“The radiation-damaged state of selected actinide-containing minerals: Mechanical and structural properties”

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by

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Contents

1. Objectives

1.1. General introduction and background

The globally increasing generation of nuclear waste (see, e.g., Ewing 2015, Diaz-Maurin et al. 2021 and references therein, Li et al. 2021, IAEA Nuclear Energy Series 2022) from civil and military use (e.g., nuclear power plants, medical and scientific applications, and nuclear weapons programs); renders its secure long-term disposal in a durable matrix medium of high importance (see, e.g., Ewing and Lutze 1991, Zhang et al. 2022). Further, knowledge about how radiation damage in general affects a material is crucial estimating its durability and improving its design for operation in enhanced radiation fields (e.g., nuclear reactors, advanced nuclear fuel forms, satellites, space travel and exploration, moon and planet colonialization) (see, e.g., Narici et al. 2017, Diaz de La Rubia et al. 2000, Sickafus et al. 2007, Hands et al. 2018, Dobynde et al. 2021, Taller et al. 2021). From the point of view of fundamental research, the essential scientific question raised by radiation induced damage in materials is: Which phases form and what are their specific properties far away from the thermodynamic equilibrium state?

Radiation induced damage can strongly influence the physical and chemical properties of materials, due to extensive structural modifications (see, e.g., Holland and Gottfried 1955, Ewing 1975, Özkan 1976, Chakoumakos et al. 1991, Oliver et al. 1994, Salje et al. 2011). There are several methods for studying the interaction of radiation damage with condensed matter, e.g., particle irradiation from external sources (see, e.g., Oliver et al. 1994, Lang et al. 2010, Kinsler-Fedon et al. 2022), doping with unstable nuclei (see, e.g., Weber et al. 1986, Weber 1990, Burakov et al. 2002) or by investigating naturally actinide containing minerals (see, e.g., Holland and Gottfried 1955, Hawthorne et al. 1991, Murakami et al. 1991, Bismayer et al. 2010, Paulmann et al. 2019). The scope of this work lies solely on the last. There are various minerals in nature that contain uranium (U) and/or thorium (Th) (structural and as substitutions); serve a number of purposes, including for geological age dating and as resources for nuclear applications (Jäger and Hunziker 1979, Pidgeon et al. 1998). The alpha-decay of the unstable nucleus leads to structural damage and amorphization (so called metamictization) in these phases. The radiation damage related metamictization process has been described extensively in the literature (see, e.g, Hawthorne et al. 1991, Ewing et al. 1995, Ewing 2007a,b, 2011): During the alpha-decay process two different particles are generated: the alpha-particle (helium core with an energy of ~ 4.5 – 5.8 MeV for actinides) and the heavy recoil nucleus (~ 70 – 100 keV). On its trajectory of ~ 15 – 22 μm through the ordered crystal lattice the smaller alpha-particle displaces several hundreds of atoms (most of them at the end) and induces defects in the structure. The heavier recoil-nucleus (energy of, e.g., ~ 86 keV for ^{235}U recoil from decay of ^{239}Pu) displaces thousands of atoms on its path (~ 30 – 40 nm). For zircon ($ZrSiO_4$), for example, ~ 5000 displaced atoms have been reported per α-decay event (Farnan et al. 2007, Salje et al. 2012). The mentioned differences in total displaced atoms are due to the fact that the α-particle deposits most of its energy by ionization processes, whereas the recoil nucleus deposits its energy by elastic collisions. As a result, the recoil nuclei generate recoil cascades in the ordered structure that overlap with increasing structural damage to finally generate an amorphous (so called metamict) state (see Ewing et al. 1995, Ewing, 2007b). The described structural amorphization process leads to, e.g., swelling (known to be very pronounced for zircon), decrease in density and optical birefringence, increase in leach rate, and softening of the mechanical properties (Özkan 1976, Ewing et al. 1981, Chakoumakos et al. 1987, 1991, Murakami et al. 1991, Salje et al. 2011).

An important point is that percolation theory (percolation-type transitions) has been proposed to be appropriate to describe and to provide insights into the radiation damage related crystalline-to-amorphous transition with two percolation thresholds (at least for zircon) (see Salje et al. 1999, Trachenko et al. 2000,2003):

(i) starting from the initial highly crystalline state (crystalline matrix surrounding amorphized domains), until the 1st percolation point (p_{c1}), only the crystalline fraction percolates,

(ii) after passing this threshold, the further growing amorphous fraction also starts to percolate (i.e., both crystalline and amorphous fractions now percolate),

(iii) the 2nd percolation point (p_{c2}) demarks the threshold where the crystalline fraction ceases to percolate and an amorphous matrix is established with embedded vanishing, defect enriched, crystalline isles.

The radiation-damaged structural state is metastable and can (at least partially) be recovered by thermal annealing (see, e.g., Hawthorne et al. 1991).

Against the in this chapter summarized background, actinide (i.e., U and Th) containing minerals that often have ages in the thousands or millions of years have been proposed as adequate natural analogs to study the long-term behavior of possible crystalline ceramic host phases for nuclear waste disposal exposed to intrinsic radiation damage (Ewing and Haaker 1980, Ewing et al. 1988, Ewing and Weber 2010).

1.2. Objects of study

As mentioned above, to better understand the long-term effects of radiation damage over geological time scales (thousands or millions of years), selected naturally occurring U- and Th-bearing minerals have been investigated. Here the minerals zircon, pyrochlore and allanite have been chosen as objects of study. The ages of these minerals often exceed millions of years and they have suffered radiation damage throughout this time. Therefore, zircon, pyrochlore and allanite are ideal natural materials with which to investigate the long-term effects of intrinsic radiation damage on crystalline materials. The minerals zircon and pyrochlore [to be more precise phases with pyrochlore structure ($A_2B_2O_7$)] have been selected for study as both have already been proposed as possible crystalline matrix materials for the disposal of actinides, e.g., plutonium (e.g., Ewing 1999, Ewing et al. 2004). Allanite has been chosen to include a mineral that initially contains structural OH^- groups, which is an important part of the thermal stability of a matrix material. Further, hydrogen is assumed to act as a catalyst for annealing induced recrystallization in radiation-damaged minerals (see Salje and Zhang 2006, Salje 2010). In the following a brief overview of the structures of the selected minerals will be provided to give the reader a basic understanding [for more detailed information, see the related in this thesis cumulated papers (see chapter 1.4.) and references cited therein]:

(i) Zircon ($ZrSiO_4$) is a tetragonal nesosilicate mineral with space group $I4_1/amd$. Chains of edge-sharing ZrO_8 dodecahedra and SiO_4 tetrahedra along the c-axis and edge-sharing ZrO_8 polyhedra along the b-axis form the zircon structure (see Robinson et al. 1971). An important point is that the zircon structure can incorporate high amounts of actinides, as Zr can be completely replaced by Th, U, Np, Pu, and Am, indicated by synthesized end-member compositions (Keller 1963, Walter 1965, Speer 1980, Speer and Cooper 1982, Weber 1990,1991,1993, Anderson et al. 1993, Ewing et al. 1995, Deer et al. 1997, Burakov et al. 2002). Zircon has been found to incorporate commonly up to 5000 ppm of U and Th at the Zr site in nature, with a total concentration of up to 10 wt.% (Ewing 1999). The pioneering work of Murakami et al. (1991) ("Alpha-decay event damage in zircon") provided an excellent and very valuable basis for the thesis author's investigations of zircon.

(ii) Pyrochlore is a cubic mineral that crystallizes in the space group $Fd\bar{3}m$ with the ideal formula $A_2B_2X_6Y$ (Lumpkin 2001). This anion-deficient derivative of the fluorite structure type (AX_2) shows ordered cation sites, corner-sharing BX_6 octahedra and A_2Y chains with eight-fold-coordinated A cations that build up the structure (Chakoumakos 1984, Lumpkin and Ewing 1988, Atencio et al. 2010). For a schematic presentation it is referred to the works of Zietlow et al. (2017) and Reissner et al. (2020) (both cumulated in this thesis, see chapter 1.4.). The mineral pyrochlore has found to be able to incorporate various cations:

- on the A position: Na, Ca, U, Th, Y, and rare earth elements (REE) and in smaller quantities also Fe^{2+}, Mn, Sn^{2+}, Sb, Bi, Sr, Ba, Pb, K, and Cs (Lumpkin and Ewing 1988)
- on the B position usually elements like Nb, Ta, Ti, Fe^{3+}, Zr, and Sn^{4+} (Lumpkin and Ewing 1988)

Lumpkin (2001) reported an actinide content of up to 9 wt.% ThO_2 and 30 wt.% UO_2 for natural pyrochlore. Oxygen can occupy the X and Y positions and can be replaced by hydroxyl-groups and fluorine-ions on the latter (Lumpkin and Ewing 1988).

(iii) Allanite, a member of the epidote-super group, is a monoclinc mineral with space group $P2_1/m$ and the general formula $^{A1}(Ca)^{A2}(REE)^{M1,M2}(Al)_2{}^{M3}(Fe^{2+})[SiO_4][Si_2O_7]O(OH)$ (Armbruster et al. 2006, Bonazzi et al. 2009, Mills et al. 2009). The crystal structure is built up as follows [see Dollase 1973, Ercit 2002 and for a schematic presentation Reissner et al. 2019 (the latter cumulated in this thesis, see chapter 1.4.)]:

- a framework of two types of edge-sharing octahedral chains (single M1 octrahedra chain and multiple chains of M2 and peripheral M3 octahedra) cross-linked by SiO_4 and Si_2O_7 groups
- M1 site can be occupied by Al, Fe, Mg, Mn, Ti, Cr, and V
- M3 site by Fe, Mn, Mg, Al, Cu, Cr, and V
- M2 site is usually only occupied by Al.
- M3 octahedra's corners link to the Si sites from polyhedral (A1 and A2) positions that host Ca, Mn, and Na (A1), and Ce or other lanthanides, as well as U and Th or other cations (e.g., Sr, Pb, and Cd) (A2)
- a proton is attached to the O10 atom of the M2 octahedron

If Ce is the dominant REE in allanite, as in the present studies, it is termed allanite-(Ce) (Ercit 2002, Armbruster et al. 2006) and has been found to incorporate up to 5 wt.% ThO_2 (Exley 1980, Gieré and Sorensen 2004).

1.3. Objectives in detail

The present cumulative habilitation thesis comprises selected scientific work from the past seven years, undertaken with the overall aim to better understand how the mechanical properties of actinide containing initially crystalline ceramic (like) materials are affected by intrinsic radiation damage (mainly alpha-decay) and in part by subsequent thermal annealing. Further, detailed insights into the radiation damage related transition mechanisms are expected to be obtained. Knowledge about the radiation damage induced crystalline-to-amorphous transition, and vice-versa (induced by subsequent thermal annealing), of condensed matter is of crucial importance for the design and development of, e.g., suitable nuclear waste matrix materials and advanced nuclear fuel forms (Weber et al. 1998, Sickafus et al. 2007). As mentioned above, the minerals zircon, pyrochlore and allanite served as natural model substances in the studies.

1.3.1. Zircon

Detailed investigations of the evolution of the elastic modulus (E) (here the Young´s modulus), hardness (H) and fracture toughness (K_c) with increasing radiation damage of zircon should be enabled by nanoindentation (including pillar-splitting) measurements (Beirau et al. 2016, 2018a,b, 2019a,2021). Objects of study were single crystal zircon samples (at least initially, before radiation damage) that cover the main part of the crystalline-to-amorphous transition, comparable in chemistry, orientation and age, but with an increasing amount of incorporated uranium and thorium (hence degree of radiation damage) (Beirau et al. 2016, 2018a,b). Further, a zoned zircon sample, from the same locality as the other studied zircons and with same orientation has been studied. The zonation is due to varying amounts of incorporated U and Th and hence suffered radiation damage (see Beirau et al. 2019a, 2021). Hence, this single sample can be used to follow the effects of alpha-decay radiation-damage on mechanical properties, covering already a large part of the crystalline-to-amorphous transition (Beirau et al. 2019a). It should be noted that the main advantage of these samples and the reason for their selection is their overall excellent comparability.

The evolution of the mechanical properties with increasing radiation dose should be monitored by nanoindentation, while the point where the mechanical properties become isotropic should be narrowed (Beirau et al. 2016). The obtained mechanical data might be used to shed some light on the damage mechanism itself (Beirau et al. 2018a), as two basic competing damage models have been suggested in the literature (i.e., double cascade-overlap and direct impact) (see, e.g., Weber 1990, Rios et al. 2000). The double cascade-overlap model (after Gibbons 1972) predicts that there is no direct amorphization in the collision cascade, but by overlap of the cascades. In contrast, the direct impact model (Gibbons 1972) proposes amorphization to occur directly in the recoil cascade.

The zoned zircon sample is of great scientific interest as it can be seen as nature's equivalent of a multilayered ceramic. Nanoindentation mapping should help to better understand the variations in *E* and *H* among different zones with different degrees of radiation damage (see Beirau et al. 2019a).

Molecular dynamic simulations of Trachenko et al. (2002) for zircon implied existing interfaces and underlying hard shells, enclosing the depleted amorphized cores (induced by the heavy recoil nucleus) in the ordered lattice. As interface phenomena can have a huge influence on the physical properties of materials (see, e.g., Aird and Salje 2000, Kityk et al. 2000, Salje 2007), one might expect also an effect on the mechanical properties of radiation-damaged zircon (see Beirau et al. 2018b,2021).

Finite element modelling work should verify the conclusions drawn from the experimental results and help to gain deeper insights (Huber and Beirau 2021). It should be investigated, whether the crystalline-to-amorphous transition can be properly described as a percolation problem with two percolation thresholds, as postulated in literature (at least for zircon) (Salje et al. 1999, Trachenko et al. 2000,2003). Further, can the earlier-mentioned assumed effect of the interfaces and hard shells convincingly be reproduced in simulations?

Microfractures across zones with a high degree of crystallinity have been observed in zoned zircon to not extend through adjacent, highly amorphized zones (Chakoumakos et al. 1987,1991). The fracturing in the higher crystalline zones has been reported to be caused by the swelling of neighboring amorphized regions (due to unit-cell expansion and the overlapping accumulation of amorphized domains) (Chakoumakos et al. 1987,1991). From their observations Chakoumakos et al. (1987) assumed an increasing fracture toughness with increasing degree of amorphization in zircon. Knowledge about fracture propagation and behavior are very important to understanding the failure mechanisms for a material. Therefore, the presented studies also concentrate on this subject (Beirau et al. 2019a,2021). As no direct measurements of the fracture toughness of zircon have been made so far, the present work should change that (Beirau et al. 2021).

1.3.2. Pyrochlore

The structural reorganization behavior of natural uranium or thorium containing pyrochlore should be followed in detail using global and local probes. Objects of study were two highly radiation-damaged pyrochlore samples, one U-rich that contains preserved crystalline domains, while the other contains Th and is completely amorphous on the X-ray diffraction (XRD) length scale (Zietlow et al. 2017). The third sample, included for comparison, is less damaged (and hence more crystalline). All samples are overall comparable in chemistry and were cut and polished plane-parallel to the same crystallographic orientation (surface).

It was the goal to learn more about the general influence of radiation induced disorder and thermally induced recrystallization on the short- and long-range order of pyrochlores with different degrees of structural amorphization and to reveal the start of the structural reorganization (Zietlow et al. 2017).

Calorimetric measurements will make it possible to follow in situ the temperature related annealing process (Zietlow et al. 2017). Additional statistical data analysis should be performed to determine the behavior of the structural reorganization process in detail and to search for similarities to structural phase transitions (Beirau et al. 2019b), as have been reported by Verner et al. (1993) for the ion-beam induced amorphization-crystallization process in semiconductors.

Further, it should be determined how the mechanical properties, i.e., E and H, are affected by radiation damage and the structural reorganization process (Reissner et al. 2020). It is of special interest, how the initially different degrees of structural disorder of the selected pyrochlore samples influence the onset of recrystallization and the reestablishment of the mechanical properties. While photoluminescence of structurally incorporated rare earth elements is a common phenomenon, it will be checked for its suitability to follow the recrystallization process in pyrochlore (Reissner et al. 2020).

Using the experimentally obtained data, finite element modelling work should verify if the crystalline-to-amorphous transition in pyrochlore can also be properly described as a percolation problem with two percolation thresholds (Beirau and Huber 2021), as suggested in the literature (Lumpkin et al. 2018). The other question to answer is, could we reveal a possible influence of the percolation thresholds on the recrystallization kinetics (Beirau and Huber 2021)?

Interesting elastic phenomena that will be revealed during the step-wise annealing room-temperature mechanical testing experiments, should be additional followed in-situ to obtain deeper insights (Beirau and Carpenter 2022).

An important parameter for structural reorganization is the duration of the annealing process. Based on the results of the previously undertaken mechanical experiments (Reissner et al. 2020), a suitable pyrochlore sample should be selected and studied after step-wise annealing for a shorter period of time, enabling detailed information of the time-temperature dependence of the recrystallization process (Beirau et al. 2022).

1.3.3. Allanite

As a catalytic effect of hydrogen-ions on the recrystallization of radiation-damaged minerals has been assumed in the literature (Salje and Zhang 2006, Salje 2010), annealing experiments of the mineral allanite (containing structural OH^- groups, Fe and Th) should provide some insights (Reissner et al. 2019). Three highly disordered allanite samples have been found appropriate for detailed experimental analysis. We propose to use the step-wise annealing related evolution of the mechanical properties (i.e., E and H) to follow the structural reorganization process and to determine the region of its onset. The thermally induced recrystallization of radiation-damaged allanite is known to be a complicated process including, e.g., oxidation, dehydration and decomposition (Cobic et al. 2010). The goal was to develop a comprehensive understanding, considering all these aspects, of the overall behavior of highly radiation-damaged allanite under thermal treatment (Reissner et al. 2019).

Further, in situ annealing calorimetric data, should be followed and statistically analyzed for analogies to the behavior of pyrochlore and structural phase transitions (Beirau et al. 2019b). It is of interest, if avalanches [sudden jumps of an observed quantity (here energy), so-called jerks (see Salje and Dahmen 2014)] can be detected during the annealing related combined decomposition and crystallization process in allanite and, if so, what is the behavior of the energy of the thermal spikes.

1.4. Published cumulated work and individual contributions

The research presented in this habilitation thesis was undertaken by the author in the frame of the following third party funded projects:

i) Funding: Deutsche Forschungsgemeinschaft (DFG) - Project number 374360049

Program: Research Grants

Principal investigator: Dr. Tobias Beirau

Project: “Mechanical properties of radiation damaged geomaterials”

Location: Martin Luther University Halle-Wittenberg

Duration: 2017 - present

(funding included a PhD student position and a nanoindentation device)

ii) Funding: German Academic Exchange Service (DAAD), German Federal Ministry of Education and Research (BMBF) and the European Union (EU/FP7/Marie Curie Actions/COFUND)

Program: Postdoctoral Researchers International Mobility Experience (PRIME)

Principal investigator: Dr. Tobias Beirau

Project: “Radiation damage in minerals”

Location (foreign): Stanford University (USA)

Duration: 2015-2016

The research results in this project were acquired in close cooperation with national and international colleagues and published in internationally recognized peer-reviewed journals. These publications (underlined when cited in this thesis to simplify identification) are listed below with comments on the individual contributions of the thesis author (in *italics*: former PhD student of the thesis author, who defended successfully in 2021). Parts of this research have been published in the PhD theses of Dr. P. Zietlow (PhD University of Hamburg in 2016) and Dr. C.E. Reissner (PhD Martin Luther University Halle-Wittenberg in 2021).

(Individual contributions of Dr. Tobias Beirau on joint publications:

Predominant contribution → contribution > 70%; Major contribution → contribution 30% - 70%; Minor contribution → contribution < 30%)

Beirau, T., *Reissner, C.E.*, Pöllmann, H., and Bismayer, U. (2022)

Partially disordered pyrochlore: Time-temperature dependence of recrystallization and dehydration.

Zeitschrift für Kristallographie – Crystalline Materials, published online.

<u>Predominant contribution to:</u> writing and revising the manuscript, design of experiments, data interpretation, preparing figures, supervision of PhD student Reissner, C.E. in performing experiments and data evaluation

<u>Major contribution to:</u> data evaluation

Beirau, T., and Carpenter, M. (2022)

High-temperature resonant ultrasound spectroscopy of highly radiation-damaged pyrochlore: Structural reorganization and high acoustic loss.

Applied Physics Letters, 120, 231901.

Major contribution to: writing and revising the manuscript, design of experiments, preparing figures, data interpretation

Beirau, T., Rossi, E., Sebastiani, M., Oliver, W.C., Pöllmann, H. and Ewing, R.C. (2021)

Fracture toughness of radiation-damaged zircon studied by nanoindentation pillar-splitting.

Applied Physics Letters, 119, 231903.

Predominant contribution to: writing and revising the manuscript, preparing figures

Major contribution to: data evaluation, data interpretation, design of experiments

Beirau, T. and Huber, N. (2021)

Percolation transitions in pyrochlore: Radiation-damage and thermally induced structural reorganization.

Applied Physics Letters, 119, 131905.

Predominant contribution to: writing and revising the manuscript, preparing figures

Major contribution to: data evaluation, design of experiments, data interpretation

Huber, N. and **Beirau, T.** (2021)

Modelling the effect of intrinsic radiation damage on mechanical properties: The crystalline-to-amorphous transition in zircon.

Scripta Materialia, 197, 113789.

Major contribution to: writing and revising the manuscript, data interpretation

Minor contribution to: design of experiments

Reissner, C.E., Roddatis, V., Bismayer, U., Schreiber, A., Pöllmann, H. and **Beirau, T.** (2020)

Mechanical and structural response of radiation-damaged pyrochlore to thermal annealing.

Materialia, 14, 100950.

Predominant contribution to: design of experiments, supervision of PhD student Reissner, C.E. in performing experiments and data evaluation

Major contribution to: writing and revising the manuscript, data interpretation

Beirau, T., Shelyug, A., Navrotsky, A., Pöllmann, H. and Salje, E.K.H. (2019b)

Avalanches during recrystallization in radiation-damaged pyrochlore and allanite: Statistical similarity to phase transitions in functional materials.

Applied Physics Letters, 115, 231904. **[Featured Article]**

Predominant contribution to: writing and revising the manuscript, design of experiments, performing statistical analysis, preparing figures

Major contribution to: data evaluation, data interpretation

Minor contribution to: performing experiments

Beirau, T., Oliver, W.C., *Reissner, C.E.*, Nix, W.D., Pöllmann, H. and Ewing, R.C. (2019a)

Radiation-damage in multi-layered zircon: Mechanical properties.

Applied Physics Letters, 115, 081902.

Predominant contribution to: writing and revising the manuscript, data evaluation, data interpretation, preparing figures, supervision of PhD student Reissner, C.E. in performing dose calculations

Major contribution to: design of experiments

Reissner, C.E., Bismayer, U., Kern, D., Reissner, M., Park, S., Zhang, J., Ewing, R.C., Shelyug, A., Navrotsky, A., Paulmann, C., Skoda, R., Groat, L., Pöllmann, H. and **Beirau, T.** (2019)

Mechanical and structural properties of radiation-damaged allanite-(Ce) and the effects of thermal annealing.

Physics and Chemistry of Minerals, 46, 921.

Predominant contribution to: design of experiments, supervision of PhD student Reissner, C.E. in performing experiments and data evaluation

Major contribution to: writing and revising the manuscript, data interpretation

Beirau, T., Nix, W.D., Ewing, R.C., Pöllmann, H. and Salje, E.K.H. (2018b)

Radiation-damage-induced transitions in zircon: Percolation theory applied to hardness and elastic moduli as a function of density.

Applied Physics Letters, 112, 201901. **[Editor's Pick]**

Predominant contribution to: writing and revising the manuscript, design of experiments, performing experiments, data evaluation, preparing figures

Major contribution to: data interpretation

Beirau, T., Nix, W.D., Pöllmann, H. and Ewing, R.C. (2018a)

Radiation-induced effects on the mechanical properties of natural ZrSiO4: double cascade-overlap damage accumulation.

Physics and Chemistry of Minerals, 45, 435.

Predominant contribution to: writing and revising the manuscript, design of experiments, performing experiments and calculations, data evaluation, data interpretation, preparing figures

Zietlow, P., **Beirau, T.**, Mihailova, B., Groat, L.A., Chudy, T., Shelyug, A., Navrotsky, A., Ewing, R.C., Schlüter, J., Skoda, R. and Bismayer, U. (2017)

Thermal annealing of natural, radiation-damaged pyrochlore.

Zeitschrift für Kristallographie – Crystalline Materials, 232, 25.

Major contribution to: writing and revising the manuscript, data interpretation

Minor contribution to: design of experiments

Beirau, T., Nix, W.D., Bismayer, U., Boatner, L.A., Isaacson, S.G. and Ewing, R.C. (2016)

Anisotropic mechanical properties of zircon and the effect of radiation damage.

Physics and Chemistry of Minerals, 43, 627.

Predominant contribution to: writing and revising the manuscript, design of experiments, performing experiments, data evaluation, data interpretation, preparing figures

2. Conclusions

In the following the individual major conclusions drawn from the undertaken studies (see chapter 1.4.) will be given separately for each investigated mineral, i.e., zircon, pyrochlore, and allanite, as they are very different in structure and chemical complexity. The undertaken research enabled significant progress in the understanding of intrinsic alpha-decay damage in minerals (and hence ceramic materials). In the second part (2.2.) some general conclusions will be presented. It should be noted that no assessment of or support for a specific mineral's suitability as matrix materials will be made. The selected minerals have been taken as natural laboratories to increase the overall knowledge about the effect of intrinsic radiation damage and to better understand the metamictization process within specific phases and in general.

2.1. Individual conclusions

2.1.1. Zircon

Highly crystalline natural zircon is an initially remarkably stiff and hard material (with $E_{[001]}$ ~ 426 GPa, $E_{[100]}$ ~ 340 GPa, $H_{[001]}$ ~ 23 GPa, $H_{[100]}$ ~ 20 GPa) (Beirau et al. 2016,2018b). Nanoindentation studies revealed that zircon is, at least from mechanical point of view, a relatively durable phase with respect to intrinsic radiation damage induced amorphization, showing a decrease in stiffness and hardness of ~ 54% and 48%, respectively (for indentation along [100]) (Beirau et al. 2016,2018b), while Poisson's ratio ($\nu_{[100]}$) was found to increase by ~ 54%. A maximum life-time alpha-decay event dose of ~ 6.3×10^{18} α-decays/g has found to be definitely sufficient for the mechanical properties of the investigated zircons from Sri Lanka to become isotropic (Beirau et al. 2016,2018a). The isotropification of ν indicates that the measured lateral strain in the presence of a uniaxial applied stress becomes equal in all directions for zircon at least at doses of ~ 6.3×10^{18} α-decays/g (Beirau et al. 2018a). Nanoindentation mapping of a comparable but zoned zircon specimen from the same locality showed that E and H of each individual zone depend on its degree of crystallinity influenced by the amount of suffered radiation damage (~ 3.7× to 7.5×10^{18} a-decays/g) due to the individual U- and Th-content and age (Beirau et al. 2019a). An important aspect of this study is the possibility to directly study how a multilayered ceramic (in this case represented very well by a naturally zoned zircon as an extreme case) accommodates volume expansion and changes in mechanical properties as a function of radiation damage.

Further, the evolution of the mechanical properties of zircon during the radiation damage related crystalline-to-amorphous transition showed an overall good agreement with the double cascade-overlap damage accumulation model (Beirau et al. 2018a). A damage process mainly driven by double cascade-overlap amorphization has also been suggested for $AmAlO_3$ (Vigier et al. 2019).

The undertaken mechanical properties measurements and additional mechanical modelling work (Beirau et al. 2018b,2019a, Huber and Beirau 2021) confirmed the suitability of percolation theory (two percolation thresholds) postulated in the literature (Salje et al. 1999, Trachenko et al. 2000,2003) to describe the crystalline-to-amorphous transition in zircon. The exact positions of the percolation thresholds depend on the applied model.

The recoil cascades have been reported to consist of a densified outer layer populated by SiO_n polymers and an atomically depleted core (Farnan and Salje 2001, Trachenko et al. 2002). A combined effect of these "hard shells" and the interface to the surrounding crystalline material is assumed to cause the experimentally observed stabilization of the hardness of zircon during the metamictization process (Beirau et al. 2019a). This effect has been verified by mechanical modelling (Huber and Beirau 2021). This is a highly interesting material behavior and, up to now, is unique with respect to radiation damage (not to be confused with the commonly known effect of radiation hardening in materials at lower doses).

Nanoindentation pillar-splitting enabled the measurement of the fracture toughness (K_c) of zones with different degree of structural disorder (amorphous fractions of all zones have overcome at least the first percolation point) in the zoned zircon specimen (Beirau et al. 2021). The across these zones measured increase in K_c with increasing degree of amorphization confirmed experimentally the effect in zircon which had, until now, only been assumed based on microscopic work (Chakoumakos et al. 1991). The before-described complex microstructure of radiation-damaged zircon (i.e., preserved defect enriched crystalline material, interfaces and overlapping regions of recoil cascades with "hard shells" surrounding depleted cores) is assumed to cause an increase in stress (due to increasing disorder) that raises the ability of the structure to resist fracture, e.g., via crack deflection mechanisms (Beirau et al. 2021). This is in good agreement with Lawn (1993), who reported weak interfaces and other microstructural heterogeneities that influence the overall elastic field to be able to deflect cracks and second phases to allow for pinning and bowing of cracks. Due to the results obtained by mechanical mapping of the investigated fractured regions, the degrading effect of cracks on the mechanical properties of surrounding material could be estimated to be only local (maximum observed outreach ~ 2 µm from crack center) (Beirau et al. 2019a). Zoned zircon, with alternating self-irradiated zones (Beirau et al. 2019a,2021), can be seen as a useful natural model system for the design of, e.g., multilayer coatings and complex ceramics for proper use in high radiation environments (e.g., designed for space applications or nuclear reactors).

2.1.2. Pyrochlore

Combined diffraction, spectroscopic and calorimetric work enabled a comprehensive picture of the radiation damage state of the investigated pyrochlore samples [average composition $(Na,Ca)_2Nb_2O_6F$] and the effect of thermally induced recrystallization on the short and long-range order (Zietlow et al. 2017). The investigation revealed in detail a correlation between the initial degree of structural order and the thermally induced reorganization, showing considerable differences in the onset (Zietlow et al. 2017).

Based on these initial results, detailed nanoindentation, electron microscopic and spectroscopic measurements were undertaken, indicating a stiffening and hardening of pyrochlore after step-wise thermal annealing due to an increase in structural order (Reissner et al. 2020). The nanoindentation measurements agreed well with the assumption that the bulk annealing kinetics are directly related to the initial degree and homogeneity of the structural damage in pyrochlore (visible especially in the E behavior, a measure for the bond interconnectivity). The thermally induced structural reestablishment was found to begin > 500 K (in these pyrochlores) (Zietlow et al. 2017, Reissner et al. 2020), the temperature that demarks the upper limit to occur in a repository (Weber and Ewing 2000). For the recrystallization process of the investigated pyrochlores, at least three different regimes became visible by evaluating the mechanical properties measurements (Reissner et al. 2020):

- A distinct low *E* and *H* region of ~ 105 – 121 GPa and ~ 7.2 – 8.6 GPa, respectively that comprises the highly disordered states.
- A still crystalline but partially disturbed region in a relatively distinct modulus region of ~ 165 – 192 GPa that provided evidence for a comparable degree of reestablished bonds and increased bond strength. The hardness range showed an overall broader distribution of ~ 9.7 – 13.9 GPa. This is assumed to be due to the formation of additional grain boundaries during the polycrystalline recrystallization of the initially highest amorphized sample. Both of the two other pyrochlore samples recrystallize again to a single-crystal like state.
- A highly crystalline regime with *E* and *H* values of ~ 198 – 220 GPa and ~ 11.3 – 12.4 GPa, respectively.

The described observed regimes agree very well with the differences in the shapes of the related luminescence spectra (from Nd^{3+}) that are sensitive to the degree of local order (Reissner et al. 2020). The estimated degrees of amorphized fraction (Zietlow et al. 2017) also show a good correlation.

The reported acquired mechanical and structural data (Zietlow et al. 2017, Reissner et al. 2020) could be successfully used to model (finite element mechanical modeling) the crystalline-to-amorphous transition as a percolation problem with two percolation points (analog to zircon; see Huber and Beirau 2021) for pyrochlore (Beirau and Huber 2021). This made it possible to follow the evolution of the degree of amorphous fraction during the thermally induced step-wise structural reorganization process for the two investigated highly amorphized pyrochlore samples (Beirau and Huber 2021). One should keep in mind that for, e.g., zircon and titanite, it is known that this process is not a simple reverse process of the initial radiation damage process (see Zhang and Salje 2003). The combined results of experimental and modelling work led to the conclusion that percolation thresholds act as specific kinetic barriers during thermally induced structural reorganization in pyrochlore (see Beirau and Huber 2021).

Statistical analysis of calorimetric data made it possible to identify avalanches during the thermally induced recrystallization process of heavily radiation-damaged pyrochlore (and allanite, as reported in chapter 2.1.3.) and indicated similarities to the dynamics of phase transitions, e.g., ferroelectric and martensitic (Beirau et al. 2019b). This means that during structural reorganization, the phase fronts do move by local singularities, not smoothly, and that small regions recrystallize more often than large ones (Beirau et al. 2019b).

High-temperature resonant ultrasound spectroscopy (HT-RUS) revealed already initial high acoustic loss for highly radiation-damaged pyrochlore, probably due to internal microcracks (no obvious cracks visible to the naked eye), caused by volume expansion due to radiation induced amorphization (Beirau and Carpenter 2022). Although this prevented a conventional analysis (hence, determination of the elastic tensor was not possible), clear changes in elastic properties due to thermal treatment and an elastic softening caused by initial heating have been revealed for the radiation-damaged pyrochlore. The shear modulus of the untreated highly disordered pyrochlore showed a stronger temperature dependence than after recrystallization (Beirau and Carpenter 2022).

Insights into the time-temperature dependence of the above-described thermally induced amorphous-to-crystalline transition of pyrochlore have been achieved by comparing the reestablishment of the mechanical properties of a partially disordered sample after step-wise annealing for 1 and 16 h (Beirau et al. 2022). An annealing time of 16 h at each temperature step was found to be sufficient to ensure saturation of the thermally induced structural reorganization effect (Reissner et al. 2020).

The results of the nanoindentation measurements combined with that of mechanical modelling (Beirau and Huber 2021) indicated an annealing time dependence of the first percolation transition (coming from the state where crystalline and amorphous fractions percolate → entering the state where only the crystalline fraction percolates) (Beirau et al. 2022). This is an important point that has to be considered, when estimating microstructure behavior under elevated temperatures in high radiation environments.

Further, a dehydration process has been revealed during the thermally induced recrystallization of the pyrochlore sample (Beirau et al. 2022), supporting the catalytic effect of hydrogen-ions in radiation-damaged phases assumed by the literature (Reissner et al. 2019, Salje and Zhang 2006, Salje 2010).

2.1.3. Allanite

Thermal annealing experiments of the selected highly radiation-damaged allanite samples revealed a heterogeneous recrystallization process with a noticeable onset around ~ 550 K (Reissner et al. 2019). Nanoindentation measurements revealed that short-term annealing for 1 h at 700 K is sufficient to lead to a distinct increase in *E* and *H* of the investigated allanite samples, indicating an increasing overall structural integrity and bond strengthening (Reissner et al. 2019). The Fe^{2+} oxidation (air atmosphere) in allanite, coupled to hydrogen loss, was found to start at ~ 700 K and took place up to ~ 1000 K. One can assume that increased internal stress, due to the heterogeneous recrystallization and loss of hydrogen, caused the observed internal and surface fracturing in allanite at higher temperatures (Reissner et al. 2019). This process, reaching a maximum after annealing at 900 K, when nearly all Fe^{2+} has been oxidized and hydrogen has escaped, hindered the precise determination of *H* and *E* after step-wise annealing in the region 800 - 1000 K.

The observation that the allanite sample with the highest OH^- content showed the strongest increase in the mechanical properties after annealing at higher temperatures (Reissner et al. 2019) concurs with the assumption in the literature (Salje and Zhang 2006, Salje 2010) that hydrogen acts as a catalyst in the structural reorganization process.

Similar to pyrochlore (see chapter 2.1.2.), a statistical analysis of calorimetric data made it possible to identify avalanches during the thermally induced combined decomposition and crystallization [allanite is known to decompose and crystallize to other phases above ~ 1000 K (Cobic et al. 2010)] process of heavily radiation-damaged allanite (Beirau et al. 2019b). Further, a connection to the dynamics of phase-transitions, e.g., ferroelectric and martensitic, has been found. Hence, during thermal treatment related recrystallization and transformation, the phase fronts are assumed to not move smoothly, but instead by local singularities. As also revealed for pyrochlore (see chapter 2.1.2.), the distribution of the growth events shows power-law behavior (Beirau et al. 2019b). Hence, small regions recrystallize more often than larger ones.

2.2. General conclusions

The following general conclusions can be drawn from the cumulated work in this thesis:

- nanoindentation has found to be a suitable and sensitive method and the measured parameters (elastic modulus and hardness) are excellent parameters to monitor the effect of radiation damage and subsequent thermally induced recrystallization in minerals
- interfaces can play important part for the bulk material behavior
- the mechanical modelling approach used in this work provides a sufficient approximation to simulate the effects of radiation damage on the mechanical properties (at least) for ceramic materials
- statistical analysis of calorimetric data is a useful tool to obtain deeper insights into the thermally induced recrystallization process

- dehydration during thermally induced recrystallization has a considerable effect on the mineral's structure

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A. Published cumulated papers

Beirau, T., Nix, W.D., Bismayer, U., Boatner, L.A., Isaacson, S.G. and Ewing, R.C. (2016)
Anisotropic mechanical properties of zircon and the effect of radiation damage.
Physics and Chemistry of Minerals, 43, 627.
https://doi.org/10.1007/s00269-016-0822-9

Abstract: This study provides new insights into the relationship between radiation-dose-dependent structural damage due to natural U and Th impurities and the anisotropic mechanical properties (Poisson's ratio, elastic modulus and hardness) of zircon. Natural zircon samples from Sri Lanka (see Muarakami et al. in Am Mineral 76:1510–1532, 1991) and synthetic samples, covering a dose range of zero up to 6.8×10^{18} α-decays/g, have been studied by nanoindentation. Measurements along the [100] crystallographic direction and calculations, based on elastic stiffness constants determined by Özkan (J Appl Phys 47:4772–4779, 1976), revealed a general radiation-induced decrease in stiffness (~54 %) and hardness (~48 %) and an increase in the Poisson's ratio (~54 %) with increasing dose. Additional indentations on selected samples along the [001] allowed one to follow the amorphization process to the point that the mechanical properties are isotropic. This work shows that the radiation-dose-dependent changes of the mechanical properties of zircon can be directly correlated with the amorphous fraction as determined by previous investigations with local and global probes (Ríos et al. in J Phys Condens Matter 12:2401–2412, 2000a; Farnan and Salje in J Appl Phys 89:2084–2090, 2001; Zhang and Salje in J Phys Condens Matter 13:3057–3071, 2001). The excellent agreement, revealed by the different methods, indicates a large influence of structural and even local phenomena on the macroscopic mechanical properties. Therefore, this study indicates the importance of acquiring better knowledge about the mechanical long-term stability of radiation-damaged materials.

Zietlow, P., Beirau, T., Mihailova, B., Groat, L.A., Chudy, T., Shelyug, A., Navrotsky, A., Ewing, R.C., Schlüter, J., Skoda, R. and Bismayer, U. (2017)

Thermal annealing of natural, radiation-damaged pyrochlore.

Zeitschrift für Kristallographie – Crystalline Materials, 232, 25.
https://doi.org/10.1515/zkri-2016-1965

Abstract: Radiation damage in minerals is caused by the α-decay of incorporated radionuclides, such as U and Th and their decay products. The effect of thermal annealing (400–1000 K) on radiation-damaged pyrochlores has been investigated by Raman scattering, X-ray powder diffraction (XRD), and combined differential scanning calorimetry/thermogravimetry (DSC/TG). The analysis of three natural radiation-damaged pyrochlore samples from Miass/Russia [6.4 wt% Th, $23.1 \cdot 10^{18}$ α-decay events per gram (dpg)], Panda Hill/Tanzania (1.6 wt% Th, $1.6 \cdot 10^{18}$ dpg), and Blue River/Canada (10.5 wt% U, $115.4 \cdot 10^{18}$ dpg), are compared with a crystalline reference pyrochlore from Schelingen (Germany). The type of structural recovery depends on the initial degree of radiation damage (Panda Hill 28 %, Blue River 85 % and Miass 100 % according to XRD), as the recrystallization temperature increases with increasing degree of amorphization. Raman spectra indicate reordering on the local scale during annealing-induced recrystallization. As Raman modes around 800 cm^{-1} are sensitive to radiation damage (M. T. Vandenborre, E. Husson, Comparison of the force field in various pyrochlore families. I. The $A_2B_2O_7$ oxides. J. Solid State Chem. 1983, 50, 362, S. Moll, G. Sattonnay, L. Thomé, J. Jagielski, C. Decorse, P. Simon, I. Monnet, W. J. Weber, Irradiation damage in $Gd_2Ti_2O_7$ single crystals: Ballistic versus ionization processes. Phys. Rev. 2011, 84, 64115.), the degree of local order was deduced from the ratio of the integrated intensities of the sum of the Raman bands between 605 and 680 cm^{-1} divided by the sum of the integrated intensities of the bands between 810 and 860 cm^{-1}. The most radiation damaged pyrochlore (Miass) shows an abrupt recovery of both, its short- (Raman) and long-range order (X-ray) between 800 and 850 K, while the weakly damaged pyrochlore (Panda Hill) begins to recover at considerably lower temperatures (near 500 K), extending over a temperature range of ca. 300 K, up to 800 K (Raman). The pyrochlore from Blue River shows in its initial state an amorphous X-ray diffraction pattern superimposed by weak Bragg-maxima that indicates the existence of ordered regions in a damaged matrix. In contrast to the other studied pyrochlores, Raman spectra of the Blue River sample show the appearance of local modes above 560 K between 700 and 800 cm^{-1} resulting from its high content of U and Ta impurities. DSC measurements confirmed the observed structural recovery upon annealing. While the annealing-induced

ordering of Panda Hill begins at a lower temperature (ca. 500 K) the recovery of the highly-damaged pyrochlore from Miass occurs at 800 K. The Blue-River pyrochlore shows a multi-step recovery which is similarly seen by XRD. Thermogravimetry showed a continuous mass loss on heating for all radiation-damaged pyrochlores (Panda Hill ca. 1 %, Blue River ca. 1.5 %, Miass ca. 2.9 %).

Beirau, T., Nix, W.D., Pöllmann, H. and Ewing, R.C. (2018a)

Radiation-induced effects on the mechanical properties of natural ZrSiO4: double cascade-overlap damage accumulation.

Physics and Chemistry of Minerals, 45, 435.
https://doi.org/10.1007/s00269-017-0931-0

Abstract: Several different models are known to describe the structure-dependent radiation-induced damage accumulation process in materials (e.g. Gibbons Proc IEEE 60:1062–1096, 1972; Weber Nuc Instr Met Phys Res B 166–167:98–106, 2000). In the literature, two different models of damage accumulation due to α-decay events in natural $ZrSiO_4$ (zircon) have been described. The direct impact damage accumulation model is based on amorphization occurring directly within the collision cascade. However, the double cascade-overlap damage accumulation model predicts that amorphization will only occur due to the overlap of disordered domains within the cascade. By analyzing the dose-dependent evolution of mechanical properties (i.e., Poisson's ratios, compliance constants, elastic modulus, and hardness) as a measure of the increasing amorphization, we provide support for the double cascade-overlap damage accumulation model. We found no evidence to support the direct impact damage accumulation model. Additionally, the amount of radiation damage could be related to an anisotropic-to-isotropic transition of the Poisson's ratio for stress along and perpendicular to the four-fold c-axis and of the related compliance constants of natural U- and Th-bearing zircon. The isotropification occurs in the dose range between 3.1 × and 6.3×10^{18} α-decays/g.

Beirau, T., Nix, W.D., Ewing, R.C., Pöllmann, H. and Salje, E.K.H. (2018b)

Radiation-damage-induced transitions in zircon: Percolation theory applied to hardness and elastic moduli as a function of density.

Applied Physics Letters, 112, 201901.
https://doi.org/10.1063/1.5030626

Abstract: Two in literature predicted percolation transitions in radiation-damaged zircon ($ZrSiO_4$) were observed experimentally by measurement of the indentation hardness as a function of density and their correlation with the elastic moduli. Percolations occur near 30% and 70% amorphous fractions, where hardness deviates from its linear correlation with the elastic modulus (E), the shear modulus (G) and the bulk modulus (K). The first percolation point p_{c1} generates a cusp in the hardness versus density evolution, while the second percolation point is seen as a change of slope.

Reissner, C.E., Bismayer, U., Kern, D., Reissner, M., Park, S., Zhang, J., Ewing, R.C., Shelyug, A., Navrotsky, A., Paulmann, C., Skoda, R., Groat, L., Pöllmann, H. and Beirau, T. (2019)

Mechanical and structural properties of radiation-damaged allanite-(Ce) and the effects of thermal annealing.

Physics and Chemistry of Minerals, 46, 921.
https://doi.org/10.1007/s00269-019-01051-z

Abstract: The onset of thermally induced, heterogeneous structural reorganization of highly radiation-damaged allanite-(Ce) begins at temperatures below 700 K. Three strongly disordered allanite samples (S74 20414: ~ 0.55 wt% ThO_2, 22.1 wt% REE oxides, and maximum radiation dose 3.5 × 10^{18} α-decay/g; LB-1: ~1.18 wt% ThO_2, 19.4 wt% REE oxides, and maximum radiation dose 2.0 × 10^{19} α-decay/g; R1: ~ 1.6 wt% ThO_2, 19.7 wt% REE oxides, and maximum radiation dose 2.6 × 10^{18} α-decay/g) were step-wise annealed to 1000 K in air. Using orientation-dependent nanoindentation, synchrotron single-crystal X-ray diffraction (synchrotron XRD), X-ray powder diffraction (powder XRD), differential scanning calorimetry and thermogravimetric analysis (DSC/TG), mass spectrometry (MS), ^{57}Fe Mössbauer spectroscopy and high-resolution transmission electron microscopy (HRTEM), a comprehensive understanding of the structural processes involved in the annealing was obtained. As a result of the overall increasing structural order, a general increase of hardness (pristine samples: 8.2–9.3 GPa, after annealing at 1000 K: 10.2–12 GPa) and elastic modulus (pristine samples: 115–127 GPa, after annealing at 1000 K: 126–137 GPa) occurred. The initially heterogeneous recrystallization process is accompanied by oxidation of iron, the related loss of hydrogen and induced stress fields in the bulk material, which cause internal and surface cracking after step-wise annealing from 800 to 1000 K. HRTEM imaging of the pristine material shows preserved nanometer-sized crystalline domains embedded in the amorphous matrix, despite the high degree of structural damage. The results show that hardness and elastic modulus are sensitive indicators for the structural reorganization process.

Beirau, T., Oliver, W.C., Reissner, C.E., Nix, W.D., Pöllmann, H. and Ewing, R.C. (2019a)

Radiation-damage in multi-layered zircon: Mechanical properties.

Applied Physics Letters, 115, 081902.

https://doi.org/10.1063/1.5119207

Abstract: Nanoindentation high-resolution mapping has been used to probe the mechanical properties [elastoplastic factor (S^2/P, where S is the contact stiffness and P is the load), indentation hardness (H), and elastic modulus (E)] of a natural, highly zoned zircon ($ZrSiO_4$). The zoning, on a scale of ~ 5 to 400 μm, is due to variations in the U and Th concentrations, resulting in a range of α-decay event doses of ~ 3.7× to 7.5 × 10^{18} α-decays/g. Thus, this single, zoned zircon crystal can be used to investigate the effects of α-decay radiation-damage on mechanical properties. The results also illustrate how multilayered ceramics accommodate volume expansion and change in mechanical properties as a function of radiation dose. Further, the detailed investigation of fractures in the lesser damaged, higher crystalline domains provides a better understanding of crack propagation in the initially crystalline material due to the strain induced by heterogeneous damage distribution. This is an important consideration in designing materials for the immobilization of plutonium from dismantled nuclear weapons, as plutonium decays by α-decay events. The directly measurable stiffness²/load (S^2/P) provides a useful estimate of the degree of radiation-damage. The evolution of E provides experimental evidence for the predicted second percolation transition that denotes the end of percolation of the crystalline fraction.

Beirau, T., Shelyug, A., Navrotsky, A., Pöllmann, H. and Salje, E.K.H. (2019b)

Avalanches during recrystallization in radiation-damaged pyrochlore and allanite: Statistical similarity to phase transitions in functional materials.

Applied Physics Letters, 115, 231904.
https://doi.org/10.1063/1.5133439

Abstract: Differential scanning calorimetry has been employed to analyze the jerky behavior of exothermic, structural reorganization processes of the highly disordered radiation-damaged uranium or thorium containing minerals pyrochlore and allanite. The thermal signals occur as thermal spikes forming crackling noise spectra. The energy of the thermal spikes follows power-law behavior with an exponent $\varepsilon \sim 1.61–1.65$, which is in good agreement with force integrated energy distributions predicted by mean field theory. The recrystallization is hence statistically identical to the collapse of martensites under external pressure and the switching of ferroelectric materials.

Reissner, C.E., Roddatis, V., Bismayer, U., Schreiber, A., Pöllmann, H. and Beirau, T. (2020)

Mechanical and structural response of radiation-damaged pyrochlore to thermal annealing.

Materialia, 14, 100950.
https://doi.org/10.1016/j.mtla.2020.100950

Abstract: Nanoindentation has been employed to probe the mechanical properties [indentation hardness (H) and elastic modulus (E)] of radiation-damaged pyrochlore before and after step-wise thermal annealing up to 900 K. Three natural U and/or Th containing samples with increasing degree of disorder have been investigated (i.e., Panda Hill: 1.8 wt% ThO_2, maximum lifetime alpha-decay event dose ~1.6 x 10^{18} α-decay g^{-1}; Blue River: 11.9 wt% UO_2, maximum lifetime alpha-decay event dose ~115.4 x 10^{18} α-decay g^{-1}; and Miass: 7.2 wt% ThO_2, maximum lifetime alpha-decay event dose ~23.1 x 10^{18} α-decay g^{-1}). Complementary investigations by photoluminescence and Raman spectroscopy and in-situ annealing transmission electron microscopy (TEM) allowed us to follow the structural evolution. Therefore, a comprehensive understanding of the thermally induced structural reorganization process was obtained. Recrystallization has found to start above 500 K in the pyrochlores. Due to the increasing structural order a general hardening of the mechanical properties was observed. Miass pyrochlore (highest degree of structural damage of the investigated samples) reaches a polycrystalline state after annealing. While lesser damaged, but also highly disordered Blue River pyrochlore (containing small preserved crystalline domains) has found to transform into a single crystal. The recrystallization of both pyrochlore samples was followed by in-situ TEM at 800 and 750 K, respectively.

Huber, N. and Beirau, T. (2021)
Modelling the effect of intrinsic radiation damage on mechanical properties: The crystalline-to-amorphous transition in zircon.
Scripta Materialia, 197, 113789.
https://doi.org/10.1016/j.scriptamat.2021.113789

Abstract: Mechanical modelling using the level-cut Gaussian random field approach has been employed to simulate the effect of radiation induced amorphization on the Young´s modulus, Poisson´s ratio and hardness of zircon ($ZrSiO_4$). A good agreement with previous nanoindentation experiments has been achieved. Two percolation transitions occur at ~16% and ~84% amorphous volume fraction, leading to deviations from linearity in the evolution of the Young´s modulus. Interface regions between crystalline and amorphous areas stabilise the hardness for a considerable amount of amorphous fraction. The modelling approach is promising for predicting the intrinsic radiation damage related evolution of the mechanical properties of various materials.

Beirau, T. and Huber, N. (2021)

Percolation transitions in pyrochlore: Radiation-damage and thermally induced structural reorganization.

Applied Physics Letters, 119, 131905.
https://doi.org/10.1063/5.0068685

Abstract: Finite element mechanical modeling is used to follow the evolution of the hardness (H), Young's modulus (E), and Poisson's ratio (v) during the radiation-damage related crystalline-to-amorphous transition in pyrochlore (average main composition $Ca_2Nb_2O_6F$). According to the model, two percolation transitions have been identified around 16% and 84% amorphous volume fraction, respectively. In this context, earlier results from thermally induced recrystallization experiments have found to indicate noticeable modifications on the short- and long-range order by passing the percolation thresholds. Both percolation points have found to act as specific kinetic barriers during stepwise annealing induced structural reorganization. As phases with pyrochlore structure have been considered as host structures for the long-term disposal of actinides, it is essential to gain better knowledge of their mechanical behavior under radiation-damage and subsequent temperature treatment. The obtained results validate the used models' robustness in predicting radiation-damage related mechanical modifications, at least for ceramics.

Beirau, T., Rossi, E., Sebastiani, M., Oliver, W.C., Pöllmann, H. and Ewing, R.C. (2021)

Fracture toughness of radiation-damaged zircon studied by nanoindentation pillar-splitting.

Applied Physics Letters, 119, 231903.
https://doi.org/10.1063/5.0070597

Abstract: Nanoindentation micro-pillar splitting was employed to measure the fracture toughness (KC) of growth-zones in radiation-damaged zircon with varying degrees of disorder (~45%–80% amorphous fraction). The radiation-induced amorphization is caused by α-decay events from incorporated U and Th (~0.22–0.43 wt. % UO_2 and ~0.02–0.08 wt. % ThO_2). K_C has been found to increase with the increase in the amorphous fraction (~2.39 to 3.15 MPa*$m^{1/2}$). There is a good correlation with the modulus/hardness (E/H) ratio evolution over the investigated zones. As zircon has been proposed as a nuclear waste form for the incorporation and disposal of Pu, a deeper knowledge of K_C as a function of radiation damage is important, as radiation-induced cracking provides diffusion paths for the release of incorporated actinides. Zoned zircon provides a model for the development of multilayer coatings and complex ceramics that can be designed to be resistant to crack propagation.

Beirau, T., and Carpenter, M. (2022)

High-temperature resonant ultrasound spectroscopy of highly radiation-damaged pyrochlore: Structural reorganization and high acoustic loss.

Applied Physics Letters, 120, 231901.
https://doi.org/10.1063/5.0096735

Abstract: High-temperature resonant ultrasound spectroscopy (HT-RUS) has been employed to follow in situ the thermally induced structural reorganization of highly radiation-damaged pyrochlore. The investigated sample with average composition $(Na,Ca)_2Nb_2O_6F$ contains ∼12 wt. % UO_2 and has an amorphous fraction of ∼95%. The sample displays high acoustic loss, but an unconventional use of HT-RUS (monitoring the variation of the respective measured spectra's overall integrated intensity) nevertheless allows the thermally induced structural reorganization process to be followed in some detail. The recrystallization process is accompanied by clear changes in elastic properties, while initial heating causes elastic softening of the radiation-damaged pyrochlore. The results imply a general applicability of HT-RUS to in situ monitoring of the thermal behavior of highly attenuating materials.

Beirau, T., Reissner, C.E., Pöllmann, H., and Bismayer, U. (2022)

Partially disordered pyrochlore: Time-temperature dependence of recrystallization and dehydration.

Zeitschrift für Kristallographie – Crystalline Materials, 237, 287.
https://doi.org/10.1515/zkri-2022-0006

Abstract: The comparison of the evolution of the mechanical properties (elastic modulus and hardness) after step-wise thermal annealing for 1 and 16 h up to 900 K of a radiation-damaged pyrochlore (~35% amorphous fraction; 1.8 wt% ThO_2) provides insights to the time-temperature dependence of the recrystallization behavior. Especially the elastic modulus, directly related to interatomic bonding, enables the correlation with the amount of amorphous fraction. From this a pronounced effect of the annealing time on percolation behavior could be deduced. Evolved gas analysis indicate dehydration in the course of the structural reorganization process.

B. Curriculum vitae

- omitted for data protection reasons -

C. Eidesstattliche Erklärung / Declaration under Oath

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