Journal of Nuclear Materials 446 (2014) 224–231

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Ion beam irradiation effects in strontium zirconium phosphate with NZP-structure type

Daniel J. Gregg [a,*], Inna Karatchevtseva [a], Gordon J. Thorogood [a], Joel Davis [a], Benjamin D.C. Bell [b], Matthew Jackson [b], Pranesh Dayal [a], Mihail Ionescu [c], Gerry Triani [a], Ken Short [a], Gregory R. Lumpkin [a], Eric R. Vance [a]

[a] Institute of Materials Engineering, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia
[b] Department of Materials, Imperial College, London SW7 2BP, United Kingdom
[c] Institute of Environment Science, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

A R T I C L E I N F O

Article history:
Received 15 October 2013
Accepted 29 November 2013
Available online 7 December 2013

A B S T R A C T

Ceramics with the sodium zirconium phosphate or NZP type structure have potential as nuclear waste form and inert matrix materials. For both applications the material will be subjected to self-radiation damage from α-decay of the incorporated actinides. In this study, ion-beam irradiation using Au- and He-ions has been used to simulate the consequences of α-decay and the effects of irradiation on the structural and macroscopic properties (density and hardness) have been investigated. Irradiation by Au-ions resulted in a significant volume contraction of ~7%, a reduction in hardness of ~30% and a loss in long-range order at fluences above 10^{14} Au-ions/cm^2. In contrast, little effect on the material properties was noted for samples irradiated with He-ions up to a fluence of 10^{17} ions/cm^2. Thermal annealing was investigated for the highest fluence Au-ion irradiated sample and significant decomposition was observed.

1. Introduction

The sodium zirconium phosphate ($NaZr_2(PO_4)_3$, or NZP) family of ceramics has received significant attention in recent years for its use as ionic conductors and as materials for oxidation resistant coating applications on carbon–carbon composites [1]. The properties of this family of compounds include low thermal expansion, high chemical and temperature stability, and superionic conductivity. Crystalline compounds with the NZP structure have also long been proposed as candidates for the immobilization of radioactive waste [1–6] and more recently have shown potential as candidate inert matrix fuels (IMF) [7,8]. For both of these applications the material will be subjected to self-radiation damage from α-decay of the incorporated actinides, and this may affect the performance of the actinide-bearing phase. The evaluation of the effect of radiation on the crystalline phase is therefore of critical concern for these applications. Of course, in addition to the self-radiation damage from α-decay there will be substantial radiation damage during reactor irradiation of the inert matrix fuels. In this work we present a basic study to establish the tolerance of NZP type ceramics to α-decay in order to investigate its potential candidacy as a waste form for the immobilization of radioactive waste and as an IMF for actinide burning.

NZP crystallizes in the rhombohedral space group $R\bar{3}c$ with a structure consisting of vertex linked ZrO_6 octahedra and PO_4^{3-} tetrahedra. The basic unit of the network consists of two octahedra and three tetrahedra $(Zr_2P_3O_{12})^{-1}$, which form chains aligned along the *c* axis. These chains are joined perpendicular to the *c* axis by PO_4^{3-} tetrahedra to produce a three-dimensional network. There are two kinds of cavities, M1 and M2, and the Na cation occupies the M1 cavities in NZP, which also align along the *c* axis. The symmetry is lowered to $R\bar{3}$ when the Na cation is substituted by a divalent cation such as Sr, as an ordering of cations and vacancies in the M1 cavities occurs [9]. A unique feature of the NZP structure is its flexibility as it can incorporate a vast array of cations within framework or inter-framework positions, and as such can potentially accommodate both the fission products and the actinides [10–12] within its crystal structure. The literature includes many examples of synthetic NZP type compounds with tetravalent actinides incorporated in framework positions [13–17]. In addition, the existence of several compounds with trivalent or tetravalent actinides incorporated within interframework sites has been described [10,12].

Several studies have investigated the effect of γ-radiation on the structure of NZP type materials and have shown that the action of external γ-radiation from a ^{60}Co source (dose up to 5×10^9 Gy) on NZP itself does not result in phase degradation or changes in the composition and structure [17–19]. Further, the water resistance of the $CsZr_2(PO_4)_3$ structure as well as the Cs leaching were shown

* Corresponding author. Tel.: +61 2 9717 7075; fax: +61 2 9717 9225.
E-mail address: daniel.gregg@ansto.gov.au (D.J. Gregg).

0022-3115/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnucmat.2013.11.048

not to be affected by the γ-radiation. There are limited studies however on the radiation effects in NZP structure type materials using ion irradiation. $CsZr_2(PO_4)_3$ was irradiated by 3 MeV Ar ions and found to become X-ray amorphous at ~0.1 displacements per atom [6]. The radiation damage was shown to increase the dissolution rates of the material in both deionised water and brine at 100 °C. The influence of 50 MeV Li^{3+} ion irradiation was investigated on the series $Ca_{0.5-x}Sr_xZr_2(PO_4)_3$ for $0 \leqslant x \leqslant 0.5$ [20]. X-ray diffraction showed the irradiation had produced some amount of amorphous material in amongst the crystalline material at a fluence of 10^{14} ions/cm^2. The degree of amorphization depended on the Ca/Sr substitution ratio. Another method to examine the long-term effects of α-decay events is to incorporate short-lived actinides within the structure, such as ^{238}Pu which has a half-life of 87.7 years (compared to ^{239}Pu which has a half-life of 24,100 years) [21], and provides up to $\sim 10^{19}$ α-decay events/g in a matter of several years. The most significant study of this kind on NZP structure type materials was carried out by Orlova et al. [17]. Trigonal $NaPu_2(PO_4)_3$ was formed after heat treatment at 1100 °C and was found using X-ray diffraction to become amorphous after 9.3×10^{18} α-decay events/g.

The process of α-decay involves the release of a high energy (~4–5 MeV) α-particle together with a low energy (~70–100 keV) recoil atom [22]. In general terms for minerals, the large recoil nucleus has a range of 20–25 nm and typically displaces on the order of 1000 atoms primarily by nuclear stopping processes. The α-particle however has a much longer range of around 10–15 μm and loses most of its energy through electronic interactions before displacing on the order of 100 atoms near the end of its track [22]. In this study, ion-beam irradiation using Au- and He-ions has been used to simulate the consequences of cumulative α-decay on the structure and properties of an NZP structure type material. $Sr_{0.5}Zr_2(PO_4)_3$ (SrZP) has been chosen due to the enhanced thermal stability of NZP structured $AE_{0.5}Zr_2(PO_4)_3$ (where AE = alkaline earth) [23] and the separate use of Au- and He-ions has allowed discrimination between damage caused by the recoil nucleus and the α-particle.

2. Experimental

2.1. Sample preparation

The samples were prepared by a modified alkoxide route. Stoichiometric amounts of tetrabutyl zirconate (TBZ) $[Zr(OC_4H_9)_4]$ were dissolved in isopropanol and intimately mixed with aqueous solutions containing $Sr(NO_3)_2$ and 85% H_3PO_4 in a stainless-steel beaker. The mixture was heated to dryness with stirring on a hot plate at ~110 °C. The dried powder was subsequently calcined in air for 20 h at 700 °C. The calcined powder was then milled using yttria-stabilized zirconia balls in cyclohexane for 16 h and dried at ~110 °C. The powder was uniaxially pressed at 5 MPa and sintered at 1500 °C for 24 h to provide ~1 g pellets (~10 mm diameter and ~3 mm thick). One face of each of the resulting pellets was polished to a 1 μm diamond finish in preparation for irradiation. Archimedes' method in distilled water was used to measure sample density (Table 3).

2.2. Characterization

XRD patterns were measured using a BRUKER D8 Advance diffractometer, utilizing Cu $K\alpha_{1,2}$ radiation and a SOL-XE energy dispersive detector over an angular range of 5–120° 2θ, with a step size of 0.02° and a counting time of 20 s per step. Refinements were carried out by the Le Bail method [24] using the RIETICA program (version 1.7.7) [25]. The peak profiles were approximated by the Pseudo–Voigt function. The lattice parameters were refined with the gradual addition of parameters and continuous graphical modelling of the background until the *R* factors ceased to change. Grazing incidence X-ray diffraction (GI XRD) characterized only the irradiation-damaged thickness on the sample surface. The diffractometer was fitted with an incident beam Gobël mirror and 0.18 parallel-plate collimator for parallel beam conditions. The incident angle was set at 3° to achieve a maximum extinction of X-rays at approximately 2–3 μm below the surface, the depth of the Au irradiated layer. The acquisition conditions were 10–80° 2θ range with a step size of 0.03° and a counting time of 20 s per step.

A Zeiss Ultra Plus SEM operating at 15 kV and equipped with an Oxford Instruments X-Max 80 mm^2 SDD X-ray microanalysis system was used for microstructural and phase-composition analysis. Samples were mounted in an epoxy resin and polished to 1 μm diamond finish. A carbon film (~5 nm) was deposited onto the polished surface. Changes in crystallographic contrast at high resolution were observed in the SEM using backscattered electron channelling contrast imaging with an ASB (angular selective backscatter) detector [26].

Raman spectra were collected using a Renishaw inVia Raman spectrometer equipped with the Argon ion laser (514 nm) and a Peltier cooled CCD detector. Stokes shifted Raman spectra were collected in the range of ~100–1200 cm^{-1} with a spectral resolution of ~1.7 cm^{-1} for the 1800 l/mm grating. The spot size was around 1.2 μm for 50× magnification.

Density variations were determined from the irradiation-induced step height on the sample surface following a similar method described in Refs. [27–29]. A mask was placed over the sample prior to irradiation. Ion irradiation caused densification of the material and the appearance of steps along the masked region. The step height was measured using Atomic Force Microscopy (AFM) and the change in density determined using $\Delta\rho/\rho = \Delta V/V = (100 \times Z)/P$, where *Z* is the step height (nm) and *P* the ion irradiation depth (nm). The ion irradiated region is estimated as the point at which the nuclear or electronic energy loss calculated by SRIM 2013 decreases to 5% of the maximum value (3.20 μm for Au irradiation).

Atomic force microscopy 2D and 3D images were obtained on a D 3000 Scanning Probe Microscope with a Nanoscope III controller. Scans were made on 5 × 5 μm^2 areas in tapping mode using a standard etched silicon tapping-mode tip. Feedback of the AFM tip oscillation amplitude was set to 60% of the free oscillation amplitude, providing a reliable topographic image of the sample surface.

An Agilent Nano Indenter G300 [30] with MTS TestWorks 4 (version 4.10A) software [31] was used to measure the surface hardness of the irradiated pellets. The nano-indenter has a displacement resolution of <0.01 nm and a load resolution of around 50 nN. A minimum of ten indentations were made using a Berkovich indenter for each sample from both irradiated and unirradiated regions. The continuous stiffness measurement (CSM) technique [32] was used for all indents with a depth limit of 2.5 μm. With the CSM technique, each indentation test gives continuous measurement of the hardness with increase in the penetration depth. Grain boundaries could not be avoided. Sampling followed a grid fashion with a spacing of 160 μm between each indentation to ensure plastic zones did not overlap.

2.3. Ion beam irradiation

In order to simulate the effect of α-decay, two sets of ion irradiation experiments were carried out on the samples: (a) 12 MeV Au ions to simulate the α-recoil nucleus which has energy between 70 and 100 keV; and (b) 5 MeV He ions to simulate the α-particles. The kinetic energy from these particles is deposited in the host