Nuclear Instruments and Methods in Physics Research A 486 (2002) 278–282

NUCLEAR
INSTRUMENTS
& METHODS
IN PHYSICS
RESEARCH
Section A

www.elsevier.com/locate/nima

Charge-transfer luminescence and spectroscopic properties of Yb^{3+} in aluminium and gallium garnets

N. Guerassimova[a,b,*], C. Dujardin[a], N. Garnier[a], C. Pédrini[a], A.G. Petrosyan[a,c], I.A. Kamenskikh[b], V.V. Mikhailin[b], I.N. Shpinkov[b], D.A. Spassky[b], K.L. Ovanesyan[c], G.O. Shirinyan[c], R. Chipaux[d], M. Cribier[d], J. Mallet[d], J.-P. Meyer[d]

[a] *LPCML, UCB Lyon 1, UMR 5620 CNRS, Domaine Scientifique de La Doua, Villeurbanne 69622, France*
[b] *Physics Department, Synchrotron Radiation Laboratory, Faculty of Physics, Moscow State University, Moscow 11989, Russia*
[c] *Institute for Physical Research, Armenian National Academy of Science, Ashtarak-2 378410, Armenia*
[d] *Commisariat à l'Énergie Atomique, DSM/DAPNIA, CE-Saclay, 91191 Gif sur Yvette, France*

Abstract

Luminescence of Yb^{3+} from the charge-transfer state with broad emission bands and short radiative lifetimes (few to tens of nanoseconds depending on the host lattice and the temperature) is attractive for the development of fast scintillators capable of discriminating very short events. The most important currently considered application is that in solar neutrino (ν_e) real-time spectroscopy, since the ν_e capture by ^{176}Yb is followed by a specific emission signature which can accordingly excite the Yb^{3+} fluorescence. Studies on scintillation and luminescence in aluminium garnets containing Yb^{3+} have shown that these materials meet some of the required properties for such scintillators.

In defining our priorities, the best compromise between host crystal, Yb^{3+} concentration, production method, post-growth treatment and performance is to be considered based on the studies of charge-transfer luminescence and quenching mechanisms. The experiments have been extended to a large number of compounds: YAG:Yb–YbAG, YGG:Yb–YbGG, YAP:Yb–YbAP, $LaYbO_3$ in the form of single crystals and/or powders. In garnets, the temperature-dependent fluorescence intensity and decay time under X-ray and VUV excitations decrease at low temperatures ($T < 100\,K$) and demonstrate the important role played by the traps. The thermoluminescence peaks show a strong dependence on the crystal history, composition and impurities introduced intentionally. The fluorescence intensity and decay time are also dependent on Yb^{3+} concentration and the presence of Yb^{2+}. The results trace the major directions to optimised scintillators in terms of their efficiency and lifetime. © 2002 Published by Elsevier Science B.V.

PACS: 72.20.Jv; 78.60.Ya

Keywords: Yb^{3+}; Garnets; Charge transfer; Trapping effects

1. Introduction

An increasing interest to the fast luminescence of Yb-containing compounds is connected with possibility of their application to low-energy

---

*Corresponding author. Physics Department, Synchrotron Radiation Laboratory, Faculty of Physics, Moscow State University, Moscow 119899, Russia. Tel.: +7-095-939-3169; fax: +7-095-939-2991.

E-mail address: nvg@opts.phys.msu.su (N. Guerassimova).

0168-9002/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0168-9002(02)00718-0

neutrino (ν_e) detection based on the reaction of ν_e with ^{176}Yb [1]:

$$\nu_e + {}^{176}\mathrm{Yb} \rightarrow {}^{176}\mathrm{Lu}^* + e^- \quad (Q = 301\,\mathrm{keV}),$$
$$^{176}\mathrm{Lu}^* \rightarrow {}^{176}\mathrm{Lu} + \gamma \quad (E_\gamma = 72\,\mathrm{keV}).$$

A prompt electron plus a delayed γ-signal is the signature of neutrino event. A delayed coincidence within 50 ns is required to have good discrimination power against background noise. Thus, requirements for such a crystal are high Yb concentration, fast time response, and large light yield.

The charge-transfer luminescence (CTL) of Yb^{3+} because of its short radiative lifetimes (few to tens of nanoseconds depending on the host lattice and the temperature) is attractive for the development of fast scintillators capable of discriminating very short events. Among a large variety of Yb^{3+}-doped crystals, the CTL of YAG:Yb exhibits the most short fluorescence decays [2]. Studies on scintillation [3] and luminescence [4] in aluminium garnets containing Yb^{3+} have confirmed that these materials meet some of the required properties for such scintillators.

2. Experimental

The YAG:Yb–YbAG and YAP:Yb crystals (except YAG:Yb 15%) were grown by the Bridgman method under inert/reducing atmosphere and using molybdenum crucibles. Thermal annealing at 1200°C in air has been applied to stimulate $Yb^{2+} \rightarrow Yb^{3+}$ transitions and to remove the crystal colour. YAG:Yb 15% was grown using the Czochralski method.

Excitation and reflection spectra and decay profiles under VUV excitation were measured at the Superlumi station, Desy, Hamburg [5]. The experimental details for luminescence, thermoluminescence and decay measurements under X-ray excitation can be found in Ref. [4]. The light yield was determined as an integrated intensity of charge-transfer (CT) luminescence measured under X-ray excitation on powder samples placed in the same fixed position.

3. Results and discussion

The CT luminescence of Yb^{3+} in YAG shows two broad emission bands with maxima near 335 and 485 nm due to transitions from the charge-transfer state (CTS) to $^2F_{7/2}$ and $^2F_{5/2}$ states of Yb^{3+}.

Figs. 1 and 2 show decay profiles of CT-emission in Yb-containing aluminium garnets. Under 210 nm exitation (direct excitation of Yb^{3+} to CTS) the profiles exhibit nearly exponential shape with initial rapid part (Fig. 1); the input of this rapid part increases with Yb concentration. The energy transfer between Yb-ions may be responsible for the observed shapes of decay profiles. The interband excitation when the host lattice absorbs the excitation energy (110 nm, 65 nm, X-ray excitation) leads to non-exponential decay profiles and a long component appears (Fig. 2).

The temperature dependencies of CT-emission-integrated intensity and of CT-emission decay time under 210 nm excitation are of the same shape and demonstrate a classical thermal quenching

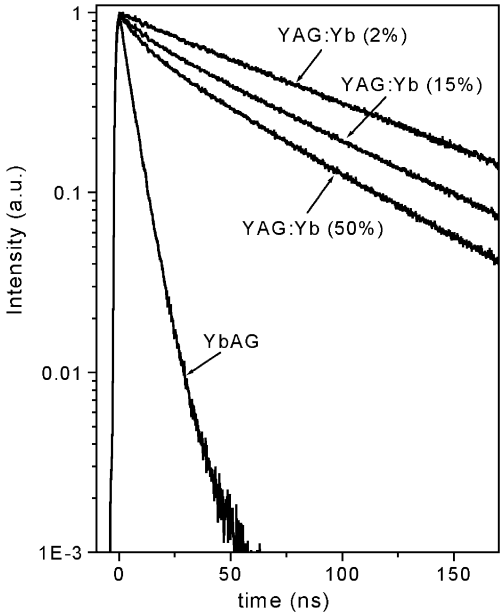

Fig. 1. Decay profiles of YAG:Yb CT-emission after 210 nm excitation at 12 K.

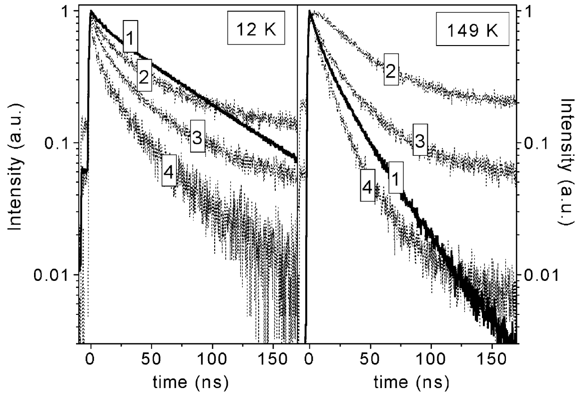

Fig. 2. Decay profiles of YAG:Yb (15%) CT-emission after: 210 nm (1), 110 nm (2), 65 nm (3) and X-ray (4) excitations.

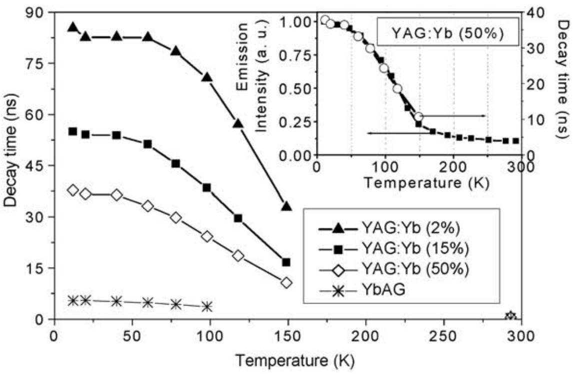

Fig. 3. Temperature dependencies of CT-emission decay time and of CT-emission-integrated intensity (insertion) under 210 nm excitation.

behaviour reflecting the increase of non-radiative transitions to the ground state with temperature (Fig. 3). Under interband excitation the temperature dependencies of CT-emission-integrated intensity and of CT-emission decay time are quite different as compared to those under direct excitation to CTS: X-ray excitation leads to decrease of intensity and of decay time with temperature decrease in the range below 150 K (Fig. 4a and b). This behaviour indicates the occurrence of an additional source of quenching at low temperatures.

The thermoluminescence measurements under X-ray excitation (Fig. 4c) show the presence of a

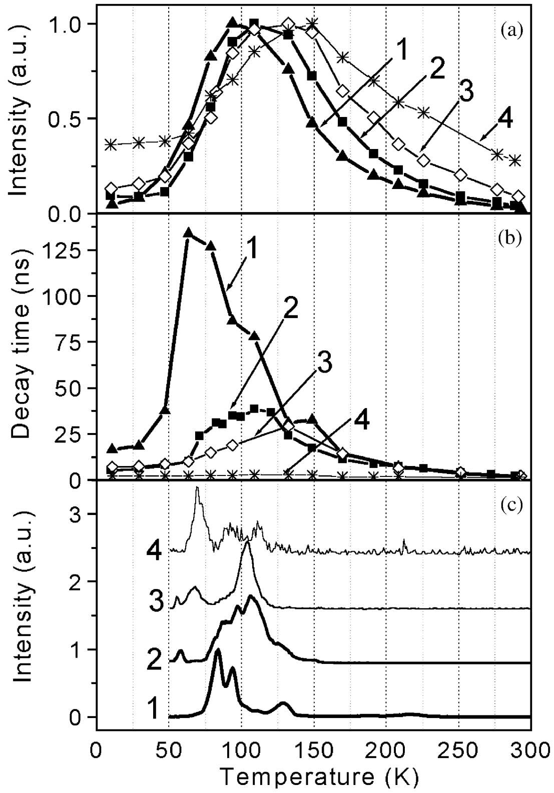

Fig. 4. Temperature dependencies of CT-emission-integrated intensity (a) and of CT-emission decay time (b), and thermoluminescence (c) under X-ray excitation of YAG:Yb 2% (1), YAG:Yb 10% (2), YAG:Yb 50% (3), YbAG (4).

number of glow peaks in the temperature region below 150 K indicating the presence of traps. X-ray excitation creates electrons and holes which can excite Yb^{3+} centres through sequential capture of electrons and holes, but also can be trapped causing strong quenching below 150 K. The UV excitation with energy less than the band gap cannot produce electrons and holes. The Yb^{3+} centres are directly excited and traps do not play any role in the fluorescence quenching process. Appearance of a long component in decay profiles under excitations with energies higher than the band gap (110 nm, 65 nm, X-ray excitation) is also due to the trapping effect. This slow emission results from thermally stimulated release of trapped carriers with subsequent retrapping and emission at luminescence centres.

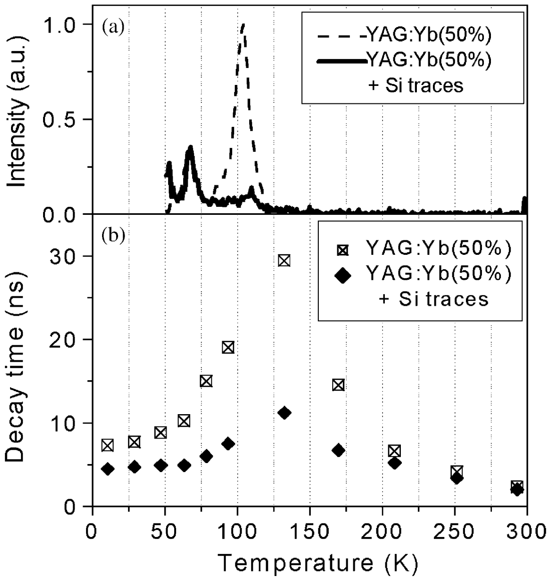

Fig. 5. Thermoluminescence (a) and CT-emission decay time (b) of YAG:Yb (50%) and YAG:Yb (50%) + Si traces, after X-ray excitation.

Table 1
Light yield of Yb-containing compounds at 300 K

Sample	Light yield (% BGO)
YAG:Yb (2%)	0.094
YAG:Yb (10%)	0.125
YAG:Yb (15%)	0.127
YAG:Yb (50%)	0.054
YbAG	0.044
YAP:Yb (8%)	0.073
$LaYbO_3$	0.016
$Y_3Ga_5O_{12}$:Yb (2%)	0.248
$Y_3Ga_5O_{12}$:Yb (15%)	0.045
$Yb_3Ga_5O_{12}$	0.055

One of the steps we have done to optimize scintillators in terms of their efficiency and lifetime is the introduction of Si into YAG:Yb which leads to the redistribution in structure and population of the electron levels in the forbidden band. As a result the thermoluminescence peak around 100 K is suppressed for the sample with Si and decay time in this temperature range is significantly lower than that for samples grown without Si (Fig. 5).

We have compared the light yield of a number of Yb-containing compounds: YAG:Yb–YbAG, YGG:Yb–YbGG, YAP:Yb, $LaYbO_3$ at 300 K (Table 1). For the YAG:Yb–YbAG crystals, the light yield at 300 K as a function of Yb concentration is maximal at around 15% Yb. Among all the investigated systems the low-concentrated gallium garnet $Y_3Ga_5O_{12}$:Yb (2%) shows the highest value of light yield (twice higher than the most efficient Yb-doped aluminium garnet).

4. Conclusions

The charge-transfer fluorescence in Yb-containing garnets is strongly temperature dependent. The CT-fluoresence in YAG:Yb is significantly quenched at room temperature. In addition, under VUV and X-ray excitations the quenching due to the trapping effect occurs at low temperatures. Intentionally, added impurities, such as Si, are capable of modifying crystal properties. Concentration quenching in YAG:Yb is observed above 15–20 at% Yb. Thus, YAG doped with 20–30% Yb cooled to 100–120 K seems to be a promising material for neutrino detection. Another system of interest for further investigations is Yb-doped gallium garnet which shows at room temperature and low Yb concentrations a more efficient fluorescence as compared to YAG:Yb.

Acknowledgements

The present work has been motivated by the LENS (Low-Energy Neutrino Spectroscopy) project and was performed within the framework of the Crystal Clear Collaboration, CERN Research and Development Project RD-18. The work was partly supported by CEA Saclay (DAPNIA). The support of grants Deutsche Forschungsgemeinschaft DFG No 436 RUS 113/437 and YSF 00-35 (N.G.) are acknowledged. The authors are also grateful to Pr. J.-F. Cavaignac from ISN-Grenoble and Dr. B. Ferrand from LETI-Grenoble for supplying one of the samples investigated.

References

[1] R.S. Raghavan, Phys. Rev. Lett. 78 (1997) 3618.

[2] L. van Pieterson, M. Heeroma, E. de Heer, A. Meijerink, J. Lumin. 91 (2000) 177.

[3] G. Bressi, G. Carugno, E. Conti, C. Del Noce, D. Iannuzzi, Nucl. Instr. and Meth. A 461 (2001) 361; P. Antonini, G. Bressi, G. Carugno, D. Iannuzzi, Nucl. Instr. and Meth. A 460 (2001) 469.

[4] N. Guerassimova, N. Garnier, C. Dujardin, A.G. Petrosyan, C. Pédrini, Chem. Phys. Lett. 339 (2001) 197.

[5] G. Zimmerer, Nucl. Instr. and Meth. A 308 (1991) 178.