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Discovery of a maximum damage structure for Xe-irradiated borosilicate glass ceramics containing powellite

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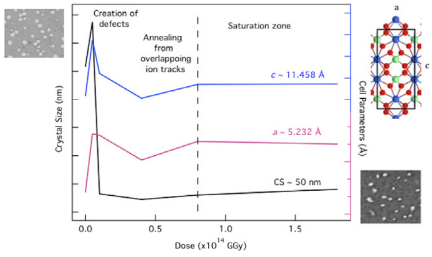
HIGHLIGHTS

- Radiation response of $CaMoO_4$ bearing glasses examined using XRD, SEM, and Raman.
- Minor amorphization of crystallites detected, but bulk of particles show resistance.
- Modifications to crystallinity and amorphous network saturate for doses > 4×10^{13} ions/cm^2.
- Saturation caused by competing processes of damage creation and thermal recovery.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to increase the waste loading efficiency in nuclear waste glasses, alternate glass ceramic (GC) materials are sought that trap problematic molybdenum in a water-durable $CaMoO_4$ phase within a borosilicate glass matrix. In order to test the radiation resistance of these candidate wasteforms, accelerated external radiation can be employed to replicate long-term damage. In this study, several glasses and GCs were synthesized with up to 10 mol% MoO_3 and subjected to 92 MeV Xe ions with fluences ranging between 5×10^{12} to 1.8×10^{14} ions/cm^2. The main mechanisms of modification following irradiation involve: (i) thermal and defect-assisted diffusion, (ii) relaxation from the ion's added energy, (iii) localized damage recovery from overlapping ion tracks, and (iv) the accumulation of point defects or the formation of voids that created significant strain and led to longer-range modifications. Most significantly, a saturation in alteration could be detected for fluences greater than 4×10^{13} ions/cm^2, which represents an average structure that is representative of the maximum damage state from these competing mechanisms. The results from this study can therefore be used for long-term structural projections in the development of more complex GCs for nuclear waste applications.

1. Introduction

In order to increase waste loading efficiency in nuclear waste glasses, alternate glass ceramic (GC) compositions are receiving a resurgence of interest as the use of civil nuclear reactors continues

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to grow. These structures are a useful alternative as they utilize an amorphous matrix to encapsulate the majority of shorter-lived radioisotopes, while enabling actinides and poorly soluble waste components such as sulfates, chlorides, and molybdates to be contained in a more durable crystalline phase [1–3]. These composite materials are of industrial interest for future wasteforms as they can reduce the final volume of waste for storage in a geological repository, accommodate waste from fuel with a higher burn-up thus increasing fuel efficiency, or be used for existing waste streams high in insoluble species, such as those arising from post-operation clean out or legacy waste from military applications.

Vitrification of high-level nuclear waste (HLW) into a glass is the widely accepted technique used for the immobilization of radioisotopes [4,5], as glasses show good thermal and radiation resistance, chemical durability when exposed to aqueous environments, and they can incorporate a wide variety of radioisotopes [1,5,6]. While there are many benefits to using these structures for long-term radioisotope storage, waste loading is limited to ~18.5 wt% in French nuclear waste glass R7T7 [7] in order to prevent phase separation [3,8,9], which can lead to a degradation of the waste-form's physical properties [2,10]. Molybdenum is a particularly problematic fission product that limits waste loading, as it can lead to the crystallization of water-soluble alkali molybdates (Na_2MoO_4, Cs_2MoO_4), known as yellow phase [9,11]. Yellow phase can act as a carrier for radioactive cesium and strontium [1,12], and hence its formation can severely alter the safety case for geological storage. While alkali molybdates are undesired, alkaline earth molybdates such as $CaMoO_4$ are comparatively water-durable (13,500 × less soluble than alkali molybdates [13]), and can therefore be used to trap insoluble molybdenum into a stable phase within a borosilicate glass matrix. Simplified GCs limiting the formation of Na_2MoO_4 relative to $CaMoO_4$ have been successfully synthesized [9,14–16], but more important to determine is the radiation response of these composite frameworks given that nuclear waste will undergo internal radioactive decay for millennia.

Accumulated radiation damage created during the encapsulation of radioisotopes can alter the composition and structure of both crystalline and amorphous phases, which can therefore affect the long-term durability of any glass or composite wasteforms. Internal radiation created by α-decay of minor actinides and Pu, β-decay of fission products, and transitional γ-decay processes can cause atomic displacements, ionization, and electronic excitations. In glasses, these events can result in changes to volume and mechanical properties, composition, stored energy, and can also induce phase transformations, such as devitrification, bubble formation, glass-in-glass phase segregation, or clustering of cations [4,5,17,18]. The range of effects is dependent on composition [19] and can sometimes result in favorable properties, such as an increase in fracture toughness, or re-vitrification of unwanted crystalline phases [4,5]. In crystals, radiation can cause a similar range of effects, in addition to causing significant dislocation within the crystal lattice and possible amorphization [20,21].

The α-decay process, and specifically the heavy recoil nuclei, is theorized to be responsible for the greatest disruption of structural order, and hence the bulk of observed macroscopic changes [4,5]. This α-recoil (70–100 keV) interacts primarily through ballistic collisions resulting in atomic displacements, while the high-energy α-particle (He^{2+}) interacts predominantly through electronic collisions that can initiate recovery processes through the creation of latent ion tracks [4,5,22]. A generally accepted model used to describe this process is the thermal spike model, in which energy is transferred to the host lattice's electrons via electron-electron and electron-phonon coupling. These interactions translate into a small cylinder of energy characterized by a temperature of ~1000 K [23]. Theoretically, electronic stopping can lead to defect annealing, or structural reorganization and precipitate formation. Thermal spikes associated with high electronic energy loss will lead to damage generation through the creation of ion tracks, while lower electronic energy loss can cause damage recovery.

Experimentally, borosilicate glasses subjected to irradiation have thus far remained amorphous, but some changes to mechanical properties, internal energy, and density properties have been observed [4,24]. Interestingly, a saturation in property modifications could be detected for irradiation doses between 2 and 4×10^{18} α/g [5,19]. A similar saturation in structural modifications has also been observed in MD simulations [25], which further supports the formation of a equilibrium state when the processes of defect formation occur at a rate similar to that of self-healing from overlapping ion tracks. Given current waste loading standards and waste streams, this saturation in structural modifications is expected to occur following ~1000 years of storage [4,5,24]. By replicating the damage occurring within this timeframe, it is therefore possible to estimate long-term damage structures. This knowledge is essential for the evaluation of any candidate materials for nuclear waste storage.

In this paper, the damage predicted to occur around this 1000 year timeframe is replicated to assess the durability of GCs with $CaMoO_4$ crystallites embedded in a borosilicate matrix. It is a fundamental approach that mimics the effects α-decay using external swift heavy ion (SHI)-irradiation in compositions that are simplified to components known to affect the formation of $CaMoO_4$ [26,27]. This study attempts to identify if long-term radiation damage will: (i) induce phase separation in homogenous systems, (ii) propagate existing phase separation, (iii) cause remediation of glass-in-glass phase separation or amorphization of crystallites through local annealing, or (iv) some combination of the above. It further seeks to identify if the saturation in modifications observed for homogeneous systems can also be detected in GCs. It therefore attempts to provide long-term structural projections of alternative nuclear waste materials in an effort to develop wasteforms with a higher waste loading efficiency that are equally resistant to internal radiation damage.

2. Materials and experimental methodology

2.1. Composition and synthesis techniques

For this study a series of non-active glasses and glass ceramics (GCs) were synthesized to test the formation and durability of powellite ($CaMoO_4$) within a borosilicate glass network when the materials were subjected to external radiation. The normalized glass and GC compositions are given in Table 1. In order to trap molybdenum in a powellite phase, MoO_3 was added in a 1:1 ratio to CaO in a borosilicate glass normalized to SON68 (non-active form of R7T7) with respect to SiO_2, B_2O_3 and Na_2O. A simplified borosilicate glass was also prepared to test the glass-in-glass phase separation tendencies induced by irradiation in systems without molybdenum. In most cases, compositions also included 0.15 mol% Gd_2O_3. Gadolinium can act as an actinide surrogate, and therefore it can

Table 1
Sample composition in mol%.

Sample	SiO_2	B_2O_3	Na_2O	CaO	MoO_3	Gd_2O_3
CNO	63.39	16.88	13.70	6.03	–	–
CNG1	61.94	16.49	13.39	7.03	1.00	0.15
CNG1.75	60.93	16.22	13.17	7.78	1.75	0.15
CNG2.5	59.93	15.96	12.95	8.52	2.50	0.15
CNG7	53.84	14.34	11.64	13.03	7.00	0.15
CN10	49.90	13.29	10.78	16.03	10.00	–