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Structural Analysis of a Completely Amorphous ^{238}Pu-Doped Zircon by Neutron Diffraction

by

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DISCLAIMER

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ABSTRACT

The structure of a completely amorphous zircon was determined by time-of-flight neutron diffraction at Argonne's Intense Pulsed Neutron Source (IPNS). The sample of metamict zircon ($ZrSiO_4$), initially doped to 8.85 weight percent ^{238}Pu, had been completely amorphized by alpha-recoil damage since its synthesis in 1981 at the Pacific Northwest National Laboratory (PNNL). The measured diffraction structure factor, $S(Q)$, indicated a completely amorphous sample, with no signs of residual zircon microcrystallinity. The pair distribution function obtained indicated that the structure was that of an oxide glass, retaining the Si—O, Zr—O, and O—O bond lengths of crystalline zircon.

INTRODUCTION

Zircon is an intrinsically durable mineral found in some of the oldest earth rocks [1], and has been considered as a material for disposal of excess weapons plutonium [2-4]. Plutonium-loaded zircon will amorphize after extended time [4], but well before the plutonium has decayed to safe levels. We present here a structural analysis of a synthetic zircon that has been doped with ^{238}Pu and stored at ambient temperature for over 15 years, resulting in complete amorphization [5]. The use of ^{238}Pu, with its short half-life (87.75 years), has resulted in a cumulative dose of 2.8×10^{19} alpha-decays/g. This radiation exposure is nearly 3-times the dose that fully amorphized this sample [5], and this damage level is equal to that accrued by an equivalent ^{239}Pu-loaded zircon over about 5000 years, or by a natural zircon over ~100 million years. While natural zircon crystals are known to become amorphized due to alpha damage from naturally incorporated thorium and uranium (primarily ^{235}U, ^{238}U, and ^{232}Th) [5, 6] the present sample is the only true bulk amorphous zircon in existence. Natural actinide-containing zircon minerals are not completely amorphous (i.e., domains within zircon crystals containing different abundances of initial Th and U accumulate different amounts of radiation damage) [7] and generally contain numerous impurities phases. Furthermore, zircon does not quench into a glass

from the melt, phase separating instead (to crystalline ZrO_2 and amorphous SiO_2). This precludes quenching as a route to amorphous zircon (Zr-Si oxide glass) preparation [8].

The interest in this particular sample is twofold. First, as a unique amorphous material prepared from a non-glass-forming system, and second, as a surrogate for crystalline materials that may be used for disposal of surplus weapons plutonium [9]. A basic question is whether the amorphous structure induced by alpha recoil-damage, which has a volume expansion of 16.6 % relative to the crystalline structure [5], is based upon the same structural units as the crystal (Figure 1), as is typically observed in glasses and vapor-deposited amorphous solids.

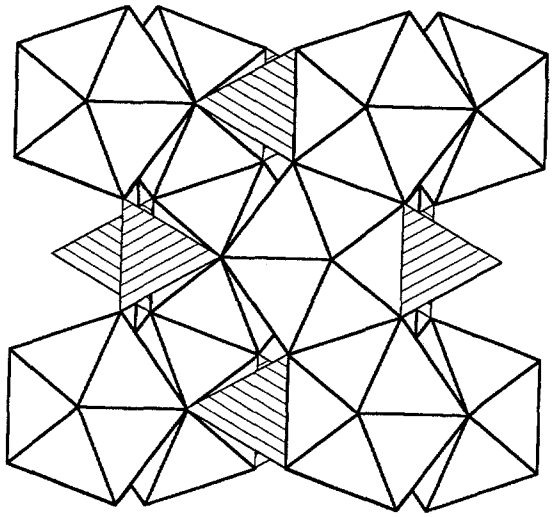

Figure 1. The crystal structure of zircon consists of chains of edge-sharing ZrO_8 triangular dodecahedra connected by isolated SiO_4 tetrahedra [10].

EXPERIMENT

Time-of-flight neutron diffraction measurements were made with the Glass, Liquid, and Amorphous Diffractometer (GLAD) at IPNS. Owing to the extreme alpha radioactivity and resultant contamination potential of this sample, double encapsulation in helium-tight vanadium containers was required. In addition, the sample was enclosed in a cryopumped furnace well at room temperature to further ensure against accidental contamination of the experimental facility. The sample was limited to 50% of the DOE Category III Limit for the nuclear material inventory at IPNS, for a total sample of only 200 mg. Scattering intensity was normalized to a vanadium reference. Standard programs for intensity, background, absorption, multiple scattering, and inelastic scattering were used to analyze and refine the data [11]. Due to nonlinear absorption of thermal neutrons by the plutonium isotopes present in the sample, small empirical corrections were made to correct an unphysical slope imposed upon the data and obtain an $S(Q)$ that oscillates properly about the value 1.0. The small sample size imposed by the radionuclide inventory limits resulted in scattering by the sample that was only 2-10% of the combined

container and background. Despite the small sample size and triple encapsulation (including the furnace well), sufficient data were collected over a seven-day period to allow determination of an experimental scattering factor, $S(Q)$.

The neutron-weighted structure factor is related to the partial structure factors by the relation

$$S(Q) = \frac{\sum_{\alpha,\beta} c_\alpha c_\beta b_\alpha b_\beta S_{\alpha\beta}(Q)}{\left(\sum_\alpha c_\alpha b_\alpha\right)^2} \quad \text{(Equation 1)},$$

where c_α is the atomic fraction, and b_α is the bound coherent scattering cross section of element α, respectively. In the case of the zircon sample studied here, this translates to

$$S(Q) = 0.38S_{O-O}(Q) + 0.22S_{Zr-O}(Q) + 0.14S_{Si-O}(Q) + 0.04S_{Si-Zr}(Q) + (terms < 0.03)$$

(Equation 2).

The corresponding pair distribution function, $g(r)$ is related to the measured scattering by the relation

$$g(r) = 1 + \frac{1}{2\pi^2\rho_0}\int_0^\infty Q^2[S(Q)-1]\frac{\sin(Qr)}{Qr}dQ \quad \text{(Equation 3)},$$

where ρ_0 is the average atomic density. The experimental $S(Q)$ is shown in Figure 2. Despite rather poor statistics, the scattering is clearly characteristic of an amorphous material. The residual features at Q = 2.91 Å^{-1} and 3.32 Å^{-1} are possibly Bragg peaks, but do *not* correspond to crystalline zircon. They are likely from the vanadium container and/or quartz, the latter suggesting possible minor phase separation. The pair distribution function, determined from the experimental $S(Q)$ by the Fourier-transform relation of Equation 3, appears in Figure 3. To reduce Fourier transform artifacts, the integrand of Equation 3 was multiplied by a Lorch termination function, $\sin(\pi Q/Q_{max})/(\pi Q/Q_{max})$ with Q_{max} ~ 10.65 Å^{-1}, and the upper limit of integration taken as Q_{max}. The peaks corresponding to the expected bond lengths of Si—O (1.63Å), Zr—O (2.12 and 2.29 Å), and O—O (2.45-2.84 Å), based upon the crystal structure [10] are indicated in Figure 3. Also indicated is the onset of next-nearest neighbor distance (nnn), where the $g(r)$ shows a remnant of the original structural order. Of particular note is the gap in $g(r)$ between ~ 2.8 and 3.4 Å, where very few bond lengths occur in crystalline zircon. It is reasonable to conclude that the local structural units of zircon are preserved upon radiation-

induced amorphization. The neutron measurements complement recent x-ray absorption fine structure (XAFS) measurements from this material [12, 13].

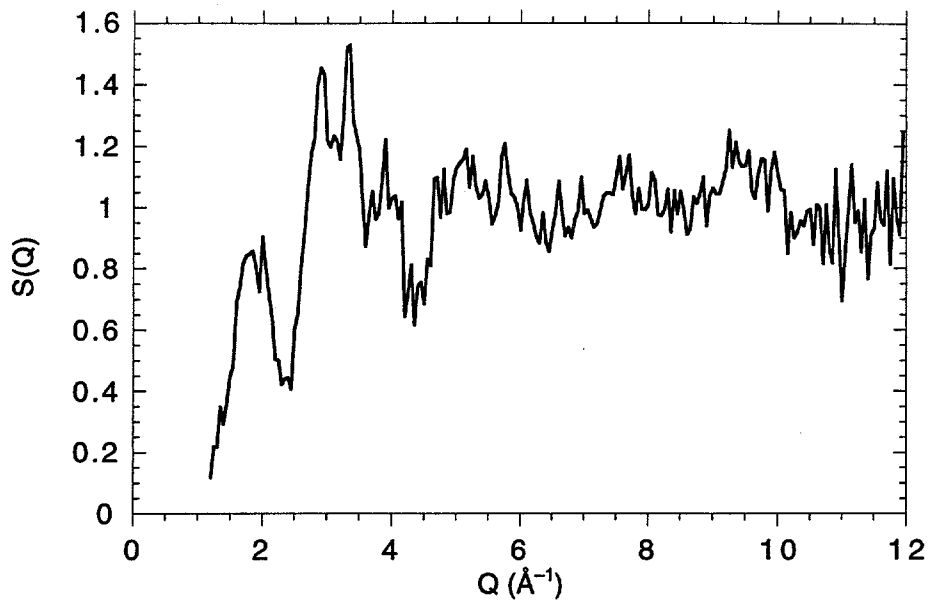

Figure 2. The experimental neutron $S(Q)$ from the amorphous zircon.

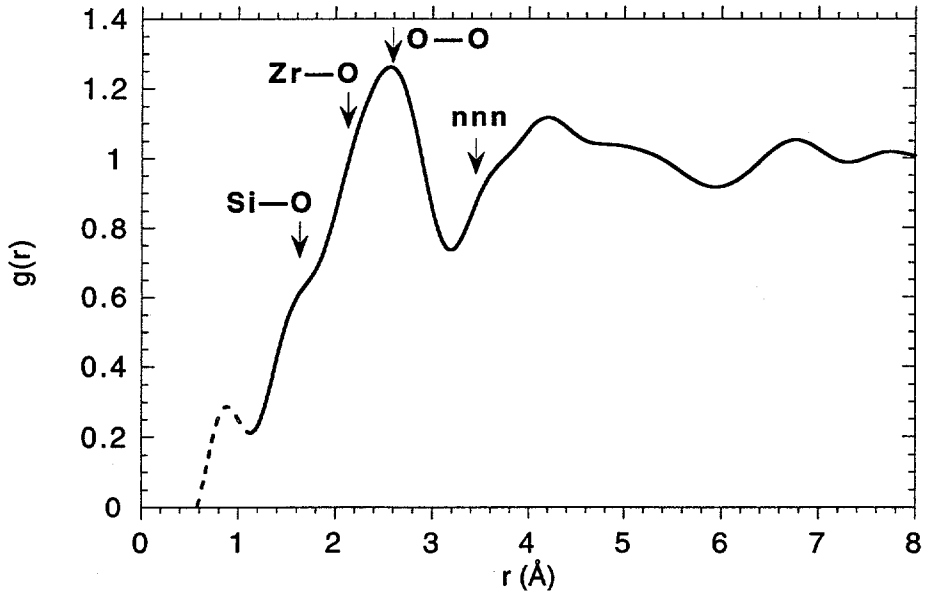

Figure 3. Experimental pair distribution function of the amorphous ^{238}Pu-doped zircon. The dashed portion below 1.2 Å represents an artifact from the Fourier transform. Bond lengths from crystalline zircon are shown.

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This work is dedicated to the memories of Jeff Lannin and Joe Hoh.

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