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2006 J. Phys.: Condens. Matter 18 L277

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LETTER TO THE EDITOR

Hydrous species in ceramics for the encapsulation of nuclear waste: OH in zircon

Ekhard K H Salje and Ming Zhang

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

Received 22 March 2006

Published 16 May 2006

Online at stacks.iop.org/JPhysCM/18/L277

Abstract

The partition of hydrous species in radiation-damaged zircon was investigated using infrared spectra from a large range of samples with different degrees of radiation damage and a variety of geological conditions. The results of the present study showed uniformly a partition coefficient of $K = 0.3$. This indicates that OH is enriched in the damaged crystalline phase and not in the amorphous phase. The uniformity of the results for all samples indicates equilibrium rather than a frozen-in kinetic behaviour. It is possible that the enrichment of OH in the damaged crystalline phase of zircon indicates a catalytic effect of hydrogen during recrystallization events.

1. Introduction

A key issue for the choice of materials suitable for the encapsulation of high level nuclear waste is its solubility in water. As it is very unlikely that nuclear deposits remain ‘dry’ over geological periods of time the problem of releasing radioactive and highly toxic elements such as Pu and other actinides into the groundwater is of paramount importance. Leaching of waste materials is significant in standard glass matrices and may also play a role in more advanced ceramic matrices. It is of significance to gain a better understanding of where hydrous species are located if the material becomes ‘wet’, and whether and how their presence may possibly affect the solubility and durability of the host phases. In previous studies the role of hydrous species in titanite has been described in great detail (Salje *et al* 2000, Zhang *et al* 2000) based on the observation that all natural titanite minerals contain significant amounts of OH and that dehydration of titanite is driven essentially by recrystallization of the radiation-amorphized regions. Similar studies in zircon are much harder because zircon generally contains much less OH, while dissolution and weathering of amorphized zircon still occurs over geological times (Balan *et al* 2001).

The dissolution and stability of zircon under hydrothermal conditions has been studied previously (Harrison and Watson 1983, Sinha *et al* 1992, Rizvanova *et al* 2000). Geisler and

collaborators (2004) have shown that hydrothermally treated zircon forms complex Lisegang-like patterns and they argued that a possible mechanism for the pattern forming mechanism is related to the fast diffusion of hydrogen and the displacement of hydrogen from growing crystallites. Geisler *et al* (2003b) studied the role of hydrogen in zircon when treated in acid solutions and relate the leaching of Zr and Si to hydrogen diffusion in the amorphous network. The probably most direct observation of coupling between solubility, hydrogen transport and the structural state of zircon was given by Geisler *et al* (2003a), who showed that reacted fractions of zircon were minute in the crystalline state with amorphous fractions below the first percolation point. The reaction rate increased in a percolation-type behaviour for intermediately damaged material and again after the second percolation point of the amorphized fraction was surpassed (Geisler *et al* 2003a). This observation agrees with those of earlier studies showing that crystalline zircon has dissolution rates below the detection limit while amorphized zircon shows dissolution rates of the order of 10^{-7} moles/m²/day at 80 °C pH 5 (Ewing 1999 for review). While this is still several orders of magnitude smaller than the value for glass it may be insufficient for some applications for encapsulation of nuclear material.

While these studies focus on the macroscopic leach rates we describe in this letter an alternative approach. We wish to understand the physical mechanisms by which hydrogen is incorporated in the various forms of zircon and how it may influence leaching processes on an atomic level. We will argue in this letter that hydrogen in geologically old samples forms predominantly OH with the surprising discovery that the OH partitioning between the damaged crystalline and the amorphous fraction zircon has apparently reached an equilibrium state in all samples which we studied so far.

2. Experimental details

Zircon samples used in this study are mainly crystals from Sri Lanka, Australia, Thailand, Uganda and unknown localities. They were chosen because of their gem quality and low levels of chemical impurities. The crystallographic orientations of the crystals were determined from the external morphology, or using x-ray precession techniques and optical polarizing microscopy. Polarized IR spectra were recorded from natural zircon crystals under vacuum using a Bruker IFS 66v spectrometer. Apertures of 2.0–2.5 mm, a KBr beam splitter, a Globar lamp, and a nitrogen-cooled MCT detector were used for the measurements. The typical spectra of natural zircon with different degrees of damage are shown in figure 1.

3. Analysis and discussion

The main component of hydrous species in zircon was found to be OH. For samples with low radiation damage, the OH ions show the features of localized defects in a crystalline matrix. The nature of these defects is not clear, although one may compare them with hydrogarnet defects in silicates (Woodhead *et al* 1991)—the SiO₄ tetrahedra are replaced by (OH)₄ groups. For samples with higher degrees of damage we find a novel, and somewhat counterintuitive, result. Samples with radiation damages higher than those of the first percolation point of the damaged regions (Salje *et al* 1999, Trachenko *et al* 2002, 2003), typical for radiation damage as expected in nuclear deposits, reveal simple spectra consisting of only two components. One component is that of full amorphized material and relates to OH in an amorphized matrix. The second component is related to crystalline but damaged material close to the first percolation point. The second component is structurally very different from the OH signal in the fully crystalline material. As one may expect, the OH ions in the amorphized regions increase with increasing radiation damage until they form the sole species for fully damaged zircon. As

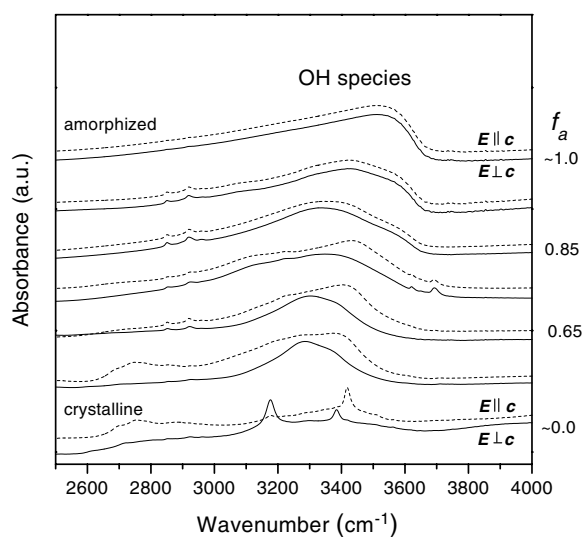


Figure 1. OH spectra of metamict zircon; f_a is the proportion of the amorphous component of the sample.

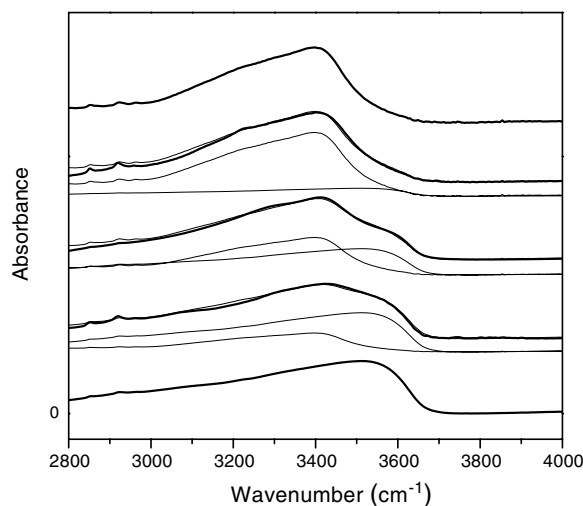


Figure 2. Infrared analysis of OH species in radiation-damaged zircon. The thick lines are measured spectra and the thin lines indicate the decomposition of the spectra into a 'crystalline' and an 'amorphous' part.

both species can be identified individually we can now ask what the partition of OH between the two states, namely crystalline (but damaged) and amorphous, is (figure 2). We define a partition coefficient K as

$$K = \frac{[\text{OH amorphous}][\text{matrix crystalline}]}{[\text{matrix amorphous}][\text{OH crystalline}]}$$

The experimentally observed partition coefficients in figure 3 show a very narrow distribution around a value of 0.3 for all samples using various methods for the calibration of the various volume proportions (Paterson 1982, Libowitzky and Rossman 1997).

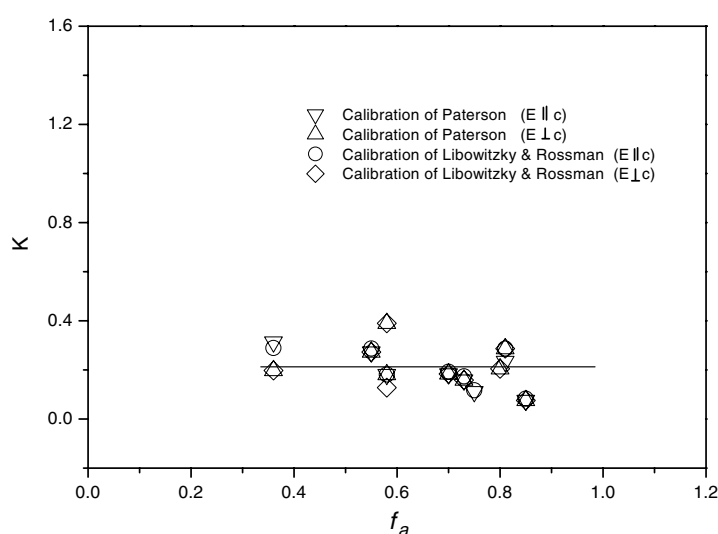


Figure 3. Partition coefficient K as a function of fraction of the amorphous phase

This result is highly significant for two reasons. First, the relatively small scatter of the data points shows that the partition has reached some thermodynamic equilibrium or steady state for all samples. The samples come from a wide variety of geological locations with very different geologies histories (Zhang and Salje 2001). Recrystallization of zircon after radiation damage is an exceedingly slow process so that one may have expected that at least some samples would show large deviations of K from its equilibrium value. For example, $K = 1$ would signify a random distribution of OH in the two states which would occur for the uniform distribution of OH in a virgin sample and subsequent random radiation damage. One could envisage this to be the initial scenario. The fact that a reasonably well defined state of equilibrium partition is observed in all samples also indicates that the hydrogen or proton is mobile enough (over geological timescales) to move from the initial distribution into the equilibrium partitioning, or diffuses from external sources into the crystals. This requires hydrogen to move between the crystalline regions and the amorphized regions through an interface. This observation can be contrasted with the behaviour of dehydration of titanite in which hydrogen moves predominantly along the interface (Salje *et al* 2000). The second important observation is the low absolute value of K . This signifies that OH is highly enriched in the crystalline matrix and depleted in the amorphized regions. This is also highly surprising in view of the higher number of trapping centres (Trachenko *et al* 2002) and holes in the amorphized parts of the samples (Rios and Salje 2004). Indeed, previous investigations of radiation damage in titanite (Salje *et al* 2000) concluded that hydrous species are enriched in the rim of the amorphized regions but not in the crystalline matrix.

This behaviour raises important questions: why do the OH species or protons prefer to stay in the crystalline matrix and how does the proton finds its way to the crystalline region. The answers remain unclear. One possibility is that trapping of hydrogen to form OH in the crystalline fraction involves defects with lower trapping energies than those in the amorphized parts of the samples. As the types of defects produced in metamictization appears highly complex (Pruneda and Artacho 2005) and are not fully understood, we cannot comment on the trapping energies in this letter.

Another possible explanation for our experimental observations is that hydrogen acts catalytically to enhance the rate of recrystallization of the amorphized material. If OH is present in the samples prior to the recoil damage process there is no reason to believe that hydrogen is systematically separated from the radionuclide. The enhanced probability to find hydrogen in the crystalline matrix would mean that the recrystallization process after the damage event is enhanced by the presence of hydrogen. This idea also concurs with the observation that the spectra of OH in the crystalline parts correspond to highly defective material rather than the virgin crystal.

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