

Metamictization of zircon: Raman spectroscopic study

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Received 30 June 1999, in final form 13 December 1999

Abstract. Raman spectroscopy of radiation-damaged natural zircon samples shows increased line broadening and shifts of phonon frequencies with increasing radiation dose. Stretching and bending frequencies of SiO₄ tetrahedra soften dramatically with increasing radiation damage. The frequency shifts can be used to determine the degree of radiation damage. Broad spectral bands related to Si–O stretching vibrations between 900 and 1000 cm⁻¹ were observed in metamict/amorphous zircon. The radiation-dose-independent spectral profiles and the coexistence of this broad background and relative sharp Raman modes in partially damaged samples indicate that these bands are correlated with amorphous domains in zircon. The spectral profiles of metamict zircon suggest that in comparison with silica, the SiO₄ tetrahedra are less polymerized in metamict zircon. This study also shows that ZrO₂ and SiO₂ are not the principal products of metamictization in zircon. No indication of bulk chemical unmixing of zircon into ZrO₂ and SiO₂ was found in 26 samples with a large variation of radiation damage (maximum dose: 23.5×10^{18} α -events g⁻¹). Only one sample showed clearly, in all measured sample areas, extra sharp lines at 146, 260, 312, 460 and 642 cm⁻¹ characteristic of tetragonal ZrO₂. The geological (and possibly artificial heating) history of this sample is not known. It is concluded that radiation damage without subsequent high temperature annealing does not cause unmixing of zircon into constituent oxides.

1. Introduction

Zircon (ZrSiO₄) is tetragonal: $I4_1/amd$ and $Z = 4$ (Hazen and Finger 1979). The ideal structure consists of a chain of alternating, edge-sharing SiO₄ tetrahedra and ZrO₈ triangular dodecahedra extending parallel to crystallographic axis c . Natural zircon commonly contains U and Th as well as other rare earth elements. Due to radioactive decay of naturally occurring radionuclides, and their daughter products in the ²³⁸U, ²³⁵U and ²³²Th decay series, the structure of zircon can be heavily damaged by α -decay events (Weber *et al* 1997). As a result, natural zircon is commonly found to be 'metamict', an aperiodic or amorphous state (Ewing 1994). Radiation effects in zircon have important implications in several application fields. Zircon has been proposed as a host phase for the disposal of excess weapons-grade Pu and other actinides (Burakov 1993, Anderson *et al* 1993, Ewing *et al* 1995, Weber *et al* 1996, Ewing 1999).

Self-radiation damage from α -decay of the incorporated actinides can affect the durability and performance of these actinide-bearing phases. The evaluation of the effect of radiation on the crystalline phase and an understanding of the damage mechanism and the structure of the damaged phase have been one of the critical concerns in this application on actinide waste form.

The effects of radiation damage on the structure of zircon can be seen as systematic changes of its physical properties: an increase in cell parameters and broadening of x-ray diffraction patterns (Holland and Gottfried 1955, Murakami *et al* 1991, Weber 1993); a decrease in IR and Raman intensities and dramatic band broadening (Vance 1975, Woodhead *et al* 1991a, Nasdala *et al* 1995, 1996, 1998); decreases in refractive index and birefringence (Holland and Gottfried 1955, Vance and Anderson 1972); absorption of hydrous species (Aines and Rossman 1986 and Woodhead *et al* 1991b); an increase in fracture toughness (Chakoumakos *et al* 1987); a decrease in density (Holland and Gottfried 1955, Murakami *et al* 1991); a variation of HRTEM diffraction patterns (Yada *et al* 1987, Murakami *et al* 1991); a variation of ^{29}Si NMR features (Farnan *et al* 1999); decreases in hardness and bulk modulus (Chakoumakos *et al* 1991); a variation of diffuse x-ray scattering from single crystals (Salje *et al* 1999) and the appearance of Huang type diffuse x-ray diffraction (Ríos and Salje 1999).

Despite extensive studies on metamict zircon, controversies concerning the structure of metamict zircon remain. In their x-ray and optical investigation, Holland and Gottfried (1955) observed in their x-ray data a systematic development and disappearance of an extra peak near 2θ of $35\text{--}36.5^\circ$ with increasing degree of α -decay radiation damage. They proposed the formation of an intermediate polycrystalline phase with intermediate dose. In an x-ray study by Murakami *et al* (1991), peak splitting was observed for most of the partially damaged samples, and this was interpreted as the coexistence of two phases with different degrees of damage. There have been reports of the presence of crystalline ZrO_2 in metamict zircon. Stott and Hilliard (1946) reported that an unheated sample gave an x-ray pattern of monoclinic ZrO_2 , while cubic and probably tetragonal ZrO_2 have been reported in different studies (Anderson 1962, Vance and Anderson 1972). In their infrared spectroscopic work Wasilewski *et al* (1973) analysed their data in terms of a two-stage damage process. In the first stage the effect of α -recoil damage on undamaged zircon is claimed to produce, throughout the lattice, highly stressed and expanded zircon with distorted SiO_4 tetrahedra, while in the second stage the recoil nucleus is thought to cause the formation of ZrO_2 , SiO_2 and probably some aperiodic ZrSiO_4 . A study by Vance (1975) indicated that the Si–O bonding in heavily damaged zircon was not too different from that in glassy SiO_2 , as infrared spectra of Si–O vibrations in heavily damaged zircon were similar to that of vitreous SiO_2 . The presence of crystalline ZrO_2 was observed in heavily damaged zircon annealed at high temperatures (Ellsworth *et al* 1994, McLaren *et al* 1994). Recently Meldrum *et al* (1998, 1999b) reported an observation of decomposition of synthetic zircon under high-temperature heavy-ion irradiation and proposed the formation of a ‘liquid-like’ state in displacement cascades and that a low cooling rate could allow the nucleation of crystalline ZrO_2 in displacement cascade regions. It has also been reported that several important similarities and differences exist among ion-irradiated specimens and minerals that undergo radiation damage from α -decay processes (Meldrum *et al* 1999a). In an x-ray absorption spectroscopic study at the Zr–K edge, Farges and Calas (1991) saw no evidence for decomposition into crystalline oxides in metamict zircon and reported a decrease in Zr–O distance of 0.1 Å while the coordination number of Zr decreased from eight to seven. An infrared study by Woodhead *et al* (1991a) reported that the structure of metamict zircon consisted of distorted and disoriented isolated silica tetrahedra with few if any undisplaced Zr cations. Raman work by Nasdala *et al* (1995) showed no indication of an amorphous phase as very heavily damaged samples still gave rise to relatively sharp

lines. Their results did not support an increasing polymerization of SiO₄ tetrahedra with increasing dose and they considered that isolated SiO₄ tetrahedra were distorted and tilted with increasing degree of damage but still isolated in a highly metamict state. Salje *et al* (1999) showed recently that metamictization in zircon could not be a phase transition driven by a critical defect concentration, but rather was a heterogeneous process of cascade formation and overlap. Instead of a 'driven phase transition' two percolation points are expected, one for the crystalline material and one for the amorphous material.

We undertook this Raman investigation of radiation-damaged zircon in order to study possible variations of local environments, the nature of the polymerization and whether metamict zircon mainly consists of ZrO₂ and SiO₂.

2. Experiment

2.1. Sample description

Zircon samples used in this study are all gemstones from Sri Lanka. The Sri Lanka zircons were selected because of their low impurities, low OH content, different degree of radiation damage, gem quality and well defined geological age (570 ± 20 million years). Among these samples twelve have been used in previous studies by Murakami *et al* (1991) and Ellsworth *et al* (1994). Other samples were characterized by electron microprobe, reflection and absorption infrared spectroscopy, x-ray diffraction and NMR. The chemical analysis has shown that the total content of impurities in any sample was less than 3 mol% and the most significant impurities are Hf, U, Th and Y. The content of individual impurities varies from sample to sample. However, for all the samples the Hf content is less than 2.5 mol%, Al < 0.1 mol%, Th < 0.8 mol%, U < 1.4 mol% and Y < 0.2 mol%. The lattice parameters of some samples were determined by x-ray Guinier powder diffraction with Si as internal standard. More detailed information on the samples is listed in tables 1 and 2.

Thermal annealing of sample 4604 was carried out between 600 K and 1700 K by step heating for one hour at each chosen temperature under N₂ flow. The samples were quenched to room temperature after each anneal.

2.2. Raman measurement

Raman spectra were recorded with a DILOR Z24 spectrometer triple monochromator in a single channel mode, coupled to a Coherent 90-3 argon ion laser. The selected incident wavelengths were 514, 488 and 457 nm in order to clearly identify the luminescence bands due to low concentration impurities. The microscope configuration was used (magnification objective 50×). Slit widths were adjusted to obtain an 8 cm⁻¹ spectral line width. In each experiment 15 scans were collected and averaged.

FT-Raman spectra were recorded at room temperature using a Bruker IFS 66v spectrometer adapted with a Bruker FRA 106 FT-Raman accessory. A silicon-coated calcium fluoride beam-splitter and radiation of 1064 nm from an Nd:YAG laser was used for the excitation laser which can produce 350 mW output. A liquid-nitrogen-cooled high sensitivity Ge detector was used. The spectra were recorded with a laser power of 45–100 mW and a back-scattering geometry. The focused beam was about 200 μm in size. For crystalline zircons 250–512 scans were used and 1000–3000 scans for heavily damaged zircons. The resolution of all the spectra was 2 cm⁻¹.

Laser power was carefully chosen to avoid potential damage to the measured areas caused by the intense local heat from the laser beam. Various laser powers were used in order to test the

Table 1. Zircon sample descriptions. Density is in units of g cm^{-3} and dosage in units of 10^{18} α -events g^{-1} .

Zircon	Locality	Density	dosage	a (Å)	c (Å)	V (Å ³)	Reference/source
4403 ^a	Sri Lanka	4.72	0.06	6.6085	5.9845	261.36	Murakami <i>et al</i> (1991), Ellsworth <i>et al</i> (1994)
Fumt10	Sri Lanka	ND	0.5	6.6046	5.9810	260.90	FUMT
3104 ^b	Sri Lanka	4.68	1.0		ND		Ellsworth <i>et al</i> (1994)
S3	Sri Lanka	ND	0.8	6.6135	5.9990	262.39	CAM
269	Sri Lanka	ND	1.8	6.6301	6.0266	264.91	NHM
4605 ^a	Sri Lanka	4.58	2.0	6.645	6.047	267.01	Murakami <i>et al</i> (1991)
4303 ^a	Sri Lanka	4.58	2.1	6.652	6.051	267.8	Murakami <i>et al</i> (1991), Ellsworth <i>et al</i> (1994)
4694	Sri Lanka	4.57	2.8	6.645	6.042	266.8	CAM
Cam26	Sri Lanka	ND	2.9		ND		CAM
4604 ^a	Sri Lanka	4.54	3.5	6.68	6.07	271	Murakami <i>et al</i> (1991)
Z5	Sri Lanka	4.36	4.2		ND		HAM
S4	Sri Lanka	ND	4.8	6.67	6.09	271	CAM
Cam25	Sri Lanka	ND	5.2		ND		CAM
4304 ^a	Sri Lanka	4.36	5.8	6.67	6.13	273	Murakami <i>et al</i> (1991)
4103 ^a	Sri Lanka	4.17	6.7	6.70	6.15	276	Murakami <i>et al</i> (1991)
Cam27	Sri Lanka	ND	5.6		ND		CAM
4105 ^a	Sri Lanka	4.25	6.3	6.70	6.13	275	Murakami <i>et al</i> (1991), Ellsworth <i>et al</i> (1994)
Ni12	Sri Lanka	4.2	7.1		ND		HAM
3107 ^b	Sri Lanka	4.12	7.2		ND		Ellsworth <i>et al</i> (1994)
Z2	Sri Lanka	4.03	8.6		ND		HAM
Ti8	Sri Lanka	4.04	9.6	unable to determine a and c			HAM
6500 ^c	Sri Lanka	ND	11.7	unable to determine a and c			Woodhead <i>et al</i> (1991a)
157	Sri Lanka	3.96	13.1		ND		NHM
Sd4	Sri Lanka	ND	15.9		ND		CAM
82988	Sri Lanka	ND	23.5		ND		NHM
Cam1	unknown	ND	ND	6.6070	6.0221	262.88	CAM

^a Measured by Murakami *et al* (1991).

^b Measured by Ellsworth *et al* (1994).

^c Measured by Woodhead *et al* (1991a).

ND = not determined.

CAM = Sedgewick Museum, University of Cambridge, UK;

FUMT = Freiberg University of Mining and Technology, Germany;

HAM = Mineralogisches Museum, Mineralogisch-Petrographisches, Universität Hamburg, Germany;

NHM = Natural History Museum, UK.

The original British Museum Catalogue numbers for the samples from NHM are: 269 = BM1920,269; 157 = BM1921,157; and 82988 = BM82988.

hypothesis that intensive laser heating could lead to unwanted annealing of radiation damage. No such effects were observed. The time dependence of FT-Raman spectrum for sample 269 and Ni12 was also examined to check whether the samples were overheated. After 2 hours of irradiation at a power of 200 mW with a beam size of $\sim 200 \mu\text{m}$, the spectra remained unchanged. Samples were checked after Raman measurements using an optical microscope. No indications of surface damage and change of colour by the laser radiation were observed.

3. Results

Theoretical analysis (Dawson *et al* 1971) predicts twelve Raman-active normal modes in zircon at $k = 0$: $2A_{1g} + 4B_{1g} + B_{2g} + 5E_g$. Raman zone-centre normal modes can also be

Table 2. Electron microprobe analyses of zircon samples that have not been characterized in previous studies.

Sample	SiO ₂	FeO	ZrO ₂	HfO ₂	CaO	Al ₂ O ₃	Y ₂ O ₃	ThO ₂	UO ₂	Total
Fumt10	33.01	—	65.85	0.81	0.01	—	0.14	0.01	0.03	99.86
S3	33.41	—	64.61	1.48	0.01	—	0.06	0.03	0.04	99.64
4605	32.16	0.04	67.03	1.23	—	—	0.07	0.05	0.21	100.79
4694	32.95	0.06	64.11	1.65	—	0.01	0.19	0.08	0.19	99.24
Cam26	33.36	0.01	65.26	1.28	0.01	—	0.03	0.03	0.18	100.16
4604	32.04	0.02	66.51	1.27	—	—	0.10	0.08	0.32	100.34
Z5	33.55	—	65.07	1.85	—	0.01	0.01	0.01	0.29	100.79
S4	33.38	—	65.15	0.99	—	0.01	0.05	0.11	0.23	99.92
Cam25	33.26	—	63.74	1.77	—	—	0.22	0.07	0.31	99.37
Cam27	33.38	—	63.26	2.81	0.01	—	0.22	0.05	0.36	100.09
Ni12	32.68	—	65.74	1.64	—	0.01	0.02	0.14	0.39	100.62
Z2	33.46	—	65.17	1.19	—	—	0.07	0.07	0.46	100.49
Ti8	32.77	0.01	64.01	2.56	0.01	0.13	0.03	0.05	0.55	100.29
157	32.48	0.01	64.85	2.36	0.05	—	0.10	0.08	0.86	100.79
Sd4	32.69	0.01	65.66	0.63	—	0.01	0.01	0.12	1.02	100.15
82988	32.91	0.01	63.08	1.80	—	—	0.47	0.30	1.38	99.95

— undetectable.

described as internal modes and external modes: internal = $2A_{1g} + 2B_{1g} + B_{2g} + 2E_g$ while external = $2B_{1g}(\text{translatory}) + 2E_g(\text{translatory}) + E_g(\text{rotatory})$.

Raman spectra of natural zircon show systematic variations with increasing degree of metamictization (figure 1). Nine of the 12 predicted Raman modes were observed in the most crystalline zircon 4403 (figure 1). They are internal modes: 1008 cm^{-1} (B_{1g} , Si–O ν_3 stretching), 975 cm^{-1} (A_{1g} , Si–O ν_1 stretching), 439 cm^{-1} (A_{1g} , Si–O ν_2 bending) and 269 cm^{-1} (B_{2g} , Si–O ν_2 bending) and external modes: 393, 355, 225, 214 and 202 cm^{-1} (Syme *et al* 1977, Hoskin and Rodgers 1996). The other predicted bands are probably too weak to be observed in our experimental set-up.

The effects of α -decay radiation damage on the structure of zircon are characterized by a decrease in Raman intensity, a decrease in phonon frequencies and line-broadening of Raman modes. Well crystallized zircon samples show sharp and well resolved Raman modes (figure 1(a) and 1(b)). With increasing α -decay radiation dose, the two Si–O stretching modes between 970 and 1010 cm^{-1} become weaker and broader while the lower-frequency modes become gradually weak and could not be analysed for high dose. These spectral variations are accompanied by a development of a broad spectral feature between 850 and 1100 cm^{-1} which can be clearly seen in heavily damaged samples (figure 1(c)). As this broad feature appears in both FT-Raman and conventional Raman spectra, we conclude that this feature is not related to impurity luminescence but seems due to the amorphous phase in damaged zircon samples.

We now analyse the spectra in terms of a simple two-phase behaviour. Phonon frequencies of crystalline/distorted crystalline zircon show a systematic variation with radiation damage (figure 2). With increasing damage, the frequencies of the Si–O stretching mode near 1008 cm^{-1} and the external vibration near 356 cm^{-1} decrease strongly at doses below $3.5 \times 10^{18}\text{ }\alpha\text{-events g}^{-1}$ and saturate at higher doses. The frequency decrease is $\sim 1.5\%$ for the Si–O stretching mode at 1008 cm^{-1} , $\sim 1.0\%$ for the Si–O stretching at 975 cm^{-1} , $\sim 0.8\%$ for the Si–O bending near 438 cm^{-1} and $\sim 2.8\%$ for the external mode at 355 cm^{-1} which is related to the motion of SiO_4 as a unit against Zr. The frequency shift for the external bands below 250 cm^{-1} is difficult to determine as their intensities and shift in frequency are too weak to allow reliable measurements.

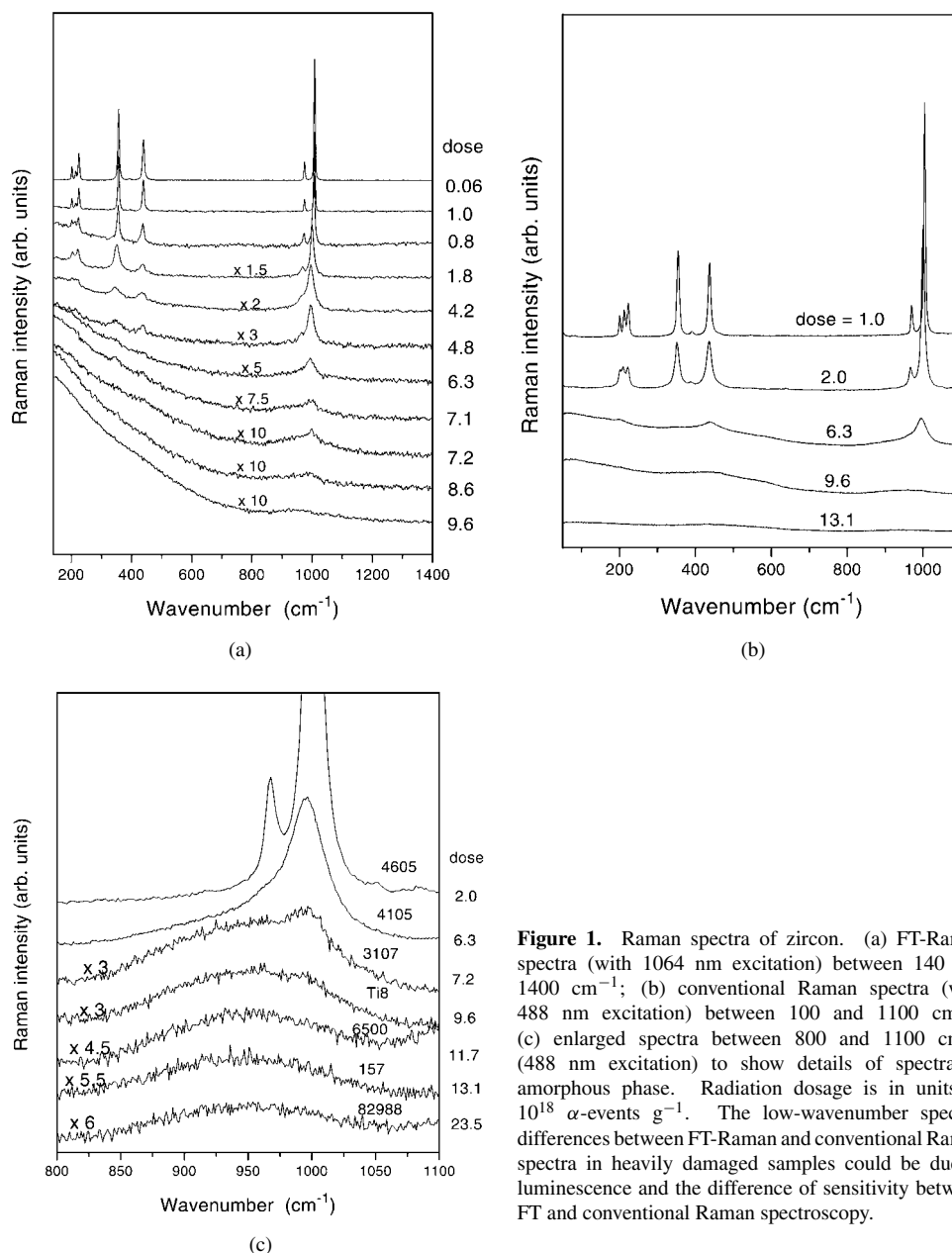


Figure 1. Raman spectra of zircon. (a) FT-Raman spectra (with 1064 nm excitation) between 140 and 1400 cm⁻¹; (b) conventional Raman spectra (with 488 nm excitation) between 100 and 1100 cm⁻¹; (c) enlarged spectra between 800 and 1100 cm⁻¹ (488 nm excitation) to show details of spectra of amorphous phase. Radiation dosage is in units of 10¹⁸ α -events g⁻¹. The low-wavenumber spectral differences between FT-Raman and conventional Raman spectra in heavily damaged samples could be due to luminescence and the difference of sensitivity between FT and conventional Raman spectroscopy.

Within experimental resolution, no clear band-splitting and no extra signals were observed that could indicate a change of symmetry of crystalline material in partially metamict zircon. Although x-ray data for the samples show a similar peak splitting for 2θ between 35 and 37° observed by Holland and Gottfried (1955), this splitting in 2θ is likely due to co-existence of areas with different degrees of damage rather than a structural phase transition as explained by Murakami *et al* (1991).

In the following we focus on spectral features related to the amorphous phase. The coexistence of the broad feature between 850 and 1100 cm⁻¹ and the Si–O stretching band near 995 cm⁻¹ in the same spectral region in samples 4105 and 3107 indicates the coexistence of

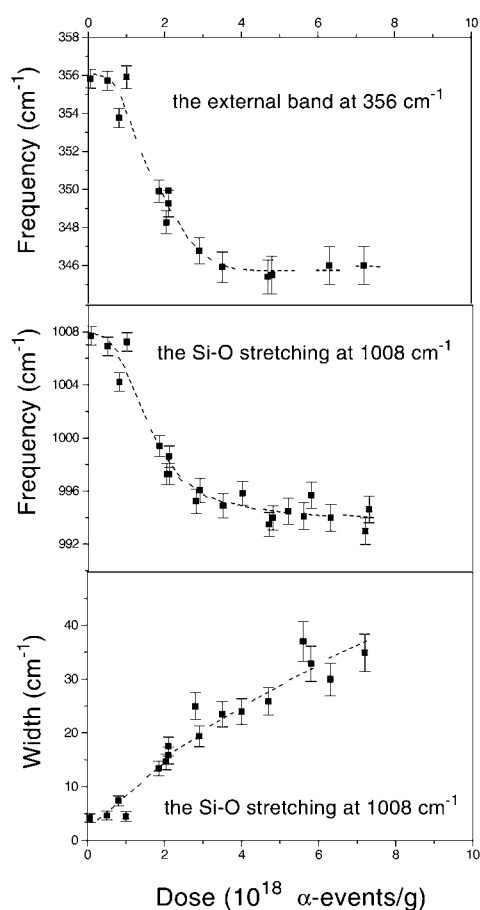


Figure 2. Phonon frequencies and width as a function of radiation dose (each point is an average of six measurements). The lines are visual guides.

the amorphous phase and damaged crystalline material (figure 1(c)). The gradual development of this background shows the accumulation of the amorphized phase with increasing radiation dose. A spectral subtraction was performed to remove the signals of the amorphized phase (sample 82988) from the measured spectra (figure 3). The comparison of the broad bands in samples 4105 and 3107 suggests that the structure of the amorphous phase is essentially identical when dose is higher than $6.3 \times 10^{18} \alpha\text{-events g}^{-1}$. Deconvolution of the spectra between 750 and 1100 cm^{-1} shows that the spectrum of the amorphous phase in this region consists of two main vibrations located at $920 \pm 15 \text{ cm}^{-1}$ and $970 \pm 20 \text{ cm}^{-1}$. Their positions and spectral features do not show a clear dose dependence. Due to its low Raman intensity this broad feature can be hardly traced in slightly or partially damaged samples with dose less than $3 \times 10^{18} \alpha\text{-events g}^{-1}$. The identical spectral features for the samples with dose higher than $10 (10^{18} \alpha\text{-events g}^{-1})$ indicates that further bombardment of the amorphous phase by α -particles does not lead to further significant changes of the structure of metamict zircon.

Among all samples studied only one sample, Cam1, shows Raman bands of zircon plus additional sharp lines at 146, 260, 312, 460 and 642 cm^{-1} which are indicative of crystalline

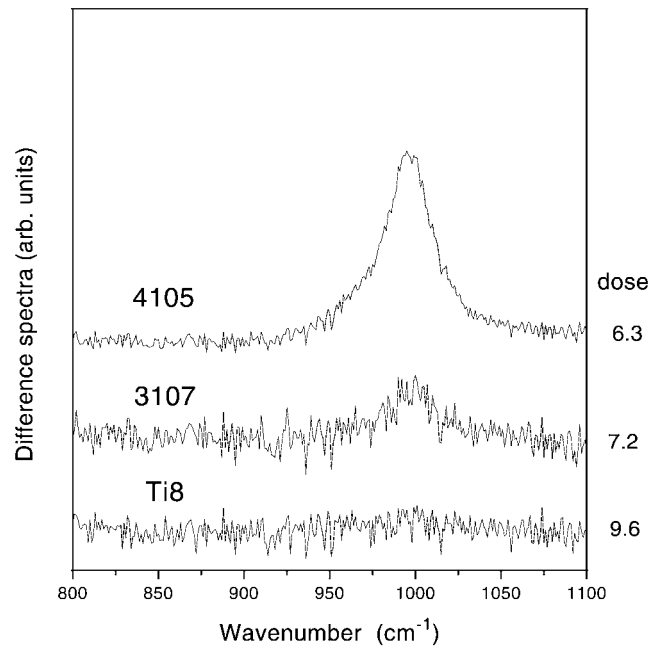


Figure 3. Difference spectra of samples 4105, 3107 and Ti8 after spectrum subtraction. Radiation dosage is in units of 10^{18} α -events g^{-1} .

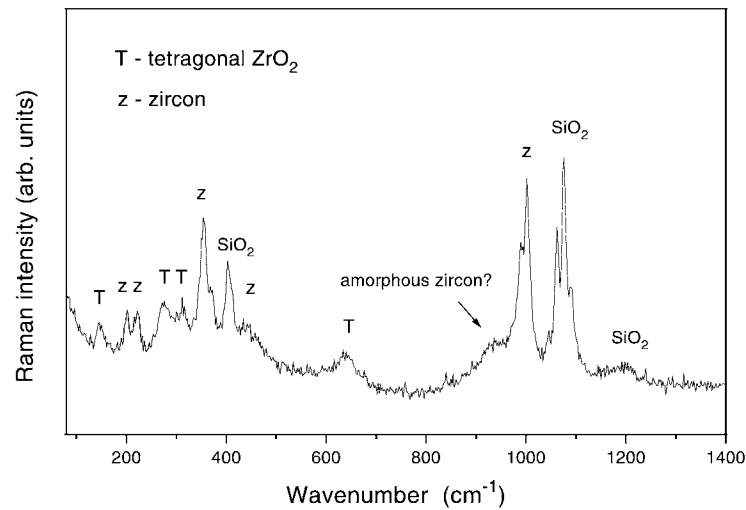


Figure 4. Raman spectrum of sample Cam1 between 80 and 1400 cm^{-1} .

ZrO_2 (figure 4). Zirconia has three polymorphs: the monoclinic, tetragonal and cubic structures (Smith and Newkirk 1965). In tetragonal ZrO_2 with space group $D_{4h}^{15}/P4_2/nmc$ ($Z = 2$), the predicted irreducible representations of optical phonons (for zero wave vector) are $A_{1g}(R) + 2B_{1g}(R) + 3E_g(R) + A_{2u}(IR) + 2E_u(IR)$ and six phonon modes are expected to be Raman active while 18 and one Raman bands are expected for monoclinic and cubic ZrO_4 , respectively (Keramidas and White 1974, Anastassakis *et al* 1975, Kim and Hamaguchi

1997). Kim *et al* (1993) have shown that tetragonal ZrO_2 doped with 2 mol% of Y_2O_3 shows characteristic bands at 145, 259, 318, 462, 606 and 641 cm^{-1} . The observed extra Raman bands in Cam1 are well consistent with those Raman bands of tetragonal ZrO_2 . Infrared powder and reflection spectra of Cam1, in fact, consist of damaged crystalline zircon, tetragonal ZrO_2 and amorphous SiO_2 . No characteristic bands from cubic and monoclinic ZrO_2 were observed in any samples.

4. Discussion

Our results show that radiation-damaged zircon samples give two signals: one from crystalline/distorted crystalline zircon and the other from amorphized zircon. The signal from the crystalline part of the sample shows a continuous decrease of the phonon frequencies and an increase of linewidths with increasing radiation dose.

The implication of the correlation between width and frequency of Raman Si–O stretching and degree of radiation dose in zircon is that it may be used for the determination of the degree of damage from Raman peak parameters for partially damaged zircon samples. The existence of impurities in natural zircon may have an additional influence on peak profiles although this effect is expected to be small for our samples for the following reasons. Firstly, the samples have low levels of impurities. The most common impurities are Hf, U and Th. The Hf content is always less than 3 mol%. This is not sufficient to cause the observed phonon frequency shifts. Secondly, if Hf were the cause of a significant frequency shift in the spectrum of zircon one would expect to see, because of the difference of the ionic radius between Zr and Hf and complex host–lattice silicate interactions, a weak increase in frequency for the Si–O stretching modes instead of the observed decrease (Nicola and Rutt 1974, Hoskin and Rodgers 1996). Thirdly, thermal treatment of a partially damaged sample (sample 4604, with dose of 3.5×10^{18} α -events g^{-1} and less than 1.10 mol% of Hf) at high temperatures results in a recovery of the damaged structure of zircon as indicated by a band sharpening and an increase of phonon frequencies up to those of well crystallized samples (figure 5).

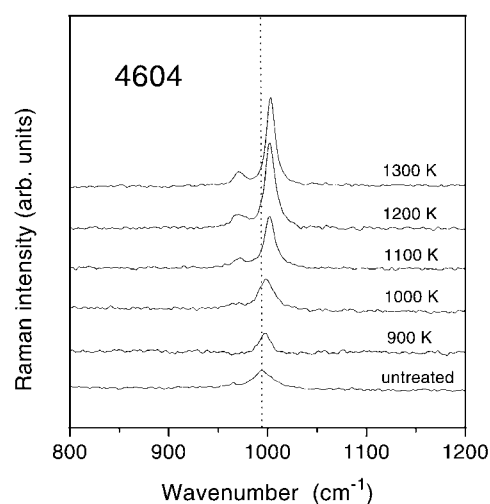


Figure 5. Spectra of zircon 4604 (dose = 3.5×10^{18} α -events g^{-1}) annealed at different temperatures for one hour.

The dose dependence of the line shift of the Si–O stretching and bending modes follows roughly the same behaviour as the increase of the unit cell volume of the crystalline part of the samples (Weber *et al* 1994). This observation probably implies that the Si–O bond strength decreases when the specific volume of the crystal increases. This may indicate that the bond distances increase or/and that the bond is depolarized by a rotation of the tetrahedra within the zircon structure. It clearly shows that the SiO₄ tetrahedra are involved in the unit cell swelling and that they act as a significant part of the zircon structure rather than isolated molecular complexes.

The saturation of the mode softening at $\sim 3.5 \times 10^{18}$ α -events g⁻¹ is understood in terms of the threshold behaviour discussed by Salje *et al* (1999). In this model, an upper limit for the local defect concentration exists in the crystalline part of the sample. If this defect concentration is exceeded by further damage the structure collapses and becomes amorphized. The characteristic dose D_s for this effect is $\sim 3.5 \times 10^{18}$ α -events g⁻¹ in zircon.

We finally discuss the question of whether increasing dose changes the structure of the amorphous component. Above 6.3×10^{18} α -events g⁻¹ the Raman spectra of the amorphous phase show no significant changes of their line profiles. The only visible change is in the intensity of the signals of the amorphous phase with no clear changes in band frequencies. This observation does not rule out subtle changes of the local structure of amorphized zircon while large changes of the interconnection of the SiO₄ tetrahedra can be ruled out. It also shows that no phase separation into a pure silica-type glass occurs unless the sample is annealed at high temperatures. The results of annealing experiments will be published in a forthcoming paper.

5. Conclusion

This study shows that two Raman signals coexist in radiation-damaged zircon due to an amorphous phase and a damaged crystalline phase. The signal from the crystalline volume shows spectral variations due to a softening of the crystal structure of zircon with increasing damage dose. A saturation of phonon frequencies was observed at dose of $\sim 3.5 \times 10^{18}$ α -events g⁻¹, and this is explained by a percolation model proposed by Salje *et al* (1999). We observed that with increasing dose from 6.3×10^{18} α -events g⁻¹ the signals from the amorphous domain remain unchanged. This suggests that when a dose is higher than 6.3×10^{18} α -events g⁻¹ the structure of the amorphous domain is essentially identical. The results from this study also show that ZrO₂ and SiO₂ are not the principal products in metamict zircon.

Acknowledgments

The authors thank Mark Welch at the Natural History Museum (London, UK), Steve Laurie at the Sedgwick Museum (University of Cambridge, UK), Jochen Schlüter at the Mineralogisches Museum (Universität Hamburg, Germany) and Andreas Massanek at Freiberg University of Mining and Technology (Germany) for providing some of the samples used in this study. We are very grateful to S J Reed for assistance with the electron microprobe analysis. This work would not have been possible without the carefully characterized samples resulting from the work of Takashi Murakami. Financial support from EU network ERB-FMRX-CT97-0108 is gratefully acknowledged. RCE gratefully acknowledges support for Basic Energy Sciences/DOE (DE-FG-02-97-ER45655).

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