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Structure refinement of zirkelite from Kaiserstuhl, West Germany

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Abstract

The crystal structure of zirkelite from Kaiserstuhl, West Germany has been refined by the full-matrix least-squares method using 949 independent reflections to a final R value of 0.052. The data were collected on a four-circle diffractometer using graphite-monochromated Mo$K\alpha$ radiation. The structure is monoclinic, space group $C2/c$ with cell dimensions a = 12.431(1), b = 7.224(1), c = 11.483(3)Å, β = 100.33(1)° and Z = 8. The results from this study show that the crystal lattice has suffered only minor damage due to an accumulated radiation dose of 1.2×10^{18} alphas per gram from the decay of natural uranium and thorium contained within the mineral. The most significant change is the increase (2–3 times) in the temperature factors. The high values of these parameters are interpreted to be the direct result of the action of alpha-recoil.

Introduction

Pyatenko and Pudovkina (1964) first proposed that zirkelite (=zirconolite), $CaZrTi_2O_7$, was closely related to the fluorite structure. They established that it had a superstructure based on a *C*-centered monoclinic lattice which is eight times the fluorite subcell such that $a_{\text{superstructure}} = -a_1 - a_2 + 2a_3$, $b_s = a_1 – a_2$, $c_s = 3/2a_1 + 3/2a_2 + a_3$, where a_1, a_2, a_3 refer to the cubic cell. Recently, the crystal structure has been solved and refined using both powder (Rossell, 1980) and single crystal X-ray techniques (Gatehouse *et al.*, 1981). The close relationship to fluorite was confirmed by these experiments. In the latter study, the site of the M4 titanium atom was found to be displaced off special position 4(*e*) at (.5, y, .25) to the general position 8(*f*) on either side of the 2-fold axis; decreasing the coordination from 6 to 5.

Zirkelite comprises about 35 percent of SYNROC, a synthetic rock designed for the immobilization of high level nuclear wastes (Ringwood *et al.*, 1979a, b). The highly radioactive actinide elements within these wastes, are partitioned into the zirkelite and perovskite phases when hot-pressed at 1100–1200°C with the SYNROC mixture. The actinides decay by a series of alpha-decays at a significant rate for a million years, during which time a large number of atomic displacements occur in the host lattice.

Natural zirkelites from the Kaiserstuhl carbonatite complex W. Germany, contain ~5 weight percent $UO_2 + ThO_2$. Oversby and Ringwood (1981) have calculated an accumulated radiation dose of 1.2×10^{18} alphas per gram for these minerals, using an age determined by the K–Ar method (Wimmenauer, 1966) of 16 million years.

In this report, a single crystal X-ray analysis has been carried out on the Kaiserstuhl zirkelite in order to examine the effects of alpha-recoil damage on the crystal lattice. The results from the single crystal refinement of a synthetic zirkelite (Gatehouse *et al.*, 1981) are used as a standard to which the natural zirkelite data can be compared.

Crystal structure analysis

The grains of zirkelite used in this study were separated from the Kaiserstuhl carbonatite (Wimmenauer, 1966), and provided by Dr. J. Keller. Many of the crystals exhibited polysynthetic twinning. Preliminary Weissenberg and precession X-ray photographs showed that reflections (*hkl*) and (*h0l*) were absent for $h + k = 2n$ and $l = 2n$ respectively. These restrictions suggested the pos-

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Table 1. Crystal data for Kaiserstuhl zirkelite

$(Ca_{.85}REE_{.02}Mn_{.01}Th_{.06}U_{.02})(Zr_{.87}Ti_{.13})$
$(Ti_{.95}Zr_{.13}Nb_{.45}Fe^{2+}_{.12}Fe^{3+}_{.25})O_7$

Monoclinic, C2/c (No. 15)

a =	12.431(1)Å	c =	11.483(3)Å
b =	7.224(1)Å	β =	100.33(1)°
V =	1014.5(5)Å^3	Z =	8
Dc =	4.9Mg m^{-3}	μ(MoKα) =	9.6mm^{-1}

μR = 0.29 (effective μR for spherical crystal with same volume as crystal used; R = radius of spherical crystal)

sible space groups *Cc* or *C2/c* in agreement with Gatehouse *et al.* (1981).

For the structure determination a crystal measuring approximately 0.05 × 0.03 × 0.08 mm was mounted on a Picker FACS-1 four-circle diffractometer with the unique axis *y* approximately parallel to the *φ* axis of the diffractometer. Lattice parameters and crystal orientation matrix were obtained by least-squares refinement of the setting angles of twelve carefully centered reflections having 2*θ* values between 49 and 60°, using Mo$K\alpha_1$ radiation (λ = 0.70926Å) reflected from a graphite-crystal monochromator (2*θ*m = 12.12). Crystal data are given in Table 1. The chemical analysis is given in Table 2.

Intensities were measured by the $\theta - 2\theta$ continuous-scan technique with a scan speed of 2° min^{-1} (2*θ*) and range from 0.8° below the $K\alpha_1$ to 0.8° above the $K\alpha_2$ peak for the reflection concerned. Stationary background counts of 20 seconds duration were made at the extreme of the scan range. Three standard reflections (800), (040), (008), showed little variation in intensity throughout the course of the data collection. 1,710 reflections having 2*θ* values between 3 and 60° were collected from the octants $hk\bar{l}$ and $h\bar{k}\bar{l}$ except those which were absent for the *C* centering condition. The data were sorted and averaged and reduced to structure amplitudes in the usual way. Data reduction procedures are described by Ferguson *et al.* (1979). Because of the small size of the crystal (μ.R = 0.29) an absorption correction was not applied. A partial compensation was achieved by averaging the intensities of equivalent reflections, $(0k\bar{l})$ and $(0\bar{k}\bar{l})$, in the monoclinic cell. (Interscale *R* factor for equivalent reflections = 0.019). After discarding reflections for which $I/\sigma(I) < 3.0$, a total of 949 were available for subsequent structural analysis. The statistical discrepancy value for this data set R_s (= $\Sigma\sigma_s(Fo)/\Sigma|Fo|$, where $\sigma_s(Fo) = \sigma(I)$ (Lp^{-1}/2|*Fo*| is the error contribution to |*Fo*| from counting statistics alone) is 0.026.

Table 2. Chemical analysis of Kaiserstuhl zirkelite. Structural formula based on 7 oxygens

Nb_2O_5	15.7	0.45
TiO_2	22.7	1.08
ZrO_2	34.8	1.08
ThO_2	4.1	.06
UO_2	1.4	.02
FeO	2.28	.12
Fe_2O_3	5.32	.25
MnO	0.2	.01
CaO	12.5	.85
REE	0.9	.02
SUM	99.90	3.94

Electron microprobe analyses by N.G.Ware;
Iron determinations by E. Kiss.

Structure solution and refinement

Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974) and were corrected for both real and imaginary anomalous components.

The refinement was carried out using the full matrix least-squares program SFLS (Prewitt, 1966) which minimizes the function $\Sigma w(|Fo|-k|Fc|)^2$, where *k* is an overall scale factor and *w* is the weight of an observation taken as unity in the initial stages.

The atomic coordinates from the synthetic zirkelite refinement in the space group *C2/c* (Gatehouse *et al.*, 1981) were used in the starting model for Kaiserstuhl zirkelite. Initially, Ca, Th and U were assigned to the M1 site, Zr to the M2 site, Ti, Nb to the M3 and M5 sites and Fe and Ti to the M4 site. The other minor cations were ignored. After several cycles of refinement and converting to anistropic temperature factors of the form,

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\right]$$

for all atoms, the conventional *R* factor decreased to 0.063. The equivalent isotropic temperature factors for individual atoms at convergence were about 2–3 times as large as those reported by Gatehouse *et* *al.* (1981). This behavior persisted in all subsequent refinements.

The significance of splitting the M4 site into two individual half atoms which occupy equivalent sites on either side of the two-fold axis as reported by Gatehouse *et al.* (1981), was checked by calculating a difference Fourier map without the M4 atoms. This showed a large region of electron density (24 e Å^{-3}) centered on 4 (*e*) at (0.5, y, 0.25) where y = 0.14. Peaks on either side of the two-fold axis were not found. This is not surprising, since the expected separation of the M4 sites ~0.5–0.8Å is close to the resolution of our data set (0.43Å). Alternatively, the M4 atoms may occupy a range of positions. The structure was therefore refined with M4 placed on special position 4(*e*). However, at convergence the *R* factor remained at 0.088, a value considerably higher than that obtained for the split site model. The M4 position for this model was (0.5, 0.121(2), 0.25) and the equivalent isotropic thermal parameter B, was 8.1Å^2. Thus, the split site model was readopted and manual adjustment and refinement of the population parameters followed.

At first, the placement of elements was guided by the previous results of synthetic zirkelite and by crystal chemical reasoning. Thus, Fe^{2+} + Fe^{3+} were restricted to occupy the M3 + M4 sites, Zr the M2, M3 and M4 sites (but mostly the M2 and M3 sites) and Ti all cation sites except for the M1 site. Refinement of the Zr population parameter in the M2 site resulted in an immediate decrease, and suggested the presence of the lighter element, Ti. In keeping with previous single crystal results, the excess Zr from the M2 site was transferred to the M3 site. Other refinements indicated that the heavy elements Zr + Nb (40 + 41 electrons respectively) did not occupy the M4 site, but were found to favor the M3 and M5 sites.

Refinement of the Nb population parameter in the M5 site was carried out; at the same time adjustments were made to the amount of Ti in M5 and Nb and Ti in M3 to maintain both the total occupancy of these sites to be 1.0 (or 0.5 in the case of the M4 site) and the unit-cell composition. The population parameter of Fe in M4 was then released and the corresponding changes to Ti and Fe were made in the M4 and M3 sites. During these final cycles it became necessary to refine separately the z positional parameter and the beta (1,3) value of M4 because of a strong correlation. The errors quoted for these two parameters in Table 3, were derived from the inverted full-matrix at the end of each

Table 3. Atomic coordinates and thermal parameters for Kaiserstuhl zirkelite, with esd's in parentheses

Atom	Site	Occupancy	X/A	Y/B	Z/C	Beq.(Å^{2})
M(1)	8(f)	0.87 Ca + 0.13 (Th,U,REE)	0.3752(1)	0.1245(3)	0.4971(1)	1.78
M(2)	8(f)	0.85 Zr + 0.15 Ti	0.1210(1)	0.1261(2)	-0.0239(1)	1.36
M(3)	8(f)	0.125 Fe + 0.375 Ti + 0.35 Nb + 0.15 Zr	0.2500(1)	0.1252(3)	0.7450(1)	1.50
M(4)	8(f)	0.33 Fe + 0.17 Ti	0.4788(8)	0.0892(6)	0.2509(5)	3.42
M(5)	4(e)	0.72 Ti + 0.28 Nb	0.0	0.1279(5)	0.25	1.60
X(1)	8(f)	1.00 O	0.3087(7)	0.1243(13)	0.2864(6)	3.10
X(2)	8(f)	1.00 O	0.4693(6)	0.1373(14)	0.0891(7)	2.75
X(3)	8(f)	1.00 O	0.2070(8)	0.0857(12)	0.5687(8)	2.84
X(4)	8(f)	1.00 O	0.3957(8)	0.1665(13)	0.7151(7)	2.97
X(5)	8(f)	1.00 O	0.7121(8)	0.1700(11)	0.5821(7)	2.51
X(6)	8(f)	1.00 O	-0.0024(7)	0.1157(14)	0.4189(6)	2.42
X(7)	8(f)	1.00 O	0.1086(8)	0.0653(13)	0.7917(7)	2.98
	U11	U22	U33	U12	U13	U23
M(1)	0.020(1)	0.019(1)	0.029(1)	0.003(1)	0.005(1)	0.004(1)
M(2)	0.017(1)	0.012(1)	0.023(1)	0.002(1)	0.004(1)	0.001(1)
M(3)	0.019(1)	0.017(1)	0.021(1)	-0.001(1)	0.005(1)	0.000(1)
M(4)	0.056(7)	0.062(3)	0.009(1)	-0.003(3)	-0.002(3)	-0.004(3)
M(5)	0.020(1)	0.020(1)	0.020(1)	0.0	0.002(1)	0.0
X(1)	0.062(6)	0.013(4)	0.042(4)	-0.004(6)	0.007(4)	-0.007(5)
X(2)	0.028(5)	0.024(5)	0.051(5)	0.002(6)	0.004(4)	0.002(5)
X(3)	0.030(5)	0.028(6)	0.048(5)	-0.007(4)	-0.001(4)	-0.007(4)
X(4)	0.035(6)	0.041(7)	0.036(5)	-0.010(5)	0.005(4)	-0.006(4)
X(5)	0.034(5)	0.027(6)	0.031(4)	0.000(4)	-0.004(4)	0.007(4)
X(6)	0.031(4)	0.028(5)	0.035(4)	0.001(6)	0.010(3)	0.005(4)
X(7)	0.026(5)	0.043(6)	0.041(5)	-0.014(5)	-0.001(4)	0.003(4)

Table 4. Interatomic distances (Å) and O–M–O angles (°) of Kaiserstuhl zirkelite, with esd's in parentheses

						M3 Octahedron			
M1	-X2	2.326(8)	M3	-X4	1.927(10)	X4	-X1		98.9(4)
	X2^1	2.371(9)		X1	1.960(9)		-X1^1		82.3(4)
	X3	2.391(9)		X1^1	1.970(9)		-X5		95.2(4)
	X3^1	2.396(10)		X7	1.975(9)		-X3		86.1(4)
	X1	2.412(7)		X5	1.983(8)	X1	-X7		86.1(4)
	X5	2.486(9)		X3	2.019(9)		-X5		92.7(3)
	X4	2.490(8)		MEAN	1.972		-X3		85.6(3)
	X6	2.532(9)				X1^1	-X7		92.5(4)
	MEAN	2.426					-X5		84.1(3)
M2	-X3	2.051(8)					-X3		97.6(3)
	X6	2.066(8)				X7	-X5		80.1(4)
	X5	2.107(8)					X3		98.8(4)
	X2	2.108(10)				M4 Trigonal bipyramid			
	X7	2.141(9)	M4	-X2	1.867(10)	X2	-X2^1		152.9(6)
	X5^1	2.314(10)		X2^1	1.873(10)		-X4		115.0(5)
	X6^1	2.340(9)		X4	2.120(11)		-X1		88.3(4)
				X1	2.239(13)		-X4^1		83.3(4)
	MEAN	2.161		X4^1	2.404(12)	X2^1	-X4		91.6(4)
				MEAN	2.10		-X1		105.4(5)
			M4 - M4		0.53(2)		-X4^1		103.1(4)
						X4	-X1		72.0(4)
							-X4^1		69.0(5)
						X1	-X4^1		131.6(4)
						M5 Octahedron			
			M5	-X7	1.941(9)X2	X7	-X7^1		88.0(6)
				X6	1.947(7)X2		-X6	x2	94.5(4)
				X4	1.965(9)X2		-X6^1	x2	81.7(4)
				MEAN	1.951		-X4	x2	95.1(3)
						X6	-X4	x2	87.6(4)
							-X4^1	x2	96.3(4)
						X4	-X4^1		81.8(6)

independent cycle and are considered to be underestimated. The least-squares refinement of all positional and anistropic thermal parameters gave a terminal *R* factor of 0.052 and a weighted R_w (= $[\Sigma w(|Fo|-|Fc|)^2/\Sigma w|Fo|^2]^{0.5}$) of 0.035, where the weighting scheme was taken as $w = {}^1/\sigma_{(Fo)}{}^2$. The standard deviation of an observation of unit weight was 3.24.

The highest peak on the final difference Fourier map was 2.2 e Å^{-3} located near the M2 (Zr) position. A refinement in the space group *Cc* resulted in an increased *R* value and retention of the 2-fold symmetry about the *y* axis. Final atomic coordinates and site occupancies are presented in Table 3. Bond lengths and angles are shown in Table 4. Table 5 gives a listing of structure factors[1]

The exact location and occupancy of the cations in the M3, M4, and M5 sites are open to debate. The final distribution was based mainly on crystallochemical reasoning combined with minimization of the *R* value.

The ANUCRYS Structure Determination Package (Whimp *et al.*, 1977), as implemented on the Univac 1100/42 computer at the Australian National University, was used throughout the structure solution.

Description of the structure

The structure of Kaiserstuhl zirkelite (Fig. 1) is similar to that reported by Gatehouse *et al.* (1981). Calcium (M1) is coordinated by eight oxygen atoms lying at the corners of a distorted cube. The large cations, Th and U substitute for Ca on this site. Zirconium (M2) is surrounded by seven oxygen atoms at the corners of a truncated cube and contains about 15 percent of substituted titanium. Of the remaining 3 cation sites, M3 and M5 are surrounded by six oxygens forming distorted octahedra while M4 is best described as occurring in trigonal bipyramidal (5-fold) coordination. Titanium, Fe, Nb and Zr occupy the M3 site, Fe and Ti the M4 site and Ti and Nb the M5 site. The two types of octahedra (M3 and M5) join together at their vertices to form three and six membered rings, similar to the planes of octahedra parallel to {111} in the pyrochlore structure. The M4 metal site is situated within the six membered ring and occupies a split position displaced towards the X4 oxygen atoms on one side of the cavity. These two equivalent M4 sites are separated by a distance of 0.53 (2)Å. The metal atoms occur in planes parallel to (001) in zirkelite and alternately contain M3, M4 and M5 or M1 and M2 cation sites. They are derived from the metal only (111) planes of the fluorite structure.

Discussion

The isotopes of uranium and thorium (U-238, 235, and Th-232) contained in natural zirkelite decay to form stable isotopes of lead by the emission of alpha- and beta-particles and gamma-rays. Damage

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[1] To receive a copy of Table 5 order Document AM-82-203 from the Business Office, Mineralogical Society of America, 2000 Florida Ave., N.W. Washington, D.C. 10009. Please remit $1.00 in advance for the microfiche.

to the crystal structure is caused predominantly by the recoil of the radioactive nucleus associated with alpha-decay. The recoil nucleus collides elastically with the surrounding atoms to a range of ~200Å and produces about 1500–2000 displacements/event (Reeve and Woolfrey, 1980; Fleischer *et al.*, 1975; Roberts *et al.*, 1981). The alpha-particle is ejected with high energies (4–6 MeV) which it loses through ionization of the atoms along its path (up to 20 μm). Most of the damage occurs near the end of its range producing 100–500 displacements/event. The effectiveness of these collisions is dependent on properties such as crystal structure and bond type. A more detailed discussion of this subject is given by Sinclair and Ringwood (1981).

Kaiserstuhl zirkelite has accumulated a radiation dose of 1.2×10^{18} alphas per gram. This dose is equivalent to the age of a SYNROC sample containing 10 percent high level nuclear waste for 1000 years (Oversby and Ringwood, 1981). The composition of the waste is calculated using U-only fuel with 3 percent enrichment of U-235, a burn-up of 33,000 MWd/MTHM, and a cooling time of 150 days before reprocessing (Cohen, 1977). In a previous study, Sinclair and Ringwood (1981) reported a decrease in intensity and slight boardening of the high angle powder diffraction maxima of Kaiserstuhl zirkelite. They also recorded a small change (<1 percent) in the unit cell volume after heating these samples at 1200°C. At higher doses of alpha-radiation, single crystal X-ray photographs of zirkelite from Jacupiranga, Brazil, displayed only the parent fluorite-type diffraction pattern which could be indexed on a face-centered cubic lattice with a = 5.06(4)Å. These observations are direct evidence of displacement damage resulting from alpha-recoil.

The major difference between the results of this refinement and those of Gatehouse *et al.* (1981) is the increased values of the temperature factors. These parameters are found to be consistently 2 to 3 times as large as those reported for the synthetic phase. The temperature factor correction is normally made to allow for the oscillating thermal motions of the atoms. These motions effectively change the scattering curve and cause the calculated structure factors to be systematically greater than the observed ones with increasing angle. The effect of alpha-recoil is to displace atoms or groups of atoms from their lattice sites. In a single crystal X-ray analysis, the displacements associated with the damaged areas averaged over the entire crystal, will be incorporated into the thermal motion and recorded as large U values. The high values of Uij (Table 3) for Kaiserstuhl zirkelite are interpreted to be the direct result of alpha-radiation damage.

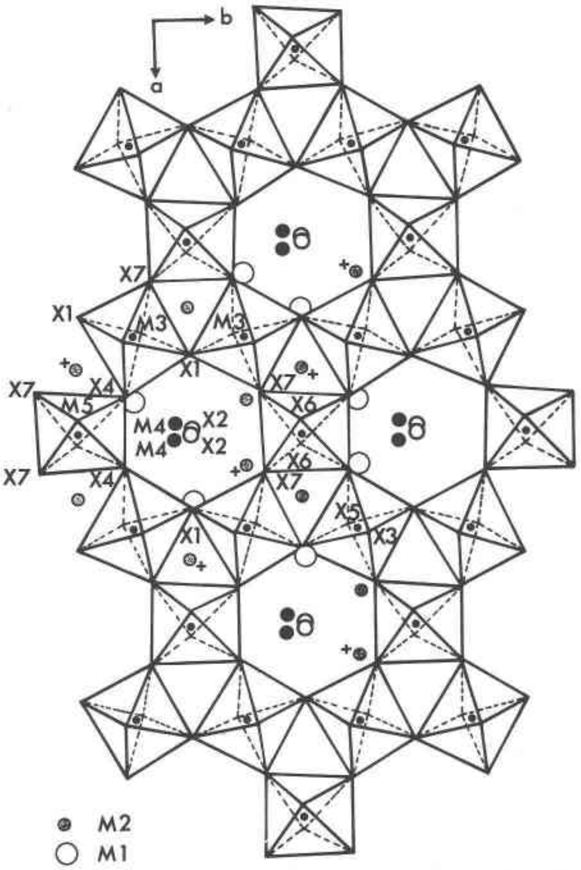

Fig. 1. Drawing of an (00l) plane of zirkelite containing M3, M4, and M5 sites. The M1 and M2 atoms occur in sites above and below the octahedral plane. M2 sites above the plane are marked. (After Gatehouse *et al.*, 1981).

Temperature factor values are also dependent on parameters such as site occupancy and absorption. However, there is evidence to suggest that these two effects have been kept to a minimum in our analysis. First, the placement of elements was well defined from previous structure determinations and from crystal chemical considerations. The changes in site occupancy made little difference to the high values of the temperature factors. Second, absorption is considered to be low because of the small size of the data crystal and the excellent agreement between equivalent reflections (interscale R = 0.019).

The results from this structure refinement are most significant for the long term stability of zirkelite in SYNROC. Although Kaiserstuhl zirkelite has received a dose of 1.2 × 10^{18} alphas per gram, equivalent to an age of SYNROC of 1000 years, a successful single crystal X-ray structure solution was completed. The analysis shows that the crystal lattice has undergone only minor changes due to the action of alpha-recoil.

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