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Silica Scintillating Materials Prepared by Sol-Gel Methods

by

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Silica Scintillating Materials Prepared by Sol-Gel Methods[1]

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ABSTRACT

Silica was investigated as a rad-hard alternative to organic polymer hosts for organic scintillators. Silica sol-gels were prepared by hydrolysis of tetramethoxysilane in alcohol solutions. Organic dyes were incorporated into the gels by dissolving in methanol at the sol stage of gel formation. The silica sol-gel matrix is very rad-hard. The radiation stability of silica scintillators prepared by this method is dye-limited. Transient radioluminescence was measured following excitation with 30 ps pulses of 20 MeV electrons.

1. Introduction

Plastic scintillating fibers and tiles based on organic dyes incorporated into polystyrene have found important applications in high energy physics experiments requiring fast detectors for ionizing particles. The fast detector-response times afforded by organic dyes with short fluorescence lifetimes provide an advantage over ionization chamber detectors and inorganic glass scintillators when time resolution is critical. The principal disadvantage of plastic scintillators is their vulnerability to radiation damage.

Efforts to develop fast-response scintillators that are also rad-hard have included the use of known rad-hard materials, especially silica. Fused silica is exceedingly rad-hard, and pure silica scintillation detectors that measure Cerenkov radiation have been demonstrated to sustain negligible degradation in performance after >1 Grad.[2] Cerenkov light yields, however, are too low for many applications. A marriage of the organic fluors and the rad-hard silica matrix was sought. Scintillation from dye-doped silica glass, prepared by adsorption of organic scintillators from solution into porous silica, has been reported.[3] We have introduced organic scintillators into silica gels at the solution stage of

silica sol-gel synthesis, analogous to literature methods.[4] This approach allows greater control of the dye concentration and is conducive to other organic modifications of the silica matrix. We have measured the transient radioluminescence from the dye-doped silica gels and determined the degradation in performance with radiation exposure.

2. Methods and Materials

Sol-gel methods encompass a wide range of synthethic techniques for fabricating inorganic glasses, ceramics and composites beginning with a liquid-phase solution, or sol.[5] In alcoholic solutions, hydrolysis of metal alkoxides ($M(OR)_n$, where M=Al, Si, Ti, etc.) is followed by polycondensation reactions that construct the three dimensional metal oxide network. The solution becomes increasingly viscous and eventually turns into a transparent amorphous solid, or gel.

Monolithic silica gels are obtained by slow drying of the wet gel to remove solvent and water. The resulting material is a porous gel. Variations of the procedure include acid or base-catalyzed hydrolysis, and different choices of metal alkoxide precursors and solvent. A polar solvent such as alcohol or ether is necessary because the metal alkoxide is not miscible with water.

Our best monolithic silica gels (round disks, 20-50 mm in diameter and 3-10 mm thick) were made by hydrolysis of tetramethoxysilane (Aldrich or Fluka) in methanol at neutral pH. The amount of water used was in a mole ratio of 2.5:1 water to tetramethoxysilane. The solutions were stirred for 0.5 h at room temperature, sealed tightly in polypropylene bottles and transferred to a 60°C oven where they gelled within 2 h. The gels were aged for 24 h at 60°C. After aging the gels, the bottle caps were replaced with plastic food wrap with one pinhole. Drying to constant weight at 60°C required 10-14 days for 20 mm diameter disks and longer for larger disks. The gels were not subjected to any further heat treatment.

The silica sol-gels are not as impervious to ionizing radiation as fused silica glass, but are considerably more rad-hard than polystyrene (Figures 1 and 2). In the first place, the UV cutoff in the virgin material is about 50 nm shorter than in unirradiated polystyrene. Loss of transmission in the near UV and visible upon irradiation with ^{60}Co γ-rays (0.4 Mrad/h) is much slower and less extensive in the silica sol-gels than in polystyrene.

Organic dyes were incorporated into the gels by dissolving the appropriate concentration of dye in the methanol solvent used in the sol. The requirement of dye solubility in a polar solvent excludes the use of some dyes; nevertheless, 1-10 wt% concentrations were achieved for some scintillators in the silica gels. Several UV-emitting

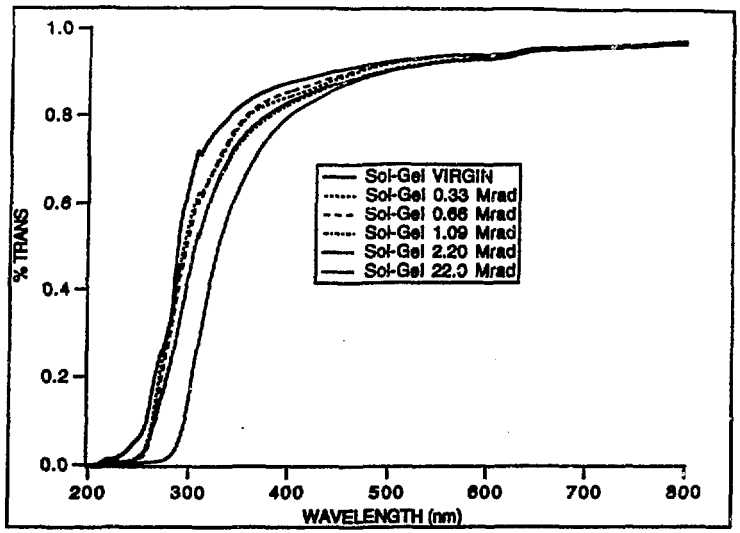

Figure 1. Transmission spectrum of silica sol-gel as a function of radiation dose (60Co γ-rays, 0.4 Mrad/h).

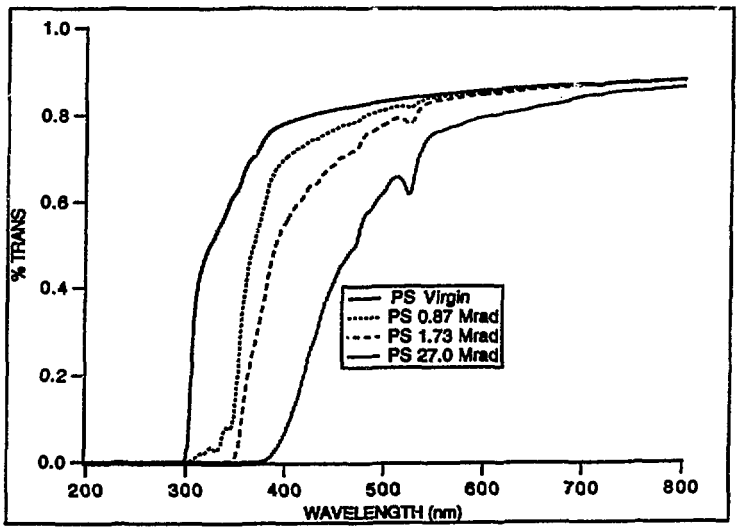

Figure 2. Transmission spectrum of polystyrene (PS) as a function of radiation dose (60Co γ-rays, 0.4 Mrad/h).

scintillators (p-terphenyl, PPO, BPBD, PBD) were used, as well as a variety of blue-emitting scintillators (coumarin-440, BBOT, Stilbene 420, LD390, LD423, BBO). Dyes were purchased from Aldrich and Exciton. Gels containing one, two or three different dyes were tested.

The possiblities for organic modifications of the metal oxide matrix using the sol-gel technique are virtually unlimited. Two simple variations involve the use of alkyl-substituted precursors (e.g., R-Si(OR)$_3$)[6] and the addition of organic molecules into the sol that may become covalently bonded to the oxide network or simply become trapped in the pores of the gel.[7] The latter approach using polyethylene glycol (MW_{av}=200) allowed us to prepare silica sol-gels containing 20-50% hydrocarbon fraction by weight with transparency equal to or better than the pure silica sol-gels. Low dose tests (0.5-1 Mrad) indicate that the incorporation of the organic component did not significantly compromise the rad-hardness of the matrix.

3. Transient Radioluminescence

Radioluminescence transients generated in sol-gel scintillators by 30 ps pulses of 20 MeV electrons (~4 krad per pulse) from an electron linac were detected with a Hamamatsu R-1328U-03 or R-1328U-02 photodiode after the light was filtered with a bandpass filter (7-12 nm width) at the emission maximum of the dye. The signals were digitized by a Tektronix 7250 transient digitizer and stored on a DEC PDP/11 computer.

Figure 3 shows the light pulse from a silica sol-gel sample containing 0.1 wt% p-terphenyl. The observed decay time was 1.1 ns compared to the p-terphenyl fluorescence lifetime of 1.05 ns in ethanol.[8] The Cerenkov light generated at the same wavelength (340 nm) in a sol-gel sample without dye is shown for comparison. The amplitude of the light pulse from the 0.1% p-terphenyl sample was approximately equal to that generated in a methanol solution with an equal concentration of p-terphenyl. In the radiolysis of alcohol solutions, the only source of solute excited states is Cerenkov excitation.[9] No energy transfer occurs from solvent excited states, and the yield of excited states from radical ion recombination is near zero. From the nearly equivalent yields of radioluminescence from methanol solutions and silica sol-gels, we conclude that the formation of scintillator excited states by other than Cerenkov excitation is negligible.

The estimated yield of p-terphenyl excited states is 0.014 per 100 eV absorbed dose or 7100 eV per excited state formed. For comparison we irradiated polystyrene samples with the same concentration of p-terphenyl (0.1%) and observed light pulses with 4-5 times greater amplitude. The solubility of p-terphenyl is considerably greater in polystyrene than

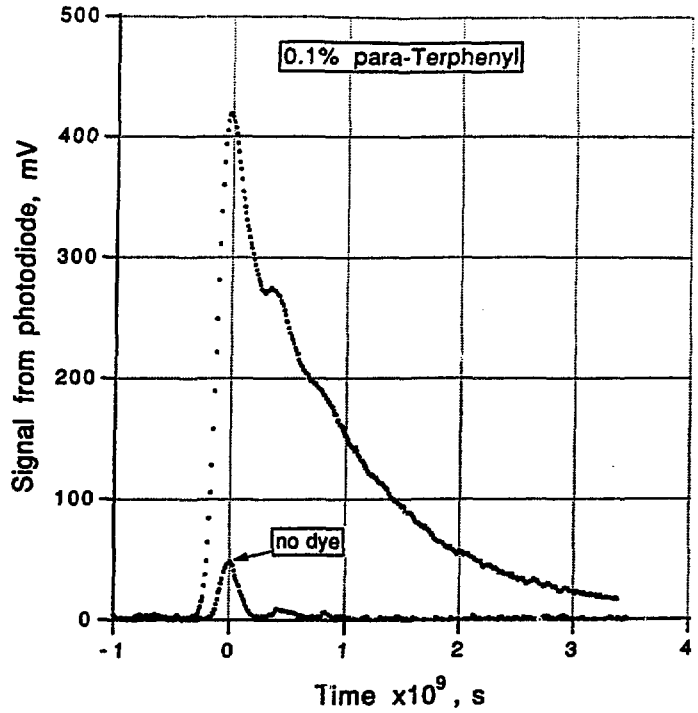

Figure 3. Fluorescence transient from silica sol-gel containing 0.1% p-terphenyl after excitation by a 30 ps pulse of 20 MeV electrons. The lower trace shows the Cerenkov light generated in a sol-gel sample without dye.

in the silica sol-gel. By increasing the p-terphenyl concentration (≥1%), the emission yields from the polystyrene samples exceeded that in 0.1% p-terphenyl (saturation) in silica by a factor of 20 or more.

Because the silica matrix itself is very rad-hard, the stability of the silica scintillator materials is dye-limited. All samples whose transient radioluminescence was measured showed decreased light output with accumulated dose. The radioluminescence transients were measured before and after delivering a dose of approximately 4.5 Mrad (1200 linac pulses). The silica samples containing UV dyes (p-terphenyl, PPO) were the most robust, showing ~50% decrease in light output after 4.5 Mrad. The degradation in light output in comparable polystyrene samples was approximately double this rate.

All blue dyes tested showed more severe damage after 4.5 Mrad. The light output fell by 75% or more. The reason for the decreased emission is a combination of dye destruction and attenuated transmission due to the growth of new absorption at the emission wavelength of the dye. Transmission scans of all irradiated silica scintillators showed evidence of the buildup of radiolysis products that absorbed at longer wavelengths than the parent dye molecules. The absorption of the radiolysis products overlaps the emission bands of the parent dyes. Such radiation-induce absorptions were not observed in silica sol-gels without dyes.

It is significant that methanol and glycerol solutions of p-terphenyl and PPO showed negligible (<2%) decrease in radioluminescence intensity after 4.5 Mrad. Clearly, the organic dyes in the irradiated silica matrix are not well protected. Further study is needed to elucidate the mechanism of dye degradation in irradiated silica and to suggest possible approaches for dye protection.

Many variations were made to try and achieve enhanced emission yields from the silica sol-gel scintillators. Table 1 shows a representative list of dyes and dye combinations that were tested. None of these gave significant improvements in light output or rad-hardness. We conclude that the silica matrix needs fundamental modification to enhance the efficiency of energy transfer and scintillator excited state formation.

Table 1: List of some of the dyes and combinations tested in silica sol-gels.

Dye	Max. Conc.(wt. %)
PTP	0.1
PPO	1
Blue dyes[a]	1
Combinations	
10% naphthalene + 0.1% PTP	
10% biphenyl + 0.1% PPO	
1% BPBD + 0.01% BBOT	
10% naphthalene + 1% BPBD + 0.01% BBOT	
10% naphthalene + 0.1% BPBD + 0.01% BBO	

[a]See 2. Methods and Materials

One way to easily and fundamentally modify silica matrices by sol-gel methods is to incorporate organic components. In this way one can hope to influence energy-transfer processes without unduly compromising the rad-hardness of the matrix. If the organic additives also provide a measure of dye protection, then the dual goals of enhanced brightness and improved rad-hardness might be achieved simultaneously.

We have demonstrated the potential of organically modified silica matrices with the addition of polyethylene glycol in amounts of 20-50%. Other details of gel formation were the same. Polyethylene glycol was chosen because of the likelihood that it participates in condensation reactions and becomes covalently bonded to the silica network. We have not demonstrated whether it does or not, but good quality, transparent disks were made and tested with various dyes. Samples containing 40 wt% polyethylene glycol and 0.1 wt% p-terphenyl were found to be approximately three times as bright as sol-gel samples without polyethylene glycol. The dye rad-hardness was also moderately improved (40% vs. 50% decrease in light output after 4.5 Mrad) compared to the samples without polyethylene glycol.

4. Summary

Scintillating materials composed of rad-hard silica doped with organic dyes can be prepared by sol-gel methods. The rad-hardness of these scintillators is dye-limited. Organic modification of the matrix is suggested as a means of dye protection and enhancing the brightness of the silica scintillators.

5. Acknowledgements

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6. References

1. Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under contract number W-31-109-ENG-38.
2. Ph. Gorodetzky, B. Grosdidier, and D. Lazic, *Radiat. Phys. Chem.* **41** (1993) 253.
3. J.-L. Nogues, S. Majewski, J. K. Walker, M. Bowen, R. Wojcik, and W. V. Moreshead, *J. Am. Ceram. Soc.* 71 (1988) 1159.

4. D. Avnir, D. Levy and R. Reisfeld, *J. Phys. Chem.* **88** (1984) 5956; R. Locher, A. Renn and U. P. Wild, *Chem. Phys. Lett.* **138** (1987) 405; T. Tani, H. Namikawa, K. Arai and A. Makishima, *J. Appl. Phys.* **58** (1985) 3559; M. Nakamura, H. Nasu and K. Kamiya, *J. Non-Crystalline Solids* **135** (1991) 1.
5. C. Jeffery Brinker and G. W. Scherer, *Sol-Gel Science* (Academic Press, New York, 1990).
6. D. Levy, S. Einhorn and D. Avnir, *J. Non-Crystalline Solids*, **113** (1989) 137.
7. T. M. Che, R. V. Carney, G. Khanarian, R. A. Keosian and M. Borzo, *J. Non-Crystalline Solids*, **113** (1988) 280.
8. I. G. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed. (Academic Press, New York, 1971).
9. M. C. Sauer, Jr., C. Romero and K. H. Schmidt, *Radiat. Phys. Chem.* **29** (1987) 261.