X-ray emission and X-ray photoelectron spectroscopy studies, *ab initio* electronic structure calculations of radiation damaged zircon and monazite

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Natural U, Th-bearing zircon ($ZrSiO_4$) and monazite ($LnPO_4$, Ln=La-Gd) minerals are widely used as geochronometers; synthetic zirconium orthosilicate and rare earth orthophosphates are potential matrices for the disposal of actinides of high-level radioactive wastes. Radiation damage is known to destroy the crystal lattice and to change physical and chemical properties of minerals; these effects may disturb the U-Th-Pb isotopic system of the geochronometers and reduce the stability of waste forms. In this study the atomic and electronic structures of radiation damaged zircon and monazite are investigated by means of the electron-induced X-ray emission spectroscopy (XES), X-ray photoelectron spectroscopy (XPES), and *ab initio* calculations (quantum-chemical cluster method of X_α discrete variation).

Electron-induced XES spectra were obtained using electron microprobe analyzer Cameca SX-100 (the depth of analysis was 3-15 μm); XPES spectra were taken using ESCALAB MK-II spectrometer (the depth of analysis was ≤10nm). Natural zircon and monazite samples of various damage degree from the Urals were investigated; some samples were irradiated with 3.0 MeV He^{2+} ions using the classic cyclotron (fluence $3 \cdot 10^{16}$ ion/cm^2, penetration depth ~7 μm). The broadening of the $\nu_3(SiO_4)$ Raman band was used to estimate the degree of radiation damage of zircon samples (following Nasdala et al., 1995).

For the XPES of zircon, the radiation damage effects are found to be most pronounced in O1*s* and Si2*p* spectra, and also in the valence band spectrum. The O1*s* band of damaged samples is a superposition of two peaks - $O_1$1*s* (~531.0 eV) and $O_2$1*s* (~532.3 eV). The first one is close in energy to that in synthetic zircon and is assigned to regular oxygen atoms $-\overset{|}{\underset{|}{Si}}-O\begin{matrix}\nearrow Zr\\ \searrow Zr\end{matrix}$. The second one is close in energy to that in quartz and is attributed to oxygen atoms Si-O-Si in amorphous and/or defect areas. The variations in O_2 concentration together with radiation damage degree (0.01-0.2 dpa) are obtained. It is found that the radiation damage of zircon structure is followed by the changes in the shape of XES SiK_β spectra. The correlation of the $SiK_{\beta 1}$-band asymmetry and the radiation damage degree is revealed.

The electronic structure and specific features of the chemical bonding (the effective charges, the electron density distributions, the electronic states spectrum) of defect areas are simulated using the models of oxygen vacancy defects in zircon (Votyakov et al., 1988). The relaxation of the zircon structure at the formation of SiO_2^0 defects is supposed to be the initial stage of the polymerization of silicon-oxygen tetrahedra. The influence of amorphization on the electronic states spectrum and chemical bonding in zircon and monazite is discussed. The possibilities of XES and XPES for the determination of the radiation damage degree are considered.

References:
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