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AUTHOR(S): F. W. Clinard, Jr., C. C. Land, D. E. Peterson, D. L. Rohr and R. B. Roof

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ALPHA DECAY SELF-DAMAGE IN CUBIC AND MONOCLINIC ZIRCONOLITE*

F. W. Clinard, Jr., C. C. Land, D. E. Peterson, D. L. Rohr, and R. B. Roof,
University of California, Los Alamos National Laboratory, Los Alamos, NM 87545,
USA

ABSTRACT

Samples of primarily-monoclinic ^{238}Pu-doped zirconolite were stored at ambient temperature to allow accumulation of alpha decay self-damage to a dose of 6×10^{24} α/m^3 (equivalent to a SYNROC age of $\sim 10^4$ y). Bulk swelling reached 2.3 vol% with no tendency toward saturation, a damage response similar to that observed for cubic Pu-doped zirconolite. X-ray volumetric swelling at 4×10^{24} α/m^3 was 1 vol%, considerably less than that for the cubic material. Changes in cell dimensions differed significantly from those reported by others for a monoclinic natural mineral. Extensive microcracking was observed, and is attributed at least partially to swelling differences between the matrix and minor phases.

INTRODUCTION

High-level nuclear waste should exhibit structural stability over geologic times, in order that fragmentation and a consequent increase in dispersion rate not occur. A major potential source of instability is self-irradiation and metamictization. Swelling in itself is not harmful, and in some ceramics is accompanied by strengthening [1]. However, anisotropic growth of non-cubic material or differential swelling of a multiphase assemblage can result in microcracking and structural degradation.

SYNROC is a promising ceramic waste form proposed by Ringwood and co-workers [2]. SYNROC B, the composition intended for immobilization of waste from commercial power plants, is made up primarily of the phases zirconolite ($CaZrTi_2O_7$), perovskite ($CaTiO_3$), and barium hollandite ($BaAl_2Ti_6O_{16}$). These supply a variety of cation sites for incorporation of metallic ions in waste calcine. Self-damage will primarily result from alpha decay of actinide ions, which results in an emitted alpha particle (helium ion) of energy ~5 MeV and an ~100 keV recoil nucleus. Reeve and Woolfrey [3] have calculated that in SYNROC phases ~90% of damage energy is induced by the recoil event. Actinide ions in SYNROC will for the most part be incorporated into the zirconolite and perovskite phases. Evaluation of mineral analogues which have suffered alpha decay self-damage from their natural uranium and thorium content show that the former phase is the more damage-prone [4].

Zirconolite with the classical composition $CaZrTi_2O_7$ has a monoclinic superlattice structure closely related to a defect fluorite structure. Rossell [5] has shown the unit cell dimensions of the monoclinic lattice to be $a=1.2445$ nm, $b=0.72734$ nm, $c=1.13942$ nm, and $\beta=100.55^\circ$. This structure can be rather accurately simulated by eight pseudo-cubic fluorite cells each with $a_c=0.505$ nm and $\alpha=92^\circ$ [6]. The principal difference in the two structures is the cation and anion disorder of the fluorite form which allows the atomic arrangement to be represented by the smaller unit cell. The cubic form of zirconolite is

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stabilized by the presence of tetravalent actinides; Kesson and Ringwood [7] found that incorporation of 4.1 mol% UO_2 was sufficient to initiate formation of the cubic phase. Some forms of SYNROC waste may contain zirconolite with a cubic or mixed cubic and monoclinic structure as a result of compositional effects.

In earlier work, the present investigators replaced the 25 mol% of ZrO_2 present in zirconolite w [illegible] mol% $^{238}PuO_2$, and investigated self-damage in the resultant cubic-structure material at high doses [8]. In that study, a highly-disordered metamict state was ultimately attained. In the work reported here, we have evaluated macroscopic swelling, x-ray lattice dilation, and microcracking in primarily monoclinic but multiphase 5 mol% $^{238}PuO_2$-doped zirconolite at lower doses. Results are compared with those for the cubic material and findings of others on self-damaged natural zirconolite.

EXPERIMENTAL PROCEDURE AND RESULTS

Powders of $^{238}PuO_2$, ZrO_2, CaO, and TiO_2 in the molar proportions 0.2:0.8:1:2 were dry ball-milled together for 24h, then cold-pressed with an organic binder at 125 MPa into cylinders of ~10 mm diameter and height. The TiO_2 used was in the form of anatase, and CaO was freshly made by air firing of $CaCO_3$. Isotopic purity of the plutonium was ~80%, with the remainder being made up of isotopes of longer half-life.

Samples were fired for 24 h at 1625 K in flowing air, and furnace cooled. Spectrochemical analysis of the fabricated material showed the major cation impurities present to be (in wt ppm): 2200 Si, 1100 Al, 40 Fe, 410 Cr, and 300 Mg. X-ray, microprobe, and metallographic analyses revealed that the resulting product was characterized by a monoclinic matrix, but contained roughly 20 vol% cubic phase. Also present were ~7 vol% TiO_2 (rutile), a lesser amount of an unidentified plutonium-bearing, low-calcium phase, and [illegible] vol% porosity. Average size of both grains and minor phases was in the range 5-10 μm. The as-fabricated structure, which was essentially crack-free, is shown in Fig. 1.

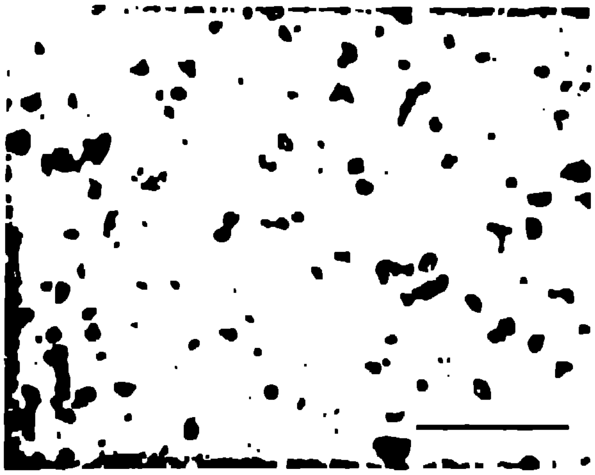

Fig. 1. Optical photomicrograph of as-sintered ^{238}Pu-doped zirconolite (unetched). Minor phases visible are TiO_2 (white) and porosity (black). Bar = 100 μm.

Plutonium was primarily partitioned between the monoclinic and cubic phases, but in unequal proportions. On the basis of four cations per molecule, the Pu content of the monoclinic phase was ~0.15 instead of the nominal value for the material as a whole of 0.20. This corresponds to a PuO$_2$ content of ~3.8 mol%, in reasonable agreement with the saturation limit of 4.1 mol% observed [7] with UO$_2$ additive in the monoclinic form. The Pu content of the cubic phase was approximately twice that of the monoclinic phase.

A cylinder of zirconolite was placed in a dilatometer the day after fabrication and macroscopic dimensional change as a function of time measured for 220 days at room temperature. The accumulated alpha decay dose of 6 x 10^{24} α/m^3 corresponds to ~10^3y of SYNROC storage age [9]. Readings were converted to volume swelling assuming expansion to be isotropic. Macroscopic swelling as a function of number of alpha decay events is shown in Fig. 2, along with results for cubic CaPuTi$_2$O$_7$ obtained earlier [8].

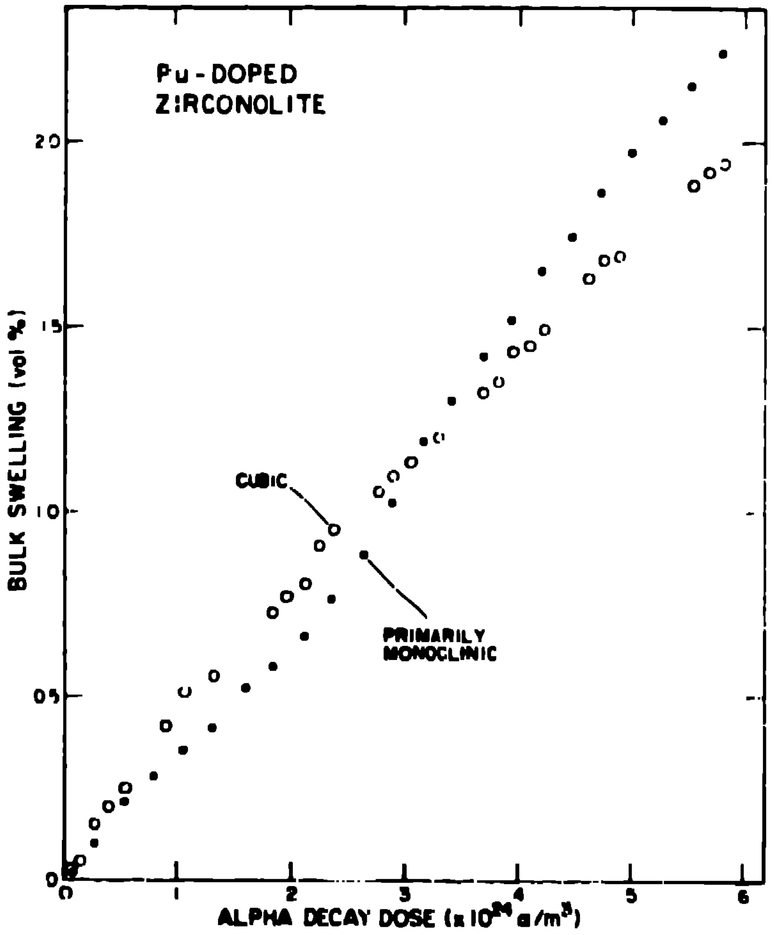

Fig. 2. Macroscopic swelling of the bulk (primarily monoclinic) material as a function of damage dose. Swelling of cubic ^{238}Pu-substituted zirconolite [8] is also shown.

A small quantity of material was crushed and packed into a capillary tube for periodic Debye-Scherrer x-ray examination, and data obtained over a period of 205 days for 13-15 reflections between 2θ values of 26° and 64°. Results were analyzed by a least-squares technique. Initial monoclinic unit cell dimensions are presented in Table I, along with those obtained for $CaZrTi_2O_7$ by Rossell [5] and for a natural zirconolite mineral by Sinclair and Ringwood [9]. As damage progressed, both fluorite-type and superlattice reflections weakened, and two of the latter ($\{11\bar{3}\}$ and $\{335,80\bar{4}\}$) disappeared. X-ray volume change with damage dose calculated from cell dimensions is shown in Fig. 3, along with that for cubic $CaPuTi_2O_7$ [8].

TABLE I
Unit cell dimensions for three forms of monoclinic zirconolite

Material	a, nm	b, nm	c, nm	β, degrees	Reference
$CaZrTi_2O_7$	1.24458	0.72734	1.13942	100.533	[5]
Pu-doped [a]	1.24[illegible]21	0.72693	1.14042	100.53	this work
Natural [b]	1.2571	7.[illegible]	11.524	100.62	[9]

[a] initial values

[b] after annealing at 147[illegible] K

A cylinder of zirconolite was sliced length-wise, mounted, and polished for periodic examination of the surface as a function of time. As swelling progressed, the material increasingly exhibited microcracking (Fig. 4). Although

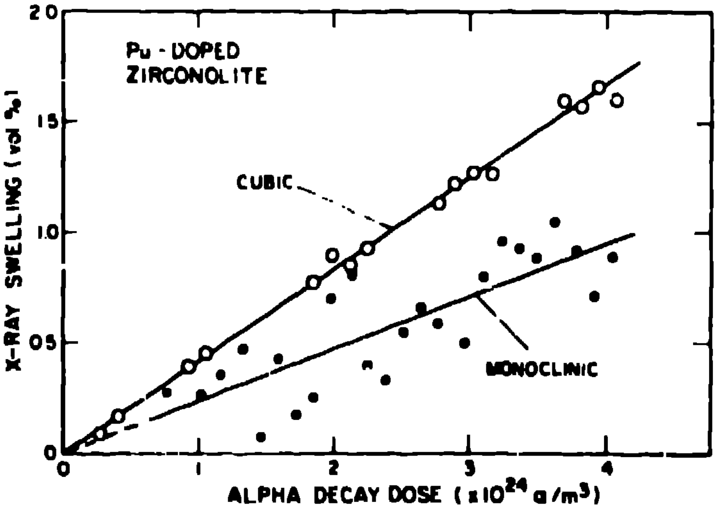

Fig. 3. X-ray swelling of the monoclinic matrix phase as a function of damage dose. Swelling of cubic ^{238}Pu-substituted zirconolite [8] is also shown.

plentiful, these cracks were not observed to open, and are therefore thought not to have contributed significantly to macroscopic swelling.

DISCUSSION

X-ray results

Initial unit cell dimensions for the monoclinic zirconolite studied here, with its 0.038 cation fraction Pu, are very close to those obtained for $CaZrTi_2O_7$ by Rossell [5] (Table I). This indicates that the structure of zirconolite is not easily perturbed by cation substitutions, as was also observed by Gatehouse et al. [10] in studies of material of varying Zr/Ti ratio. Agreement with cell dimensions of a natural zirconolite [9] was not so close, probably reflecting the high impurity content of the natural material (e.g., 15.6 wt% Nb_2O_5, 7.8 wt% FeO, and 2.9 wt% ThO_2).

In the present work, scatter of experimental data was such that only x-ray volumetric changes, rather than separate values of cell dimension a,b,c, and the angle β could be quantitatively presented as a function of damage dose (Fig. 3). However, it can be reported that all linear dimensions increased, with c showing the greatest dilation, while β was unchanged. In contrast, the zirconolite mineral examined by Sinclair and Ringwood [9] after a fluence of ~4 x 10^{24} α decays/m^3 induced by its natural UO_2 and ThO_2 content, exhibited decreases in a,b, and β and a sizeable increase in c. The overall increase in x-ray volume during irradiation for 1.6 x 10 y (measured by annealing and re-examination) was 0.7 vol%, only about half the value obtained here at that dose (extrapolated). Thus damage response for the two materials shows significant differences, most likely as a result of (1) compositional dissimilarities, (2) the factor of ~10 differences in damage rates, and/or (3) differences in storage conditions (e.g., variations in temperature and pressure over geologic times for the mineral specimen.)

X-ray vs. macroscopic swelling

Bulk swelling of the primarily monoclinic phase zirconolite studied here is similar to that observed for the cubic material [8]. The multiphase nature of

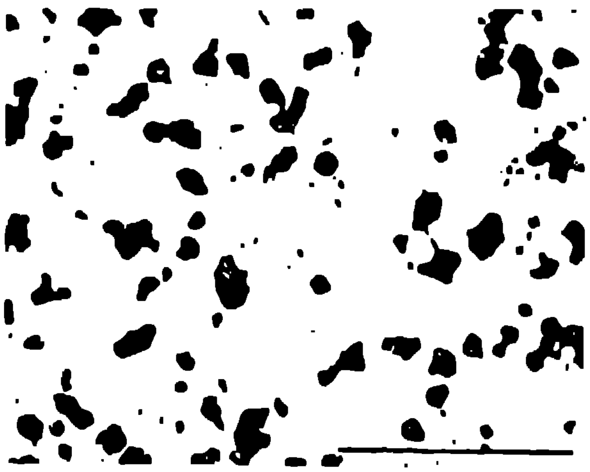

Fig. 4. Microcracks after 202 days' storage. Bar = 100 μm.

the present ceramic raises questions as to whether its macroscopic swelling is representative of that for phase-pure monoclinic zirconolite; however, recent results by Wald [11] for monoclinic material doped with 3 wt% ^{244}Cm show a swelling response similar to that reported here.

X-ray and bulk swelling are normally in approximate agreement at low damage levels, where most of the irradiated material remains strain-free [12]. As distortion increases at higher doses a discrepancy is expected, and this is observed for cubic Pu-substituted zirconolite above $\sim 7 \times 10^{24}$ α/m^3 [8]. However, in the work reported here x-ray swelling lags macroscopic swelling at the comparatively low fluences investigated (Figs. 2 and 3). Some of the difference may be attributable to a relatively large contribution to macroscopic swelling from the cubic phase, but it does not seem likely that this could fully explain the discrepancy. It should be pointed out that a difference exists between the damage response of monoclinic and cubic zirconolite: the former material first moves from the ordered to the disordered state on each sublattice (i.e., toward the cubic structure) and then undergoes the metamictization process, while the cubic material is initially disordered on each sublattice. Such a difference may affect the x-ray/macroscopic swelling relationship. Also, the theory which predicts agreement of the two types of swelling at low doses deals with materials which form distinct damage aggregates [12] rather than those which transform to the metamict state.

Sources of microcracking

Swelling in a single-crystal or cubic polycrystalline ceramic should not induce cracking, unless in the latter case internal strains arise from swelling differences between intra- and near-grain boundary regions [1]. Generalized microcracking was not observed in cubic zirconolite [8], although bulk swelling reached 4.7 vol%. On the other hand, cracking was observed in the present work even before 1 vol% swelling was attained. Either or both of two additional strain sources may be responsible: anisotropic swelling of the non-cubic matrix phase, or differential swelling within the multiphase assemblage. Anisotropic growth has been observed to lead to microcracking in polycrystalline ceramics such as Al_2O_3 [13], which has a hexagonal structure. In this material neutron irradiation-induced growth is predominantly in the c-axis direction, with resultant microfracture along grain boundaries. The degree of anisotropy is large (c/a growth ratio ≈6) at an irradiation temperature of 1000 K, but decreases markedly (to c/a ~1.6) at 650 K [14]. Thus internal strains from this source can be strongly temperature-dependent. Grain size is also an important parameter, with small grains exhibiting the greater resistance to cracking [15]. The question as to whether anisotropic swelling of the monoclinic zirconolite matrix phase is alone responsible for microcracking in the present study must await evaluation of a more phase-pure form of this material.

Microcracking from differential growth among phases in a multiphase ceramic has been observed by Matthews [16], who attributed an approximately 50% strength loss in neutron-irradiated reaction-bonded silicon carbide to this source. The material contained α-SiC (hexagonal), β-SiC (cubic), and free Si (cubic), and microcracking was attributed to differential growth between SiC and Si. It was concluded that swelling of α-SiC is nearly isotropic and equal to that of β-SiC.

In the work reported here, the presence of several phases in addition to the zirconolite matrix assures that differential swelling will have occurred. The TiO_2 phase is thought not to be responsible for the observed microcracking, since generalized cracking did not occur in cubic zirconolite which contained a similar distribution of this phase [8]. A more likely suspect is the cubic zirconolite phase, which constituted a significant fraction (roughly 20%) of the fabricated product. The cubic phase contained about twice as much damage-producing plutonium as did the matrix, and should therefore have undergone approximately twice the swelling or 4-5 vol%. (The cubic material exhibits saturation in swelling as metamictization occurs, but deviation from linearity is still small at 1.2 x 10^{25} α/m^3 [8].) The consequent maximum linear misfit strain ($\sim$0.8%) is roughly twice that thought to be responsible for microcracking in reaction-bonded silicon carbide [16], and is probably sufficient to explain the cracking observed here. Swelling mismatches at least this great can be expected in three-phase SYNROC, where hollandite will not be a host for significant concentrations of actinide ions and should exhibit low swelling [4]; thus microcracking is a likely consequence of self-damage in this waste form.

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