# Metamict zircon study using synchrotron-based Attenuated Total Reflectance (ATR) infrared microspectroscopy

# Изследване на метамиктен циркон чрез ATR – инфрачервена микроспектроскопия със синхротронно лъчение

*Rositsa Titorenkova[1], Biliana Gasharova[2], Ludmil Konstantinov[1], Boriana Mihailova[3]*
*Росица Титоренкова[1], Биляна Гашарова[2], Людмил Константинов[1], Боряна Михайлова[3]*

[1] Central Laboratory of mineralogy and crystallography, Bulgarian Academy of Sciences, 1113 Sofia;
E-mail: rosititorenkova@dir.bg
[2] Forschungszentrum Karlsruhe GmbH, ANKA synchrotron light source/Institute for Synchrotron Radiation,
P. O. Box 3640, D-76344 Eggenstein-Leopoldshafen, Germany
[3] Mineralogisch-Petrographisches Institut, University of Hamburg, Grindelallee 48, D—20146 Hamburg, Germany

**Абстракт.** Изследвани са природни циркони с различна степен на дефектност чрез ATR-инфрачервена микроспектроскопия с лъчение от синхротронен източник. Получените спектри на поглъщане се различават значително за кристали с различни акумулирани радиационни дози.

**Key words:** ATR IR microspectroscopy, synchrotron radiation, zircon

## Introduction

Natural zircon ($ZrSiO_4$) belongs to the group of metamict minerals, which are characterised by structural disorder of various degrees related to the simultaneous action of alpha decay recoil damage due to incorporated radio-nuclides and structural recovery caused by thermal annealing. Structural studies of metamict zircon are important for geochronological interpretation and for better understanding the long-term effects of structural modification, since zircon is used for a host system for disposal of radioactive waste. One of the most frequently used methods for determining the degree of structural disorder on a micron-scale level is Raman spectroscopy (Palenik et al., 2003). The structural analysis is based on the disorder-induced anomalies in phonon modes of zircon. Infrared spectroscopy, as an alternative technique for probing optical phonon modes, has also been utilised to study the structural modifications in zircon (Zhang et al., 2001; Geisler et al., 2003) however, it has not been applied so far for analysing micron-scale spatial regions of inhomogeneous natural minerals.

The objective of this study is to apply synchrotron-based attenuated total internal reflectance infrared (ATR IR) microspectroscopy to characterise natural zircon samples with different degree of structural disorder, as preliminary distinguished by electron microprobe analysis and Raman microspectroscopy. The advantages of ATR IR spectroscopy are: (i) it overcomes the necessity to use Kramers-Kronig's transformation and, thus, the uncertainty in determining the peak positions, as in the case of specular reflectance; (ii) there are no special requirements for the sample thickness as in the case of transmittance regime, where the preparation of samples thin enough for measuring the first-order infrared-active phonons is difficult to handle; (iii) high lateral resolution (approaching 3 μm) when an ATR objective is used, which was facilitated by the utilization of synchrotron radiation.

## Experimental

We studied 36 natural zircon crystals separated from various locations and type of rocks. The ATR IR spectroscopic measurements were performed at the ANKA IR beamline, using a Bruker IFS 66v/S FT-IR spectrometer equipped with a Bruker IRscope II microscope with a Ge-ATR crystal objective and a liquid $N_2$-cooled MCT detector. The refractive indices of Ge and zircon are ~ 4.01 and 1.65, respectively, i.e. the optical parameters of zircon meet the requirements for occurrence of total reflectance when Ge crystal is used. The spectral range in which Ge can be used as an ATR crystals is 600–5000 $cm^{-1}$, which allow to detect the fundamental Si-O stretching bands near 880–980 $cm^{-1}$, the infrared absorption due to multi-phonon processes and the stretching modes of hydroxyl groups. The spectra were collected in a dry $N_2$-purged chamber, with an appertture of 25 μm, spectral resolution of 2 $cm^{-1}$, by pressing the ATR crystal onto the sample with a force of

0.46 N and averaging over 512 scans. The characteristic penetration depth was approximatelly 700 nm. Polarized spectra with the light polarisation either perpendicular or parallel to the crystallographic *c*-axis of zircon were collected using KRS5 polarizers.

## Results

According to group theory, seven IR active modes ($3A_{2u} + 4E_u$) should appear in the IR spectra of zircon (Dawson et al., 1971). The modes of $A_{2u}$ symmetry are observed when the light electric vector **E** is parallel to the *c* axis, whereas the modes of $E_u$ symmetry contribute to the spectrum when measured with **E** perpendicular to the *c*-axes. The bands at 885 cm$^{-1}$ (**E** $\perp$ *c*) and 989 cm$^{-1}$ (**E** || *c*) are generated by Si-O stretching mode $\nu_3$, wheras peaks at 608 cm$^{-1}$ (**E** || *c*, $A_{2u}$ type) and 430.5 cm$^{-1}$ (**E** $\perp$ *c*, $E_u$ type) are due to O-Si-O bending mode $\nu_4$. The IR spectra reveal significant differences between the various zircon samples, depending on the accumulated radiation dose, which is linearly related with the uranium concentration in the samples and in an exponential way to their age. The accumulation of radiation damages leads to a decrease in IR absorption band intensity, shift of band positions, band broadening and/or splititing (Fig. 1). In some spectra, besides the typical zircon peaks at 885 cm$^{-1}$ (**E** $\perp$ *c*), at 989 cm$^{-1}$ (**E** || *c*) and at 608 cm$^{-1}$ (**E** || *c*), additional absorption signals were detected at 790 cm$^{-1}$ and 1050 cm$^{-1}$. The observed spectral changes are indicative for lowering of the local symmetry of $SiO_4$ tetrahedra and for a change in the connectivity of the zircon framework.

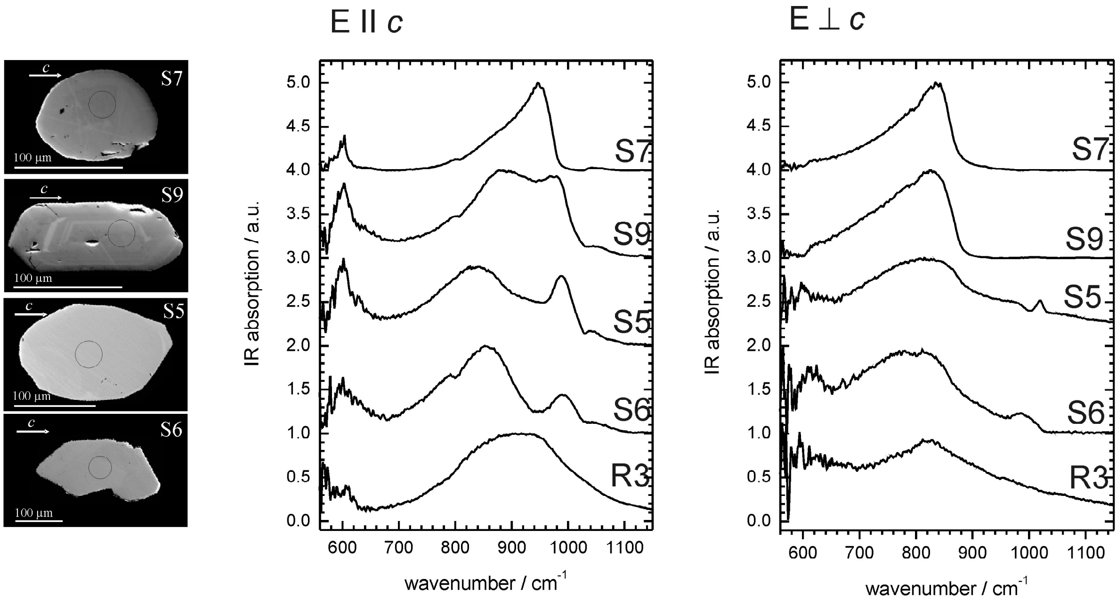


Fig. 1. Polarized ATR-IR spectra of selected zircon samples: R3 — metamict zircon from Sri Lanka with high concentration of radionuclides, corresponding to an accumulated radiation dose $D_\alpha = 5.4\times10^{15}$ α-events/mg; S6 — zircon from metamorphic rocks with $D_\alpha = 1.7\times10^{15}$ α-events/mg; S5 zircon with $D_\alpha = 0.7\times10^{15}$ α-events/mg; S9 — with $D_\alpha = 0.3\times10^{15}$ α-events/mg; S7 — from metamorphic rock without any accumulated dose

Our results clearly demonstrate that ATR IR microspectroscopy is a very sensitive method for studing the degree of structural disorder in metamict zircon. When brilliant synchrotron infrared light is used for ATR IR microspectroscopy, it further enables investigations of minerals that are inhomogenious on a micron scale.

*Acknowledgements:* We acknowledge the ANKA Angstroemquelle Karlsruhe for the provision of beamtime. This work was supported by the European Community — Research Infrastructure Action under the FP6-Programs: "Structuring the European Research Area" (through the Integrated Infrastructure Initiative "Integrating Activity on Synchrotron and Free Electron Laser Science"; Contract RII3-CT-2004-506008 (IA-SFS)). We also thank Dr. Yves-Laurent Mathis and Michael Süpfle (IR-beam group, ANKA), André Weimer (Bruker Optics GmbH) and Dr. Jochen Schlüter (Mineralogical Museum, University of Hamburg) for suport.

## References

Dawson, P., M. Hargreave, G. Wilkison. 1971. The vibrational spectrum of zircon ($ZrSiO_4$). — *J. Phys. Condens. Matter, 4*, 240—256.

Geisler, T., M. Zhang, E. Salje. 2003. Recrystallyzation of almost fully amorphous zircon under hydrothermal conditions: An infrared spectroscopic study. — *J. Nuclear Materials, 320*, 280—291.

Palenik, C., L. Nasdala, R. Ewing. 2003. Radiation damage in zircon. — *Amer. Mineral., 88*, 770—781.

Zhang, M., E. Salje. 2001. Infrared spectroscopic analysis of zircon: Radiation damage and the metamict state. — *J. Phys. Condens. Matter, 13*, 3057—3071.