Application of electron backscatter diffraction and micro-Raman spectroscopy for characterization of zircon crystallinity

Използване на дифракция на обратно отразени електрони и микро-Раманова спектроскопия за характеризиране на кристалност на циркон

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Introduction

Stability and crystallinity of zircon ($ZrSiO_4$) are repeatedly debated themes over the past 20 years, mainly in view of (i) wide application of the mineral in geochronology and geochemistry, and (ii) high potential of its structure for waste actinides immobilization. Micro-Raman spectroscopy in combination with cathode luminescence and backscattered electron imaging technique in SEM are commonly used for characterization of radiation damages (metamictization) of the mineral structure, variations in its chemical composition and phase inhomogeneity (Nasdala et al., 2001). In the present report, the authors make an attempt to combine and compare Raman spectroscopy experiments with electron backscatter diffraction (EBSD) and energy dispersive spectrometry (EDS) analysis in SEM for characterization of zircon crystallinity.

Material and methods

Crystals of zircon manually picked from the heavy fractions of granite samples of the Igralishte pluton (Southwestern Bulgaria) with age of 243 Ma, incorporated into epoxy resin pellet and polished according to preparation protocol for EBSD (Nowell et al., 2005) were used for the present study. A DigiView III camera, a part of the EDAX Trident System attached to the scanning electron microscope ZEISS SEM EVO 25LS (Institute of Mineralogy and Crystallography – BAS) was used for collection of EBSD patterns at 20 kV acceleration voltage. A single Raman spectrometer LabRAM HR Visible equipped with an optical microscope and Peltier-cooled CCD detector (Sofia University, Faculty of Physics) was applied for collection of Raman spectra using a 633 nm He-Ne laser with power on spot of 0.7 mW and 100x objective.

Results and discussion

In the first stage of our investigation, more than 80 zircon crystals were studied by EBSD technique aiming at detection in them of areas with different crystallinity. EBSD pattern presents a combination of Kikuchi bands corresponding to definite crystallographic planes; the intersections of these bands locate the position of particular axis zones as it is shown in Fig. 1b. The quality of EBSD patterns strongly depends on the degree of crystallinity of the material and the preparation technique applied. The effects of preparation were diminished by us via strictly following of the polishing protocol recommended for EBSD. Besides, we reasonably suggested that in one and the same pellet, the effect of preparation is the same for all embedded zircon crystals. However, there is no commonly accepted procedure to quantify the degree of crystallinity using EBSD data. Well contrasted Kikuchi bands with sharply outlined boundaries in EBSD pattern are an indication of high crystallinity of a material. Absence of such bands in EBSD pattern is an indication of strong structural disorder (~amorphous state) of the material. Patterns with variable diffusivity of Kikuchi bands specify intermediate structural states of the material. For the present report we adopted semi quantitative scale including 5 classes of crystallinity from 1 (high degree of crystallinity) to 5 (strong disorder). Thus specified areas with different crystallinity were later analyzed by EDS and examined by Raman spectroscopy. During the present investigation we found that:

– According to the EBSD data almost all the studied zircon crystals are characterized by variable crystallinity. The areas of different crystallinity are well outlined in secondary electron (SE) images being either randomly shaped zones or well pronounced growth zones and central cores of the crystals. This

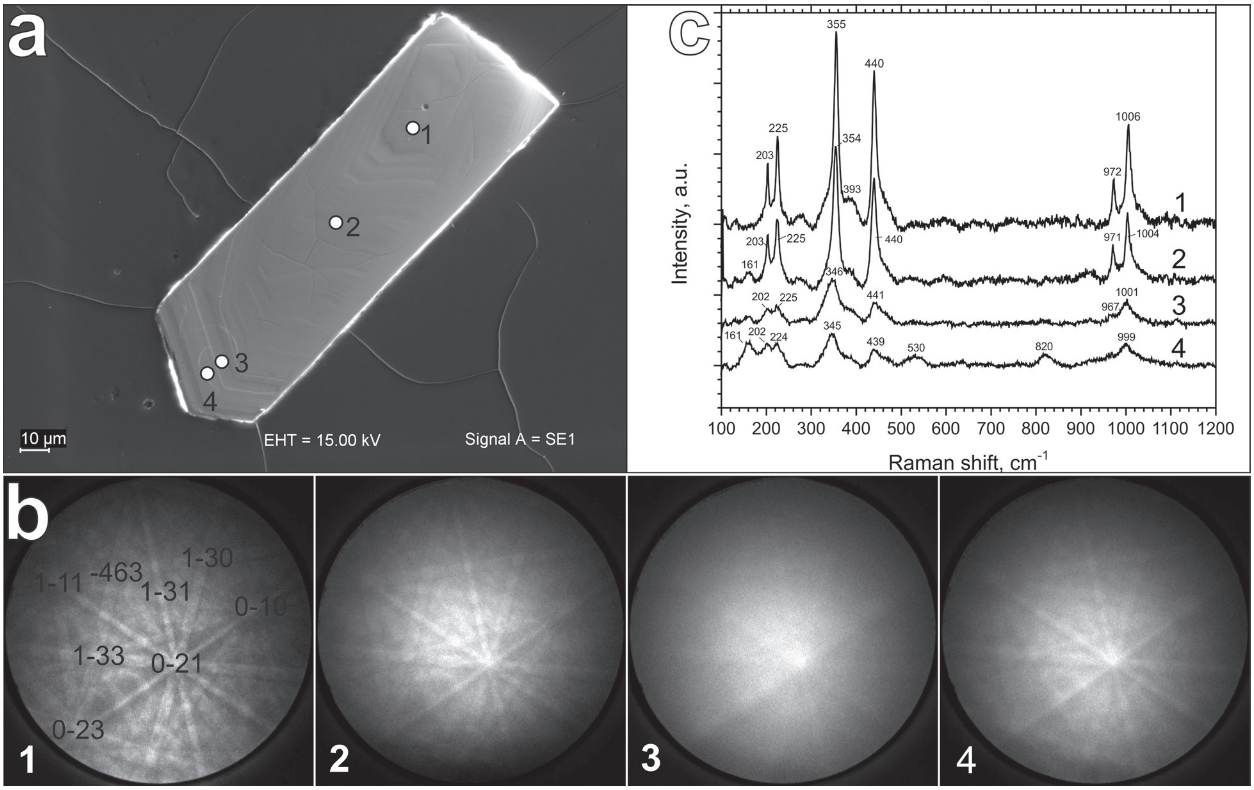

Fig. 1. (a) SE image of zircon crystal with indicated areas (1, 2, 3, and 4) analyzed by EBSD, EDS and Raman spectroscopy; (b) series of EBSD patterns indicating decrease of crystallinity from area 1 to areas 3 and 4; (c) sequence of unpolarized Raman spectra showing decrease of crystallinity from area 1 to areas 3 and 4

finding is well illustrated in Fig. 1a where a half of euhedral zircon crystal is shown with indicated places studied with EBSD, EDS and Raman spectroscopy. The obtained EBSD patterns (Fig. 1b) show decrease of crystallinity from the central part of the crystal (area 1) to its periphery (areas 4 and 3). It is well visible (Fig. 1a) that the analyzed areas are well outlined due to topography contrast as a consequence of different mechanical properties of the material resulted from the different crystallinity.

– The found variable crystallinity of the zircon crystals well correlates with the content of uranium. In the studied crystal, the highest U content is found for the area 3 (2.8 wt.%) while for the areas 1 and 2 the content of U is below 0.2 wt.%. This result unequivocally evidences for the advanced stage of radiation damage (metamictization) of the area 3.

– The recorded Raman spectra of the specified areas (Fig. 1c) well correlate with the EBSD and EDS analysis data. The reduction in the EBSD degree of crystallinity correlates with the typical for metamict zircon decrease in the intensity of Raman peaks, their broadening and shift (Nasdala et al., 2001). For example, the peak corresponding to antisymmetric stretching $\nu_3(SiO_4)$ known to be at 1008 cm^{-1} for well crystallized zircon, in the spectrum of the area 1 is situated at 1006 cm^{-1}, and gradually shifted to 999 cm^{-1} for the area 4 (Fig. 1c). Some discrepancy between the EBSD and Raman spectroscopy on the crystallinity of areas 3 and 4 most probably is related to additional alteration (or re-equilibration) processes (Geisler et al., 2007) requiring the further investigation.

Conclusion

The application EBSD and Raman spectroscopy for characterization of zircon crystallinity shows good correlation between the two methods. At the same time, further investigation is needed to clarify in more details the crystallinity of the mineral and its relation with the radiation damage and other alteration processes, including postmagmatic ones.

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