

**RADIOGENIC TRANSMUTATION EFFECTS IN A CRYSTALLINE  
ALUMINOSILICATE CERAMIC: A TEM STUDY**

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## RADIOGENIC TRANSMUTATION EFFECTS IN A CRYSTALLINE ALUMINOSILICATE CERAMIC: A TEM STUDY

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### ABSTRACT

We demonstrate the use of transmission electron microscopy (TEM) to study the effects of beta-decay of radioactive  $^{137}\text{Cs}$  to  $^{137}\text{Ba}$  in crystalline pollucite ( $\text{CsAlSi}_2\text{O}_6$ ). Most prior work on radiation effects in materials has focused on structural damage from alpha radiation. Beta radiation, on the other hand, causes little atomic displacement, but the decay transmutation, that is, the radioactive decay of a radioisotope to an isotope of another element, results in progeny with different the valence and ionic radius. Cesium-137, a fission product of uranium, is a major contaminant at U.S. Department of Energy production facilities. Pollucite is an aluminosilicate ceramic with potential use for long-term storage of  $^{137}\text{Cs}$ . We focused on one of several available  $^{137}\text{Cs}$  sources originally fabricated in the 1970s and 1980s. These sources were small, sealed, stainless steel capsules containing pollucite in which varying amounts of the natural Cs had been replaced by radioactive  $^{137}\text{Cs}$  ( $t_{1/2} = 30.13$  years). The sample chosen for TEM examination, aged for nearly 20 years, contained the most radiogenic barium—nearly 16% of the total cesium—and was expected to show the largest radiation effects. Bright field transmission images revealed a homogeneous crystalline matrix, with no evidence of distinct Ba phases or ex-solution phenomena resulting from the  $^{137}\text{Cs}$  transmutation. Electron diffraction patterns obtained from several portions of the sample were consistent with literature values for pollucite. These data suggest that little substantial damage was done to the crystal structure of this sample, despite the transmutation of nearly 16% of the cesium to barium over the elapsed 20 years. Although our observations are limited, to our knowledge these are the only available data in which transmutation effects have been isolated from other radiation damage phenomena.

### INTRODUCTION

Here, we present a study of long-term effects of transmutation on the stability of crystalline pollucite. This process is a key scientific issue in the assessment of the long-term stability, and hence performance, of a waste form. Most work on radiation effects in waste forms has focused on alpha radiation, which produces more displacements than beta radiation. However, beta radiation results in transmutation, which changes both the ionic radius and the valence of the element undergoing decay (0.160 nm for  $\text{Ba}^{2+}$  vs. 0.188 nm for  $\text{Cs}^+$ ). These changes in coordination chemistry may destabilize the waste form, permitting higher releases of radionuclide contaminants to the accessible environment.

Potential waste forms for Cs storage include silicate glass, glass-ceramics, cesium-loaded zeolites, and pollucite. Of these candidates, pollucite offers several advantages. It can accommodate more than 40 wt% Cs into its structure, thereby producing a highly dense waste form, comparable in density to glass and much denser than the glass-ceramic or zeolite alternatives. In addition, the measured and calculated solubility of pollucite and the leachability of Cs in the pollucite structure are all about three orders of magnitude less than those measured for the candidate silicate glass [1]. The manner in which pollucite responds to transmutation, however could affect these advantages. Although the pollucite structure can accommodate > 40 wt% Cs, previous data indicated that it can accommodate only about 10 wt% Ba [2].

Little is known about the mobility of Cs in pollucite. Only a few studies [3-5] have examined leaching following transmutation or irradiation of pollucite or closely related aluminosilicates, and the results seem to be contradictory. The results may indicate that prior to radiation-induced amorphization, the accumulated defects can lead to higher leachability of Cs [3], whereas once amorphization occurs, the Cs becomes trapped in the collapsed structure [2]. A more thorough analysis of the effect of accumulated defects from both transmutation and ionization processes on the pollucite structure is needed to assess the impact on Cs mobility.

## APPROACH

We selected pollucite for this study for the following reasons:

- We had access to well-characterized samples of  $^{137}\text{Cs}$ -containing pollucite that had been stored under ambient conditions for up to 20 years.
- Cesium has a high activity ( $t_{1/2} = 30.13$  years), leading to the buildup of significant levels of Ba in these samples.
- Cesium continues to be an important constituent of the waste management effort within the DOE complex.

Pollucite, also known as Cs-leucite, has a cubic symmetry (space group  $Ia\bar{3}d$ ) at temperatures above  $\sim 100^\circ\text{C}$ . The crystal structure consists of a network of vertex-sharing (Si, Al) $\text{O}_4$  tetrahedra. The Cs is contained in wide channels that are parallel to the  $\langle 111 \rangle$  directions. These channels do not intersect but are connected via  $\langle 110 \rangle$  side channels. At temperatures below  $100^\circ\text{C}$ , pollucite undergoes a reversible displacive phase transition to a tetragonal phase, which has spacegroup  $I4_1/a$ . Because the  $c/a$  ratio of the tetragonal phase is only 1.0051, it was not recognized as a distinct phase until recently [6].

If the structure of the pollucite is damaged by radioactive decay, it may be less effective at containing the  $^{137}\text{Cs}$ . We focus here on results obtained by TEM to determine whether the chemical differences between cesium and barium reduce the structural integrity of the pollucite. We have chosen a specimen from one of several  $^{137}\text{Cs}$  sources originally fabricated for tumor treatment (Figure 1). These sources were small, sealed, stainless steel capsules containing pollucite in which varying amounts of natural, nonradioactive  $^{133}\text{Cs}$  had been replaced by radioactive  $^{137}\text{Cs}$ . The stainless steel capsules were 300 micrometers thick and approximately 3 mm long and 1 mm in diameter. Inside each capsule was a loosely

consolidated pellet of pollucite, with a mass of approximately 80 mg. The available capsules ranged from 10 to 20 years old (Table 1). The amount of  $^{137}\text{Cs}$  in each capsule and the resulting decay in growth of  $^{137}\text{Ba}$  also appear in Table 1. It was expected that the decay of  $^{137}\text{Cs}$  to  $^{137}\text{Ba}$  would place the pollucite structure under significant strain, owing to the limited solubility of Ba in pollucite [2].



Figure 1. Pollucite capsule, shown with dime for scale.

Table 1. Radioactive pollucite sample identification and characteristics (as of 1999).

Series (year)	Serial number	Original activity, mCi	Present <sup>a</sup> activity, mCi	Mass fraction of total pellet, g <sup>b</sup>		Fraction of total original Cs, g <sup>c</sup>	
				Original $^{137}\text{Cs}$	Present <sup>a</sup> $^{137}\text{Ba}$	Original $^{137}\text{Cs}$	Present <sup>a</sup> $^{137}\text{Ba}$
1979	AD 92	121	78	0.0375	0.0139	0.425	0.155
1979	AE 87	44	28	0.0136	0.0050	0.154	0.057
1979	AE 53	42	27	0.0130	0.0048	0.147	0.054
1984	AE 889	4.0	2.8	0.0012	0.00035	0.0140	0.004
1984	AE 784	16	11.5	0.0051	0.0015	0.0572	0.017
1989	AG 510	6.0	4.8	0.0019	0.0004	0.0211	0.0044

<sup>a</sup> As of 1999.

<sup>b</sup> Based on 0.0844 g pollucite/pellet.

<sup>c</sup> Based on 0.0075 g total Cs/pellet.

## RESULTS AND DISCUSSION

The AD 92 sample was chosen for TEM examination because it contained the most radiogenic barium—nearly 16% of the total cesium (Table 1)—and was expected to show the largest radiation effect.<sup>†</sup> Small fragments of the AD 92 pollucite were removed from the capsule in a nitrogen-filled glove box. The pollucite fragments were embedded in an epoxy block and thin-sectioned by using a Reichert ultramicrotome. The thin sections were floated onto a carbon-coated copper TEM grid, which was then mounted in a liquid-nitrogen-cooled TEM sample holder. The samples were allowed to desiccate in the TEM under vacuum over a weekend and then were examined by using a JEOL 2000 FX Mark II TEM equipped with dual energy dispersive x-ray fluorescence spectroscopy (EDS) detectors and operated at an accelerating energy of 200 keV. The sample temperature was maintained at approximately 100 K with the liquid nitrogen coolant to minimize electron beam damage, which is often rapid in an aluminosilicate sample. Bright field transmission images revealed a homogeneous crystalline matrix, with no evidence of distinct Ba phases or ex-solution phenomena resulting from the <sup>137</sup>Cs transmutation (Figure 2). Electron diffraction patterns were obtained from several portions of the sample; the combined data appear in Table 2. Despite the liquid nitrogen cooling, the sample amorphized rapidly in the beam, allowing any spot within the beam to be examined for only about 15 seconds. Nonetheless, the excellent agreement between the observed diffraction spacings and literature values for pollucite indicates that no substantial damage was done to the crystal structure of this sample, despite the transmutation of nearly 16% of the cesium to barium over the elapsed 20 years. A systematic contraction of the observed lattice spacings by about 2% is indicated in the final column of Table 2; this contraction may have been a result of the cryogenic temperature of the experiment. These observations are in accord with independent x-ray diffraction results reported by Hess *et al.* [7], who found no evidence of a distinct Ba phase. The Hess *et al.* study did report minor unit cell volume expansion and some disordering of the (Si, Al)O<sub>4</sub> tetrahedra, compared with non-radioactive specimens [7].

## CONCLUSIONS

We used TEM to assess structural effects caused by the beta-decay transmutation of <sup>137</sup>Cs to <sup>137</sup>Ba in radioactive pollucite that had aged for nearly one half-life of the <sup>137</sup>Cs. This transmutation might affect the stability of the aluminosilicate pollucite crystal because of chemical differences between Cs<sup>+</sup> and Ba<sup>2+</sup>. Although the amount of barium exceeded the amount the structure was expected to tolerate, our observations indicate that the pollucite structure remained remarkably unaffected by the transmutation. This suggests the presence of a metastable, yet robust, state. Our observations are limited, but to our knowledge, these are the only available data in which transmutation effects have been isolated from other radiation damage phenomena. The virtual null result for transmutation effects on the pollucite is encouraging from a regulatory and modeling point of view. However, this accommodation of

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<sup>†</sup> Not all of the cesium in the samples is radioactive <sup>137</sup>Cs. Thus, some cesium will remain after the transmutation of <sup>137</sup>Cs to <sup>137</sup>Ba is complete.

excess Ba is not understood mechanistically, and it may not be characteristic of aged waste forms in general.

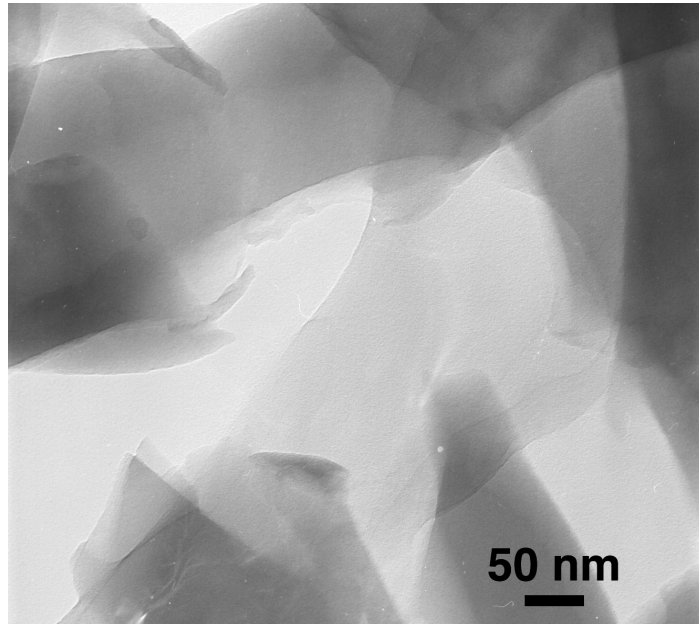


Figure 2. TEM micrograph of radioactive pollucite from the AD 92 capsule. The pollucite was shattered during the ultramicrotome process, but each of the fragments has a homogeneous appearance. There is no evidence of phase separation or ex-solution precipitation.

**Table 2. Experimental electron diffraction data from radioactive  $^{137}\text{Cs}$ -doped pollucite sample AD 92 compared with JCPDS-ICDD reference data.**

Experimental d-spacing (Å), sample AD 92	Natural Pollucite JCPDS-ICDD 25-194 d-spacing (Å) <sup>a</sup>	Synthetic Pollucite JCPDS-ICDD 29-407 d-spacing (Å) <sup>a</sup>	Ratio (experimental/reference) <sup>b</sup>
5.47	5.56 vf 4.83 vf	5.58 4.84 vf	0.980
3.54	3.65 *	3.66 *	0.973
3.56			
3.57			
3.30	3.42 3.23 vf 3.06 vf	3.42 *  3.06 f	0.965
2.86	2.913 *	2.914 *	0.982
2.82			
	2.791 vf		
2.62	2.682 2.497 vf 2.416 2.218 2.162 1.897	2.684 2.499 2.419 * 2.220 2.018 1.975 vf 1.897 vvf	0.977
1.813	1.860 * 1.736 * 1.709	1.862 * 1.737 * 1.709	0.974
1.652	1.683 1.634 1.589 1.548 1.529	1.684 vf 1.635 1.549 1.529	0.982
1.429			

<sup>a</sup> Major peaks in JCPDS-ICDD reference data (= 30% most intense) are labeled by “\*.” Very faint peaks are indicated by “vf”; extremely faint peaks are indicated by “vvf.”

<sup>b</sup> The final column gives the ratio of the experimental data to the average of the corresponding reference values. The TEM specimen was liquid-nitrogen-cooled to ~100 K, whereas the reference samples were measured at ambient temperature. This ratio may reflect thermal expansivity effects.

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