Structural evolution under gamma ray irradiation of zircon originated from Hainan province, China

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Abstract: In order to investigate the structural evolution and the capability of resistance to γ-ray irradiation of natural minerals, the zircon from metamorphic rock in the middle region of Hainan was investigated. The morphologic characteristic of cracked rocks was observed and zircon crystals were selected under a multifunctional microscope. All the samples were irradiated using a ^{60}Co γ-ray source to 576 kGy. Phases and structures of the as-gained samples were characterized by X-ray diffraction (XRD) and Raman spectroscopy (Raman) before and after γ-ray irradiation. Moreover, the chemical compositions of zircons were analyzed by electron probe micro-analyser (EPMA) as well. The results show that the as-gained crystals which come from metamorphic rock undergone near 1483 million years geological evolvement and still contained UO_2 and ThO_2 with the contents of 0.3074 *wt*%. In addition, the samples had good crystallinity. No obvious damage to the structure is found in the zircon irradiated by γ-ray with 576 kGy, however the disorder degree of crystal has a slight increase.

Introduction

With the application of nuclear fission technology, nuclear waste production is always unavoidable. The treatment and disposal of nuclear waste have hence become the focus of nuclear industry [1-3]. Nowadays, numerous scholars consider that mineral crystal lattice immobilization is an excellent technique due to that it is convenient in handling, transportation, storage and disposal of the waste [4,5]. Ceramics (zirconolite and phosphate) are reliable matrices for the nuclear waste due to their excellent mechanical, thermal, chemical and radiation stability [6,7].

Zircon ($ZrSiO_4$) consists of triangular dodecahedral ZrO_8 groups which form edge-sharing chains parallel to the *a*- and *b*-axis, and SiO_4 tetrahedral monomers which form edge-sharing chains with alternating ZrO_8 groups parallel to the *c*-axis [8]. Natural zircon contains U and Th could to 5000 ppm, and it undergoes self-radiation damage via alpha decay over millions of years [9]. Zircon has long been recognized as a host material for the high-level nuclear waste (HLW), owing to the possibility of introducing large amounts of radionuclides into its crystal structure [10,11]. However, the final stability of the artificial waste forms could be guided a lot by the performance of natural minerals (such as zircon). Especially , the capability of resistance to irradiation will directly affect the final safety of the high-level radioactive waste. Therefore, the research of natural zircon is necessary [12].

In this article, zircons collected from the middle of Chinese Hainan (formed from about 1483 Ma [13]) were selected as investigative object. The chemical compositions of zircons were analyzed by electron probe micro-analyser (EPMA). All the samples were irradiated using a ^{60}Co γ-ray

source with 576kGy doses. Phases and structures of the as-gained samples before and after γ-ray irradiation were characterized by XRD and Raman.

Experimental

Metamorphic rocks (Biotite plagioclase gneiss) were collected from the eastern highway Changzheng farm of Hainan side of the quarry. Metamorphic rocks were broken, elutriated and choosing pure zircon crystals named WB. The samples irradiated using a ^{60}Co γ-ray source with 576 kGy doses were named FB. The γ-ray energy was 1.33 Mev, and the activity of radiation source was 150000 Ci (5.55 × 1015 Bq).

The Laborlux 12 pol multi-functional microscope (Germany Leitz) was adopted to characterize the metamorphic rocks. The phase structures of sample WB and FB were characterized by an X-ray diffractometer (X'pert MPD Pro, Netherlands) with Cu Kα radiation (The accelerating voltage of 40 kV). Continuous scans were used for qualitative phase record in the 2θ = 3 ° to 80 ° at a scanning rate of 25 °/min. Electron probe micro-analyser (EPMA, JXA-8800R, Japan) was exploited to analyze the chemical compositions of zircons originating from natural rocks. The Raman spectra were recorded at room temperature using Invia Raman microscope system (Renishaw, UK). The 514.5 nm line from He-Ne laser was used as the excitation line. Laser power of 0.306 mW was focused to a spot of about 10 lm and a standard 50 objective lens was used for the collection of back-scattered Raman signal.

Results and discussion

The photos of samples under the multi-functional microscope are shown in Fig.1. It could be found that the mineral compositions mainly involve black mica, plagioclase, microcline, quartz, Zircon, apatite, magnetite and so on.

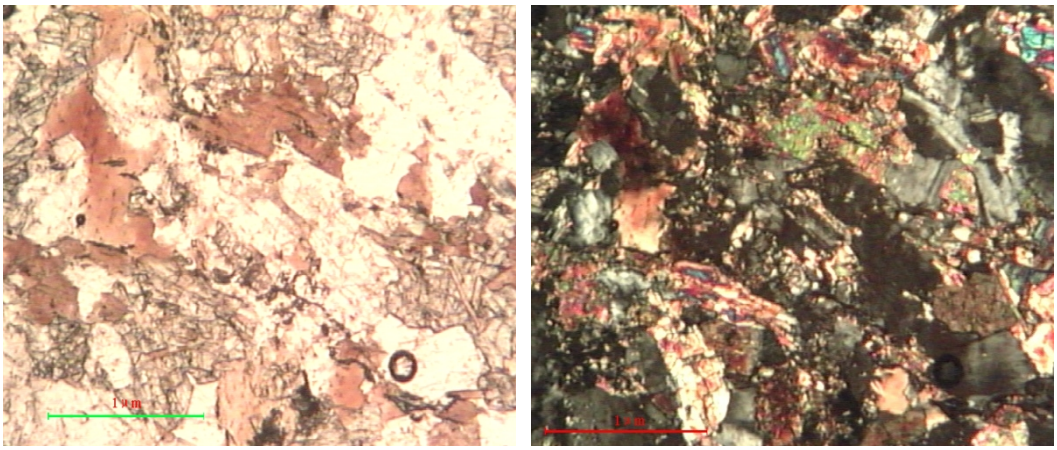

Fig.1. Images of sample metamorphic rock under a multi-functional microscope

The samples which were randomly chosen from WB were analyzed by EPMA and the results were shown in Tab.1. It can be observed that the relative contents of ZrO_2, SiO_2, HfO_2, Y_2O_3, UO_2, ThO_2 and PbO_2 are 64.8510, 32.3560, 1.3900, 0.0122, 0.2868, 0.0206 and 0.0074 *wt*%. Radioactive UO_2 and ThO_2 are important point of our attention. The as-gained crystals contain UO_2 and ThO_2 with the total contents of 0.3074 *wt*%, after 1483±13 million years of geological evolution.

Tab.1. Chemical composition of sample WB

Station	ZrO_2	SiO_2	HfO_2	Y_2O_3	UO_2	ThO_2	PbO_2
1-1	64.83	32.20	0.56	0.1220	1.5410	0.0790	0.0161
1-2	65.02	32.17	1.15	0.0000	0.0280	0.0030	0.0062
1-3	64.60	32.59	1.01	0.0000	0.0520	0.0120	0.0028
2-1	64.24	31.88	1.27	0.0000	0.1130	0.0050	0.0083
2-2	65.29	31.81	1.44	0.0000	0.1890	0.0090	0.0064
2-3	65.57	32.69	1.49	0.0000	0.3360	0.0150	0.0106
2-4	64.17	32.38	1.82	0.0000	0.2860	0.0050	0.0096
3-1	65.42	32.34	1.68	0.0000	0.1900	0.0580	0.0053
3-2	64.65	32.79	1.77	0.0000	0.0920	0.0200	0.0049
3-3	64.72	32.71	1.71	0.0000	0.0410	0.0000	0.0039
Average	64.8510	32.3560	1.3900	0.0122	0.2868	0.0206	0.0074

Fig. 2 shows the powder XRD patterns of WB and FB. It can be seen from Fig.2 that $ZrSiO_4$ phase accounts for the major part in WB and FB. And characteristic peak is very sharp, which shows that the samples had good crystallinity. By comparing the two XRD patterns, it can be found that FB diffraction peaks exhibit a slight decline. This shows that the disorder degree of crystal FB sample has a slight increase.

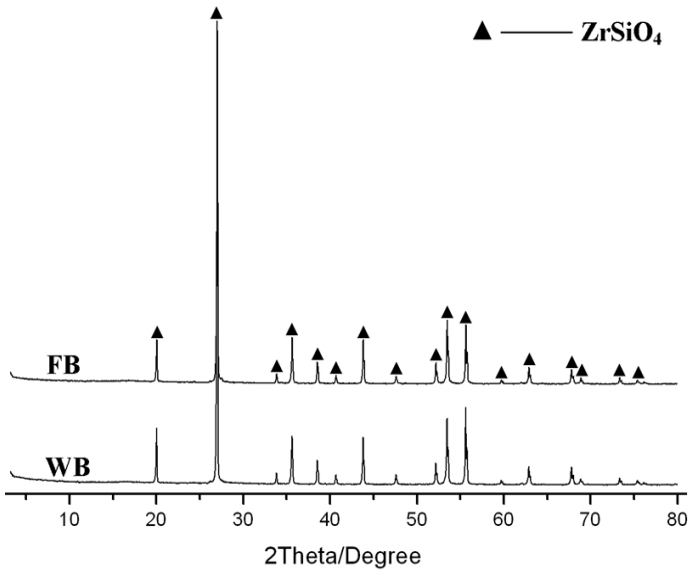

Fig.2. The XRD spectra of WB and FB samples

Fig. 3 shows the Raman spectra of WB and FB samples. It could be found that three dominant peaks arises at about 356, 439 and 1008 cm^{-1}, these peaks are interpreted by Nasdala ***et al.*** [14] as representing the internal vibrations of SiO_4 tetrahedra. The OMNIC software is used to fit the FWHM (W) with the most intense peak at 1008 cm^{-1}, the results are shown in Tab.2. It can be

observed from Tab.2 that the FWHM (W) of WB and FB samples are 7.84308 and 8.54955. The ratio of intensity of peak (H) to FWHM (W) which is shown as H/W in Tab.2 decreases from 13847.2386 to 10680.8078. This result demonstrates that the disordering degree of zircon induced by gamma ray irradiation is enhanced.

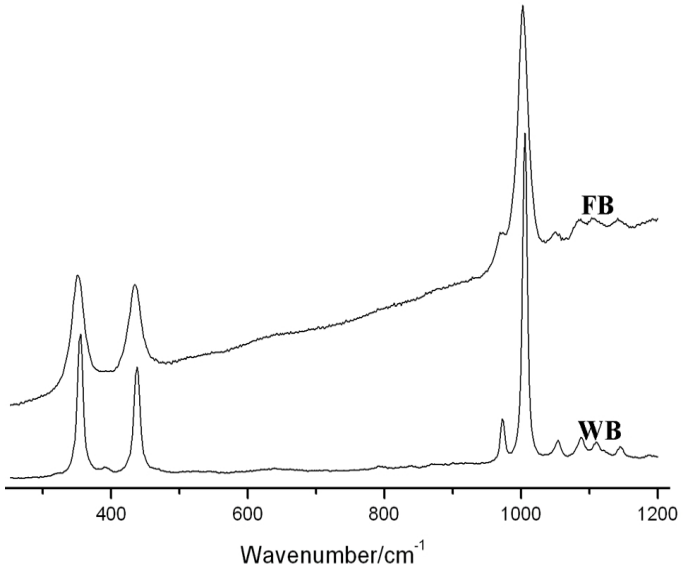

Fig.3. The Raman spectra of WB and FB samples

Tab.2. Calculated H/W of Raman spectrum near 1000^{-1} for samples

Sample	Station/cm^{-1}	H	W/cm^{-1}	H/W
WB	1005.91	108605	7.84308	13847.2386
FB	1005.89	91316.1	8.54955	10680.8078

Conclusions

In this study, zircons were successfully collected from the middle of Hainan province, China. The results show that the as-gained crystals which come from metamorphic rock undergone near 1483 million years geological evolvement and still contained UO_2 and ThO_2 with the contents of 0.3074 *wt*%, besides the samples had good crystallinity by the XRD analysis. The samples were irradiated using a ^{60}Co γ-ray source with 576 kGy doses. The disorder degree of irradiated sample has a slight increase from XRD and Raman analysis.

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