THE RELATIVE RADIATION RESISTANCE OF ZIRCONOLITE, PYROCHLORE AND PEROVSKITE TO 1.5 MeV Kr\(^+\) IONS* 

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INTRODUCTION

Zirconolite (CaZrTi₂O₇), pyrochlore (VIII₈A₂⁷VI₂B₂¹IV₆X₆Y) and perovskite (CaTiO₃) are candidate phases for the immobilisation of rare earth elements (REEs) and actinides (ACTs) in various high level radioactive waste (HLW) forms [1]. The effect of radiation damage on the structure and consequently on the durability of these phases is important to predictive modelling of their behaviour in the repository environment and risk assessment.

METHODOLOGY

In this study, long term radiation damage effects at room temperature were simulated in six fabricated zirconolites (of various compositions and structures), one fabricated pyrochlore and one natural perovskite, by irradiating samples with 1.5 MeV Kr+ ions using the HVEM-Tandem User Facility (HTUF) at Argonne National Laboratory. The HTUF consists of a modified AEI high voltage transmission electron microscope interfaced to a 2 MeV tandem ion accelerator. Selected area diffraction patterns (SADs) of individual grains of each material were monitored as a function of dose to establish the critical dose for amorphisation (Dc).

RESULTS

Damage ingrowth in all zirconolite, pyrochlore and perovskite samples is revealed by the following progressive changes in the SAD patterns: weakening of some classes of reflections with respect to others, appearance of diffuse rings which increase in intensity with dose, disappearance of specific classes of reflections, then the disappearance of remaining reflections leaving only diffuse rings. In zirconolite and pyrochlore, the reflections which remain at high doses are representative of their fluorite sublattices. In perovskite, the reflections which remain at high doses are cubic sub-cell reflections.

A representative SAD sequence for zirconolite is shown in Figures 1 and results for all samples are summarised in Table 1. We found that i) Dc(zirconolite) varies by a factor of ≈2 (from ~4 to 7 x 10⁴ ion cm⁻²), but that it is independent of the atomic weight of dopants in zirconolite and the mean atomic weight of the sample, ii) Dc(pyrochlore) ≈ Dc(zirconolite) and iii) Dc(perovskite) = 3.5 x Dc(zirconolite).

DISCUSSION

Within experimental error, our Dc(undoped zirconolite) value agrees with that measured by Ewing and Wang ([2], 4 x 10¹⁴, 1.5 MeV Kr+ ions cm⁻²) and disagrees with that measured by White et al. ([3], 1 x 10¹⁵, 1.5 MeV Kr+ ions cm⁻²). However on the basis of computer simulations of ion irradiation Smith et al. [4] suggest that White et al.'s Dc(undoped zirconolite) value may be high. If that were true, it may also explain why White et al.'s data suggested that Dc(zirconolite) depended on the atomic weight of dopant species, which is in contradiction to the trend we observed.

Data from previous studies agree with our result that Dc(pyrochlore) = Dc(zirconolite). Studies of natural minerals showed that zirconolite and pyrochlore [5] require approximately the same alpha dose (1 x 10¹⁶ α/mg) to be rendered amorphous. Synthetic Cm-doped Gd₂Ti₂O₇ (pyrochlore) and CaZrTi₂O₇ (zirconolite) became amorphous at alpha doses of 3.8 and 5 x 10¹⁵ α/mg respectively (i.e. less variation than we see with zirconolite)[6]. Ion irradiation studies of zirconolite and pyrochlore [7, 8] show that the radiation resistance of pyrochlore and zirconolite vary by a factor of between 2 and 4.

We found that Dc(perovskite) = 2.5 x Dc(zirconolite). Previous findings are divided. Data from natural samples suggest that Dc(perovskite) = 0.5-2 x Dc(zirconolite)[4]. Karioris et al. and Weber et al.'s Ar ion irradiation studies suggest that Dc(perovskite) = 0.25-0.5.
Table 1. Compositions, mean atomic numbers, and critical amorphization doses of samples.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Atomic no. (10^4 ions cm^-2)</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dacrite (2,7 fresh)</td>
<td>11.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Sodapine (2,7 fresh)</td>
<td>11.3</td>
<td>8.0</td>
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<td>8.0</td>
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</tbody>
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Figure 1. [111] 010 SAD patterns of a zirconolite grain (a) before irradiation and (b) after doses of 5E+17 and (c) 5E+17 ions cm^-2.

References


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