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Irradiation effect on natural quartz from Zambia

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Abstract

The effects of high gamma-irradiation doses (50-300 kGy) on natural quartz crystals have been investigated by ESR technique. The ESR spectrum carried out at low temperature (120 K) displayed lines group of Al center. The higher amount of gamma doses affected ESR spectra by increasing of intensity, especially the increasing intensity in the range of the Al center. The complex ESR spectra of Al center observed to contain 9 peaks that did not reach saturation even though the level of gamma-irradiation dose was as high as 300 kGy. The total area under ESR spectra of Al center was increased as a polynomial function of irradiated dose. The overlapping of ESR signal from defects in the range of Al center was also investigated.

Keywords: Al center; ESR; gamma-irradiation; natural quartz

1. Introduction

Quartz (SiO_2) is the most abundant mineral that found on the earth's surface [1]. The appearance of natural quartz can be found in geological materials (rocks, faults and sediments) etc. [2]. On this world there are many source of minerals especially, southern Africa. Zambia is a landlocked country in central southern Africa (see Fig. 1) which is bordered by Angola, the Democratic Republic of Congo (DR

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Congo), Tanzania, Malawi, Mozambique, Zimbabwe, Botswana and Namibia [3]. In central and eastern Zambia the Muva consists of meta-pelites and meta-quartzites, whereas in northern Zambia it consists of sediments such as sandstones, quartzites, mudstones and conglomerates [4].

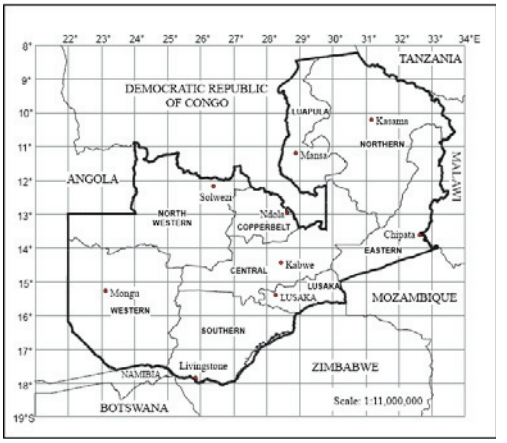

Fig. 1. Map of Zambia [4]

The SiO_2 is a half-covalent and half-ionic crystal and polymorphous i.e. α-quartz, β-quartz, tridymite, cristobalite, etc. [2]. The α-quartz as a gemstone is a special type of silicate that is stable at atmospheric pressures. In various natural quartz studied, the irradiation or heating process was method to investigate the change of the point defect, intrinsic and impurity defects, in natural quartz crystal [5-7].

Several point defects in quartz were investigated by spectroscopy. Especially, the paramagnetic defects concerned with intrinsic or associated-impurity defects have been widely studied by electron spin resonance (ESR) spectrometer. Defects in quartz can be used determine the ages of volcanic material, fault formation, and presumably sedimentation, based on different mechanisms.

The E' center, the peroxy center or oxygen hole center, etc. are examples of intrinsic defects which were well-known. Particularly, the E' center which is an unpaired electron at the oxygen vacancy was various position of an unpaired electron trapped in or nearby an oxygen vacancy of the SiO_2 lattice, e.g. E_1' , E_2' , E_4' or etc. [2, 8]. The ESR intensity signal of E_1' center was historically used to determined the age of geological or archeological material; natural quartz in granites, sediments or rock, etc. [9-10]. J. Bartoll, et.al. reported that the ESR signal of E_1' center in unstrained geological quartz grains from weathered rock of Cretaceous age disappeared when the samples were irradiated with gamma dose about 200 kGy and its signal can be regenerated by heated at 310 °C [11].

In addition, the impurity-associated defect such as the Al center is one of point defect that is alternatively used for ESR dating. The Al center is a trivalent aluminum ion Al^{3+} that substitute a Si^{4+} site in the ionic crystal scheme of the SiO_2 lattice. The ESR spectra of this center can appear at low temperature. M. Lin et al. studied the ESR intensity signal of Al center after irradiated with 60 kGy gamma doses [12]. It found that no saturation of the Al center signal and the range of ESR signal of the Al center and E_1' center were overlapping. Then, it was difficult to examine the amount of ESR intensities. In this work, we will present the effect of high gamma-irradiation does to the ESR signal of Al center and overlapping of other point defect in range of Al signal.

2. Experimental details

All natural quartz crystals were cleaned with 10 wt% nitric (HNO_3) acid and soaked in ultrasonic bath with 30 minutes for remove trace element on the quartz's surface. The chemical composition of quartz sample was collected by energy dispersive X-ray fluorescence (EDXRF, Panalytical-minipal4) spectroscopy. The quartz samples were divided into 4 groups The natural quartz crystal samples were irradiated by ^{60}Co gamma ray with different dose (i.e. 0, 50, 150, and 300 kGy) at Gem Irradiation Center, Thailand Institute of Nuclear Technology (TINT). After gamma irradiation, all samples were ground into fine powder using alumina motor for investigated by X-ray diffraction (XRD) to confirm structure and the electron spin resonance (ESR) for paramagnetic defect.

The crystal structure of the quartz samples were characterized by X-ray diffractometer (Bruker, D8 Advance) with CuK_α radiation, 40kV, 20 mA at 0.02 degree per step, a step time of 2 s and scan time of 1.23 h. The XRD pattern was recorded in the 2-theta range of 20°-70°.

For ESR measurements, the ESR intensity of natural quartz powder was measured at room temperature and low temperature (120 K) with ESR spectrometer (Bruker E500 CW) and the microwave frequency in X-band range (~ 9.84 GHz). Approximately 0.249 g of each sample was filled in a fused quartz tube of 3 mm internal diameter. Then, the sample tube was positioned in such a way that sample was situated symmetrically with respect to the cavity center. Standard rectangular cavity operating in TE_{102} mode was selected. DPPH with a g factor of 2.0036 was used as an internal standard for g factor calculations. The ESR signal intensities of all samples were normalized with the ESR signal from un-irradiated samples.

3. Results and discussion

The elemental composition of natural quartz samples from Zambia that used in this work is SiO_2 (99.2%), CaO (0.28%), Fe_2O_3 (0.431%), and CuO (0.0624%), other element (0.0266%) which the quartz samples were colorless. The XRD pattern of un-irradiated natural quartz was shown in Fig. 2. It indicated that the structure of silicon dioxide (SiO_2) which matched JCPDS file number 46-1045. After gamma irradiation, the XRD patterns of quartz samples were also displayed in Fig. 2. The characteristic of XRD pattern were similar with un-irradiated sample. It indicated that the structure of quartz were not change when were irradiated by high gamma-doses. The ratios of *c/a* were almost constant with different gamma irradiated dose.

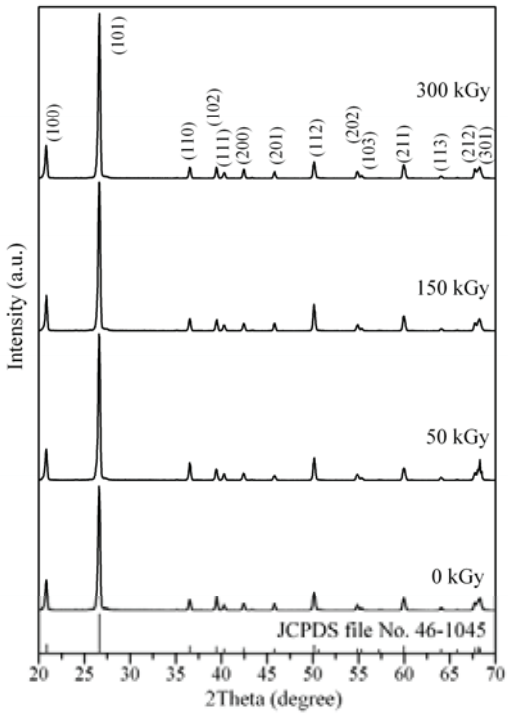

Fig. 2. The X-ray powder diffraction patterns obtained from the natural quartz samples with un-irradiated and different gamma irradiation (50, 150,300 kGy)

The ESR spectrum of natural quartz samples at low temperature (-153 °C) are displayed in Fig. 3. It shows inconspicuous lines of Al center. When the samples were irradiated with gamma ray, the ESR spectra; at 10 mW microwave power, can be clearly observed as shown in Fig. 4.

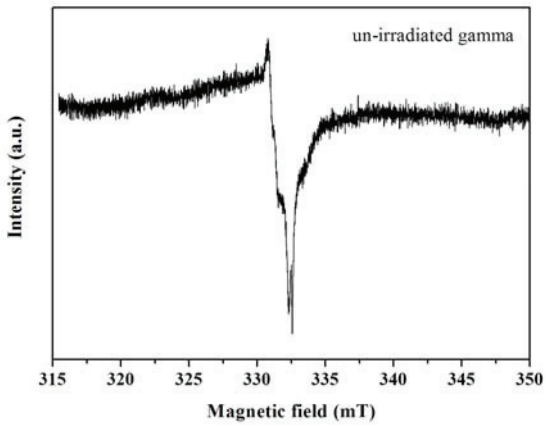

Fig. 3. The ESR spectrum of un-irradiated natural quartz sample at low temperature

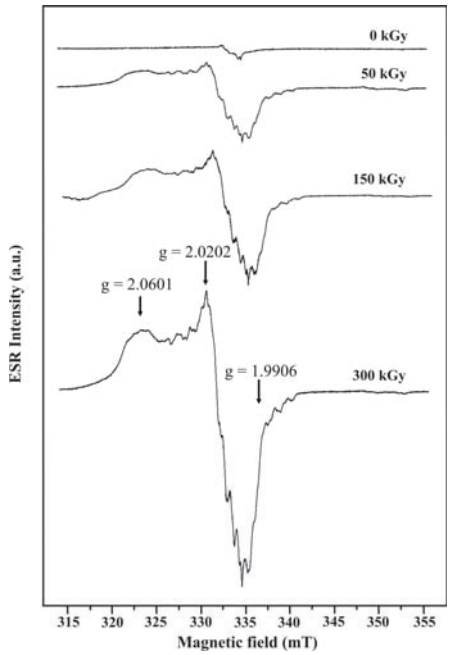

Fig. 4. The dependence of the ESR spectra of various γ-irradiated dose (i.e. 0, 50, 150, and 300 kGy) at low temperatures

The Al center could be distinctively that the ESR intensity increased with the increasing of the γ-irradiated doses observed in the magnetic fields range of 315 – 350 mT. The influence of overlapping from any defects in ESR signal range of Al center; the complex lines group, should be observed with partial peaks of 9 apparent peaks at different *g*-value from 1.9906 to 2.0202. Also at g = 2.0601, the intensity of Al center raised with doses. In the first derivative form, the ESR intensity height of each lines of Al center is measured from the top of the first peak to the bottom of the last peak. The increase of line-widths was small in comparison to the increase of its intensities and area; the multiplication of the line-width with the intensity.

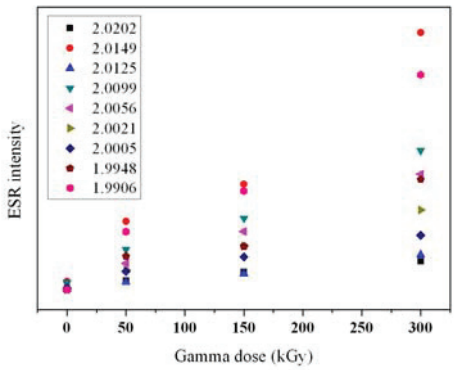

Fig. 5. The relation between the γ-irradiated dose with the intensity of each *g*-value of the Al center peaks at 120 K temperature, 10 mW microwave powers

In general, the intensity of the ESR signal increased with γ-irradiated increase while the line-width is almost kept constant. As well as in this study, the ESR signals show that continues to increase. The small increases in line-width from our results are attributed to broken bonds from Si-O network which giving g-values of approximately 2.00 as the result of high dose. The rising tendency of ESR intensity signals over the level of irradiation, especially for the peaks at *g*-value of 2.0149 and 1.9906 were showed the higher increase than the other peaks was illustrated in Fig. 5.

From the results, three types of overlapping to Al center were indentified as E_1', peroxy and OHC center, which correspond with Toyoda and Falgueres (2003) reported the overlapping of the first two centers in the region from the 7th to the12th peaks of Al center, as displayed in our results [13]. In addition, the ESR signal at g-value of 2.012, which is often called oxygen hole center (OHC), can be observed in this work. The peroxy signal at g-value of 2.067 and the Al center signal at g-value of 2.0602 were overlapping in magnetic field range of 315-325 mT. The microwave power affects the signal of E_1' center which shows high signal intensity at 0.10 mW of microwave power. While the suitable microwave power for measuring Al and OHC center are from 1.0-10 mW [2]. Even with suitable microwave power and ESR condition i.e. temperature were selected for Al defect, the lines group of Al center still can not avoid the overlapping of signals. This suggests the difficulty face in using Al center as the ESR dating.

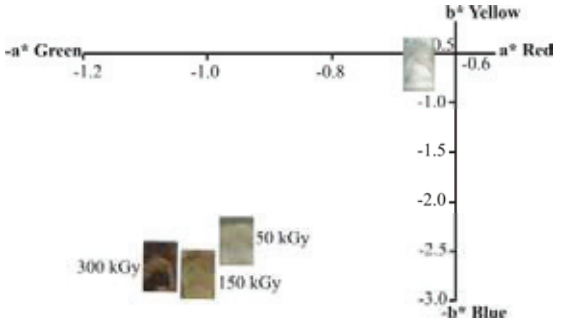

Fig. 6. The CIE L*a*b* color scale of quartz samples for different γ-irradiated doses

The γ-irradiation dose effected to the color of natural quartz samples which displayed in Fig. 6. The colors of all samples were almost colorless but the brightness, L* were decreased with higher γ-irradiation dose.

4. Results and discussion

For natural quartz samples from Zambia, the increasing ESR intensity signal of Al center was not saturated even though the gamma-irradiation dose was increased up to 300 kGy, especially for the peaks at g-value of 2.0149 and 1.9906 were showed the higher increase than the other peaks. The total area under Al center lines group was increased as a polynomial function over dose level. The signal intensity of E_1', peroxy and OHC center were observed in natural quartz with high gamma doses and theirs peaks overlapped with the ESR signal of Al center. This indicates that ESR dating determined from Al center is rather complicate and may be of confusing in some cases.

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