

Single-Crystal Neutron Diffraction Study of Metamict Zircon up to 2000 K

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Abstract

High-temperature single-crystal measurements of metamict zircon were performed up to 2000 K and the recrystallization was monitored using the width and intensity of selected peaks. Full data sets were collected at room temperature, 1573 and 1823 K. The changes in the probability density function (p.d.f.) of the O atoms revealed important features of the recrystallization. The measurements were done in air using a mirror furnace and performed on the D19 four-circle diffractometer at the ILL equipped with a vertically curved two-dimensional position-sensitive detector.

Introduction

Natural zircon (ZrSiO_4 , $I4_1/amd$, $Z = 4$) occurs with various degrees of crystallinity depending on the amount of radiation damage it has suffered through α events due to the substitution of Zr mainly by U and Th. This has led to the use of zircon as a dating mineral in geochronology (Headley, Ewing & Haaker, 1981). The physical properties of this so-called metamict zircon are very different from synthetic samples (Speer, 1982). EXAFS and XANES measurements suggest that 'metamict zircon shows a significant decrease in its Zr—O bond distances accompanying an increase in distortion of the Zr—O polyhedra as compared with crystalline zircon' and 'the coordination number around Zr in the metamict states may be less than that in the crystalline state' (Nakai *et al.*, 1987). Furthermore, the structure of the second-nearest-neighbour shell is perturbed. The metamict state has also been observed in other systems, *e.g.* pyrochlores (Gregor, Lytle, Chakoumakos, Lumpkin & Ewing 1985).

Metamictization may thus be characterized as a sort of composite crystal where slightly misorientated

crystallites of zircon are separated by areas with varying disorder depending on the radiation damage. The metamictization process may lead to disordered zircon, zircon glass and/or amorphous ZrO_2 and SiO_2 (Speer, 1982; Lumpkin & Chakoumakos, 1988). According to Swanson, Parson & Hoelke (1971), it is due to a spontaneous collapse of the long-range order when the local defect concentration increases that the free energy approaches a value close to the free energy of the amorphous state. As a consequence, materials with macroscopically crystal-like habit only show very broad reflections.

A hydrous component (OH^- or H_2O) seems to stabilize the metamict state by compensating local charge imbalances (Aines & Rossmann, 1986; Caruba, Baumer, Ganteaume & Iaconi, 1985; Lumpkin & Chakoumakos, 1988). On heating, there seems to be a dehydration process which speeds up near 1200 K, *i.e.* the temperature at which recrystallization occurs (Aines & Rossmann, 1982). The structure of heat-treated zircon is, however, not necessarily the same as that of the premetamict state (Ewing & Ehlmann, 1975). The differential thermal analysis (DTA) of metamict zircon shows an exotherm peak at 1143 K attributed to the recrystallization process (Lipova, Kusnetsova & Makarov, 1965). This process is of fundamental interest since it is a phase transition from a disordered or amorphous state to a crystalline one.

Diffraction experiments on metamict crystals of zircon should help clarify the ordering phenomena taking place during the recrystallization. Generally, disorder phenomena manifest themselves by a diffuse-scattering contribution which has to be distinguished from the broadening of the Bragg reflections due to mosaicity. The Bragg intensities, however, also contain information about the disorder in an averaged manner. This information can be extracted by analysing the atomic displacement parameters including anharmonic terms and/or split-atom models. Such

studies should preferably be done with neutrons since the scattering powers of the three elements are similar, they are independent of the scattering angle and the absorption effects are small.

Experimental

We performed structure refinements of metamict crystals (provenience: Ratnapura, Sri Lanka) at room temperature, 1573 and 1823 K. In addition, some reflections were selected and their three-dimensional shapes, reflecting the degree of disorder, were monitored in smaller temperature steps. Such an experiment was possible using D19 at the ILL in combination with a mirror furnace previously used in powder experiments (Frey, Boysen & Vogt, 1990; Boysen, Frey & Vogt, 1991). All the high-temperature measurements were done in air.

The furnace was developed by Lorenz (1988) and later improved (Lorenz, Neder, Marxreiter & Schneider, 1992). It makes use of the focusing properties of a rotational ellipsoid. Two ellipsoidal mirrors made of AlMg_5 are joined together, having a common focal point in which the sample is put (Fig. 1). In the other two focal points, two 1000 W halogen lamps are located, which emit the light that is reflected onto the sample. The furnace is cooled by a water-flow system

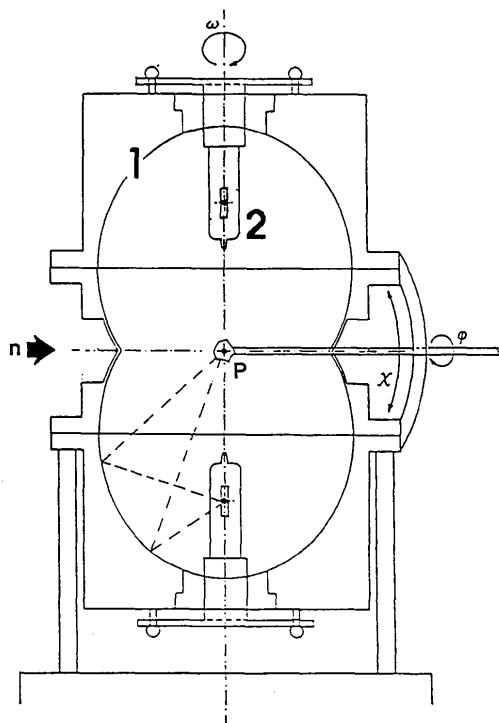


Fig. 1. Schematic plan of the mirror furnace showing the mirror (1), halogen lamps (2) and sample position (P). (Taken from Lorenz, 1988.)

inside the aluminium blocks. This type of furnace has been widely employed for single-crystal growth from melts (see *e.g.* Eyer, Zimmermann & Nitsche, 1975; Watanabe & Shimazu, 1976). The crystal is glued onto an Al_2O_3 tube in which a Pt/Pt-10at.%Rh thermocouple is placed. We used a glue based on Al_2O_3 . Temperature control was achieved using a PID controller with a thyristor varying the current sent to the halogen lamps. The temperature stability was ± 3 K. This type of furnace is easy to set up, has a very low background, can be run in air or, if modified suitably, in any desired atmosphere and is connected to a standard 220 V net voltage supply. D19 is a single-crystal diffractometer with a vertically curved two-dimensional position-sensitive detector (PSD) (Thomas *et al.*, 1983; Maier & Blank, 1988). The PSD is built up of 16 cathode (γ direction in Fig. 2) and 512 anode wires (ν direction in Fig. 2) and situated 1.15 m from the sample having a solid angle of 4° (γ) horizontally and 64° vertically (ν).

The detector is filled with ^3He at 6 atm pressure as a detection gas and argon at 1 atm as quench gas. The detector stability is roughly 1%.

The furnace can be accommodated on an Eulerian cradle with an offset ϕ axis and the two-dimensional detector allows data collection in various geometries. Owing to the limitation in χ imposed by the geometry of the furnace, we measured in parallel-beam geometry at $\chi = 90^\circ$, finding reflections by varying ω and ϕ , using a wavelength of 1.043 \AA . A single ω scan gives

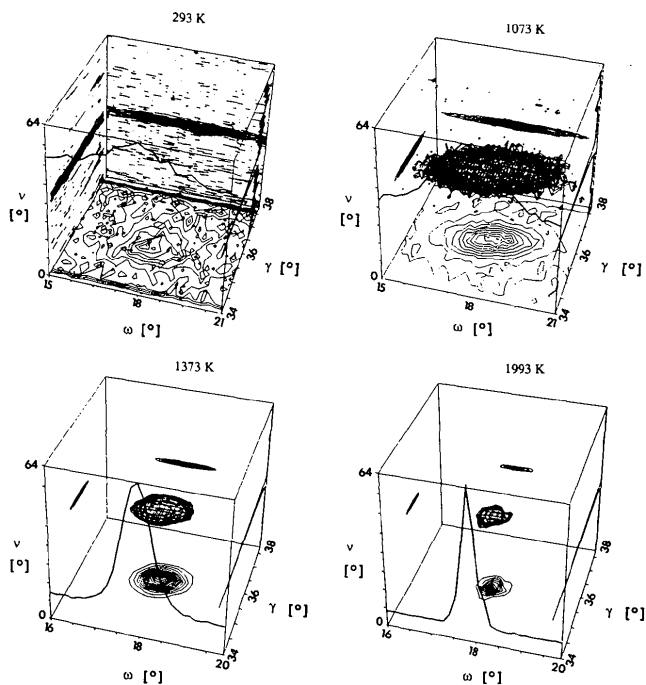


Fig. 2. The 132 reflection at 293, 1073, 1373 and 1993 K. Note the different scales, especially the compressed ν scale.

information about three directions in reciprocal space rather than one with a single detector. This allows one to observe extended diffuse scattering, twinning, co-existing phases, mosaicity *etc.* at the same time.

Results and discussion

Fig. 2 shows the shape of a three-dimensional Bragg reflection at different temperatures before and after the recrystallization. It is displayed in a three-dimensional array of ω , γ and ν . This figure shows a contour plot of the reflection and the projections on the $\omega - \gamma$, $\omega - \nu$, $\gamma - \nu$ planes and the projected intensities $I(\omega)$ and $I(\nu)$. The increasing degree of order in ZrSiO_4 is monitored by the narrowing of the peak along ω accompanied by an increase of the integrated intensity as shown in Fig. 3. Note that even at room temperature localized Bragg reflections occur, although broadened in all directions. This allows the refinement of an averaged structure. The broadening along ω and ν might be attributed, at least partly, to misorientations of the crystallites, while the broadening along γ shows inherent features like size effects or strains. One observes that the recrystallization starts noticeably near 1100 K as known from the literature. The diagram seems to suggest a two-stage recovery process with a first process finishing near 1250 K. Vance & Anderson (1972) measured the variation of the density during isochronal recovery of metamict zircon and also obtained a curve suggesting that the recrystallization is a two-stage process. The first recovery stage in their study peaked at 1320 K close to where we observe a discontinuity in the slope of the integrated intensity and full width at half-maximum (Fig. 3). Weber (1990) found the same behaviour in Pu-doped zircon.

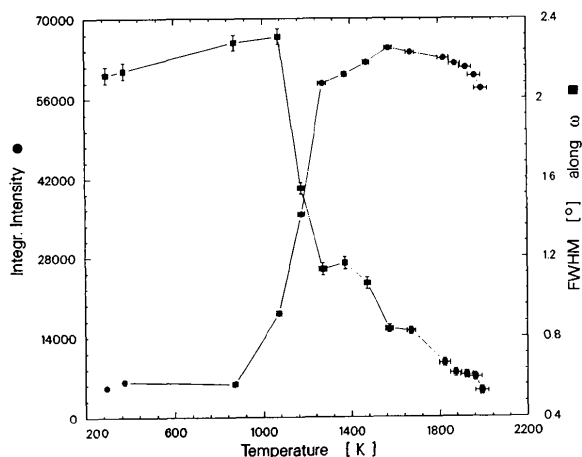


Fig. 3. The variation of the integrated intensity and full width at half-maximum along ω of the 132 reflection with temperature. (The lines are drawn to guide the eye.)

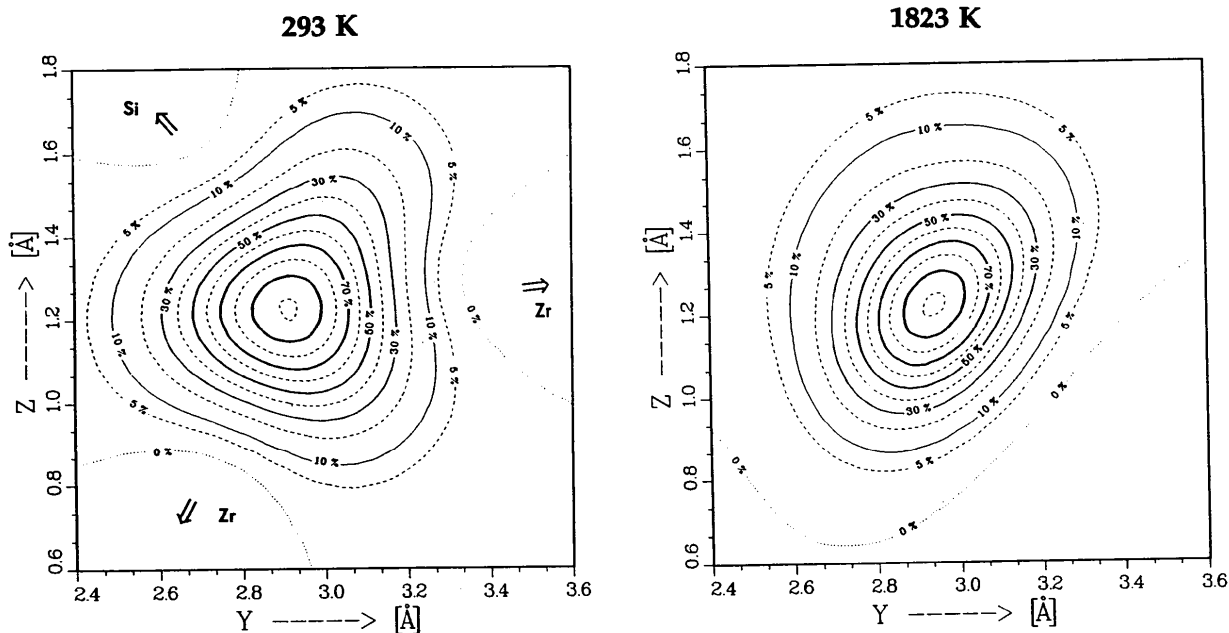
We measured four data sets of metamict zircon: two at room temperature using different crystals with different degrees of metamictization to be able to judge sample dependence and two at high temperatures after recrystallization.* We checked all the ω scans for powder lines and other parasitic scattering by displaying each scan with the help of a specially written colour graphics program (Richard, 1990). The integrated intensities were extracted as described by Wilkinson & Khamis (1983). With a two-dimensional detector, very weak reflections are measured much more reliably and with smaller errors since the background is better defined. A correction for absorption was applied. Refinements were done using the *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983) program allowing one to take into account terms of the anharmonic thermal displacement parameters. Table 1 summarizes the results of the four refinements at three different temperatures. Note that there is no significant difference between the results of the two room-temperature data sets.

Fig. 4 shows the probability density functions (p.d.f.) of the O atoms at the different temperatures. The room-temperature measurements show the same features: the oxygen p.d.f.'s have minima in the direction towards the cations. At higher temperatures, after the recrystallization, these minima disappear and there is an increased density shifted towards the Si atom. This behaviour can be understood as a consequence of the two different types of bonding involved in ZrSiO_4 . There are two types of Zr—O bonds in the dodecadeltahedron. If one describes this dodecadeltahedron as two interpenetrating tetrahedra, one obtains corner-linked and edge-sharing ZrO_4 tetrahedra with the SiO_4 tetrahedron. The thermal responses of these two linkages are different. We know from a powder study on synthetic non-metamict zircon (Mursic, Vogt & Frey, 1992) that in the temperature range where metamict zircon recrystallizes a structural relaxation exists. The sudden expansion of the Si—O bond and of the SiO_4 tetrahedral volume in this temperature region allows the smaller corner-sharing ZrO_4 tetrahedra to rotate. Thus, the strain due to the structural disorder present in the metamict state is released and crystallization is promoted *via* a rearrangement of the Zr—O subunit. In the metamict state, the disorder created by the recoiling nuclei after an α event leads to a frozen-in disordered state in which the polyhedra are disordered on an averaged scale. The minima in the oxygen p.d.f. in direction towards the cations at room temperature arise from the static disorder of

* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54983 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Summary of the refinements on ZrSiO_4 (values of C_{ijk} are multiplied by 1000)

		Space group $I4_1/amd$ (No. 141, origin at centre)			
		Zr atoms on 4(a)	0, 3/4, 1/8,	site symmetry $4m2$	
		Si atoms on 4(b)	0, 1/4, 3/8,	site symmetry $4m2$	
		O atoms on 16(h)	0, y, z,	site symmetry m .	
Data set		293 K (I)	293 K (II)	1573(20) K	1823(15) K
Measured reflections		575	60	127	117
Unique reflections		61	45	39	39
R (merge) (%)		1.7	—	1.3	1.3
$\sin(\theta_{\max})/\lambda$ (\AA^{-1})		0.77	0.77	0.80	0.70
R (weighted) (%)		1.4	1.2	1.3	1.3
Goodness of fit		2.6	2.9	2.1	2.1
Lattice constants (\AA)					
a		6.610(5)	6.608(6)	6.640(6)	6.649(6)
c		6.001(5)	6.002(6)	6.033(7)	6.040(7)
Positional parameters					
O	y	0.0646(4)	0.0655(3)	0.0661(1)	0.0660(1)
	z	0.1967(3)	0.1954(2)	0.1995(8)	0.1996(7)
Atomic displacement parameters U_{ij} (\AA^2) and C_{ijk}					
Zr	U_{11}	0.025(1)	0.0050(5)	0.0176(4)	0.0190(4)
	U_{33}	0.024(1)	0.0071(5)	0.017(1)	0.017(1)
Si	U_{11}	0.026(1)	0.0050(9)	0.0176(6)	0.0192(6)
	U_{33}	0.022(2)	0.0044(9)	0.017(2)	0.015(2)
O	U_{11}	0.0336(7)	0.0116(5)	0.0413(7)	0.0457(7)
	U_{22}	0.0241(7)	0.0066(5)	0.0179(4)	0.0196(4)
	U_{33}	0.0250(5)	0.0072(3)	0.0233(6)	0.0255(6)
	U_{23}	-0.0022(5)	-0.0009(2)	-0.0053(4)	-0.0059(4)
	C_{333}	0.007(2)	—	0.005(2)	0.006(2)
	C_{112}	-0.004(1)	—	—	—
	C_{223}	0.0017(4)	0.0026(6)	0.0027(8)	0.0027(7)
	C_{233}	-0.009(2)	-0.0011(5)	—	-0.0016(8)

Fig. 4. Probability density function p.d.f. of the O atom in the bc plane ($x=0$) at room temperature and 1823 K.

slightly disordered crystalline regions within the crystallites. The reordering to a coherent single crystal during annealing is shown by the narrowing of the reflections. We explain the increased density of the O-atom p.d.f. towards the Si atom after annealing as the result of an increasing stability of the SiO₄ tetrahedra compared with the two interpenetrating ZrO₄ tetrahedra with increasing temperature. This may be seen as a precursor effect of the following decomposition. After decomposition, the first crystalline phase observed is tetragonal ZrO₂ (Mursic, Vogt & Frey, 1992). Under this aspect, the decomposition of ZrSiO₄ may be considered as a phase transformation where Zr changes the coordination polyhedron but maintains the coordination number.

A more detailed description of the mechanism is beyond the scope of this paper and is given elsewhere (Mursic, Vogt & Frey, 1992).

Concluding remarks

We have shown that, with a fairly simple experimental set-up, high-temperature single-crystal diffraction studies up to 2000 K can be done in air. A few advantages of a two-dimensional PSD are pointed out: direct visualization of a reflection in three dimensions; easy recognition of parasitic or genuine weak and diffuse scattering, in particular thermal diffuse scattering; and easy monitoring of Bragg reflections in the vicinity of phase transitions without readjusting instrumental parameters if the order parameter is strongly correlated with the unit cell. These advantages provide an easy access to more studies on disordered materials such as liquid crystals and fibres.

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