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Short communication

Probing structural disorder in zircon by electron backscatter diffraction (EBSD): Radiation damage and Kikuchi pattern

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ABSTRACT

Electron backscatter diffraction (EBSD) was employed to probe the structural order of a zoned radiation-damaged zircon ($ZrSiO_4$) on the sub-micron scale. The amorphous fraction of the growth-zones is in the range of ~45–80%, due to variations in the amount of incorporated uranium and thorium (~0.22–0.43 wt% UO_2 and ~0.02–0.08 wt% ThO_2) and the resulting alpha-decay events over time. The obtained Kikuchi patterns' band contrast (*bc*) and band slope (*bs*) are indicative of the degree of atomic-scale order. The excellent correlation of both parameters with the evolution of the elastic modulus validates the methods reliability.

Electron backscatter diffraction (EBSD) is a well-established technique in the frame of scanning electron microscopy (SEM) applications in materials and natural sciences, e.g., for micro texture analysis and crystal morphology. When back-scattered electrons from electron microscope measurements fulfill the Bragg conditions (*i.e.*, constructive interference), Kikuchi bands can be detected that form a Kikuchi pattern (e.g., [1,2]). The patterns are correlated with the lattice planes in the material and become visible as fluorescence of the e^- on a phosphor screen. They contain all necessary crystallographic information to determine a material's atomic structure and orientation. Hence, decreasing structural order (e.g., due to radiation damage) will decrease the signal-to-noise ratio of the Kikuchi pattern until no diffraction signal is evident (i.e., high degree of amorphization).

Advance in probing structural disorder, or rather order, is essential to facilitate verification of the integrity and to generally better understand the behavior of materials that are, e.g., exposed to high radiation fields; like nuclear fuel, reactor materials, materials designed for radiation shielding, and nuclear waste forms (see, e.g., [3,4]). Taking this into account, the following questions arise: (i) is EBSD a useful technique to easily probe varying degrees of atomic-scale disorder in materials; (ii) if so, how accurately can this be done and (iii) what is the influence of the surface quality?

In this letter, we focus on the mineral zircon ($ZrSiO_4$) to address these questions. While zircon itself has already been proposed as a possible host matrix for the immobilization of actinides like plutonium [5], it commonly incorporates up to 5000 ppm of U and Th in nature [6,7]. As an object of study we choose a very well investigated zoned radiation-damaged zircon sample (#4601 from the Ratnapura district in Sri Lanka; (100) oriented polished thin section; for further details, see [8–12]). The ~5–30 µm wide zones are caused by variations in the uranium and thorium distribution that lead to different degrees of amorphization. The α-decay events of the incorporated actinides cause structural damage and finally lead to an amorphous (metamict) state [5]. The studied area comprises ~10 obvious zones with varying UO_2 and ThO_2 concentrations between ~0.22–0.43 wt.% and ~0.01–0.08 wt.% (determined by electron microprobe analyses), respectively [8]. The resulting degree of amorphization over the investigated zones ranges from ~45 to ~80% ± 5% amorphous fraction (f_a) [12]. This makes the zoned sample an ideal layered ceramic model material to investigate the varying effect of structural amorphization with the advantage of using only a single sample to enhance comparability.

The EBSD technique, using a Tescan Clara field emission scanning electron microscope equipped with an Oxford Symmetry 2 detector (experimental parameters: EBSD camera pixels: 156 × 128, mode: Speed 2, exposure time: 3.00 ms, camera gain: 1, and frame averaging: 10 frames), was used to probe variations in structural order of the zoned radiation-damaged zircon. Therefore, we monitored the obtained Kikuchi patterns' band contrast

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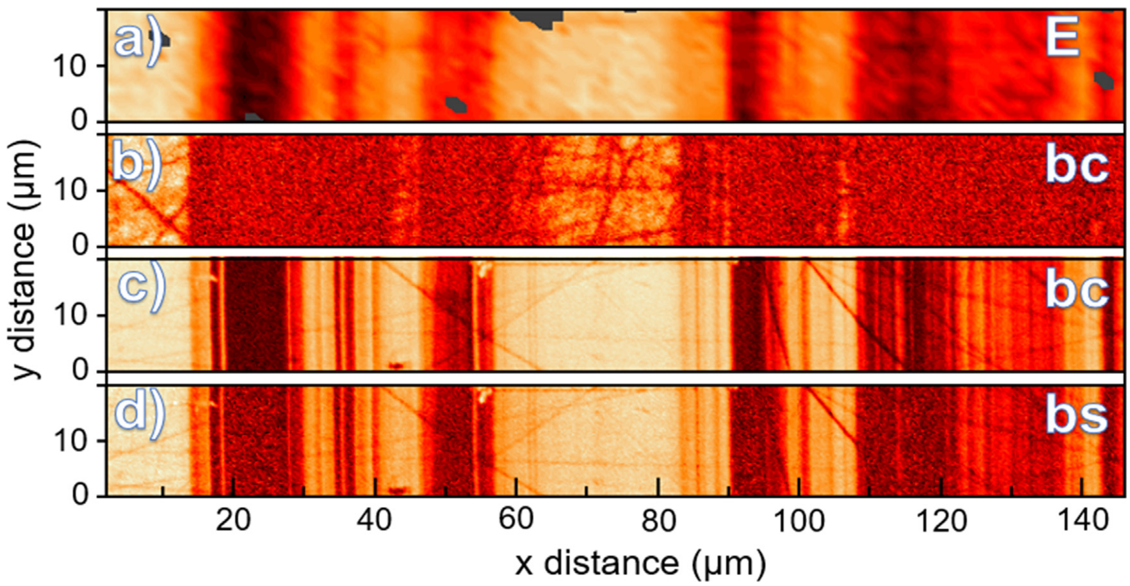

Fig. 1. Mapped variations of (a) elastic modulus (*E*) (data from [11]; areas where no data could be collected are gray), (b) the Kikuchi band contrast (*bc*) before, and (c,d) band contrast and band slope (*bs*) after re-polishing of the zoned zircon specimen (color code: brighter → higher degree of crystallinity, *i.e.*, higher *E*, *bc*, and *bs*; damage due to α-decay).

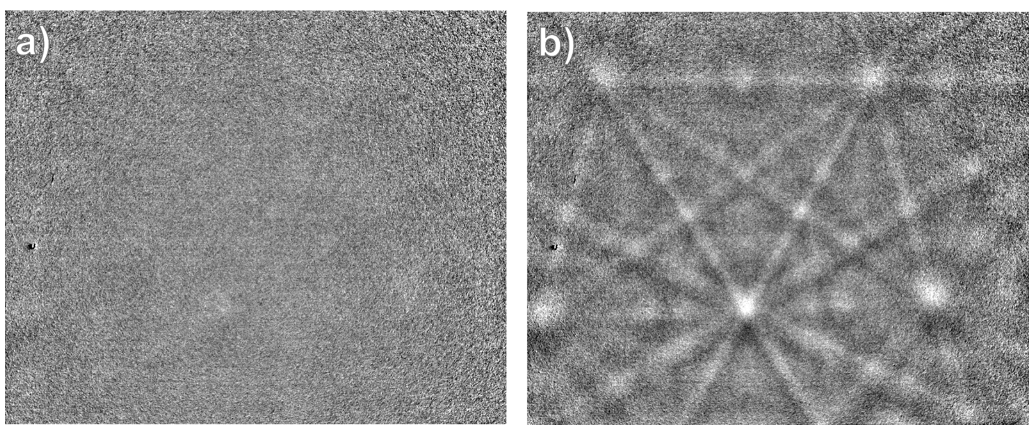

Fig. 2. Exemplary Kikuchi pattern from (a) a highly (~80% f_a) and (b) a lesser (~45% f_a) amorphized zone (located around $x = 23$ µm and 77 µm in Figs. 1 and 3, respectively).

(*bc*; also known as image quality) and band slope (*bs*) (Fig. 1b–d). Both parameters have been reported as quality indicators for Kikuchi patterns [13]. While *bc* denotes the average intensity of the Kikuchi bands compared with the gross intensity of the measured pattern, *bs* is a qualitative measure of the overall sharpness of the bands [2]. EBSD mapping was conducted with a stage tilt angle of 70°, an accelerating voltage of 20 kV, incident beam current of 10 nA, and a step seize of 0.25 µm. The raw data were analyzed with the Oxford software package Aztec to deduce *bc* and *bs* values.

Although EBSD is known to be highly sensitive to sample surface quality, we can show that even a mechanically polished thin section [8] provides already useful information about the variations in degree of crystallinity, visible in the obtained *bc* map (Fig. 1b). To get a more detailed picture, the sample was mechanically (¼ micron diamond paste) and chemically (colloidal silica) re-polished (Fig. 1c and d). Due to the improved resolution of detected zones visible in the corresponding *bc* and *bs* maps (Fig. 1c and d), we focus on the re-polished sample results in the following. Fig. 2a and b show exemplary Kikuchi patterns from a highly and a lesser amorphized zone (*i.e.*, ~80% and ~45% ± 5% f_a, respectively [12]).

As a measure of structural integrity for comparison, we chose the evolution of the elastic modulus (*E*) (Fig. 1a) that is directly related to materials' interatomic bonding, deduced form earlier nanoindentation mapping of the same zones (see [11]).

Fig. 3 shows the excellent correlation between the evolution of the avarege *E* and average *bc* (see also Fig. 1a and c).

In summary, we successfully showed the excellent applicability of the EBSD technique to map and monitor variations in a zoned zircon's degree of radiation damage on the sub-micron scale, using the Kikuchi band contrast or band slope as a measure. The very good correlation of both parameters (i.e., *bc* and *bs*) with the evolution of the elastic modulus (see Figs. 1 and 3), measured over the different zones, validates the obtained results and the relation to radiation damage. Hence, the shown technique could be used to access the structural state of a material against a known reference sample (same material, measured with exactly the same EBSD setup), as one has to keep in mind that absolute values of *bc* and *bs* are also influenced by measurement and sample condi-

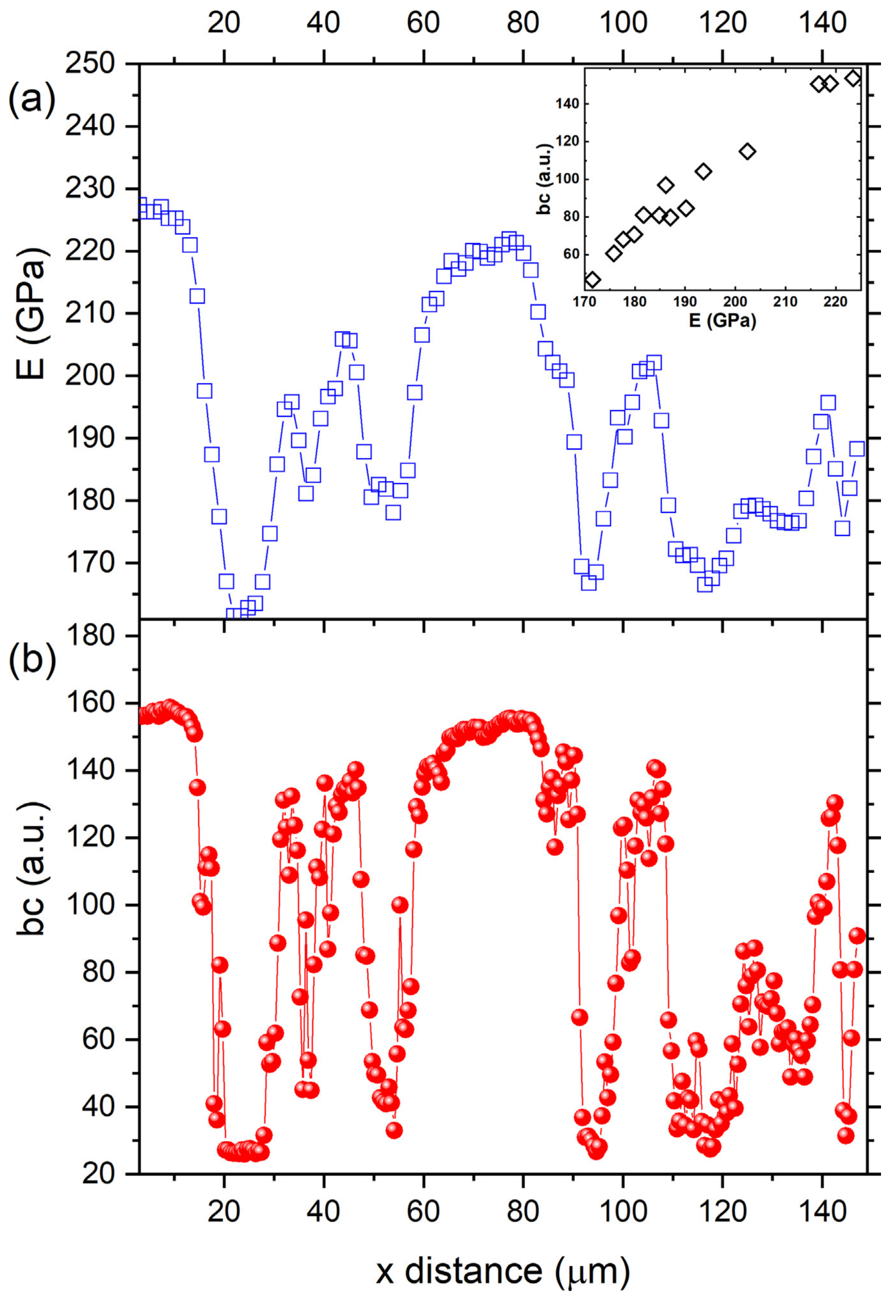

Fig. 3. (a) Evolution of average *E* (open boxes) and (b) average *bc* (closed circles) for the zoned area (see Fig. 1a and c). Inset: *bc versus E* (open diamonds), spatially averaged over 10 μm bins. Lines are a guide to the eye.

tions. This indicates the potentially great benefit for the broad field of radiation effects in nuclear material, particularly for the analysis of composite materials. EBSD *bc* and/or *bs* data can provide useful additional information about the local degree of structural order of, *e.g.*, nuclear fuels and the fuels-cladding interface regions that are already commonly investigated by SEM [14].

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Tobias Beirau reports financial support was provided by German Research Foundation. Michael Stipp reports financial support was provided by German Research Foundation.

CRediT authorship contribution statement

Tobias Beirau: Conceptualization, Validation, Formal analysis, Writing – original draft, Visualization, Funding acquisition. **Rüdiger Kilian:** Methodology, Software, Validation, Formal analysis, Investigation, Writing – review & editing. **Michael Stipp:** Resources, Writing – review & editing. **Rodney C. Ewing:** Resources, Writing – review & editing.

Data Availability

Data will be made available on request.

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