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Thermal diffusion of mixed valence Ce in ^{6}Li loaded silicate glass for neutron imaging

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ABSTRACT

The creation and characterization of Ce doped surface regions in ^{6}Li enriched silicate glasses for cold neutron detection is described. A diffusion layer of a dried solution containing cerium III acetylacetonate hydrate was thermally diffused into monolithic glass samples under a reducing atmosphere. The diffusion characteristics of the mixed valence cerium compound were assayed with Rutherford Backscattering Spectrometry. The Ce diffusion activation energy within the glass was found to be 411 ± 53 kJ/mol (4.26 ± 0.55 eV). Radiation induced color centers formed on the diffusion samples as an effect of using alpha bombardment measurements. The ratio of Ce valence states of the diffused cerium was assayed as a function of depth with X-ray Photoelectron Spectroscopy, and the signal from Ce for the color centers was compared to the unirradiated sample surface.

1. Introduction

Neutron imaging is a unique utility for nondestructive analysis, specifically where cold neutrons are able to penetrate many dense materials, while remaining sensitive to low atomic mass materials [1]. This results in the ability to assay an object even when it is found inside of an X-ray opaque housing material. Enabled by advanced neutron sources available internationally, neutron imaging is progressing the scientific community's understanding of advanced materials, next generation energy storage systems, precision manufacturing technologies, aerospace components, metallic additive manufacturing, plant physiology, and geosciences [2].

In spite of all the successes that neutron scattering science facilities have enabled in recent years, even higher-impact research is limited by the current spatial resolution of neutron detection devices. While X-ray imaging can resolve spatial features well below the micron level, the state-of-the-art for neutron scattering instrumentation is approximately 10–15 μm. High resolution neutron imaging represents a challenge since neutrons do not possess charge. So, their detection often relies on nuclear capture reactions that produce heavy charged particles (HCPs) that can then be detected using scintillation materials. Currently, the spatial resolutions of cold neutron imaging methods are fundamentally limited by the variance introduced by the tracks of these charged particles. Therefore, we are developing and experimentally characterizing micro-structured arrays of scintillating ^{6}Li silicate optical fibers that are capable of particle tracking. In past work, we used simulation and modeling to investigate an approach to reach spatial resolution down to ~1 μm using a scintillating lithium loaded glass microfiber array in combination with charged particle tracking, in order to determine the interaction site of each individual event [3].

Creating a thin region of scintillation (that could be tens to hundreds of microns thick, depending on the application) within a neutron-sensitive material could be used to avoid light loss arising from optically coupling conversion layers and scintillating films. Whereas some structured detectors such as patterned thin film, composites, and microchannel plate detectors have been researched for position-sensitive neutron detection, little effort has been made to create selective scintillating regions within structured detectors. This is likely because most commercially available glass scintillators, such as ^{6}Li enriched silicates, are drawn from a melt that uniformly contains an activator, with Ce being one of the most common activators used in neutron sensitive glasses. More specifically, cerium (III) oxide, Ce_3O_2, constitutes ~0.1 of the molar ratio or 3.8–4.6 wt% in the melt of common lithium and boron loaded glass scintillators [4]–[6].

As seen in Fig. 1, the proof-of-concept system employs an Intensifying Charge Coupled Device (ICCD), which is sensitive to single photons, to collect the scintillation light. However, placing an ICCD directly into a neutron beam line is deleterious, sometimes irreparably,

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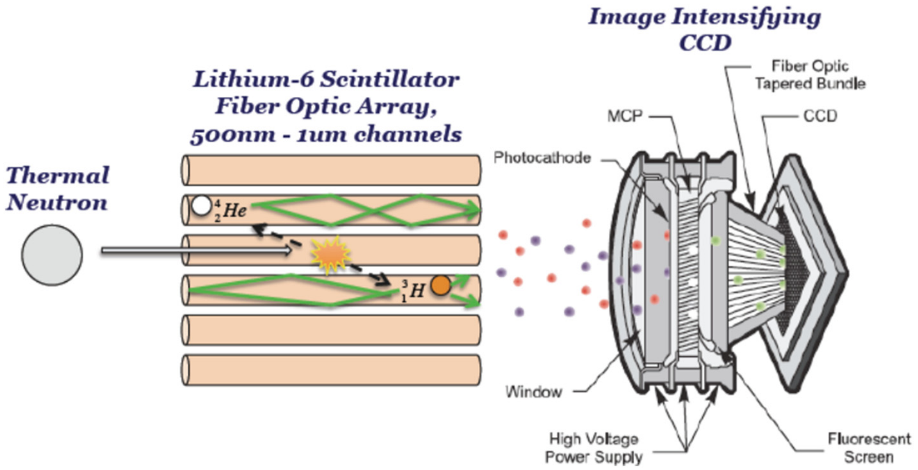

Fig. 1. When neutrons are absorbed by the ^{6}Li loaded glass microfibers, the resulting reaction emits an alpha and a triton back-to-back. The heavy charged particles produce scintillation light, which is channeled down a waveguide comprised of the ^{6}Li glass cores surrounded by optical cladding glass, to be collected at an ICCD.

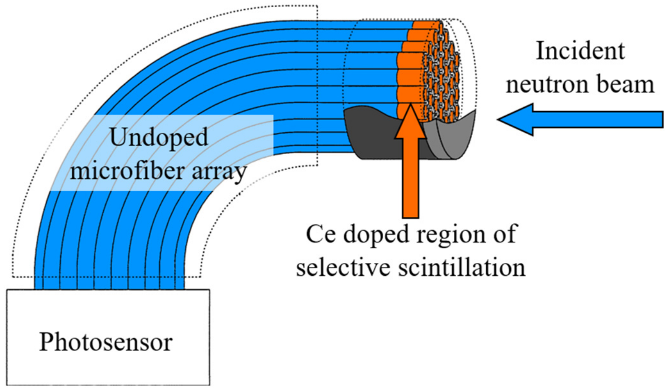

Fig. 2. Illustration of a high resolution lithium-glass microfiber array, selectively doped only at the neutron detection end, designed to function as a waveguide to bend and taper scintillation light towards a position sensitive photosensor. Schematic edited from [7].

to the photosensor. To avoid light loss and to prevent damage to the photosensor, we intend to directly couple a bent, microstructured fiber array to the photosensor (see Fig. 2). However, neutron captures along the arc of the bent fibers will create position confusion, as there would not be a one–to–one relationship. To avoid this loss of spatial resolution, we propose to selectively dope Ce as an activator into only the ends of the fibers. This concept is being investigated through controlled diffusion of Ce^{3+} into the surface of undoped, samples produced without the Ce activator, ^{6}Li loaded glass (fabricated by Nucsafe Inc., Oak Ridge, TN, USA) that is similar to the well-known GS20 scintillating glass.

In our recent research [8], we showed that Ce metal can be thermally diffused into the surface of undoped ^{6}Li-loaded glass. After using an AJA sputtering system to coat samples of monolithic ^{6}Li loaded glass with Ce metal, the samples were each heated, and the diffusion profiles of Ce for different heating temperatures (500–600 °C) and durations (1–4 h) were studied using Rutherford Backscattering Spectrometry (RBS). From experimental results it was observed that: 1) longer annealing times are required to reach micron-scale diffusion depths, 2) more controls are necessary to allow uniform charge transport across the insulating glass samples, and, most importantly, 3) while sputtering from metallic Ce results in moderately successful thermal diffusion into the lithium-glass, it does not allow for precise control of the Ce charge state in the glass. This work addresses these issues by evaluating selective doping techniques using controlled thermal diffusion of a Ce (III) acetylacetonate solution into the surface of undoped, ^{6}Li-loaded glass.

Herein, we present our doping technique, the results of micron-scale Ce diffusion concentration and depth assayed with RBS, an analysis of trivalent Ce content via X-ray Photoelectron Spectroscopy (XPS), and the creation of radiation-induced defects related to the reducibility of Ce^{IV} to Ce^{III}.

2. Fabrication methods

A. Diffusion layer

Since trivalent Ce is needed for scintillation, we used a Ce liquid solution that is unreactive with air, and is therefore expected to be better capable of maintaining the 3+ charge state throughout diffusion. Specifically, cerium III acetylacetonate hydrate [Ce(acac)$_3$(H$_2$O)$_2$] (Aldrich Prod. No. 381403), commonly referred to as “Ce acac,” is used to coat our undoped ^{6}Li loaded glass with a Ce diffusion layer. Since Ce acac powder is not able to be sputtered, coating is accomplished from a liquid form. To find a stable solution, Ce acac was dissolved into several solvents, yielding success with a toluene solvent. The solution was not viscous enough to be spin coated onto the samples in a reasonable timeframe. So, the solution was directly air dried onto the glass for the first batch (B1) of 6 irregular monolithic undoped ^{6}Li loaded glass samples (S1-S6). The synthesis was later refined by drying 24 mg of the Ce acac precipitate from the toluene solution in an open air-beaker at 80 °C, similar to the work described in [9], where the dehydration stability of Ce acac was noted. The brownish amber precipitate was dissolved back into 0.5 mL of acetone and 15 mL of toluene before again being air dried onto the surface of a second batch (B2) of 4 monolithic undoped ^{6}Li loaded glass samples (S0-S3). Drying is expected to be responsible for an approximate $\leq$30% loss of the Ce concentration [10].

B. Active reduction during annealing

Most samples in B1 and B2 were annealed in a two step, drive-in and soak, heat cycle process. The annealing was performed in a MTI GSL1500X High Temperature Vacuum Tube Furnace with pressures around several mTr while flowing a nonflammable 2% H and 98% N reducing gas mixture. None of the B1 samples possessed visual clarity as the initial diffusion layer coating readily blackened. With the aforementioned changes to the diffusion layer that coated onto B2 samples, the samples better retained some transparency. Four samples in B2 were thermally annealed in two heat cycles, the drive-in and soak cycles at pressures between 5 and 10 mTr. The drive-in annealing