American Mineralogist, Volume 94, pages 856–858, 2009

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

MING ZHANG,[1,*] RODNEY C. EWING,[2] LYNN A. BOATNER,[3] EKHARD K.H. SALJE,[1] WILLIAM J. WEBER,[4] PHILIPPE DANIEL,[5] YANWEN ZHANG,[4] AND IAN FARNAN[1]

[1]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.
[2]Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109-1005, U.S.A.
[3]Oak Ridge National Laboratory, Materials Science and Technology Division, Oak Ridge, Tennessee 37831-6056, U.S.A.
[4]Pacific Northwest National Laboratory, P.O. Box 999, Richland, Washington 99352, U.S.A.
[5]Laboratoire de Physique de l'Etat Condensé (LPEC), UMR CNRS number 6087, Université du Maine, Faculté des Sciences, Av. Olivier Messiaen, 72085 Le MANS Cedex 9, France

We appreciate the opportunity to respond to the discussion by Nasdala (2009) concerning our interpretation of infrared spectra used to investigate the change in the structure of Pb-irradiated zircon as a function of increasing flux (Zhang et al. 2008a, 2008b). Nasdala is correct in cautioning experimentalists to carefully match the analytical technique to the expected irradiation damage profile to optimally probe the irradiation effects, and in fact, this point was emphasized by Ewing et al. (2003) in a review of radiation effects in zircon. However, Nasdala's discussion fails to fully appreciate three important points. (1) There is a difference between in situ irradiations of TEM samples that must be electron transparent, ~200 nm thick, as were completed by Weber et al. (1994), and more bulk-like irradiations that were completed in the Zhang et al. (2008a, 2008b) studies. (2) The particle-solid interactions change along the path of an implanted ion, that is the distribution and nature of the damage changes with depth as the ion loses energy, resulting in the greatest number of ballistic interactions near the end of the particle trajectory (see Fig. 1 of Ewing et al. 2003). (3) In comparing natural zircon damaged by alpha-decay events with ion-irradiated zircon, one must be aware that the recoil nucleus and the alpha particle cause different types of damage, and the use of the Pb-implantation experiment is meant to simulate only the alpha-recoil damage.

Pb-implanted vs. metamict zircon

Nasdala disagrees with our conclusion that there is a difference between Pb-implanted and metamict zircon. Although similarities are found between metamict zircon and Pb-irradiated (as well as Au-irradiated) zircon, it has been observed that ion irradiation does not cause the same extent of change in band frequency and width as those seen in metamict zircon, especially for the Raman v_3 band (Zhang et al. 2008a). The work of Zhang et al. (2008b) simply reported a lack of significant change in IR band wavenumbers, and it stated clearly that the issue had been studied and discussed in the work of Zhang et al. (2008a), whose conclusions, in fact, were based on Raman data of the v_3 band (it is not IR-active). The band is the strongest Raman band of zircon and is located near 1008 cm^{-1} with a FWHM of about 2–3 cm^{-1} in synthetic zircon. It remains intense in metamict zircon, but it is located in a low-frequency region (down to 995–955 cm^{-1}) (Nasdala et al. 1995; Zhang et al. 2000; Geisler et al. 2001) with a FWHM as large as 30 cm^{-1}. However, the significant change of the v_3 Raman band was not observed in the Au- and Pb-irradiated zircon specimens. This shows that the phonon band is less affected by the ion irradiation than by the alpha-decay events that cause metamictization in natural zircon. The discrepancy between Au- and Pb-irradiated zircon and metamict zircon is well discussed in Zhang et al. (2008a) and briefly addressed in Zhang et al. (2008b). A less defective structure and a lack of alpha-particle damage in the ion irradiation and strain release were proposed as the possible causes. Additional studies are underway to further explore these possible effects.

Additional experimental evidence has emerged that confirms the lack of a significant change of frequencies in ion-irradiated zircon. During the preparation of this reply, we noted a recent study (Lang et al. 2008) that reported Raman data for a synthetic zircon crystal (30 μm thick), which was entirely exposed to a defocused centimeter-sized ^{132}Xe-beam of energy 1.47 GeV (at 5×10^{12} ions/cm^2) with a calculated penetration depth of about 60 μm, i.e., the ions completely passed through the sample. While TEM revealed that the crystalline zircon was heavily damaged, the Raman data showed that the v_3 Raman band in an unirradiated synthetic crystal is located near 1008 cm^{-1} (Fig. 2a of Lang et al. 2008), and the value of the band frequency for the irradiated zircon is about 1006 cm^{-1} (Fig. 3a of Lang et al. 2008). This work clearly shows that high-energy ion irradiations do not produce the same degree of change in band frequencies (as well as widths) as observed in metamict zircon. This is consistent with our observations and conclusions in Zhang et al. (2008a, 2008b).

Metamict zircon vs. glass structure of quenched $ZrSiO_4$

Nasdala (2009) also takes issue with our conclusion that there is a difference between the aperiodic structure of metamict zircon and glass-like or glassy $ZrSiO_4$ produced by melting and quenching. We based our conclusions on the significant spectral differences observed in the Raman spectra of the two materials (Zhang et al. 2008a). On this point, Nasdala does not provide evidence that the two types of aperiodic states are the same. This is in fact a very difficult distinction to make; however, a careful study by Sales et al. (1989) has unequivocally established that the aperiodic state created by ion irradiation of lead pyrophosphate does not have the same structure as the glass produced by quenching this phase from a melt. The results of Sales et al. (1989) show that the structural state produced by displacive ion damage of a single crystal is actually "more disordered" or "more amorphous" than the thermally quenched glass formed from the same composition. Although these results are for a different

* E-mail: mz10001@esc.cam.ac.uk

0003-004X/09/0506–856$05.00/DOI: 10.2138/am.2009.542

material, a phosphate, they do show that very different aperiodic structures can result from different processes, such as ion beam irradiation vs. quenching from a melt.

There is also substantial evidence indicating differences between the two types of aperiodic state (metamict vs. quenched glass). Examples include: (1) spectral and structural differences (e.g., Sales et al. 1989; references in Zhang et al. 2008a); (2) ion irradiation can cause significant changes in glasses (e.g., Magruder et al. 1990, 1993); (3) metamict minerals tend to recrystallize epitaxially (e.g., McLaren et al. 1994; Capitani et al. 2000) while glasses commonly undergo a glass transition when heated to high temperatures; and (4) glasses have a roughly defined glass transition temperature, while metamict zircon shows very different responses at different temperatures (different defects may be annealed at different temperatures; and dehydroxylation and decomposition can occur) (e.g., Vance 1975; Woodhead et al. 1991; Ellsworth et al. 1994; see the discussion of the transition point by Salje et al. 1999).

The application of IR-spectroscopy to ion-implanted samples

The IR-reflection technique, which is similar to that employed in our study (Zhang et al. 2008a, 2008b), has been used to characterize ion-beam-irradiated surface and subsurface by several different research groups (e.g., Arnold and Peercy 1980; Sood et al. 1984; Baars et al. 1988; Arnold et al. 1990; Magruder et al. 1990, 1993; Zorba et al. 1996; Tung et al. 1998; Key et al. 2000; Chang et al. 2002; Brink et al. 2004; Vodopyanov and Kozyrev 2006). As compared with other analytical methods, infrared spectroscopy, as well as Raman spectroscopy, has proven to be useful in distinguishing differences between the crystalline and aperiodic structures because it is mainly dependent on atomic masses and the length and strength of interatomic bonds, and not primarily on the long-range periodicity of the structure. IR analysis provides valuable information on the local structure, bond strength, and composition of the sample. These previous studies have led to undeniably important observations and findings. The key to the successful application of IR spectroscopy is the use of weak signals from the damaged layers that are indicative of irradiation-induced changes. This is well demonstrated by various studies (e.g., Arnold and Peercy 1980; Sood et al. 1984; Arnold et al. 1990; Magruder et al. 1993; Tung et al. 1998; Brink et al. 2003). In the studies of Zhang et al. (2008a, 2008b), infrared specular (or external) and micro-reflection spectroscopy were applied. A grazing angle objective was used, which has two advantages: (1) improved sensitivity because a novel two-pass configuration (the IR beam passes the sample surface twice); and (2) grazing angle incident increasing the travel distance of the IR incident beam in the layers. Our analysis and description of the spectra are fully consistent with those of other previous studies (see earlier references). Referring to the comments by Nasdala (paragraphs 2 through 8), it appears that he has misunderstood the experimental configuration (external reflection, IR microscope, and a grazing angel incident objective) that we used. Furthermore, we clearly discussed and indicated the thickness of the amorphized layer that was examined in our two studies (Zhang et al. 2008a, 2008b).

We agree with Nasdala (2009) that IR-penetration depth is a complex issue. It is a measure of how deep electromagnetic radiation can penetrate into a material. It is defined as the depth at which the intensity of the radiation inside the material falls to 1/e of the original value at the surface. According to the Beer-Lambert Law, the intensity of infrared radiation inside a material falls off exponentially from the surface. For a given material, the penetration depth can generally vary for different wavelengths of radiation, the refractive indices and absorption coefficients of the media involved, incident angle, and polarization conditions. The shorter wavelength radiation penetrates less into the sample (this is why we mainly focused on implantation-induced bands in the high-frequency region where the depth is less). Infrared radiation with a larger incident angle (such as grazing angel incidence) has a shallower depth.

However, we wish to point out that for ion-irradiated materials (especially the Pb-irradiated zircon), the determination of the penetration depth becomes far more complex than that described in Figure 1 of Nasdada (2009). Not only the depth, but also the optical path of infrared radiation will be changed by the Pb-implantation. The effects can come from several factors. (1) Ion irradiation causes changes of the refractive indices and the absorption coefficient. The change depends on the irradiation dose and the type of ions implanted (Townsend et al. 1994). (2) Refractive index shows a distribution as a function of depth and an "optical barrier" could form (similar to the observation of Babsail et al. 1991) (Townsend et al. 1994). (3) Domains and clusters of newly formed phases (such as SiO_2, ZrO_2, and lead silicates) cause additional reflection and refraction when infrared radiation travels between these phases with different refractive indices. (4) At higher ion fluxes, more Pb-nanoparticles, as seen by Lian et al. (2003), are expected to form in the Pb-irradiated zircon, and they can simply stop some infrared radiation from further penetrating the sample. (5) Due to local stresses, scattering of light can occur (even in the strained crystalline zircon), which makes the radiation more likely to be absorbed. And (6), the reflected light from the bulk is expected to be disturbed again by the previously noted factors as the radiation leaves the crystal. The consequence of these effects is that less incident radiation may reach the deeper bulk material underneath the amorphized layer. Unfortunately, apart from the work of Babsail et al. (1991) on optical properties of He-implanted zircon, these effects have not been investigated, especially for heavy ion implanted zircon.

Spectrum assignments

Nasdala assigns the IR spectra presented by Zhang et al. (2008b) to crystalline zircon underneath the surficial amorphous, implanted layer (Nasdala 2009). The assignment is problematic for several reasons: (1) Irradiation-induced additional weak bands in the high-frequency region are very important to the type of application, as shown by the previous applications (see earlier references), but they were simply ignored. (2) Some additional features are relatively intense (e.g., the band near 1270 cm^{-1}) and are not allowed by the tetragonal symmetry ($I4_1/amd$) of zircon. (3) The effect of strain is not expected to cause changes as seen in the Pb-irradiated zircon (so far pressure-induced new phases in $ZrSiO_4$ have been seen at pressures as high as 19–20 GPa, which are too high for the ion irradiation to produce). (4)

The assignment cannot offer a proper explanation on the increase in reflectivity below 250 cm^{-1} (Fig. 1b of Zhang et al. 2008b), which is not seen in crystalline or metamict zircon.

We attribute the reflection spectrum of the zircon irradiated with Pb^+ in Zhang et al. (2008a, 2008b) to signals from the amorphous layer (amorphous phases that are at least in principle similar to those in metamict zircon and other ion-irradiated zircon specimens), additional phases or species and remnants, and the bulk underneath the ion implantation. Nasdala maintains that we have misinterpreted the spectra. In fact, our understanding and description of the spectra are correct. For the amorphized phases, we focused mainly on those weaker bands in the high-frequency region, and none have the same band frequencies of crystalline zircon. This is also clearly evident in the comparison of some frequencies between the irradiated and untreated crystalline zircon, as is shown by the fact that none of the bands was used for determining the volume fraction of the amorphous phase.

REFERENCES CITED

Arnold, G.W. and Peercy, P.S. (1980) Crystallization of ion-implanted $Li_2O{\cdot}2SiO_2$ and SiO_2 glasses. Journal of Non-Crystalline Solids, 41, 359–379.

Arnold, G.W., Brow, R.K., and Myers, D.R. (1990) Characterization of the near-surface region of glass implanted with light elements. Journal of Non-Crystalline Solids, 120, 234–240.

Baars, J., Seelewind, H., Fritzsche, Ch., Kaiser, U., and Ziegler, J. (1988) Arsenic ion implantation in $Hg_{1-x}Cd_xTe$. Journal of Crystal Growth, 86, 762–767.

Babsail, L., Hamelin, N., and Townsend, P.D. (1991) Helium-ion implanted waveguides in zircon. Nuclear Instruments and Methods in Physics Research, B59/60, 1219–1222.

Brink, D.J., Camassel, J., and Malherbe, J.B. (2004) Formation of a surface SiC layer by carbon-ion implantation into silicon. Thin Solid Films, 449, 73–79.

Capitani, G.C., Leroux, H., Doukhan, J.C., Ríos, S., Zhang, M., and Salje, E.K.H. (2000) A TEM investigation of natural metamict zircons: structure and recovery of amorphous domains. Physics and Chemistry of Minerals, 27, 545–556.

Chang, W., Feng, Z.C., Lin, J., Liu, R., Wee, A.T.S., Tone, K., and Zhao, J.H. (2002) Infrared reflection investigation of ion-implanted and post-implantation-annealed epitaxially grown 6H-SiC. Surface and Interface Analysis, 33, 500–505.

Ellsworth, S., Navrotsky, A., and Ewing, R.C. (1994) Energetic of radiation-damage in natural zircon ($ZrSiO_4$). Physics and Chemistry of Minerals, 21, 140–149.

Ewing, R.C., Meldrum, A., Wang, L.M., Weber, W.J., and Corrales, L.R. (2003) Radiation effects in zircon. In J.M. Hanchar and P.W.O. Hoskin, Eds., Zircon, 53, p. 387–425. Reviews in Mineralogy and Geochemistry, Mineralogical Society of America, Chantilly, Virginia.

Geilser, T., Pidgeon, R.T., van Bronswijk, W., and Pleysier, R. (2001) Kinetics of thermal recovery and recrystallization of partially metamict zircon. European Journal of Mineralogy, 13, 1163–1176.

Key, P.H., Sands, D., Schlaf, M., Walton, C.D., Anthony, C. J., Brunson, K.M., and Uren, M.J. (2000) Infra-red reflectivity of ion-implanted and pulsed excimer laser irradiated 4H-SiC. Thin Solid Films, 364, 200–203.

Lang, M., Zhang, F., Lian, J., Trautmann, C., Neumann, R., and Ewing, R.C. (2008) Irradiation-induced stabilization of zircon ($ZrSiO_4$) at high pressure. Earth and Planetary Science Letters, 269, 291–295.

Lian, D., Rios, S., Boatner, L.A., Wang, L.M., and Ewing, R.C. (2003) Microstructural evolution and nanocrystal formation in Pb^+-implanted $ZrSiO_4$ single crystals. Journal of Applied Physics, 94, 5695–5703.

Magruder, R.H., Morgan, S.H., Weeks, R.A., and Zuhr, R.A. (1990) Effects of ion implantation on intermediate range order: IR spectra of silica. Journal of Non-Crystalline Solids, 120, 241–249.

Magruder, R.H., Henderson, D.O., Morgan, S.H., and Zuhr, R.A. (1993) Optical spectra of Pb implanted fused silica. Journal of Non-Crystalline Solids, 152, 258–266.

McLaren, A.C., Fitz, J.D., and Williams, I.S. (1994) The microstructure of zircon and its influence on the age determination from Pb/U isotopic ratios measured by ion microprobe. Geochimica et Cosmochimica Acta, 58, 993–1005.

Nasdala, L. (2009) Pb^+ irradiation of synthetic zircon ($ZrSiO_4$): Infrared spectroscopic investigation—Discussion. American Mineralogist, 94, 853-855.

Nasdala, L., Irmer, G., and Wolf, D. (1995) The degree of metamictization in zircon: a Raman spectroscopic study. European Journal of Mineralogy, 7, 471–478.

Sales, B.C., Ramey, J.O., Boatner, L.A., and McCallum, J.C. (1989) Structural inequivalence of the ion-damage-produced amorphous state and the glass state in lead pyrophosphate. Physical Review Letters, 62, 1138–1141.

Salje, E.K.H., Chrosch, J., and Ewing, R.C. (1999) Is "metamictization" of zircon a phase transition? American Mineralogist, 84, 1107–1116.

Sood, A.K., Umadevi, V., Kesavamoorthy, R., and Venkataraman, G. (1984) Infrared studies on ion irradiated quartz. Pramana, 23, 573–593.

Townsend, P.D., Chandler, P.J., and Zhang, L. (1994) Optical effects of ion implantation. Cambridge University Press, U.K.

Tung, Y.-S., Ueda, A., Mu, R., Wu, M., Chen, J., Gu, Z., Henderson, D.O., Collins, W.E., White, C.W., and Zhur, R. (1998) Annealing behavior of tin implanted silica. Nuclear Instruments and Methods in Physics Research, B141, 279–283.

Vance, E.R. (1975) α-recoil damage in zircon. Radiation Effects, 24,1–6.

Vodopyanov, L.K. and Kozyrev, S.P. (2006) Infrared reflection spectroscopy of ion-implanted n-$Hg_{0.8}Cd_{0.2}Te$. Physica Status Solidi (a), 72, 737–744.

Weber, W.J., Ewing, R.C., and Wang, L.-M. (1994) The radiation-induced crystalline-to-amorphous transition in zircon. Journal of Materials Research, 9, 688–698.

Woodhead, J.A., Rossman, G.R., and Thomas, A.P. (1991) Hydrous species in zircon. American Mineralogist, 76, 1533–1546.

Zhang, M., Salje, E.K.H., Farnan, I., Graeme-Barber, A., Daniel, P., Ewing, R.C., Clark, A.M., and Leroux, H. (2000) Metamictization of zircon: Raman spectroscopic study. Journal of Physics: Condensed Matter, 12, 1915–1925.

Zhang, M., Boatner, L., Salje, E.K.H., Ewing, R.C., Daniel, P., Weber, W.J., Zhang, Y., and Farnan, I. (2008a) Micro-Raman and micro-infrared spectroscopic studies of Pb- and Au-irradiated $ZrSiO_4$: Optical properties, structural damage, and amorpization. Physical Review B, 77, 144110.

Zhang, M., Boatner, L., Salje, E.K.H., Honda, S., and Ewing, R.C. (2008b) Pb^+ irradiation of synthetic zircon ($ZrSiO_4$): Infrared spectroscopic investigation. American Mineralogist, 93, 1418–1423.

Zorba, T.T., Mitsas, C.L., Siapkas, I.D., Terzakis, G.Z., Siapkas, D.I., Pacaud, Y., and Sorupa, W. (1996) An infrared study of Ge^+ implanted SiC. Applied Surface Science, 102, 120–124.