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RESEARCH INVESTIGATION ON DENSE SCINTILLATION GLASS FOR USE IN TOTAL ABSORPTION NUCLEAR CASCADE DETECTORS

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I. Introduction

The purpose of this investigation was to produce a glass for use in a Total Absorption Nuclear Cascade (TANC) detector. Such a glass would meet the following requirements: modest scintillation efficiency, good optical transmission, scintillation decay time substantially less than one micro-second, availability in large pieces, high density, and short radiation length. The only known scintillation activator for glass was cerium in the trivalent state. Silicate and borate glasses, activated with cerium and loaded with high thermal neutron cross-section isotopes, had been used as neutron scintillators. These glasses fulfilled all the desired criteria except for high density and short radiation length. High density and short radiation lengths were considered to be equivalent for purposes of this investigation. The investigation, therefore, was centered upon scintillator glasses with high density.

Three approaches were followed: First, the cerium-activated silicate scintillation glass was investigated to determine the limitation of density increase while retaining scintillation efficiency. Second, the scintillations efficiency of silver in a silicate glass was determined. Third, the scintillation efficiency-density relationship of borate glasses containing silver was established.

Since facilities were not available at Bausch & Lomb for scintillation measurements, preliminary measurements were limited to ultraviolet excited fluorescence and final scintillation measurements were carried out at a NASA activity at the University of Arizona under the direction of Dr. E. P. Krider. Within the cerium activated glass systems it was known that impurities reduced both ultraviolet fluorescence and scintillation efficiency by the same amounts. Fluorescent materials which did not show scintillation had been eliminated by an earlier work. Silver in a silicate system had not been tested and was therefore included in this investigation.

II. Experimental Procedure

A. Silver Diffusion

Boules of sodium-aluminum silicate and sodium-zirconium were fabricated (75 mm dia. x 38 mm high), placed in a bath of silver chloride and held for 21 days at a temperature of 500°C. During this period the silver diffusing into the sample replaced the sodium atoms to a depth of approximately 10 mm. The silver concentration gradient was determined by electron microprobe measurements. Sections of these samples perpendicular to the gradient were made and measurements of transmission, fluorescence, density and scintillation were made for correlation with silver concentration. In addition, one sample after removal from the silver chloride bath was further heat treated for 14 days at 500°C. A uniform homogenized silver content of 10 weight % was obtained in this sample.

B. Hot Pressing

A frit consisting of a high density glass (Schott LaF-10) and cerium activated silicate glass was prepared by ball milling each glass separately, sieving to separate particle size, decanting and then mixing together. Each frit then contained a mixture of 50% by weight of each material in various particle size ratios. After these mixtures were cold compacted they were hot pressed at 5000 lbs/sq. inch at 820°C for a period of 10-30 minutes, annealed then ground and polished. Some thirty samples were prepared and measured for density and fluorescences. In an effort to remove the trapped air between the particles several runs were attempted in which a vacuum of 50 microns of Hg was maintained as the powder was being heated and during the pressing operation.

C. Glass

Borate System

Some 112 melts were made to determine the glass field of the systems boron-lanthanum-tantalum-niobium and boron-lanthanum-tantalum. Initial melts were done in air. When a satisfactory composition was attempted in a reducing atmosphere, the system containing niobium was discarded because of absorption in the wavelength range of the cerium tri-valent ion. When cerium in the form of the oxalate was added to the glass system boron-lanthanum-tantalum, there still persisted slight traces of yellow due to the cerium being in the four plus state. This resulted in a low level of fluorescence. An improvement was noted with the introduction of the cerium as a metal powder into the batch. The final melts were then made in a controlled atmosphere furnace continually being flushed with forming gas (95% N_2 - 5% H_2). The glass composition is as follows:

B_2O_3	35	Weight Percent
Ta_2O_5	10	
La_2O_3	54	
Ce_2O_3	.1	

The cerium metal was mixed with the last batch fill. All 148 melts were made in either 50cc or 2-1/2" platinum pots. The batch materials were all of high purity. Before each melt the platinum pots were cleaned in HF then in a boiling solution of 10% nitric and 90% concentrated hydrochloric acid.

Silicate

Some one hundred melts have been made to determine the limits of the glass forming field as tungsten-niobium-tantalum and lanthanum were added to a magnesium-lithium-aluminum silicate glass. Because of either low solubility limits, devitrification or ultra-violet absorption, tungsten, niobium and their combinations were eliminated. However, both tantalum and lanthanum alone when added to the glass proved to be quite soluble up to 57 and 40 weight percent respecitvely. As in the case of the borates, the initial melts were made in air. The most promising compositions were then made in the controlled atmosphere furnace using the technique of pumping the residual gases and back filling with a reducing atmosphere (95% N_2 - 5% H_2). This atmosphere was bled in continuously over hot carbon. Periodically, during the melt the unit was pumped down to prevent any oxygen from entering. The unit was always maintained under a slight vacuum. The glass compositions were:

Li_2O	- 1.7		Li_2O_3	- 2.6	
Al_2O_3	- 4.5		Al_2O_3	- 6.2	
MgO	- 9.4	and	MgO_2	- 13.0	weight
SiO_2	- 26.4		SiO_2	- 37.2	percent
Ta_2O_5	- 57.0		La_2O_3	- 40.0	
Ce_2O_3	- 1.0		Ce_2O_3	- 1.0	

The cerium was added in the form of metal powder. All of the batch materials were of high purity.

III. Apparatus & Measurements

U. V. transmittance measurements were made on a Bausch & Lomb 505 spectrophotometer equipped with a deuterium light source.

The fluorescence emissions spectra were measured on a 505 spectrophotometer. The excitation illumination was from a Xenon source in a high intensity B&L grating monochromator. This U.V. light was passed through a Corning wide band U.V. filter to remove any higher orders.

Total fluorescence intensity was measured as the output current of a 1P28 photomultiplier detector by a No. 610 Keithley electrometer. The source for the ultra-violet excitation energy was a super pressure mercury lamp through a broad band ultra-violet filter.

Decay times for the silver and cerium fluorescent activators were measured on a Tektronix 7704 oscilloscope. The illumination for the excitation was provided by a 20 nanosecond spark gap pulser.

The controlled atmosphere furnace used in these experiments consisted of a stainless steel tank capable of being pumped down to 10^{-5} mm of Hg and then backfilled with any atmosphere. Melting is done using RF induction heating directly coupled to the platinum crucible. Batch material from a hopper located in the unit may be fed directly into the pot. Facilities are also available to stir and cast without disturbing the atmosphere.

IV. Results

A. Silver Diffusion

Sodium aluminum silicate glasses were prepared into which silver could be diffused. This process resulted in an increase of the density from 2.46 g/cc to 2.69 g/cc for an approximate 10 weight percent of silver. Sodium zirconium silicate glasses were also found in which the sodium could be replaced by silver by diffusion. For an approximate 12 weight percent increase of silver the density of the glasses changed from 2.76 g/cc to 2.87 g/cc. Both glasses exhibited fluorescence from an ultra-violet source with a measured decay constant of 45 nanoseconds. However, neither glass indicated scintillation from high energy sources.

B. Hot Pressing

In these experiments a mixture by weight of 50% LaF-10 density of 4.568 g/cc and 50 cerium activated silicate glass, density or 2.66 g/cc resulted in pressed glass with a density of about 3.6 g/cc. The finished pieces, however, contained many bubbles and reflecting interfaces due to the difference in index of refraction of the two glasses. Gas bubbles could not be removed even when pressed under a partial vacuum. In addition, there was occasional cracking due to the difference in coefficient of expansion of the two materials. Although the resultant products were translucent and showed some fluorescence, the efficiency did not appear high and they were not tested for scintillation. An attempt was made to stir in grains of the high melting cerium activated silicate glass into a low melting high density glass. The cerium along the surface of the grains was oxidized to the four valance level resulting in absorption and low fluorescence and the approach was abandoned.

C. Glass

Borate - Experiments with the glass system boron-tantalum-niobium-lanthanum melted under reducing conditions showed no absorption-free glasses. The glass with 35% boron oxide, 10% tantalum oxide and 55% lanthanum oxide had an ultra-violet transmission cutoff at 260 nm, which was not influenced by melting atmosphere. The density of this glass was 4.26 and the fluorescence intensity was about half that of the cerium-silicate glasses. However, there was no indication of scintillation when irradiated with high energy particles.

Silicate - All of the heavy elements added to the magnesium-lithium-aluminum silicate glass with the exception of either tantalum or lanthanun resulted in glasses that divitrified, absorbed in the ultra-violet or were too low in density and so were discontinued. Tantalum up to 57 weight percent could be dissolved in this glass melted in air or under reducing atmospheric conditions. This glass had a density of 4.26 g/cc. Lanthanum could be dissolved in the base glass up to 40 weight percent of the oxide again in either air or under reducing atmospheric conditions. The density of this glass was 3.7 g/cc. Thus, the density of the base silicate glass may be continuously varied from 2.6 g/cc to 4.2 g/cc.

Both of these glasses with the addition of 1 weight percent of cerium fluoresced when excited with ultraviolet light with a decay time of approximately 60 nanoseconds. As in the case of the borates, no scintillation was detected when irradiated with high energy particles.

V. Conclusion

Three approaches to the development of a high density scintillation glass were investigated: The increase of density of glass systems containing cerium—the only systems which had been known to show scintillation, the testing of a novel silicate glass system containing significant concentrations of silver produced by ion exchange and never tested previously, and the hot pressing of a diphasic compact of low density scintillation glass with high density passive glass. In first two cases, while ultraviolet excited fluorescence was maintained in the glasses showing high density, scintillation response to high energy particles was not retained in the case of the cerium containing glasses or developed in the case of the silver containing glasses. In the case of the compacts, the extremely long path length caused by the multiple internal reflections which occur in such a body resulted in attenuation even with glasses of high specific transmission.

It is not clear why the scintillation efficiency is not maintained in the higher density cerium containing glasses. It would appear that there is either inhibition of energy transfer in the presence of heavy elements or there exists a permitted radiationless transition in the presence of these elements.