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Positron annihilation lifetime study of radiation-damaged natural zircons

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HIGHLIGHTS

- Study of a range of naturally occurring zircons damaged by alpha radiation.
- Characterised using a range of techniques, including PALS spectroscopy.
- Effects on hydrous material appear important, rather than direct radiation damage.
- Annealing is shown to remove the observed voids.

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ABSTRACT

Zircons are a well-known candidate waste form for actinides and their radiation damage behaviour has been widely studied by a range of techniques. In this study, well-characterised natural single crystal zircons have been studied using Positron Annihilation Lifetime Spectroscopy (PALS). In some, but not all, of the crystals that had incurred at least half of the alpha-event damage of ~10^{19} α/g required to render them structurally amorphous, PALS spectra displayed long lifetimes corresponding to voids of ~0.5 nm in diameter. The long lifetimes corresponded to expectations from published Small-Angle X-ray Scattering data on similar samples. However, the non-observation by PALS of such voids in some of the heavily damaged samples may reflect large size variations among the voids such that no singular size can be distinguished or. Characterisation of a range of samples was also performed using scanning electron microscopy, optical absorption spectroscopy, Raman scattering and X-ray scattering/diffraction, with the degree of alpha damage being inferred mainly from the Raman technique and X-ray diffraction. The observed void diameters and intensities of the long lifetime components were changed somewhat by annealing at 700 °C; annealing at 1200 °C removed the voids entirely. The voids themselves may derive from He gas bubbles or voids created by the inclusion of small quantities of organic and hydrous matter, notwithstanding the observation that no voidage was evidenced by PALS in two samples containing hydrous and organic matter.

1. Introduction

Zircon has been suggested as a nuclear waste form for the immobilisation of actinides [1]. Zircon is not easily made by an oxide route but sol–gel methods can give high zircon yields [2–4]. Natural zircons experience lattice damage due to radioactive decay of substitutional U, Th and their daughter products over geological periods of time, and this phenomenon has been studied for many years [5]. Damage is manifested as a lowering of bulk density of up to ~16% and broadening and ultimately vanishing of the X-ray diffraction (XRD) peaks [6,7]. Subsequently, the details of the

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damage process have been elucidated through Transmission Electron Microscopy (TEM) [8,9], solid state ^{29}Si nuclear magnetic resonance [10,11], infrared and Raman spectroscopy [12–14], as well as other techniques [15]. Thus lattice damage is largely caused by the ~80 keV recoil alpha nuclei, with a range of ~20 nm, rather than the longer-range ~5 MeV alpha particles, and if enough U/Th is present, this damage gradually aggregates until any traces of crystallinity are below the detectable limit. There is some debate regarding whether this process occurs quasi-continuously or in stages [8,12,13]. More recently there has been evidence [16–18] from Small-Angle X-ray Scattering (SAXS) of voids or regions of low electron density (and scattering factor) in radiation-damaged natural zircons that had incurred damage levels in excess of half those required for full amorphism (~10^{19} α/g). Such voids, ~1 nm in size, have not been reported in TEM studies, though their observation would be difficult due to general lattice damage. Although large voids, 50–100 nm in size, have been reported in TEM for one severely damaged zircon, no such voids were observed in a second severely damaged specimen in the same work [8]. In another report [19], it was stated that although ~30 nm-sized microvoids were observed in euxenite, no such voids were observed by TEM studies in (radiation-damaged) silicates.

One method to observe nanovoids in solids is via Positron Annihilation Lifetime Spectroscopy (PALS) [20]. In this technique, positrons are injected into a material where they thermalise on a timescale of a few pss in the case of well-crystallised ionic solids. Defects, such as cation vacancies and voids, act as traps for the thermalised positrons or orthopositronium, due to the absence of positively charged nuclei at these sites. As a result of the reduced electron density at these sites, the positron annihilation lifetime is increased for these trapped positrons, and can be related to the size/type of defect. Annihilation is detected as a function of time through the observation of the resultant 511 keV gamma rays, giving rise to a timing spectrum which is then deconvoluted to determine the lifetimes present. To our knowledge, no PALS measurements have been reported on zircons except on a single sample which had experienced very little natural damage [21]. The major lifetime component in this case was ~0.18 ns and other smaller components were observed. Thus, in this work, PALS measurements were undertaken to try to detect voids in a suite of damaged natural zircons. For the measurements presented here, eight samples (see Table 1) were chosen for study on the basis of Raman scattering or XRD that indicated the following: three samples incurred relatively little damage, one had incurred nearly half the amorphisation dose of 10^{19} α/gram and the other four had incurred more than half the amorphisation dose, as indicated in Table 1. The doses in our samples were deduced by comparison of the Raman scattering or XRD patterns with previous results [14]. The samples were also characterised by Scanning Electron Microscopy (SEM) to detail their chemical composition, plus infrared absorption spectroscopy where appropriate.

2. Experimental

The smaller of the zircon single crystal samples were 5–6 mm in size and broadly ellipsoidal in shape. These were cut in half down the long axis to produce surfaces which were polished down to a 1 μm diamond finish. The other samples were larger and again polished faces were prepared for examination.

Beam based PALS measurements were carried out using the apparatus recently constructed by the Centre for Antimatter Matter Studies (CAMS) at the Australian National University [22]. The apparatus utilises a ^{22}Na source moderated by solid Ne to produce a continuous beam of low energy positrons. This is then trapped using a buffer gas trap and released as a pulsed beam with a repetition rate of around 1.5 kHz and pulses of ~800 ps FWHM. A customised analysis software package uses the annihilation in a reference sample to establish the instrument function of the positron pulse (which is non-Gaussian, and not easily approximated using a functional form). This is then used in a fitting routine which convolutes the instrument function with one or more lifetimes to find the best fit to the sample lifetime data. Typical spectra contain over 1 million counts, and errors are given through the least squares fitting process employed in the data analysis. For the present samples, the shortest lifetime observed was 290 ps for Zircon 11 after treatment at 700 °C (see Section 3, Table 2), which is at the lower limits of the possible resolvable lifetimes in this system.

Measurements on samples Zircon 19 and Zircon 26 were carried out prior to the samples being cut, although this had a negligible effect on the results. Measurements were carried out with a positron implantation energy of 5 keV, giving the implantation profile shown in Fig. 1. While positron diffusion to the surface and subsequent trapping may also cause the appearance of a lifetime in the spectra, this was not observed in the current study. A preliminary study was also made on the unheated two larger samples, Zircon 10 and 11, with a conventional fast–fast coincidence lifetime spectrometer [23] with a time resolution of ~220 ps, also within the CAMS collaboration, at the University of Western Australia. In this case. a 30 μCi source encapsulated in an 8 μm Kapton foil was used in a standard sandwich geometry. Fast–fast coincidences were obtained from two BC418 plastic scintillators coupled to Burle 8850 photomultiplier tubes (Burle Industries, Inc., Lancaster, PA) to acquire the lifetime spectra. In this case, the analysis was performed using the well established PALSfit software package (Version 1.64) [24], with careful account taken of any source contribution effects.

SEM was carried out on all samples mounted in epoxy resin and

Table 1
Hf, U and Th concentrations as substitutional impurities in zircon samples, determined by SEM microanalysis. The α-dose has been determined by the Raman scattering and estimates from X-ray diffraction, and the amorphisation dose is ~10 × 10^{18}/g.

Sample	HfO_2 (wt %)	UO_2 (wt %)	ThO_2 (wt %)	α-dose (10^{18}/g)	Provenance
Zircon 10	0.91	0.16	<0.01	6.5	–
Zircon 11	1.64	0.24	"	4.0	–
Zircon 19	0.94	0.43	"	2.1	–
Zircon 26	0.90	0.21	"	4.5	–
D23524	2.30	0.35	0.1	~3	Sri Lanka
D29620	0.44	<0.05	0.2	~1	Madagascar
Cam27[a]	2.81	0.36	0.05	5.6	–
Cam 27[b]	2.60	0.35	0.1	–	–
No.2[a]	1.86	0.47	0.5	7	–
No.2[b]	1.70	0.60	0.2	–	–

[a] [9].
[b] Current measurements, averaged over 5 or 6 points on polished samples.