO<sub>3</sub> scintillator can replace BGO in the PET machines due to a higher density (8.4 g/cm<sup>3+</sup>, i.e. 120% of BGO), a much faster decay time (20–40 ns, i.e. more than 10 times), and a higher light yield (1.5–4 times). Today PET machines are used in more than 100 hospitals or medical research centres of the world. These scintillations can be applied also in geology, aggressive chemistry, etc. Besides medical tomography, YAlO<sub>3</sub>:Ce crystals can be used in backscattering electron detectors for electron microscopy, where even a small shortening of the luminescence decay time can give a huge economic effect. To achieve a high spatial resolution in combination with sufficient absorption of X-rays, which is necessary for X-ray screens intended for microtomography, materials with a high effective atomic number (like Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce) can be successfully used.

High light yield PbWO<sub>4</sub> crystals can compete with BGO for selected industrial applications due to a higher density (115% of BGO), fast leading scintillation decay components (below 10 ns), and much lower production costs (3–5 times at least). This scintillator can be used in very large (whole body) PET machines. A light yield improvement can be achieved by the introduction of additional emission centres like  $(MoO_4)^{2-}$ . Co-doping (e.g., with Nb<sup>5+</sup>, Y<sup>3+</sup>, Gd<sup>3+</sup>)

allows maintaining high radiation hardness and suppressing considerably the slow decay components.

High light yield rare-earth doped or/and phosphate containing glasses can compete with NaI:Tl scintillators, plastic scintillators, and classical (silicate) glass scintillators, due to their favourable density (3–4 g/cm³) and low production cost, in many applications in industrial defectoscopy, material sorting (coal industry), densitometry (sugar industry), radiation intensitometry (radiation protection, military applications), and security systems (custom checking in airports, country borders, etc., applied to luggage, cars, trucks, containers, etc.). Hundreds of different X-ray cameras are annually produced for these purposes. Due to an efficient  $Gd^{3+} \rightarrow Ce^{3+}$ ,  $Tb^{3+}$ ,  $Mn^{2+}$  energy transfer, the Gd-rich phosphate glasses were proposed to achieve an efficient radioluminescence in the ultraviolet, green, and red spectral regions, respectively.

# 3. RESEARCH METHODS

In Tartu, luminescence of crystals and glasses (in the 1–5 eV spectral range) was studied in a wide temperature range (0.35–500 K) both by the time-resolved spectroscopy methods and at the steady-state conditions, under excitation by photons of 2–11.5 eV energy. The following main setups were used.

- 1. A setup, based on two monochromators for the *steady-state* emission and excitation spectra measurements in the energy range 1–6.2 eV under excitation with deuterium or mercury lamps.
- 2. A setup, based on two monochromators for the study of *time-resolved* emission and excitation spectra and decay kinetics of luminescence in the microsecond–second time range under excitation by a xenon flash lamp FX-1152 (EG&G) with a pulse duration of about 1 μs and registration of the decay curves with the PC plug-in card multichannel scaler MCS-plus (EG&G) with a minimum dwell time of 2 μs.
- 3. A setup on the basis of a vacuum monochromator VMR-2 with the hydrogen discharge open-capillary lamp for the study of photoluminescence and thermally stimulated luminescence characteristics and defect creation processes under excitation/irradiation of samples in the VUV–UV spectral range (3.5–11.5 eV).

The experiments at temperatures from 0.35 to 500 K were performed

- (i) with the use of a helium refrigerator for the experiments at 0.35–80 K; in this refrigerator temperatures down to 0.35 K were obtained by pumping <sup>3</sup>He vapours;
- (ii) with the use of an immersion helium cryostat where the temperatures down to 1.7 K can be obtained by pumping <sup>4</sup>He vapours;
- (iii) with the use of vacuum nitrogen cryostats for experiments in the 80–500 K temperature range.

# 4. RESULTS AND CONCLUSIONS

The main goals of the project were achieved. For most of the systems studied the optimum chemical composition and preparation conditions were established. New information was received on the origin of luminescence centres and mechanisms of various physical processes taking place in these materials.

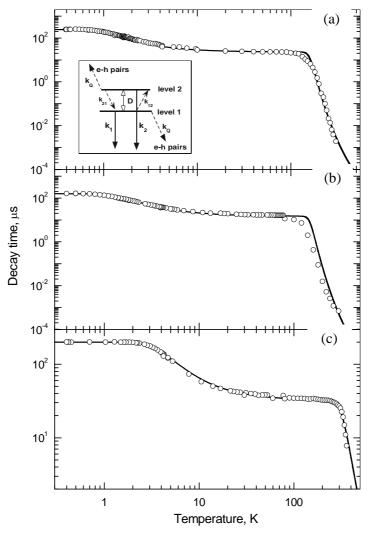
The following main results were obtained in the framework of the project with the participation of the Tartu team members.

1. In PbWO<sub>4</sub> crystals, two types of green emission centres were found. The centres of *the first type* are responsible for the low-temperature green emission. The decay kinetics of this emission was studied in the 0.35–300 K temperature range (see, e.g., Fig. 1a) and was found to be similar to the decay kinetics of the blue self-trapped exciton (STE) emission of PbWO<sub>4</sub> crystals arising from the WO<sub>4</sub><sup>2-</sup>-type exciton state. From temperature dependences of the green luminescence intensity and decay time, the structure of the corresponding relaxed excited states was established for several undoped and doped PbWO<sub>4</sub> crystals and the parameters of these states were calculated (see inset in Fig. 1a). The values of the parameters together with those obtained for the STE state are shown in Table 1. For comparison, the same study was carried out for PbMoO<sub>4</sub> (Fig. 1b), ZnWO<sub>4</sub> (Fig. 1c), and CdWO<sub>4</sub> crystals. The parameters of the relaxed excited states responsible for the green emission in the crystals of

**Table 1.** Parameters of the relaxed excited states responsible for the green emission. For notations, see the inset in Fig. 1a and the figure caption. K is a "zero temperature" rate related to  $k_{12}$  and  $k_{21}$ ;  $E_a^{\text{def}}$  is the activation energy for the defect creation process

Crystal	D,	$k_1, \\ \mathbf{s}^{-1}$	$k_2, s^{-1}$	<i>K</i> , s <sup>-1</sup>	$w_0$ ,	$E_{\mathrm{Q}}$ ,	$E_{\rm a}^{\rm def}$ ,
	meV	$s^{-1}$	$s^{-1}$	$s^{-1}$	$\frac{w_{Q}}{s^{-1}}$	eV	eV
Scheelite structure							
$PbWO_4$	0.3	$4.05 \times 10^{3}$	$1.0 \times 10^{5}$	$0.6 \times 10^{5}$	$1 \times 10^{8}$	0.1	0.215
PbWO <sub>4</sub> :Cr	0.33	$4.72 \times 10^{3}$	$1.2 \times 10^{5}$	$1.0 \times 10^{5}$	$1 \times 10^{8}$	0.1	0.20
PbWO <sub>4</sub> : Mo	0.35	$4.1 \times 10^{3}$	$0.8 \times 10^{5}$	$3.0 \times 10^{5}$	$7 \times 10^{12}$	0.26	0.26
PbWO <sub>4</sub> blue STE emission	0.45	$39 \times 10^3$	$3.7 \times 10^5$	$5.0 \times 10^5$	10 <sup>12</sup>	0.2	0.125
PbMoO <sub>4</sub>	0.37	$6.3\times10^3$	$1.3 \times 10^{5}$	$1.0 \times 10^{5}$	$5 \times 10^{13}$	0.26	no defects created
Wolframite structure							
$GdWO_4$	1.2	$3.1 \times 10^{3}$	$9.5\times10^4$	$1.2\times10^5$	_	-	no defects
$ZnWO_4$	1.0	$5.0\times10^3$	5.8 × 10 <sup>4</sup>	$1.0\times10^5$	$7 \times 10^8$	0.29	no defects created

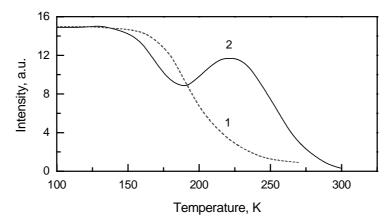
the scheelite (PbWO<sub>4</sub> and PbMoO<sub>4</sub>) and wolframite (ZnWO<sub>4</sub> and CdWO<sub>4</sub>) structure were found to be very different (see Table 1). It was concluded that the green emission of the first type does not arise from PbWO<sub>4</sub> crystal regions, having the wolframite structure, and that the defects responsible for this emission are different in different PbWO<sub>4</sub> crystals. This emission is considerably quenched at T > 220 K (Fig. 2, curve 1). The green



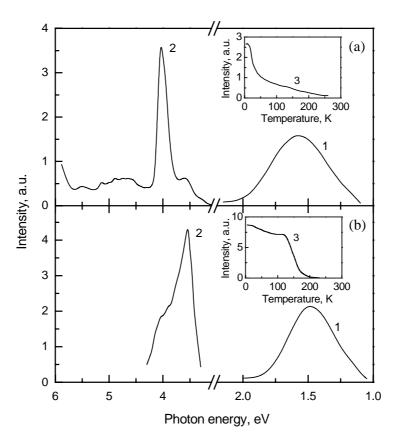
**Fig. 1.** Temperature dependences of the green emission decay times of (a) PbWO<sub>4</sub>: Mo, (b) PbMoO<sub>4</sub>, and (c) ZnWO<sub>4</sub> crystals. Circles represent experimental data and solid lines are calculated using the parameters reported in Table 1. The inset in (a) shows the sketch of the model used and the rates of the radiative  $(k_1, k_2)$  and one-phonon nonradiative  $(k_{12}, k_{21})$  processes from the lower and the upper excited levels, respectively, the energy difference (D) between these levels, the rate of the emission thermal quenching process  $k_Q = w_Q \exp(-E_Q/kT)$  with activation energy  $(E_Q)$  and frequency factor  $(w_Q)$ .

emission of the first type in PbWO<sub>4</sub> crystals was assumed to arise from the states of the  $WO_4^{2-}$ -type exciton localized near a defect. In PbWO<sub>4</sub>: Mo crystals, this emission may arise from the  $MoO_4^{2-}$  states. The defects responsible for the green emission of *the second type* appear only at higher temperatures (Fig. 2, curve 2) where the exciton state decomposition is possible. The appearance of these defects is connected with the thermal destruction of  $Pb^+$ – $WO_3$  centres. The defects responsible for the green emission of the second type can be created only in the crystals containing oxygen vacancies. The data obtained allow us to ascribe them to the  $WO_3$ -type groups. It is just the green emission of the second type that influences strongly the scintillation characteristics of the undoped crystals at room temperature.

- 2. Red emission centres of two types were found in PbWO<sub>4</sub> crystals, and their luminescence characteristics were studied at steady-state conditions (Fig. 3) as well as by the time-resolved spectroscopy methods. In some crystals the intensity of relatively slow red emission is comparable at room temperature with the intensity of blue or green emission, thus it may considerably influence the scintillation characteristics of PbWO<sub>4</sub>. Detailed comparison of luminescence characteristics of different crystals allowed the conclusion that the red emission of the first type, which is present in most of the crystals studied, arises from lead vacancies. The red emission of the second type, observed only in a PbWO<sub>4</sub>:Mo<sup>6+</sup>, Y<sup>3+</sup> crystal, was ascribed to the associates of lead vacancies with trivalent impurity ions.
- 3. For various undoped and  $Mo^{6+}$ -,  $Cd^{2+}$ -,  $Ba^{2+}$ -,  $Cr^{3+}$ -,  $Mo^{6+}$  and  $Nb^{5+}$ -, or  $Mo^{6+}$  and  $Y^{3+}$ -doped PbWO<sub>4</sub> crystals, the photostimulated creation of defects was studied under irradiation of a crystal in the exciton and in the defect-related absorption bands at T > 100 K. The formation of defects reveals itself in the appearance of the thermally stimulated luminescence



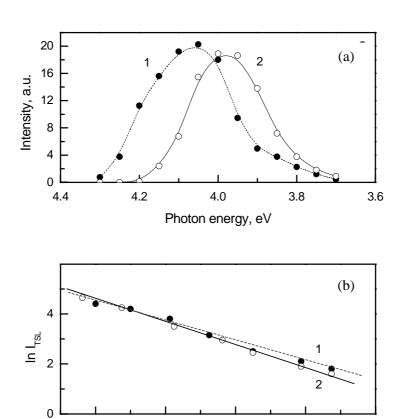
**Fig. 2.** Temperature dependence of intensity of the green emission of the first type (curve 1) and of the second type (curve 2).



**Fig. 3.** Emission (curves 1) and excitation (curves 2) spectra at 4.2 K and temperature dependences of the emission intensity (curves 3) measured for the red emission of the first type (a) and the second type (b).

(TSL), whose intensity (I) depends on the irradiation energy ( $E_{\rm irr}$ ) and temperature ( $T_{\rm irr}$ ). The defect creation spectra  $I_{\rm TSL}(E_{\rm irr})$  were measured for each TSL peak observed (see, e.g., Fig. 4a) and the activation energies ( $E_{\rm a}^{\rm def}$ ) for the defect creation processes were calculated from the  $\ln I_{\rm TSL}(1/T_{\rm irr})$  dependences (see, e.g., Fig. 4b). The values of  $E_{\rm a}^{\rm def}$  are also shown in Table 1. From these data suggestions were made on the origin of the defects responsible for the green emission of the first type, on the decomposition of exciton states and photoionization of defect states, and on the origin of the optically created defects responsible for the recombination luminescence of the crystals studied. In the PbWO<sub>4</sub>:Mo crystals studied defect-related centres of different types (with  $E_{\rm a}^{\rm def}$  varying from 0.08 to 0.35 eV) were detected.

4. For the Gd-rich phosphate glasses of the Na(K)GdCe, NaGdTb, and NaGdMn types, energy migration through the Gd<sup>3+</sup> ion sublattice and the following energy transfer from Gd<sup>3+</sup> to Ce<sup>3+</sup>, Tb<sup>3+</sup> or Mn<sup>2+</sup> impurity ions,



**Fig. 4.** (a) Defect creation spectra ( $I_{TSL}$  vs  $E_{irr}$ ) obtained at  $T_{irr}$  = 140 K and (b) dependences ln  $I_{TSL}$  vs  $1/T_{irr}$  measured for TSL peaks at 200 K (curves 1) and 225 K (curves 2) for the undoped PbWO<sub>4</sub> crystal grown by the Bridgman method and then annealed in air (2 h, 600 °C) to create oxygen vacancies.

0.0072

0.0068

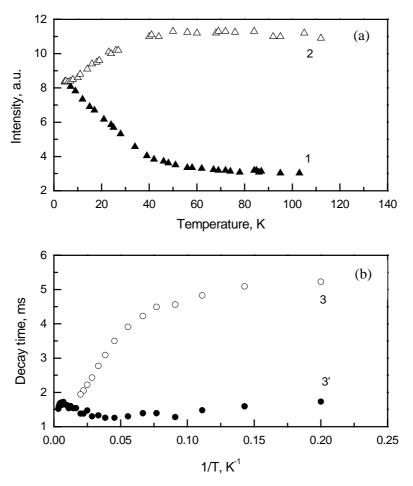
0.0076

1/T, K<sup>-1</sup>

0.0080

0.0084

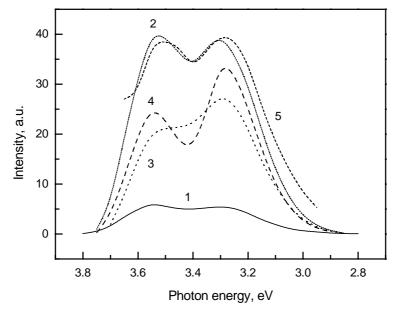
and the dependence of the efficiency of these processes on the glass composition and temperature were studied. For example, the decrease in the  $Gd^{3+}$  emission intensity accompanied with the increase in the  $Tb^{3+}$  emission intensity with the increasing temperature, observed under excitation in the  $Gd^{3+}$ -related absorption band and shown in Fig. 5a, is one of the evidences for the  $Gd^{3+} \to Tb^{3+}$  energy transfer. The appearance of two components in the  $Gd^{3+}$  emission decay and strong temperature dependence of the slower component decay time (Fig. 5b) are another evidence for this process. A significant increase (several times) in the impurity luminescence intensity was achieved for Gd-containing matrix with respect to Gd-free samples. The absolute maximum was obtained for the composition of about 30 mol%  $Gd^{3+}$  and of about 3 mol%  $Ce^{3+}$ ,  $10 \text{ mol}\%\ Tb^{3+}$ , and  $10 \text{ mol}\%\ Mn^{2+}$ . The most efficient energy transfer and



**Fig. 5.** Temperature dependences of (a) the  $Gd^{3+}$  (curve 1) and  $Tb^{3+}$  (curve 2) emission intensities and (b)  $Gd^{3+}$  emission decay times (curves 3, 3') measured for a NaGdTb phosphate glass under excitation in the  $Gd^{3+}$ -related 4.5 eV absorption band.

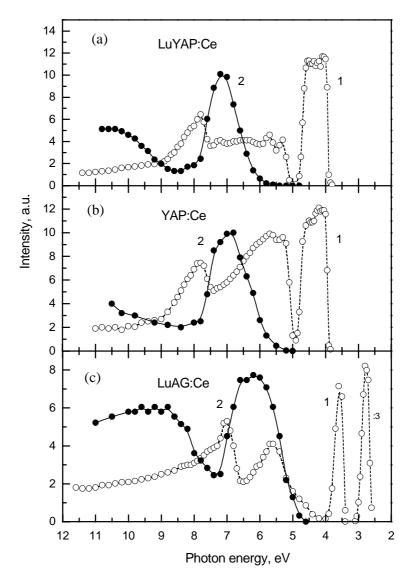
- intense fast impurity luminescence was observed for  $Ce^{3+}$ -doped glasses. In these systems, also the reverse  $Ce^{3+} \rightarrow Gd^{3+}$  transfer was detected. Conclusions were made on possible mechanisms of energy transfer in different systems studied.
- 5. For the YAP:Ce and LuYAP:Ce single crystals, the positive influence of Zr<sup>4+</sup> co-doping on luminescence yield and decay kinetics and on defect creation efficiency was observed, and optimum concentrations of Ce<sup>3+</sup> ions and Zr<sup>4+</sup> ions were found. The mechanism of this influence was clarified. It was shown that not only the excess charge of the co-doping ion but also its size is important to improve the scintillation characteristics of the material. The presence of Ce<sup>3+</sup> ions with different surroundings was observed both in YAP:Ce and LuYAP:Ce crystals. The influence of the

- co-doping  $Zr^{4+}$  ions on the luminescence characteristics and defect creation processes was found to be much stronger in LuYAP:Ce (see, e.g., Fig. 6) than in YAP:Ce. This allowed us to make a conclusion about a close location of  $Ce^{3+}$  and  $Zr^{4+}$  ions in the LuYAP:Ce crystal lattice. No clear influence of the  $Ce^{3+}$  ion surroundings on the luminescence spectra of YAG:Ce and LuAG:Ce crystals was detected.
- 6. Luminescence characteristics of undoped YAG and LuAG crystals, measured under excitation in the 6.0–11.5 eV energy range for the samples with strongly different concentrations of crystal structure defects, were quantitatively compared. It was concluded that both ultraviolet emission bands of these crystals (peaking at 4.8–4.9 eV and 3.65–3.95 eV) belong to the same centres and most probably arise from the excitons localized at the antisite (Y<sub>Al</sub><sup>3+</sup>, Lu<sub>Al</sub><sup>3+</sup>) defects. Due to the presence of these defects, the self-trapped exciton emission in the single crystals is strongly suppressed. In Ce<sup>3+</sup>-doped garnets, the antisite defects compete with Ce<sup>3+</sup> centres in the energy transfer processes. It was concluded that for the improvement of scintillation characteristics of YAG:Ce and LuAG:Ce crystals, the antisite defects should be removed. The most effective way for that is the preparation of thin crystalline films from these materials.



**Fig. 6.** Emission spectra of LuYAP:Ce crystals co-doped with 1000 ppm (curve 1), 300 ppm (curve 2), 100 ppm (curve 3), and 0 ppm (curve 4)  $ZrO_2$ , measured at the same conditions under 4.05 eV excitation. Curve 5 is measured for the LuYAP:Ce 300 ppm  $ZrO_2$  sample under 3.8 eV excitation. T = 4.2 K.

7. In the Ce<sup>3+</sup>-doped yttrium aluminium and lutetium aluminium perovskites and garnets, the creation of defects was observed not only under irradiation in the band-to-band transitions region, but also in the Ce<sup>3+</sup>-related absorption bands (see, e.g., Fig. 7). Defect creation by the vacuum ultraviolet radiation can be caused by the photoionization of the 6s <sup>2</sup>S<sub>1/2</sub> excited state of the Ce<sup>3+</sup> ion or by the photostimulated transfer of an electron from the Ce<sup>3+</sup>-perturbed oxygen state to an oxygen vacancy and the following trapping of the produced mobile hole by a Ce<sup>3+</sup> ion. The



**Fig. 7.** Excitation (curve 1) and defect creation (curve 2) spectra of LuYAP:Ce (a), YAP:Ce (b), and LuAG:Ce (c) crystals at 80 K. Emission energy  $E_{\rm em} = 3.3$  eV (a, b) and 2.8 eV (c).

tunnelling recombination of the electrons from oxygen vacancies with the Ce<sup>4+</sup> centres results in the appearance of the Ce<sup>3+</sup> luminescence. It was concluded that to decrease the role of the undesirable slow recombination processes, the concentration of oxygen vacancies should be decreased by introduction of suitable co-doping ions (e.g., Zr<sup>4+</sup> ions) into the crystal.

# **ACKNOWLEDGEMENTS**

The work was supported by the NATO Science for Peace Project No. 973510 "SfP-Scintillators" and the Estonian Science Foundation project No. 5045.

# REFERENCES

- Nikl, M., Mares, J. A., Mihokova, E., Nitsch, K., Solovieva, N., Babin, V., Krasnikov, A., Zazubovich, S., Martini, M., Vedda, A., Fabeni, P., Pazzi, G. P. and Baccaro, S. Radio- and thermoluminescence and energy transfer processes in Ce<sup>3+</sup>(Tb<sup>3+</sup>)-doped phosphate scintillating glasses. *Radiat. Meas.*, 2001, 33, 593–596.
- 2. Mares, J. A., Nikl, M., Nitsch, K., Solovieva, N., Krasnikov, A. and Zazubovich, S. A role of Gd<sup>3+</sup> in Tb-doped Na-Gd phosphate glasses. *J. Lumin.*, 2001, **94–95**, 321–324.
- Pazzi, G. P., Fabeni, P., Susini, C., Nikl, M., Mihokova, E., Solovieva, N., Nitsch, K., Martini, M., Vedda, A., Baccaro, S., Cecilia, A. and Babin, V. Defect states induced by UV-laser irradiation in scintillating glasses. *Nucl. Instrum. Methods Phys. Res. B*, 2002, 191, 366–370.
- Nikl, M., Mares, J. A., Chval, J., Mihokova, E., Solovieva, N., Martini, M., Vedda, A., Blazek, K., Maly, P., Nejezchleb, K., Fabeni, P., Pazzi, G. P., Babin, V., Kalder, K., Krasnikov, A., Zazubovich, S. and D'Ambrosio, C. An effect of Zr<sup>4+</sup> co-doping of YAP: Ce scintillator. *Nucl. Instrum. Methods Phys. Res. A*, 2002, 486, 250–253.
- Mihokova, E., Nikl, M., Bohacek, P., Babin, V., Krasnikov, A., Stolovits, A., Zazubovich, S., Vedda, A., Martini, M. and Grabowski, T. Decay kinetics of the green emission in PbWO<sub>4</sub>: Mo. J. Lumin., 2003, 102–103, 618–622.
- Babin, V., Krasnikov, A., Mares, J. A., Nikl, M., Nitsch, K., Solovieva, N. and Zazubovich, S. Luminescence spectroscopy of the Gd-rich Ce<sup>3+</sup>-, Tb<sup>3+</sup>- and Mn<sup>2+</sup>-doped phosphate glasses. *Phys. Stat. Sol.* (a), 2003, 196, 484–495.
- Nikl, M., Bohacek, P., Mihokova, E., Babin, V., Stolovits, A., Krasnikov, A., Zazubovich, S., Pazzi, G. P., Fabeni, P., Vedda, A. and Martini, M. Excited state dynamics of luminescence centres in PbWO<sub>4</sub> single crystals. *Functional Materials*, 2003, 10, 105–110.
- Krasnikov, A., Savikhina, T., Zazubovich, S., Nikl, M., Mares, J. A., Blazek, K. and Nejezchleb, K. Luminescence and defects creation in Ce<sup>3+</sup>-doped aluminium and lutetium perovskites and garnets. *Nucl. Instrum. Methods Phys. Res. A*, 2004 (accepted).
- Bohacek, P., Ishii, M., Kiisk, V., Krasnikov, A., Nikl, M., Sildos, I., Usuki, Y. and Zazubovich, S. Red emission of PbWO<sub>4</sub> crystals. *Radiat. Meas.*, 2004, 38, 623–626.
- Babin, V., Bohacek, P., Krasnikov, A., Mihokova, E., Nikl, M., Stolovits, A., Usuki, Y. and Zazubovich, S. Decay kinetics of the green emission in tungstates and molybdates. *Radiat. Meas.*, 2004, 38, 533–537.
- Blazek, K., Krasnikov, A., Nejezchleb, K., Nikl, M., Savikhina, T. and Zazubovich, S. Luminescence and defects creation in Ce<sup>3+</sup>-doped Lu<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> crystals. *Phys. Stat. Sol. (b)*, 2004, 241, 1134–1140.
- 12. Di Martino, D., Krasnikov, A., Nikl, M., Vedda, A. and Zazubovich, S. The 3.83 eV luminescence of Gd-enriched phosphate glasses. *Phys. Stat. Sol.* (a), 2004, **201**, R38–R40.

13. Babin, V., Krasnikov, A., Nikl, M., Savikhina, T., Voloshinovskii, A. and Zazubovich, S. Luminescence of undoped LuAG and YAG crystals. *Phys. Stat. Sol. (c)* (accepted).

# Uued stsintillatsioonimaterjalid teaduslikeks, meditsiinilisteks ning tööstuslikeks rakendusteks

# Svetlana Zazubovitš

Artikkel sisaldab infot NATO projekti "Science for Peace" kohta, mis oli pühendatud mõnede uute ja/või parendatud karakteristikutega stsintillatsiooni materjalide otsimisele ja uurimisele. Lühidalt on kirjeldatud selle töö tähtsamad tulemused, mis saadi 2000.–2003. a. Tartu Ülikooli Füüsika Instituudis koostöös kolleegidega Itaaliast ja Tšehhi Vabariigist mitteaktiveeritud ning ioonidega Mo<sup>6+</sup>, Cr<sup>3+</sup>, Cd<sup>2+</sup>, Ba<sup>2+</sup>, Mo<sup>6+</sup> ja Y<sup>3+</sup> ning Mo<sup>6+</sup> ja Nb<sup>5+</sup> aktiveeritud pliivolframaatkristallide, mitteaktiveeritud ning Ce<sup>3+</sup>-ioonidega aktiveeritud ütriumalumiiniumperovskiit-, ütrium-luteetsium-alumiiniumperovskiit-, ütrium-alumiiniumgranaat- ja luteetsium-alumiiniumgranaatkristallide ning Ce<sup>3+</sup>-, Tb<sup>3+</sup>-, Mn<sup>2+</sup>-ioonidega aktiveeritud gadoliiniumirikaste fosfaatklaaside uurimisel.