

ANNUAL PROGRESS REPORT

for the

US Department of Energy

SCINTILLATION MATERIALS FOR MEDICAL APPLICATIONS

Grant no: DE-FG02-90ER61033

January 1, 1991 to December 31, 1992

A.Lempicki and A.J.Wojtowicz

TABLE OF CONTENTS

1. INTRODUCTION 2

2. ACCOMPLISHMENTS 2

 2.1. Studies of physical processes 3

 2.2. Development of methodology 4

 2.3. Search for new materials 4

 2.4. Academic accomplishments 5

3. FUTURE WORK 5

4. BIBLIOGRAPHY 6

5. APPENDICES 7

 Appendix A.

 "Scintillation Mechanism in $Ce_xLa_{1-x}F_3$ Monocrystals",
 submitted to *Phys. Rev.* 7

 Appendix B.

 "Stoichiometric cerium compounds as scintillators
 part II: CeP_5O_{14} " accepted for publication in
 IEEE Trans. Nucl. Sci. 8

 Appendix C.

 "Scintillation mechanism in stoichiometric cerium compounds",
 to be published in the *Workshop Proceedings, International
 workshop on heavy scintillators for scientific and industrial
 applications, Chamonix, France, Sept. 22-26, 1992.* 15

 Appendix D.

 "*Cerium-Doped Orthophosphates: New Promising
 Scintillators*", to be published in the *Conference
 Record of the 1992 IEEE Nuclear Science Symposium
 and Medical Imaging Conference, Oct.27-31, 1992,
 Orlando, Florida USA.* 20

Reprints
+
Preprints
Removed

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

eb

1. INTRODUCTION.

When we started this Program three years ago, scintillators were beginning to attract a renewed attention after a long period of stagnation, because of two developments. First there was the realization that the modern High Energy Physics accelerators were placing unprecedented demands of quantity and quality of detector materials. Secondly Positron Emission Tomography, (PET), was entering the medical field with a great, albeit not yet fully realized promise as a research tool and eventually superior diagnostic method. Both applications required materials for scintillator detectors with properties beyond those delivered by traditional scintillators. Thallium doped halides were very efficient, but slow and chemically unstable, [1]. Plastic scintillators were very fast but limited in stopping power for high energy gammas. A very significant addition was the inorganic crystal, BGO, which had remarkable stopping power, but was still limited in speed, [2]. At about the time we entered the field, there were two modern developments, namely the very fast BaF_2 , which owed its success to the newly discovered crossover transitions, [3], and CeF_3 , which carried a promise of "fast components", more practical wavelengths and attractive, if not supreme efficiency, [4]. The juxtaposition of the Old and the New, carried a certain aura of excitement, characteristic of a field of somewhat haphazard physics in which discoveries were often accidental. It became therefore our stated goal to organize this field, based on experience in Solid State Physics and Luminescence. Taking a cue from whatever was known, we came to the conclusion that in order to arrive at scintillators which may, one day, approach a theoretical maximum performance, one has to:

- * Limit the research to inorganic crystals;
- * Consider only optically allowed transitions;
- * Maximize the conversion of deposited energy into light.

Our reasoning was transparently clear: traditional scintillators (Tl doped halides) are very efficient, and could be even more efficient at larger concentrations of Tl, if it were not for the unfortunate circumstance of concentration quenching. However Tl transitions are spin forbidden and slow. Both ills could be remedied by replacing Tl with Ce, whose transitions are allowed and which is known to form fully concentrated compounds of high photoluminescent efficiency and no quenching. These materials, plus new Ce-doped materials, exhibiting highly promising properties for medical applications, became the target of our Program, "Scintillator materials for medical applications", under the grant no: DE-FG02-90ER61033.

2. ACCOMPLISHMENTS

This report covers the third year of our work in the Program. The three main goals of the Program were specified as follows:

- 1). Determination of physical processes involved in the scintillation effect,
- 2). Development of methodology to evaluate the physical limitations of potential scintillation materials,
- 3). Search for new materials with PET as a prime target.

We have concentrated on the following Ce-activated materials:

- A) Ce-La-trifluorides
- B) Ce-La-pentaphosphates
- C) Ce-doped, RE-based orthophosphates, (RE = Y, La, Lu, Yb, Gd).

2.1. Determination of physical processes

Under this goal our efforts have concentrated on optical and ionizing radiation spectroscopy and included luminescence, luminescence excitation, transmission, time resolved luminescence spectra, decays, light output measurements, and temperature dependences of all the above. The interpretation of these experiments has characterized some interactions important for the performance of studied materials:

1. electronic interactions in Ce^{3+} ion,
 2. electron-phonon coupling,
 3. interactions between "regular" and "perturbed" Ce in Ce-La-trifluorides,
 4. radiation trapping in Ce-La-pentaphosphates and trifluorides,
 5. lattice - Ce^{3+} ion energy transfer,
 6. energy migration in Ce-La-pentaphosphates and trifluorides,
- 1.2 The splittings and positions of d- and f-levels, as well as their coupling to the lattice, determine the positions and widths of absorption and emission bands. Large d-splittings cause a shift of emission to the red (at the same time, unfortunately, increasing the radiative lifetime through the Lorentz correction for the local field). We were thus able to explain the differences in radiative lifetimes between different Ce-emissions, [5]. We have analyzed oscillator strengths of transitions between different Kramers' doublets in absorption and emission, which determine the measured decay times, [5]. An electron-phonon interaction, as described by the Huang-Rhys parameter S , strongly influences the values of appropriate overlap integrals, [5], important for various processes to be discussed briefly in 3, 4 and 5.
- 3 The interactions between regular and perturbed Ce ions in Ce-La-trifluorides determine the spectroscopy of those materials. An efficient energy transfer between unperturbed and perturbed Ce ions has a strong influence on decays and luminescence spectra. We were first to explain the origin of the ultrafast component in the decay of the Ce-emission and the long risetime observed for the perturbed Ce emission in Ce-La-trifluorides, [6,7]. Using the Inokuti-Hirayama model of the D-A energy transfer and our calculations of D-A transfer rates, we were able to estimate the concentrations of perturbed Ce ions and suggest fluorine vacancies as an explanation of the origin of the perturbing species, [5].
- 4 Strong overlaps between absorption and emission bands of regular Ce ions in Ce-La-pentaphosphates are responsible for radiation trapping, which distorts emission spectra and prolongs observed decay times, [8]. None of those effects were observed in fluorides. Our calculations of overlap integrals are consistent with these experimental observations, [5].
- 5 An efficient lattice-to-ion energy transfer provides a mechanism to create a characteristic volume, (CV), important for the high light output under ionizing radiation excitation, [9]. This problem and our contributions to its solution are discussed in appendices.
- 6 Contrary to some published opinions, [10], we excluded an energy migration between Ce ions. Our experimental observations, including the ultrafast component in Ce trifluoride as well as lack of observable concentration quenching in the two stoichiometric materials, prove that there is no fast energy migration among Ce ions. This conclusion has been confirmed by our calculations which clearly indicate that transfer rates among Ce ions are insignificant on the time scale of their radiative lifetimes, [5].

2.2. Development of methodology

We have made a significant contribution towards a development of methodology for dealing with known and future scintillators. This methodology is based on an analysis of the scintillation process in the given material. Here we summarize briefly the steps in the scintillation process and material constants important for their optimization:

1. Conversion step. Efficiency β can be estimated using van Roosbroeck and Robbins procedure, [11,12]. It depends on dielectric constants, phonon frequencies and the bandgap energy. We have calculated β for all materials we have studied.
2. Transfer step. This is the step which has been most neglected and which we recognized as the most important remaining problem. Some of the understanding we have reached is presently at a phenomenological level. In particular, overlap integrals, involving excitonic emission and Ce absorption should be helpful in determining the efficiency S of this step. The significance of the localization process of excitons needs some clarification: On one hand the lack of significant lattice relaxation would increase mobilities of excitons and/or holes thus increasing the CV through excitonic diffusion and/or hole capture. On the other hand this would also increase a non-radiative excitonic and/or electron-hole recombination and increase the contribution of the slow and trap-dependent scintillation mechanism based on electrons and holes. For good scintillators some compromise in the amount of lattice relaxation is therefore necessary. The amount of this relaxation may prove to be the key factor determining the performance of Ce-based scintillators. The proof of this hypothesis and a quantitative formulation of material requirements belong to the new program proposed in the Renewal Proposal, submitted with this Report.
3. Emission step. This step is characterized by a quantum efficiency Q of the luminescence center. A temperature dependence of the decay time provides the simplest way to quickly evaluate this parameter. We have used this to characterize Q for all materials studied.

Using this methodology we have analyzed all the materials studied in our previous program. In particular we have studied the problem of CeF_3 in great detail, [5]. Based on all available experimental information and given the present properties of the Optovac-grown crystals, we conclude that the light output of this material, (some 3000 photons/MeV), is not likely to be improved. This is because, in our judgement, the transfer step in this material is limited to direct excitation of Ce ions, all other more efficient processes are not operational. This makes CeF_3 a rather unique and extreme case. However, since this important conclusion is based on reasoning that is not yet completely verified, this material will be the subject of further studies.

2.3. Search for new materials

While pursuing the goals driven by fundamental problems and questions in the area of scintillators (briefly described above), we also have been actively looking for new materials to fulfill our promise of targeting medical applications. In this area we claim a discovery of a new scintillator material, Ce:LuPO_4 , cerium doped lutetium orthophosphate, which is reasonably dense (6.53 g/cc), fast (25 ns), and efficient (17,200 photons per MeV), [9]. The figure of merit for this material, defined as a number of photons per ns per MeV is about 700 photons/ns/MeV, which compares favorably with that for BGO (about 27). Despite some difference in density we do not expect too much loss in spatial resolution while the improvement in timing should be enormous, thus responding to basic needs expressed by designers of the new generation of PET cameras. In Table I we compare some of important parameters of Ce:LuPO_4 and BGO.

TABLE I Comparison of Ce:LuPO₄ (LOP) and Bi₄Ge₃O₁₂ (BGO).

Material	wave-length nm	dec. time ns	light output ph/MeV	density g/cc	ref. index	att. length cm	fig. of merit ph/MeV/ns
BGO	480	300	8200	7.13	2.15	1.10	27
LOP	360	25	17,200	6.53	1.7	1.43	680

In order to obtain an authoritative statement on the applicability of LOP to the technology of PET, we have asked C. Burnham of MGH to provide an assessment. This is what he says:

"In comparison to BGO, LOP has great advantages for PET. LOP's short decay time is of particular advantage to reduce dead time and to a lesser extent to minimize coincidence resolving time. When using a position sensitive detector the short dead time is very important in extending the count rate capability. The light output of 2.2 times BGO is useful to increase the resolution of position sensitive detectors. The 360 nm peak wavelength is getting close to the UV for some PMT's. The low refractive index will be of benefit in coupling the light from the detector, for example, to fiber optics. The stopping power is a little less than that of BGO but better than GSO and CeF₃. The calculated spatial resolution is close to that of BGO.

LOP is a great advance, however a comparison must be made to LSO with greater light output and similar characteristics".

We can only add to these remarks that LOP is twice as fast as LSO with the result that in terms of photons/ns/MeV, the two are equivalent. What will probably make the biggest difference is the availability and cost. At the present time we are investigating the possibilities of growing larger crystals and are looking for crystal growers who would be willing to undertake this problem on a commercial scale.

2.4. Academic accomplishments

Contribution to education of the new generation of scientists and engineers in the key areas of modern technology is a high priority goal of the university based research programs funded by the Department of Energy. We report that a graduate student supported by this grant, Edward Berman, was awarded a PhD for a thesis entitled "Stoichiometric Cerium Compounds as Scintillators for High Rate Gamma Counters" in May 1992. Although this Program did not provide for support of more graduate students we have engaged a second graduate student, Marcin Balcerzyk, whose support comes from the different source but who will graduate in the area covered by it. We expect this to happen in the next few months. Thus two new PhDs will be awarded under the Program.

During the third year of this Program we have written four papers (included in this report), some of which were also presented at conferences in the USA and Europe.

3. FUTURE WORK

This annual performance report is submitted with a Renewal Proposal, accompanying this report. It covers extensively the plan for continuation and extension of this work.

4. BIBLIOGRAPHY

- [1]. R.Hofstadter, Phys. Rev. 74, 100 (1948).
- [2]. M.J.Weber and R.R.Monchamp, "Luminescence of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$: Spectral and Decay Properties", J. Appl. Phys., 44, 5495 (1973).
- [3]. M.Laval, M.Moszynski, R.Allemand, E.Cormoreche, P.Guinet, R.Odru, J.Vacher, "Barium fluoride – inorganic scintillator for subnanosecond timing", Nucl. Instr. and Meth., 206, 169 (1983).
- [4]. D.F.Anderson, "Properties of the high density scintillator cerium fluoride" IEEE Trans. Nucl. Sci. NS-36, 137 (1989); W.W.Moses S.E.Derenzo, "Cerium fluoride, a new, fast, heavy scintillator", IEEE Trans. Nucl. Sci. NS-36, 173 (1989); D.F.Anderson, "Cerium fluoride: a scintillator for high-rate applications", Nucl. Instr. and Meth., A287, 606 (1990).
- [5]. A.J.Wojtowicz, M.Balcerzyk, E.Berman and A.Lempicki, "Scintillation Mechanism in $\text{Ce}_x\text{La}_{1-x}\text{F}_3$ Monocrystals", submitted to Phys. Rev.
- [6]. A.J.Wojtowicz, E.Berman, Cz.Koepke and A.Lempicki, "Stoichiometric Cerium Compounds as Scintillators part I: CeF_3 ", IEEE Trans. Nucl. Sci., 39, 494 (1992).
- [7]. A.J.Wojtowicz, E.Berman, Cz.Koepke and A.Lempicki, "Cerium compounds as scintillators", Conference Record of the 1991 IEEE Nuclear Science Symposium and Medical Imaging Conference", Nov.2–9, 1991, Santa Fe, New Mexico USA.
- [8]. A.J.Wojtowicz, E.Berman and A.Lempicki, "Stoichiometric Cerium Compounds as Scintillators part II: $\text{CeP}_5\text{O}_{14}$ " IEEE Trans. Nucl. Sci., accepted for publication.
- [9]. A.Lempicki, E.Berman, A.J.Wojtowicz, and M.Balcerzyk, "Cerium-Doped Orthophosphates: New Promising Scintillators", Conference Record, 1992 IEEE Nuclear Science Symposium and Medical Imaging Conference, Oct.27–31, 1992, Orlando, Florida USA; an extended version submitted to IEEE Trans. Nucl. Sci.
- [10]. C.Pedrini, B.Moinet, J.C.Gacon and B.Jacquier, "One- and two-photon spectroscopy of Ce^{3+} ions in $\text{LaF}_3\text{--CeF}_3$ mixed crystals", J. Phys: Condens. Matter 4, 5461 (1992).
- [11]. D.J.Robbins, "On Predicting the Maximum Efficiency of Phosphor Systems Excited by Ionizing Radiation", J. Electrochem. Soc., 127, 2694 (1980).
- [12]. W. van Roosbroeck, "Theory of the Yield and Fano Factor of Electron-Hole Pairs Generated in Semiconductors by High-Energy Particles", Phys. Rev., A139, 1702 (1965).

END

**DATE
FILMED**

7 / 15 / 93

