Synthesis of Glass Hybrid and Organic-inorganic Hybrid Scintillation Materials with a Sol-Gel Technique

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Synthesis of Glass Hybrid and Organic-inorganic Hybrid Scintillation Materials with a Sol-gel Technique

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Introduction:

A scintillator is a material able to convert energy of absorbed ionizing radiation into a number of photons of much lower energy in the visible or near visible frequency range; these photons can be easily detected using devices such as photomultipliers. Presently, the scintillation materials with high scintillation light output, high detection efficiency are greatly required. Among the various ionizing radiation, gamma-ray, high-energy X-ray and neutron are selected as the research target in our research.

For gamma-ray detection, rare earth-doped inorganic scintillators have been widely applied due to maintaining the high *Z*-value of the constituents. However, the limitations of conventional scintillation materials include their low rare earth (RE) concentration, inhomogeneous distribution of RE ions, and high manufacturing cost. These limitations have restricted their scintillation properties.

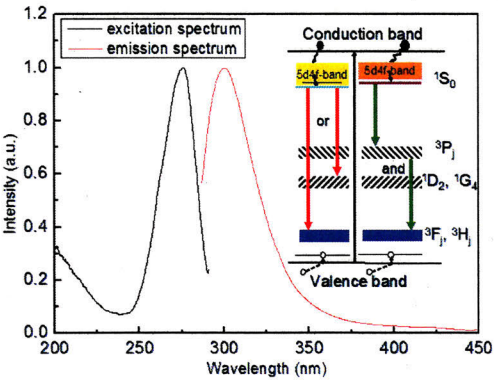

Fig. 1. Room-temperature PL and excitation spectrum of a Pr-doped glass sample with 1×10-2 Pr:Si molar ratio (T_d = 750 ℃). Transition types of Pr^{3+} ions (inset): *5d4f* emission (left); Photon cascade emission (right)

Synchrotron radiation is in a wide range of materials and life science. A fast-response detector for synchrotron radiation is needed for the accurate measurement of incident beams or photons emitted with plastic scintillators (PSs) are suitable for realizing a fast response. To measure

X-rays ad neutron produced by synchrotron radiation, key atomic elements are necessary to lead to high detection efficiency. However, because of the low detection efficiency resulting from the low concentration of key atomic elements, the application of conventional PSs has been greatly limited.

The objective of this work is to overcome the above-mentioned drawbacks. Here, we proposed some new approaches based on sol-gel method for its following advantages: (i) it is possible to incorporate the essential elements in a large amount. (ii) Organic fluor can be doped in the host matrix without degradation for its low temperature fabrication processes. (iii) Scintillating material can be synthesized in desired forms. Hence, the sol-gel method can be respected as a candidate to solve the problem of the commercial scintillator for the target radiations.

The fabrication processes and properties of scintillation materials, which are produced by sol-gel method, are stated in three parts, respectively.

1. Glass scintillation materials

In this section, Pr^{3+} ions were selected as luminescence center for the fast 5*d*-4*f* transition of Pr^{3+} ions. Pr-doped scintillators were fabricated by sol-gel method.

[Experimental] Silica gels were prepared by using tetraethoxysilane (TEOS) and $Pr(NO_3)_3 \cdot 6H_2O$ as precursors. The gel was obtained after gelation and drying in a thermostatic chamber at 35 °C. The glass samples were obtained by a thermal treatment, and the densification temperature was up to 985 °C.

[Results and Discussion] Fig. 1 shows the photoluminescence (PL) and photoluminescence excitation (PLE) spectra of a Pr-doped glass sample with a Pr:Si molar ratio of 1×10^{-2}; the PLE wavelength is 273 nm (at 4.50 eV). In the case of Pr^{3+} ions, the radiation transition can be attributed to either broadband emission or photo cascade emission. The position of the $^1S_0$ level is independence of the surrounding levels, since the 4f orbital of the $^1S_0$ energy level is well shielded by the outer orbital electrons. On the basis of the Dieke diagram, the $^1S_0$ energy level was determined to be around 5.67 eV [1] above the $^3H_4$ energy level. Apparently, the PLE energy level of the Pr-doped silica glass was less than that of the $^1S_0$ energy level. Hence, the possibility of photon cascade emission is eliminated for Pr-doped glass samples, and the luminescence of Pr^{3+}-doped silica

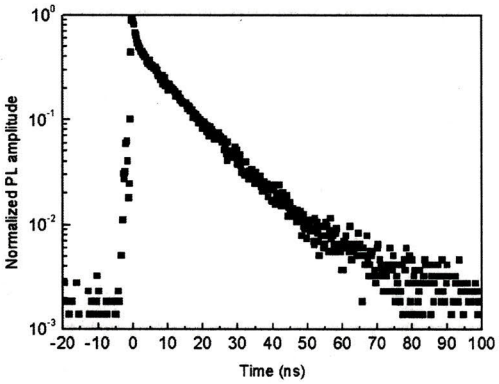

Fig. 2. Normalized PL time response for a Pr-doped glass sample with 1×10^{-2} Pr:Si molar ratio (T_a = 450 ℃).

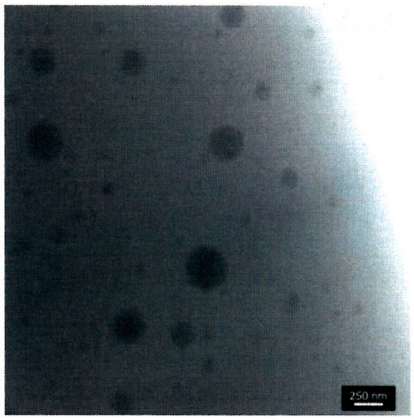

Fig. 3. TEM image of scintillation material doped with 10 wt% Hf.

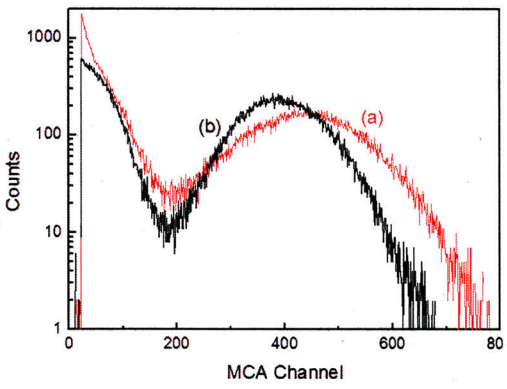

Fig. 4. Pulse-height of (a) 10 wt.% Hf-doped hybrid scintillator and (b) the commercial scintillator – NE142 (Pb 5 wt.%)

glasses is attributed to broadband emission. Fig 2 shows the scintillation time profile of 1 mol% Pr-doped silica glass scintillators. A second order exponential decay time that could be attributed to data deconvolution was observed. The time constant (τ) thus obtained was 1.3 and 14 ns. This decay is faster than that of single crystal Pr:LuAG (25 ns) [2]. The multiple decay components can also be ascribed to the different surroundings of Pr^{3+} ions in the glass.

2. Hybrid Scintillators for high-energy X-ray detection

In this part, high-Z elements have high interaction probability with X-ray photons based on the photoelectric effect. Therefore, hafnium ions (Z = 72) are selected as the key atomic element source. Because its energy of K absorption edge is located at 65 keV and high detection efficiency with Hf-doped scintillators-composed system can be respected for the target 67.4 keV X-ray photons.

[Experimental] Phenyltrimethoxysilane (PhTMOS) and $HfOCl_2 \cdot 8H_2O$ was added to a tetrahydrofuran solution of polystyrene (PS) followed by an addition of 0.1M HCl as catalyst. The mass ratio of PhTMOS to PS was 1.0. The mixture solution was heated at 35 °C for one day and then gradually raised to 80 °C. the maximum Hf-content of the final sample was 10 wt.%

[Results and Discussion] A TEM micrograph of the Hf-doped sample is presented in Fig. 3. The TEM image provides direct evidence of the formation of nanoparticles. The nanoparticle sizes range from several tens to several hundreds of nanometers. In order to investigate the composition of the nanoparticles, TEM-EDX spectrum was measured. The EDX spectrum indicates that the nanoparticles were composed of hafnium, silicon, and oxygen. Therefore, $Hf_xSi_{1-x}O_2$ nanoparticles are evidently dispersed in the polymer matrix. Fig. 4 presents the pulse-height spectra of the $Hf_xSi_{1-x}O_2$ and NE142. On the basis of the location of peak channels, the scintillation light output of the Hf-doped sample was estimated to be 120% that of NE142. Furthermore, the detection efficiency of the 0.6 mm thick Hf-doped sample was calculated to be 2.6%. The detection efficiency of a 1-mm thick Hf-doped sample was estimated to be 4.4%, which was two times better than that of NE142.

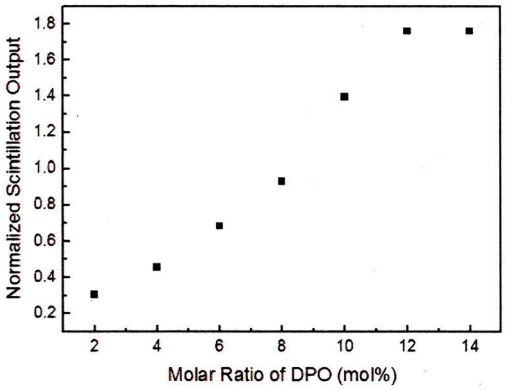

Fig. 5. RL intensity of DPO and POPOP-doped samples after normalization with that of BC454

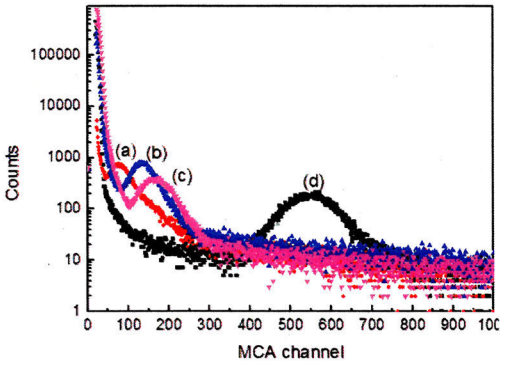

Fig. 6. Pulse-height spectra of DPO-doped samples: (a)4 mol%; (b)10 mol%; (c) 12 mol% and (d) BC454 under thermal neutron radiation

3. Hybrid Scintillators for neutron detection

Because neutrons have no electric charge, a neutron capture isotope such as ^{10}B, ^{6}Li is required to convert neutrons to detectable charged particles. Boron element is selected as the neutron capture isotope for a high cross section and relative low manufacture cost.

[Experimental] For synthesis processes, polystyrene (PS), 2,5-Diphenyloxazole (DPO), 1,4-bis(5-phenyloxazol-2-yl) benzene (POPOP), tetrahydrofuran, H_2O, and

N,N'-dimethylformamide were mixed as the starting solution. Then, trimethylborate and tetramethoxysilane were added to this solution until the PS was completely dissolved. After gelation, drying and aging processes, transparent and crack-free plastic scintillation samples were obtained. The boron in weight ratio reached 7 wt.% in the final samples.

[Results and Discussion] The RL intensities of the samples with various DPO concentrations were normalized with that of BC454 and are illustrated in Fig. 5. For DPO molar ratios up to 10 mol%, RL intensities higher than that of BC454 were observed. Thus, hybrid plastic scintillators with better scintillation efficiency than BC454 have been successfully synthesized by the sol-gel method. The height-pulse spectra of DPO-doped samples and the commercial scintillator, BC45, were shown in Fig. 6 when thermal neutron impinged. Firstly, thermal neutron had been successfully detected by all the fabricated samples. Secondly, the scintillation light output of the DPO-doped samples was enhanced by increasing DPO-content. In comparison with BC454, the maximum scintillation light output of DPO-doped sample was obtained around 1/3 of the BC454.

4. Conclusion

The target scintillation materials were successfully synthesized via sol-gel method. A fluorescence band was obtained ascribed to the 5*d*4*f*-transition, and relatively fast response time of 1.4 and 13 ns were obtained. The detection efficiency of Hf-doped hybrid scintillator was improved and estimated approximately 2-time better than that of commercial scintillator – NE142 in 1-mm thickness. The scintillation efficiency of boron-doped hybrid scintillator was higher than that of BC454. The detection efficiency of thermal neutron was still need to improve.

1 M. Gaft, R. Reisfeld, and G. Panczer, *Modern Luminescence Spectroscopy of Minerals and Materials*. (Springer, 2005).

2 M. Nikl, H. Ogino, A. Krasnikov, A. Beitlerova, A. Yoshikawa, and T. Fukuda, physica status solidi (a) **202** (1), R4 (2005).

論文審査結果の要旨

シンチレータは，放射線検出に用いられる蛍光体であり，基礎科学から核医学に至る広汎な分野で利用されている．近年では，放射光施設における高エネルギーX線や，核破砕中性子源からの中性子ビームなど，高強度かつ時間構造を持つ高度な放射線源の開発が進んできており，本論文は，主としてこれらを検出対象とする新規シンチレータを構成するための材料開発を，ゾルゲル法という溶液ベースの手法で行った成果に関するものである．

第二章には，Pr イオンを発光中心としてドープしたガラスシンチレータの開発成果が述べられている．ここでは，透明かつ稠密なガラスを得るための最適な焼成条件が提示され，その発光およびシンチレーション特性が報告されている．蛍光スペクトルや励起スペクトルの解析から，観測された発光は Pr^{3+} イオンでの 5d-4f 遷移による発光であると同定された．また，発光量はやや小さいものの，短い発光寿命が得られた．

第三章には，放射光施設での高エネルギーX線検出を想定した，有機無機ハイブリッド材料からなるシンチレータ材料開発の成果が述べられている．高エネルギーX線との相互作用機能を担う Hf 酸化物ナノ粒子と，発光機能を担うポリマーとに相分離した構造を有するシンチレータ材料において，市販の高エネルギー光子検出用プラスチックシンチレータを凌駕する性能が得られたと報告されている．

第四章には，中性子検出用の有機無機ハイブリッドシンチレータ材料の開発成果が述べられている．ここでは，ホウケイ酸ガラスの部分が中性子検出機能を，ポリマー部が発光機能を，各々担う．ポリマー部におけるエネルギー移動が定量的に解析され，最適な蛍光体濃度が決定された．また，市販品を上回る発光量が得られたことが報告されている．

本研究成果は，シンチレータ材料開発における新たな手法を提案するものである．特に，ナノ構造を有するシンチレータ材料開発事例は，その有効性にも拘わらず，本研究を含めても非常に少ない．本研究は，材料化学と放射線工学との融合領域を開拓する新たな研究展開として位置づけられる．

よって，本論文を博士(工学)の学位論文として合格と認める．