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DIFFERENTIAL SCANNING CALORIMETRY OF METAMICT Pu-SUBSTITUTED ZIRCONOLITE*

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ABSTRACT

Samples of $\text{CaPuTi}_2\text{O}_7$ were prepared by cold pressing and sintering. Plutonium was substituted for zirconium in order to characterize radiation damage effects. The energy stored in a sample which had reached saturation in swelling after storage at ambient temperature was measured with a differential scanning calorimeter. The total energy of 6.6 ± 0.1 cal/g is released over the range $485\text{--}715^\circ\text{C}$. The activation energy of annealing of the damage is 1.22 ± 0.05 eV. The temperature dependence of the rate constant is described by

$$k_T = 5.96E4 \exp(-1.22/k_B T) \text{ s}^{-1}$$

where k_B and T are the Boltzmann's constant and temperature (K) respectively. A sample stored at 600°C was similarly evaluated and showed no release of stored energy to the precision of the apparatus (± 0.1 cal/g). These results are applied to analysis of waste incorporation in SYNROC and are correlated with analogous parameters for other materials.

INTRODUCTION

The mechanism by which energy from alpha-decay is stored in a crystal lattice is of theoretical interest in characterizing the nature of condensed matter. Radiation damage in materials is also of importance in developing nuclear fuels and waste forms. Increases in structural degradation as a result of radiation could compromise the usefulness of a fuel form.

Materials exposed for extended periods to alpha decay from actinide components often do not show an X-ray pattern due to extensive damage of the crystal lattice. The substance is then referred to as residing in a metamict state. Macroscopic effects associated with this metamict transformation include swelling, fracturing, and decreased thermal conductivity. The metamict state is not well understood, often showing anomalous effects. Factors such as composition or structure probably contribute to the susceptibility of a substance to radiation damage [1]. One means of characterizing the metamict state has been to examine the minerals existing in nature that contain U or Th. Many of these minerals have retained the component actinides for millions of years even though subjected to severe geothermal and

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leaching conditions. Susceptibility to radiation damage is an important criterion in the selection of an appropriate nuclear waste form.

Based on the favorable response of some natural minerals in retaining actinides, Ringwood [2] proposed ceramic waste forms called SYNROC. These materials are intended to immobilize high level wastes produced by commercial power reactors by incorporating these wastes into stable analogues of natural minerals. The basic SYNROC formulation consists of a synthetic assemblage of three minerals: hollandite, $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$; perovskite, CaTiO_3 ; and zirconolite $\text{CaZrTi}_2\text{O}_7$. Since the zirconolite will contain many of the actinides which upon alpha decay induce self-damage, it is important to determine the irradiation response of this phase.

Comparison of the effects of metamictization in zirconolite to that in alternative waste forms should assist in the selection of the best possible waste material. Ringwood [3] and Ewing et al. [1] have examined radiation damage in naturally occurring zirconolites under storage temperatures and sample compositions determined by geological conditions. Microstructural effects of alpha-recoil in synthetic zirconolites doped with actinides have been studied by Clinard and coworkers [4] and by Gray et al. [5].

It was found [6] that Pu-substituted zirconolite aged at ambient temperature swelled extensively (5.5 vol%) and reached swelling saturation at 2.4×10^{25} alpha decays/m³ (180 days' storage). At this damage level the structure consisted of an amorphous matrix containing small untransformed crystalline domains. The same material held at 600°C for 224 days has swelled only 0.4 vol% and exhibited a crystalline lattice containing isolated defect clusters.

The level of stored energy in metamict zirconolite has been quantitatively measured in this study by use of a differential scanning calorimeter (DSC). Atoms displaced by alpha decay are easily restored to their normal lattice positions by heating to a sufficiently high temperature whereupon the damage enthalpy is released. Comparison of the magnitudes of the heat released and the activation energy of annealing for various waste forms will help characterize the relative responses to radiation damage. Samples of Pu-substituted zirconolite ($\text{CaPuTi}_2\text{O}_7$) that had been stored for extended periods at ambient temperature and at 600°C were examined in the DSC. The results of these measurements were then correlated with other physical property changes and with analogous measurements conducted on other metals, ceramics, minerals, and waste forms.

EXPERIMENTAL APPROACH

Samples of ^{238}Pu -substituted zirconolite used in this study were prepared by cold-pressing and sintering. Details of the synthesis and analyses of these specimens are described in another paper [6] presented at this symposium. Effects of substituting Pu for Zr on the phase behavior and crystal structure of zirconolite have been previously reported [3]. The sample pellets were held at ambient temperature for 201 days (2.7×10^{25} alpha decays/m³) and at 600°C for 220 days (3.6×10^{25} α/m^3) before the stored energy was measured. With the latter material the DSC measurement was made within a day after cooling to ambient temperature to minimize subsequent damage at the lower temperature. Corresponding Pu substituted zirconolite samples stored at ambient and 300°C had been shown to become metamict (i.e., highly disordered [3]) after about 100 and 180 days respectively. The heats released during the metamict to crystalline transition of the ambient temperature and 600°C samples were measured with a Perkin Elmer differential scanning calorimeter (Model DSC-2). The maximum sensitivity of this unit is 0.1 mcal/n for full scale deflection and the maximum temperature available is 727°C.

High purity metals and inorganic oxides were used to calibrate the temperature and energy scales. The standards used in this work, their melting points ($^{\circ}\text{C}$) and heats of fusion, $\Delta H_{\text{fus}}^{\circ}$ (cal/g), are as follows: In (156.63, 6.80); Pb (417.50, 5.50); and K_2CrO_4 (670.5, 8.50). The calibration constant, k_c , for the DSC was then calculated from the relationship,

$$k_c = \frac{\Delta H_{\text{fus}}^{\circ} m_c}{A_c} \quad (1)$$

where m_c is the calibrant mass and A_c is the peak area of the thermogram corresponding to the $\Delta H_{\text{fus}}^{\circ}$ value. This peak area was determined by integrating the region between the heat release peak and an interpolated base line.

An empty Au sample pan was placed in the DSC unit and a linearized base line recorded. The sample pellet stored at ambient temperature was crushed and 3 fractions encapsulated in Au pans. These were exposed to heating rates in the DSC and the heat released measured over the temperature range 50–727 $^{\circ}\text{C}$. The initial sample weighed 5.63 mg and was run at a heating rate of 40 $^{\circ}/\text{min}$ and a sensitivity of 10 mcal/s. The second sample weighed 7.70 mg and was run at 40 $^{\circ}/\text{min}$ and 2 mcal/s whereas the remaining fraction weighed 3.94 mg and was run at 10 $^{\circ}/\text{min}$ and 2 mcal/s. Each thermogram of a particular sample was repeated under the same conditions and the area between these traces integrated with a planimeter. This procedure was then again performed with the sample stored at 600 $^{\circ}\text{C}$. The sample fraction used in this measurements weighed 11.6 mg, the heating rate was 40 $^{\circ}/\text{min}$ and the calorimeter sensitivity was set at 1 mcal/s. The areas obtained from these measurements were combined with the calibration constant determined using the standards in order to calculate the heat released from the Pu-substituted zirconolite samples. The relationship used was

$$H = \frac{k_c C_s r_s M A_s}{C_c r_s m_s} \quad (2)$$

where C_c and C_s are the chart speeds for the calibrant and sample runs respectively, r_s and r_c are the sensitivity ranges, M is the molecular weight of the sample, m_s is the sample mass and A_s is the peak area of the heat released during the sample thermogram.

The deflection above the base line at a particular temperature is proportional [8] to the rate of heat release, $(dE/dt)_T$, which is in turn proportional to the annealing rate. Hence the temperature dependent rate constant, k_T , is equivalent to

$$k_T = \frac{(dE/dt)_T}{E_T} \quad (3)$$

where E_T is the total energy remaining at temperature T . This relationship was used to calculate rate constants as a function of temperature for annealing of the sample stored at ambient temperature. The deflection above a base line was measured at 10 degree intervals to determine values of the heat release rate. The corresponding energy remaining in the sample at this temperature was obtained by combining the integrated fractional area of the thermogram with the calibration constant. An activation energy of annealing, E_a , and a pre-exponential factor, A , were then obtained from the Arrhenius equation,

$$k_T = A \exp(-E_a/k_B T) \quad (4)$$

where k_B is Boltzmann's constant. A plot of $\log k_T$ vs $1/T$ was made based on the measurements of heat released from the Pu-substituted zirconolite sample that had been stored at room temperature. Values of E_a and A were obtained from the slope and intercept respectively of a linear least-squares analysis of the data.

RESULTS

X-ray, microprobe and metallographic analyses of samples from the same pellet series as used in this study showed a nominal composition of $\text{CaPuTi}_2\text{O}_7$ as the matrix phase with 2-3 vol% PuO_2 and a lesser amount of an unidentified phase. Standardization of the DSC with In , Pb , and K_2CO_3 yielded a calibration constant, k_c , of 8.76 ± 0.05 mcal/in² as determined using equation (1). This value was independent of the calibrant used indicating that k_c is constant over the entire temperature range of the DSC-2.

The initial sample from the pellet stored at ambient temperature showed a heat release occurring over the range 547-727°C. A transition heat of 6.3 ± 0.5 cal/g was calculated from these measurements. The second sample run at a higher sensitivity revealed that the heat release occurred over the range 485-715°C and had a total stored energy of 6.6 ± 0.1 cal/g. The trace of the heat released is plotted as a function of time and temperature in Fig. 1. The trace obtained by repeating the thermogram on the now-annealed material is also shown. A plot of the logarithm of the rate constant vs the reciprocal temperature is shown in Fig. 2. The corresponding activation energy, E_a , and pre-exponential factor, A , obtained by linear least squares analysis of the data are 1.22 ± 0.5 eV and $5.96 (\pm 2.79) \times 10^4 \text{ sec}^{-1}$ respectively. The thermogram associated with the sample stored at 600°C showed essentially no heat above 0.1 cal/g was released during the heating ramp.

DISCUSSION

The metamict state in Pu-substituted zirconolite can be different from a purely amorphous substance such as a glass or quenched liquid. The metamict zirconolite analogue can still possess a considerable degree of short range order and areas of crystalline domains as revealed by electron diffraction [7,9]; therefore, one would expect the energy stored from radiation damage to be significantly less than the heat of fusion of zirconolite and also lower than for a material that is fully amorphous.

This study has shown that the degree of metamictization in Pu-substituted zirconolite can be characterized by use of a differential scanning calorimeter. Determinations of the baseline with the empty cell in place, by interpolating the trace under the thermogram peak, and by repeating the thermogram were generally consistent. Small differences between the first and last two cases are believed to be due to the heat capacity of the samples. The heat release was shown to occur over a relatively large temperature range of about 230°. This observation is not surprising since the rearranging of the atoms should be a sluggish process and the temperature range is similar to that observed by Berman [9] in studies of fission damaged material.

It is evident from this study that the energy associated with the metamict zirconolite sample stored at 600°C has annealed out. This conclusion is consistent with the swelling which maximized [6] after about 50 days at 600°C.

TABLE I
Stored energies and activation energies for recovery in various substances*

Sample	Description	Stored Energy (cal/g)	Activation Energy (eV)	Reference
Iron	Neutron irradiated	--	3.1	[10]
Nickel	Neutron irradiated	--	2.62	[10]
Copper	Neutron irradiated	--	1.95	[10]
	Deuteron irradiated	--	0.68	[10]
	Alpha irradiated	--	2.10	[11]
	Cold worked	0.2	1.02	[12]
Graphite	Neutron irradiated	150	1.4	[13]
	Neutron irradiated	--	0.75-2.1	[14]
Quartz	Neutron irradiated	--	1.6	[10]
Fused SiO ₂	Gamma irradiated	--	0.75	[15]
Germanium	Electron irradiated	--	0.7	[16]
²³⁸ PuO ₂	Self damage	--	0.17	[17]
Titano-Niobate	Metamict	21	--	[18]
Eschylite-				
Prionite	Metamict	20	--	[18]
Gadolinite	Metamict	89	--	[19]
Al ₂ O ₃	Fission fragments	14-60	--	[10]
Glasses/High				
Level Waste	²⁴⁴ Cm Doped	28	0.25	[20]
Zirconolite	²³⁸ Pu Doped	6.6	1.22	This work

*In most cases, damage doses were at moderate to high levels.

disorder. This is consistent with the relative ease with which the material becomes metamict and its ready acceptance of a variety of cations [6]. The lower stored energy for $\text{CaPuTi}_2\text{O}_7$ even than that for a waste glass clearly demonstrates this tolerance for disorder.

Pu-substituted zirconolite aged at 600°C resembles a conventional ceramic in that defects aggregate into regions of localized disorder while the lattice remains crystalline. The observation here of no detectable stored energy under these conditions contrasts sharply with the behavior of EuO [21]; after irradiation to a similar damage level and retention of crystallinity, stored energy was about 50 cal/g. It is apparent that tolerance for disorder is characteristic of Pu-substituted zirconolite whatever the mode of accommodation of displacement damage.

REFERENCES

1. R. C. Ewing and R. F. Haaker, The Metamict State: Radiation Damage in Crystalline Phases, Proceedings of the Conf. on High-Level Radioactive Solid Waste Forms, L. A. Casey, ed., NUREG/CP-0005, 651-674 (1979).
2. A. E. Ringwood In: Safe Disposal of High-Level Nuclear Waste: A New Strategy. (Canberra: Aust. Nat. Univer. Press 1978); A. E. Ringwood, S. E. Kesson, N. G. Ware, W. Hibberson, and A. Major, Nature 278, 219-223 (1978).

3. A. E. Ringwood, *American Scientist* 70, 201-207 (1982).
4. F. W. Clinard, Jr., L. W. Hobbs, C. C. Land, D. E. Peterson, D. L. Rohr and R. B. Roof, *J. Nucl. Mats.* 105, 248-256 (1982).
5. W. J. Gray, J. W. Wald, and R. P. Turcotte, "Radiation Damage Studies Related to Nuclear Waste Forms", report PNL-4145 (1981).
6. F. W. Clinard, Jr., L. W. Hobbs, D. E. Peterson, D. L. Rohr and R. B. Roof in: Scientific Basis for Nuclear Waste Management, to be published.
7. R. N. Rogers, *Anal. Chem.* 44(7), 1336-1337 (1972)
8. W. Sinclair and A. E. Ringwood, *Geochem. J.*, to be published.
9. R. M. Berman, *Am. Mineralogist* 63, 807 (1978).
10. D. S. Billington and J. H. Crawford in: Radiation Damage in Metals, (Princeton Uni. Press, Princeton, NJ 1961) p. 112.
11. G. J. Dienes and G. H. Vineyard in: Radiation Effects in Solids, Vol. 2 (Interscience Publ., New York, NY 1957) p. 157.
12. A. Lucci, M. Tamanini, L. Battezzatti, and G. Ventarello, *J. Th. Anal.* 14, 93-97 (1978).
13. T. J. Neubert and R. B. Lees, *Nucl. Sci. Eng* 2, 748-767 (1957).
14. G. Mayer, P. Perio, J. Gigon and M. Townaric, *Proc. 1st Int. Conf. Peaceful Uses At. Eng* 1, 647-653 (1955) United Nations, NY (1956).
15. J. M. Nelson and J. H. Crawford, *J. Phys. Chem. Solids* 13, 296-305 (1960).
16. W. L. Brown and R. C. Fletcher, *Phys. Rev.* 92 (3), 591-596 (1953).
17. R. P. Turcotte and T. D. Chikalla, *Rad. Eff.* 19, 99-108 (1973).
18. F. F. Morehead and F. Daniels, *J. Phys. Chem.* 56, 546-548 (1952).
19. A. Faessler, *Zelt. Crist.* 104, 81 (1942).
20. W. J. Weber and F. P. Roberts, "Radiation Effects," Section 6 of PNL-3802, PNL, Richland, Washington 99532.
21. P. M. Heuer and G. Stolarski, cited in *Studies in Radiation Effects*, Series A, Physical and Chemical, Vol. 1, G. J. Dienes, ed., Gordon and Breach, NY (1966), p. 138.0.00