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Pb^+ irradiation of synthetic zircon ($ZrSiO_4$): Infrared spectroscopic investigation—Discussion

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In a recent paper, Zhang et al. (2008b) described the results from an infrared (IR) spectroscopic study that addressed structural changes in a synthetic zircon ($ZrSiO_4$) sample that resulted from the irradiation with heavy (i.e., 280 keV Pb^+) ions. Infrared analyses of the same zircon sample have been also described by Zhang et al. (2008a). I see major problems with some of the interpretations presented in these two papers. Problems arise from the failure to consider the significant discrepancy between the sample volumes that were irradiated and analyzed, respectively. To illustrate the following discussion, a largely simplified sketch of the irradiated sample is shown in Figure 1.

On the one hand, the Pb^+-implanted sample described by Zhang et al. (2008b) has certainly experienced surficial damage, due to displacive collision events, in a surficial volume zone extending only ~0.1 μm into the sample. On the other hand, the sampling depth of infrared reflectance measurements of transparent samples with a Bruker grazing angle objective is in the micrometer-range or even larger (n.b., this depends on several factors such as the irradiation angle, optical properties of the solid to be analyzed, and especially the wavelength of the infrared light; J. Sawatzki and G. Zachmann, Bruker GmbH, personal communication; see also Brunner et al. 1997). This makes conventional IR reflectance analysis extremely difficult, or even impossible, if thin films or layers with thicknesses well below the micrometer-range, located on top of a transparent host material, are to be analyzed. The IR analysis of such samples requires the application of special preparation and/or analysis techniques (see for instance Otto and Korte 1988; Amekura et al. 2004), which have not been implemented by Zhang et al. (2008b). This discrepancy in length scales suggests that in their IR reflection measurements, Zhang et al. (2008b) have mainly analyzed the crystalline zircon host underneath the implanted surficial layer, which the authors failed to consider in the discussion and interpretation of their spectra in both papers.

My doubts are illustrated by some simple calculations. The unit cell of zircon has a volume of ~260 $Å^3$ (or ~2.6×10^{-28} m^3). A ~0.1 μm thick, surficial layer of zircon has a volume of 10^{-13} m^3, and hence contains ~3.85×10^{14} unit cells, per square millimeter of surface area. As zircon has four formula units (i.e., 24 atoms) per unit cell, there are ~9.2×10^{15} lattice atoms per square millimeter in a 0.1 μm zircon layer. This same volume area has been irradiated with 10^{13} Pb^+ ions with an energy of 280 keV (note that Zhang et al. 2008b describe IR reflectance measurements of only one sample, which was implanted with 10^{15} ions/cm^2).

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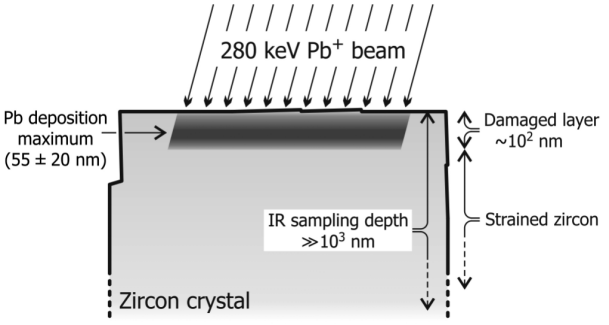

Figure 1. Sketch of the zircon sample implanted with 280 keV Pb^+ ions (simplified; not to scale), visualizing the difference of ranges of surficial implantation damage (dark gray) and IR detection.

Farnan et al. (2007) have discussed that in natural radiation-damaged zircon, an average of close to 5000 lattice atoms are permanently displaced per alpha-decay event in the U- and Th-decay chains. The majority of these displacements are located in clusters generated by recoils of heavy daughter nuclei (energies of around 100 keV). Because the 280 keV Pb^+ ions in the experiment of Zhang et al. (2008b) had much higher energy than recoiled nuclei, but similar ratio of nuclear and electronic stopping powers, it appears reasonable to assume that in the experiment of Zhang et al. (2008b), ≥10^4 lattice atoms may have been displaced per implanted Pb^+ ion. This in turn suggests that the implanted layer has experienced ≥10^{17} displacements per square millimeter. From these two values (~9.2×10^{15} lattice atoms and ≥10^{17} displacements), an average damage density of ≥10 displacements per lattice atom (dpa) is calculated.

However, Weber et al. (1994) have shown in a transmission electron microscopy (TEM) study that radiation-damaged zircon has fully become amorphous, without any evidence of crystalline remnants, at below 0.50 dpa. Consequently, the damage density calculated for the implanted layer in the sample of Zhang et al. (2008b) exceeds the damage density needed to amorphize this layer by more than order of magnitude.

Another, even more simple calculation considering the implantation dose per target weight, leads to a similar result. It has been shown in several studies that natural zircon from Sri Lanka has become amorphous after about ~10^{19} alpha-decay events per gram (e.g., Holland and Gottfried 1955; Chakoumakos et al. 1987; Murakami et al. 1991). Considering that the majority of structural damage created in an alpha-decay event is due to the alpha-recoil, the above value may suggest that Sri Lankan zircon

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is transformed into an amorphous state after being implanted by ~10^{19} heavy ions with energies of ~100 keV, per gram of material. That value, however, is an overestimate of the alpha-recoil dose that is actually needed to reach amorphization, because alpha doses of Sri Lankan zircon have always been calculated based on their U-Pb age (which had included the incorrect assumption that all structural damage has been accumulated since), whereas the Sri Lankan zircon has experienced significant annealing and hence represents incomplete damage storage (Nasdala et al. 2004).

In the experiment of Zhang et al. (2008b), an ~0.1 μm thick layer of zircon (weight ~4.68×10^{-7} g per square millimeter) has been irradiated with 10^{13} Pb^+ ions per square millimeter. The ratio of the two values gives an irradiation dose of $>2 \times 10^{19}$ 280 keV Pb^+ ions per gram of the zircon target. This dose is, considering the approximately three times higher Pb^+ energy compared to energies of alpha recoils in the U and Th chains, perhaps equivalent to the damage created by $5–6 \times 10^{19}$ α/g. This clearly exceeds the amorphization dose of $<1 \times 10^{19}$ α/g.

The above calculations and considerations suggest that irradiation of zircon with 10^{15} 280 keV Pb^+ ions/cm^2 must have resulted in the formation of a ~100 nm thick, fully amorphous layer. However, spectra obtained by Zhang et al. (2008b) are those of crystalline $ZrSiO_4$, characterized by narrow internal SiO_4 vibrational bands (see strongly broadened IR spectra of amorphous $ZrSiO_4$; Woodhead et al. 1991; Zhang et al. 2000). The main deviation of their spectra from those of the un-irradiated analog is loss of absorbance. I assign the IR spectra presented by Zhang et al. (2008b) to crystalline zircon underneath the surficial, amorphous, ion-implanted layer. The surficial layer itself, in contrast, is most likely an insignificant contribution to the integrated IR spectra, apart from some effect on the intensity of the detected IR light (e.g., change of surface properties, light reflection both at the surface and the internal amorphous-crystalline boundary, etc.) and hence the detected absorbance. This is supported by the facts that (1) the irradiation-amorphized layer is estimated to make up less than 10 vol% of the probed sample volume and (2) the vibrational absorption of amorphous materials is in general much lower that that of their crystalline analogs.

The crystalline zircon host underneath the surficial, amorphized, layer is expected to deviate from the un-irradiated sample insofar as it must be affected by intense strain, and this strain is likely to have notable effects on IR spectra. Recall that the irradiation-induced transformation of zircon into the amorphous state is connected with strong volume expansion. The expansion of the surficial, irradiation-damaged layer is—especially parallel to the surface/layer plane—partially suppressed by the underlying host zircon, resulting in compressive strain of the amorphous layer. The underlying host, in turn, must be affected by dilative strain caused by the somewhat volume-expanded surficial layer. It appears most worthwhile to check, for instance by means of TEM imaging, whether the strong strain gradient near the amorphous-crystalline boundary has resulted in the formation of fractures (compare Chakoumakos et al. 1987; Lee and Tromp 1995) with dimensions in the micrometer or submicrometer range. Such fractures, if present, would be perfect pathways for the secondary uptake of non-formula elements, as for instance hydrogen. High-resolution TEM analyses might also be useful to address the question whether there is indeed a nanometer-sized Pb silicate phase in the amorphous layer. Zhang et al. (2008b) have interpreted weak shoulders in the range 800–1050 cm^{-1} to "confirm" the presence of Pb silicate. This interpretation, however, is inconclusive because not only crystalline Pb silicates (Furukawa et al. 1979), but other silicate phases, show their most intense IR bands in this spectral region (E. Libowitzky, personal communication).

In summary, I strongly disagree with one of the main conclusions of Zhang et al. (2008a, 2008b). These authors claim to have found that the response of zircon to Pb^+ irradiation is notably different from the metamictization process, and that natural self-irradiation would eventually lead to an amorphous structural state that is different from that of glassy $ZrSiO_4$. Instead, their IR spectroscopic results simply indicate that the structural state of strained crystalline zircon underneath a surficial layer of amorphous $ZrSiO_4$ (produced by either irradiation or laser-melting and quenching) is different from the structural state of (bulk) metamict zircon.

Irradiation experiments are an excellent means to study radiation effects in natural minerals or their synthetic analogs. In the selection of analytical techniques to be applied, however, sampling volumes need to be carefully considered in view of trajectory lengths of implanted ions and the analytical method used to make the measurements. Vibrational spectroscopy has been shown (Krickl et al. 2008) to be most useful in studying mineral samples irradiated with MeV-range He ions, whose penetration depth (several tens of micrometers) is large compared to the volume resolution of light spectroscopy techniques. For the investigation of surficial damage with thicknesses in the 0.1 μm range, in contrast, techniques such as TEM (e.g., Weber et al. 1994) or micro Rutherford back-scatter/channeling (e.g., Grambole et al. 2007) might be more promising.

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