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The structure of ion beam amorphised zirconolite studied by grazing angle X-ray absorption spectroscopy

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ABSTRACT

Ti K edge X-ray absorption spectroscopy (XAS) was applied to determine the Ti co-ordination environment in the surface amorphised layer formed on zirconolite ceramics by 2 MeV Kr^+ irradiation, to a fluence of 5×10^{15} ions cm^{-2}. The application of XAS in a grazing angle geometry was demonstrated to be essential in order to probe only the surface damaged layer (<1000 nm thick), in isolation of the undamaged interior of the specimen. 2 MeV Kr^+ irradiation induced a change in the Ti co-ordination environment from majority six fold to majority five fold in the amorphised surface layer. This finding is consistent with the formation of five fold Ti in metamict natural zirconolite, as reported previously and confirmed in this study, despite the difference in dose rate of at least 10^{12} between ion beam irradiated and naturally metamict materials. This study therefore opens the door to systematic investigation of composition – structure – property relations in materials designed for radioactive waste immobilisation, through the combined application of ion beam irradiation and grazing angle XAS.

1. Introduction

The UK holds a considerable stockpile of separated plutonium, in excess of 100 tonnes of heavy metal, arising from over 50 years of civil nuclear fuel reprocessing [1]. A proportion of this stockpile may be used in future MOx or inert matrix fuels, however, a significant fraction (up to 5% of the stockpile) is unsuitable for fuel manufacture. This material will require immobilisation in a passively safe and proliferation resistant wasteform, suitable for interim storage and final disposal. Future Generation III+ and IV nuclear systems will also require an immobilisation strategy for inevitable actinide wastes and plutonium of unfavourable isotopic composition for further recycle [2]. Our investigation has centred on the disposition of plutonium (and other actinides) in ceramic wasteform materials. A key concern is to understand the long term impact of radiation damage, arising from α-decay of the immobilised actinides, on the stability of such materials. For example, α-decay of Pu-239 affords an energetic 5.2 MeV α-particle and an 86 keV U-235 daughter. The α-particle deposits its energy in ionisation processes over $\sim 10^2$ μm, generating $\sim 10^2$ atomic displacements; whereas, recoil of the daughter atom produces $\sim 10^3$ atomic displacements, through ballistic collision, within a $\sim 10^2$ nm cascade [3]. Defect accumulation and cascade overlap eventually result in amorphisation of the initially crystalline host material, analogous to metamictisation of natural U and Th bearing minerals. The safe disposal of actinide wasteform materials will require a predictive model based on a mechanistic understanding of the effects of such radiation damage on the composition, microstructure and corrosion resistance of ceramic wasteforms, over geological timescales. Systematic studies of the radiation damage in model materials are a necessary first step to building the required mechanistic understanding for a predictive physical model. Extensive investigation of metamict mineral analogues of actinide ceramic wasteforms has provided fundamental insights into radiation damage and recovery kinetics, and retention of actinide species over >100 Ma as, for example, reviewed by Lumpkin et al. [4]. Metamict minerals also provide a useful validation of systematic laboratory studies involving accelerated dose rates achieved by doping with short half life actinides (e.g. Pu-238 or Cm-244) or charged particle irradiation (e.g. by heavy Kr, Xe or Pb ions). Actinide doping accurately reproduces the combined effect of ionisation and ballistic damage but requires access to specialist laboratory facilities, which is not routine. In contrast, ion beam irradiation may effectively simulate α-recoil damage in materials which are subsequently handled without restriction (α-particle damage can also be simulated by combined He implantation, if required). However, ion irradiation produces a thin damaged or

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amorphised layer, typically less than 1000 nm thick that is not straightforward to characterise.

X-ray absorption spectroscopy (XAS) is a useful technique for the study of amorphous, aperiodic and metamict materials, providing information on the local structure around an absorber atom (i.e. number, distance and type of co-ordinating atoms; for a recent overview see [5]). XAS has been successfully applied to determine the co-ordination environment of actinide and matrix forming elements in both radiation damaged synthetic wasteforms and natural metamict minerals (in the context of this work, see [6–8]). Such investigations are essential for understanding of the relationship between the radiation amorphised structure and aqueous dissolution mechanism, for example. Clearly, the combination of XAS and ion beam irradiation offers the potential to systematically study the effect of radiation damage on materials structure at the atomic level. However, until now, it has not been demonstrated that reliable XAS data may be obtained from thin radiation damaged surface layers, in isolation of the undamaged substrate. Previous total electron yield XAS studies of Pb-implanted $SrTiO_3$, for example, were complicated by the X-ray sampling depth significantly exceeding the thickness of the damaged surface layer [9]. Here, we demonstrate the application of grazing angle XAS (GA-XAS) to the study of the ~1000 nm thick surface amorphised layer on zirconolite, $CaZrTi_2O_7$, produced by 2 MeV Kr^+ irradiation. This material is of key interest as a Pu immobilisation matrix in both single phase and multiphase ceramic wasteforms, such as Synroc [10]. The crystal structure of zirconolite, shown schematically in Fig. 1, is derived from the well known pyrochlore structure, as described by Ringwood et al. [10]. This structure is characterised by three unique Ti co-ordination polyhedra, comprising two fully occupied octahedral sites and a half occupied trigonal bi-pyramidal site. The Ca and Zr cations are eight and seven fold co-ordinate respectively. Previous studies demonstrated that Ti speciation in model oxide compounds may be determined by careful quantitative analysis of Ti K edge XANES spectra [11,12]. Furthermore, it has been demonstrated that accumulated radiation damage in metamict zirconolite minerals leads to the formation of five fold co-ordinate Ti species, at the expense of six fold co-ordinate Ti [13]. In this contribution, we demonstrate that 2 MeV Kr^+ ion beam irradiation of zirconolite reproduces this change in Ti speciation, despite the difference in dose rate of at least 10^{12}. Key to the success of this study is the acquisition of XAS data in grazing angle geometry to probe only the amorphised surface layer, in isolation of the undamaged substrate. This methodology offers the opportunity for systematic and quantitative studies of the structure of model crystalline wasteform materials, amorphised by ion beam irradiation and, ultimately, will assist in the development of coupled physical models to support disposal of actinide ceramic wasteforms.

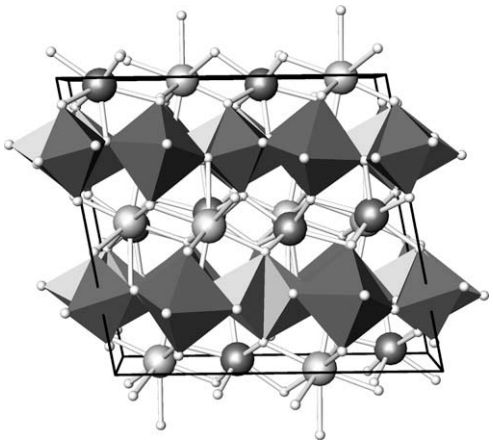

Fig. 1. Crystal structure of zirconolite viewed down [0 1 0]. Light and dark grey polyhedra represent TiO_6 and TiO_5 units, respectively. Small grey spheres represent O, large light and dark grey spheres represent Ca and Zr, respectively. Bold lines define the unit cell.

2. Experimental methods

$CaZrTi_2O_7$ was prepared by solid state reaction between $CaCO_3$, ZrO_2 and TiO_2 in stoichiometric ratio. Reagents were intimately mixed using a rotary ball mill with ZrO_2 media and isopropanol as a carrier. The mixed powder was calcined at 1200 °C for 4 h, reground using a planetary ball mill with a ZrO_2 pot and 3 mm ZrO_2 balls at 500 rpm for 2 h. 20 mm diameter pellets were formed and cold isostatically pressed at 200 MPa. Pellets were sintered at 1450 °C for 8 h and the final ceramic density was 98% theoretical. 1.0 mm thick specimens were cut from sintered pellets using a diamond saw and polished to an optical finish with SiC paper and diamond paste (to 0.25 μm grade). Specimens were annealed at 1200 °C for 4 h to relieve possible surface strain induced by polishing and reveal the grain structure. X-ray diffraction patterns were acquired using Cu K_α radiation in Bragg–Brentano or grazing angle geometry using a Siemens D5000 diffractometer, operating at 40 kV and 30 mA, with a graphite diffracted beam monochromator. Secondary electron microscopy images were acquired using a JEOL 6400 SEM operating at a voltage of 15 kV and a working distance of 17 mm.

Ion beam irradiations were performed at the Ion Beam Centre (IBC) at the University of Surrey, Guildford, UK. The entire cross sectional area of each ceramic specimen was irradiated with 2 MeV Kr^+ ions to a fluence of 5×10^{15} ions cm^{-2}. Ti K edge XAS spectra were acquired on beamline X23A2 of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), USA. Data were acquired in transmission mode using a finely ground specimen of $CaZrTi_2O_7$ dispersed in BN to achieve a thickness of one absorption length. Conventional fluorescence mode data were acquired by mounting ceramic specimens at 45° to the incident X-ray beam and detector. Grazing Angle XAS data were acquired using a motor-driven goniometer stage, permitting *x*, *y*, *z* translation and rotation about *z*-and *x*-axes (assuming conventional right handed system). Samples were first aligned parallel with the X-ray beam and then translated in the vertical to bisect the beam, the angle (α) about the goniometer axis (x) was then set to the desired grazing angle to within an accuracy of 0.01°. XAS data analysis, including correction for self absorption effects, was performed using the programs Athena, Artemis and Hephaestus [14].

3. Results and discussion

3.1. Sample characterisation

Powder X-ray diffraction confirmed the synthesis of single phase zirconolite, $CaZrTi_2O_7$: all reflections could be indexed on a C2/c cell with unit cell dimensions $a = 12.4450(16)$ Å, $b = 7.2740(6)$ Å, $c = 11.3820(10)$ Å and $\beta = 100.565(8)°$, in good agreement with previously reported data for this material [15]. Scanning electron microscopy of the sintered sample revealed a uniform microstructure comprising interlocking equiaxed grains of between 10 and 20 μm in diameter, Fig. 2a. SEM examination provided no evidence of significant porosity or the presence of secondary phases.