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X-ray diffraction and leaching of $CsAlSi_5O_{12}$ and $CsZr_2(PO_4)_3$ irradiated by argon (3 MeV) ions

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Metamict damage cross-sections for the candidate nuclear fuel waste immobilization materials $CsAlSi_5O_{12}$ and $CsZr_2(PO_4)_3$ irradiated with 3 MeV argon ions were found to be $0.6 \pm 0.2\,nm^2$ and $0.7 \pm 0.3\,nm^2$, respectively, from powder X-ray diffraction measurements. Based on caesium extraction into solution, heavy irradiation produced increases of up to a factor of 25 in the dissolution rates of the materials in deionized water and a brine at 100° C.

1. Introduction

Materials, other than glasses or cements, suggested for immobilization of radioactive ^{137}Cs or ^{135}Cs in nuclear fuel wastes include the compounds Ba-hollandite [1], pollucite [2], $CsAlSi_5O_{12}$ [3] and $CsZr_2(PO_4)_3$ [4, 5]. Radioactive waste ions will cause self-irradiation effects in the solidified waste; β- and γ-processes will give rise mainly to ionization phenomena, whereas α-decays will cause atomic displacements as well as ionization. Alpha-recoils are generally acknowledged to be the most important source of radiation damage in high-level nuclear waste forms. Possible adverse effects on the waste form include differential lattice expansion of different crystalline phases and an increased rate of dissolution in aqueous media. In solidified waste, the caesium-bearing phases would incur atomic displacement damage due to the decay of actinides, the actinides being either incorporated in the caesium-bearing phases or, for a ceramic, in neighbouring crystallites. However, if radiocaesium has been chemically separated from recycle wastes, as at the Hanford reservation in the US, self-irradiation in a final waste form for radiocaesium would derive only from β- and γ-radiation, which would tend to produce electronic excitation rather than atomic displacements.

Vance *et al.* [6] and Karioris *et al.* [7] carried out X-ray diffraction work on the response of pollucite and Ba-hollandite to 3 MeV argon ion irradiation. Data on the effects of irradiation on $CsAlSi_5O_{12}$ are not available and the only related result for $CsZr_2(PO_4)_3$ is that the isostructural Nasicon ($Na_{1+x}Si_xZr_2P_{3-x}O_{12}$) is sensitive to fast electron irradiation [8]. The crystal structure of $CsAlSi_5O_{12}$ has been given by Araki [9] and crystallographic work has been done on Nasicon [10, 11] as well as $CsZr_2(PO_4)_3$ [12].

In the present work, we have used 3 MeV argon ions to simulate the α-decay process in $CsAlSi_5O_{12}$ and $CsZr_2(PO_4)_3$. While clearly not as good as actinide doping, ion irradiation is generally considered to be a useful method of providing an indication of the radiation stability of a given material for the purposes of nuclear fuel waste disposal.

2. Experimental details

The caesium compounds were made by ceramic techniques and their dissolution behaviour in aqueous media has been studied previously [3–5, 13]. Fine powders were produced by dry-grinding in an agate mortar. Sedimentation techniques were used to coat aluminium-alloy plates,

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of a suitable size to fit into the X-ray diffractometer sample holder, with a layer of particles having an average thickness of ~ 2 μm (0.6 mg cm^{-2}). This thickness is approximately equal to the penetration depths of the 3 MeV argon ions into the solid materials.

Scanning electron microscopy of the loose powders revealed that the particles ranged in size from 0.5 to 15 μm, with most being in the 1 to 4 μm range. From the densities of the materials [3, 4, 9, 12] and assuming that the fine powders were regular spheres of 2 μm diameter, the specific surface areas can be calculated as ~ 1 $m^2 g^{-1}$, for both materials.

The experimental procedures for the heavy ion bombardments were described previously [7, 14, 15]. Irradiations with 3 MeV argon ions were conducted with the Dynamitron accelerator at Argonne National Laboratory. The X-ray samples were irradiated with an ion current of 2.2 μA cm^{-2}. Quantities of 50 mg of similarly sized powders were irradiated with a mean ion current of 0.06 μA cm^{-2}. In both cases, the maximum fluence was 20 ion nm^{-2}. Previous results [15] indicate that beam heating of the X-ray samples should not have exceeded ≈ 200° C and that it should have been negligible for the ~ 50 mg samples.

X-ray diffraction was performed by a conventional diffractometer using Cu*Kα* radiation with a graphite monochromator and photographically using a Debye–Scherrer camera, with the powder sample contained in a 0.3 mm capillary tube. A Dupont instrument was used for differential thermal analysis (DTA) measurements on ~ 25 mg samples, over the range 25 to 1100° C. The heating rate was 20° C min^{-1} and the reference material was Al_2O_3.

The leaching behaviour of heavily irradiated (10 or 20 ion nm^{-2}) powders was investigated with 10 to 20 mg powder immersed in 10 to 20 ml deionized water or a simulated, highly saline, granite groundwater (see Table I), the solid/solution ratio being 1 g l^{-1} in each case. The mixed solutions and powders were placed in tightly sealed Teflon containers, heated at 100° C in an oven for 7 or 14 days and gently agitated for a few seconds every second or third day. After heating, the mixtures were cooled to room temperature and the containers opened. The pH did not change by more than 0.3 units in any case. The mixtures were filtered (0.45 μm millipore) and the liquids then acidified and analysed for caesium by atomic absorption spectroscopy.

TABLE I Composition of brine*

Ion	mg l^{-1}	Ion	mg l^{-1}
Na	5 050	Si	15
K	50	HCO_3	10
Mg	200	Cl	34 260
Ca	15 000	SO_4	790
Sr	20	NO_3	50

*This brine is a simulation of natural brines found deep in the Canadian Shield; pH = 7.0 ± 0.5.

3. Results and discussion

3.1. X-ray diffraction

The unirradiated $CsAlSi_5O_{12}$ powders on the alloy plates exhibited rather broad diffraction peaks (2*θ* half-widths were ~ 0.5°), and only the strongest peaks, in the range 2*θ* = 20 to 30° were observed clearly above the background. The broadening of the diffraction lines was not evident in patterns obtained from coarser powder derived from the original sintered pellets, so the broadening in the X-ray pattern of the fine powder is attributed to grinding strains. Photographic X-ray diffraction work showed that the broadening could be partly removed by annealing at 1000° C, but it was not practical to anneal the fine powder before irradiation since appreciable sintering took place at this temperature. No significant broadening of the diffraction lines in the X-ray diffraction pattern of the unirradiated fine $CsZr_2(PO_4)_3$ powder was observed.

The intensities of the Bragg peaks in the X-ray patterns obtained from the irradiated plate samples decreased with increasing ion fluence for fluences ⩽ 5 ion nm^{-2}, but saturation values of ~ 30% of the intensities exhibited by the unirradiated samples were obtained at higher ion fluences. As in previous work [7, 14, 15], the finite Bragg intensities at high fluences are attributed to incomplete ion penetration. A build-up, with increasing ion fluence, of diffuse X-ray scattering at angles corresponding to interplanar (*d*) spacings of 0.3 to 0.5 nm was observed for $CsAlSi_5O_{12}$ and to *d* spacings of 0.25 to 0.4 nm for $CsZr_2(PO_4)_3$.

The metamict cross-section, D_m, is defined by Karioris *et al.* [7] as:

$$I = I_0 \exp(-D_m \phi) \qquad (1)$$

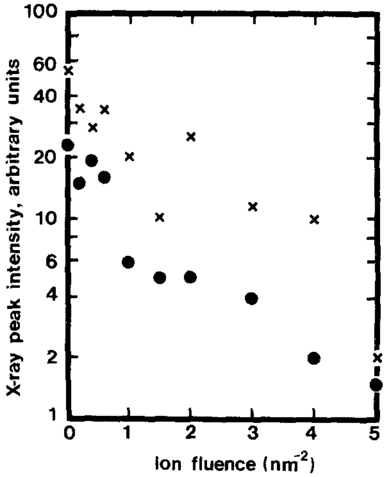

Figure 1 Intensities of Bragg diffraction peaks as a function of ion fluence for $CsAlSi_5O_{12}$ (×, (1 3 1, 2 4 0) doublet) and $CsZr_2(PO_4)_3$ (●, (1 1 6) peak). The Bragg peak intensities are measured by peak heights since no radiation-induced broadening was discernible, and their error was estimated as ± 3 units in all cases.

where I is the intensity of a given Bragg reflection after irradiation with a fluence ϕ and I_0 is the corresponding intensity for the unirradiated material. This relationship applies to a model in which irradiation produces zones of amorphous material embedded in a perfectly crystalline material. The above-mentioned build-up of diffuse scattering is also consistent with this model.

The saturation high-fluence Bragg intensities were subtracted from the low-fluence intensities and are plotted in Fig. 1 as a semilog graph for the (1 3 1, 2 4 0) doublet at $d = 0.358$ to 0.360 nm for $CsAlSi_5O_{12}$ and the (1 1 6) peak at $d = 0.298$ nm for $CsZr_2(PO_4)_3$. From the slopes of the estimated best-fit straight lines through the data points, the values of D_m are $0.6 \pm 0.2\,nm^2$ for $CsAlSi_5O_{12}$ and $0.7 \pm 0.3\,nm^2$ for $CsZr_2(PO_4)_3$.

A formal treatment of the data to find the line of best fit was not possible because subtraction of the assumed constant saturation value from each of the data points yielded some negative numbers (for fluences $> \sim 5$ ion nm^{-2}), which were not amenable to presentation on a semi-logarithmic plot. A regression analysis on the data points included in Fig. 1 (fluence $\leqslant 5$ ion nm^{-2}) determined the cross-sections for the phosphate and aluminosilicate to be 0.47 and 0.68 nm^2 ion^{-1}, respectively, when the data points were allotted statistical weights proportional to the squares of their values. However, we believe that neglecting the data at higher fluences compromises this analysis, and that the values determined in this way are underestimated. The deviations from the straight lines in Fig. 1 were about twice as large as those anticipated from the measurements of the experimental error. It is not clear whether these deviations have contributions from preferred orientation, sample thickness variation from plate to plate, or slight geometrical errors in sample placement in the diffractometer, or whether the simple model underlying Equation 1 is not entirely appropriate. However, in agreement with the implicit prediction of the model, the D_m values were independent of (h, k, l) and irradiation did not produce X-ray line broadening.

TABLE II Metamict damage cross-sections, D_m, for argon (3 MeV) ions

Material	D_m(nm^2)	Reference
Monazite, (Ce, La)PO_4	0.56 ± 0.13	[15]
Pollucite, ($CsAlSi_2O_6$)	0.8 ± 0.4	[6]
Spinel, ($MgAl_2O_4$)	$< 10^{-3}$	
Magnetoplumbite, ($CaAl_{12}O_{19}$)	~ 0.01	
Sphene, ($CaTiSiO_5$)	0.6 ± 0.2	[17]
$CsAlSi_5O_{12}$	0.6 ± 0.2	Present work
$CsZr_2(PO_4)_3$	0.7 ± 0.3	
Ba-Hollandite, ($BaAl_2Ti_5O_{14}$)	1.04 ± 0.14	[7, 14]
Zirconolite, ($CaZrTi_2O_7$)	0.11 ± 0.04	

Table II compares the values of D_m for the caesium compounds with metamict damage cross-sections of other refractory crystalline phases that have been considered for nuclear fuel waste immobilization. The values of D_m are much higher than those for structures such as spinel or magnetoplumbite.

Several irradiated samples of each compound were annealed at 400° C in air for 16 h, but no significant changes in the X-ray patterns ensued. Annealing at 600° C led to problems with oxidation and deformation of the metal plates used. Photographic diffraction data were obtained on powders irradiated with 20 ion nm^{-2} and annealed at 600 to 1000° C, but the results were inconclusive due to lack of control of sample geometries. In the DTA experiments, the $CsZr_2(PO_4)_3$, irradiated with 20 ion nm^{-2}, gave an exothermic peak at 930° C having a half-width of 30° C and an amplitude of 0.10 ± 0.01° C. No such features were observed for $CsAlSi_5O_{12}$ irradiated with 20 ion nm^{-2}. We interpret the exotherm for the irradiated $CsZr_2(PO_4)_3$ as being due to recrystallization. The absence of such an exotherm for the irradiated $CsAlSi_5O_{12}$ means either that the recrystallization occurs over a wide temperature range or that it occurs above 1100° C, the maximum temperature investigated by DTA.

The caesium compounds can, therefore, be grouped with the more structurally sensitive materials studied by the present techniques. A relevant factor is the high annealing temperature ($>400°$ C for $CsAlSi_5O_{12}$ and ~ 900° C for $CsZr_2(PO_4)_3$, based on DTA data) of radiation damage, which prevents annealing taking place during the irradiation or at ambient temperatures. The high annealing temperatures are consistent with the refractory natures of the compounds and the fact that the structures are fairly open [9–11]. This latter feature provides relatively stable interstitial sites for displaced ions. Calculations of packing factors, made using the Muller and Roy [16] compilation of ionic sizes (appropriate to the coordination numbers), yielded 47% and 52% for $CsAlSi_5O_{12}$ and $CsZr_2(PO_4)_3$, respectively. These values are significantly lower than the value of ~ 60% calculated for the close-packed spinel and magnetoplumbite structures [17]. In addition, the non-cubic structures of the caesium compounds generally favour retention of radiation damage [18].

The total number of displaced atoms per incident argon ion would be $\sim 6 \times 10^3$ and the range in the solids, would be ~ 1.5 μm [17]. Using crystallographic data [9, 12], it is easily calculated that a metamict damage cross-section of 0.6 nm^2 corresponds to the material becoming X-ray amorphous after only ~ 0.1 displacement per atom (dpa). It is assumed that no self-annealing takes place and that ionization effects do not contribute to the damage cross-section – these latter effects would lower the dpa number corresponding to X-ray amorphism.

As noted previously, the X-ray data are consistent with a model in which each argon ion produces an amorphous zone. Perhaps the low dpa number (0.1) for X-ray amorphism can be explained on the basis that long-range strains surrounding the supposed amorphous zones severely attenuate the Bragg-like X-ray scattering from the regions between the zones.

3.2. Leaching

Table III gives the concentrations of caesium dissolved in deionized water and brine for both irradiated and unirradiated samples.

Irradiation enhanced the dissolution rates by factors of 2 to 25. Quantitative theories do not exist to describe the enhancement, but qualitatively, the disruption of the bonding upon amorphorization is normally considered to increase the dissolution rate. The enhancement factors are in order of magnitude agreement with those observed after heavy-ion irradiation of certain nuclear fuel waste glasses that were leached in a 250 $g\,l^{-1}$ NaCl solution at 100° C [19–21], and with those observed in studies on naturally damaged zircons [22].

After allowing for the specific surface area (taken as geometrical), the calculated dissolution rates of the fine powders were considerably less than those found in previous experiments on $-60+100$ mesh (150 to 254 μm) powders made from the same samples [3–5, 13]. The discrepancy was 10 to 30 times for the phosphate and 5 to 10 times for the aluminosilicate. In both

TABLE III Dissolution of irradiated and unirradiated Cs compounds

Material	Ion fluence (nm^{-2})	Time (days)	Liquid	[Cs] in solution ($mg\,l^{-1}$)*	Cs extraction (%)	Enhancement factor†
$CsZr_2(PO_4)_3$	20	14	H_2O	10	4.4	10
$CsZr_2(PO_4)_3$	–	14	H_2O	1.1	0.46	
$CsZr_2(PO_4)_3$	10	7	H_2O	30	13	25
$CsZr_2(PO_4)_3$	–	7	H_2O	1.2	0.52	
$CsZr_2(PO_4)_3$	10	7	Brine	5.3	2.3	3
$CsZr_2(PO_4)_3$	–	7	Brine	1.9	0.83	
$CsAlSi_5O_{12}$	20	14	H_2O	19	8.2	2
$CsAlSi_5O_{12}$	–	14	H_2O	10	4.4	
$CsAlSi_5O_{12}$	10	7	H_2O	35	15	7
$CsAlSi_5O_{12}$	–	7	H_2O	5.1	2.2	
$CsAlSi_5O_{12}$	10	7	Brine	110	46	2.5
$CsAlSi_5O_{12}$	–	7	Brine	41	18	

*Errors in [Cs] data estimated as ± 10%, due principally to uncertainties in evaporation losses.
†Enhancement factor in dissolution rate due to irradiation; error estimated as ± 20%.

cases, prior leaching in the sedimentation process could be responsible for part of the discrepancy. However, a further possibility is that small amounts of relatively soluble, intergranular caesium-rich phases were present in the phosphate material and were preferentially separated out by the sedimentation technique: a lower caesium dissolution rate would then be expected in the present experiments. A large discrepancy in the $CsAlSi_5O_{12}$ results would not be expected from this cause since the starting material was deliberately made substoichiometric in caesium to prevent the formation of other caesium-bearing phases [3, 13].

For the unirradiated materials, the data of Table III indicate increases in the dissolution rate in brine relative to deionized water. The increases were factors of ~ 8 and < 2 for $CsAlSi_5O_{12}$ and $CsZr_2(PO_4)_3$, respectively. From previous work [5, 13], the Na^+ content of the brine, but not the Ca^{2+} content, would be sufficient to play a small part in the increase for $CsAlSi_5O_{12}$, but neither the Na^+ nor the Ca^{2+} content of the brine would have been expected to influence the dissolution rate of the unirradiated $CsZr_2(PO_4)_3$. The similarities of the caesium extractions in deionized water for the 7 and 14 day experiments on $CsZr_2(PO_4)_3$ were consistent with the results of previous work [5]. However, the reason the maximum caesium extraction was observed in both materials for the lower radiation fluence ($10\,\text{ion}\,\text{nm}^{-2}$) and smaller leaching time (7 days) is not clear.

4. Conclusions

$CsAlSi_5O_{12}$ and $CsZr_2(PO_4)_3$ appear to be fairly sensitive to atomic displacement damage when irradiated by 3 MeV argon ions, in that the D_m values lie towards the high end of values found by this technique for other refractory crystalline phases that have been considered for the immobilization of waste radionuclides. Radiation damage increased the dissolution rates of these materials in both deionized water and a brine at 100° C: the enhancement factors of 2 to 25 were in broad agreement with values obtained after heavy ion irradiation of nuclear fuel waste glasses [19–21] and for naturally damaged zircons [22].

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