Artificial luminescence center of zircon irradiated with thermal neutrons

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Abstract

Single-crystals of a pure synthetic zircon and of zircons doped with each one of B, S, Al, Ca, Mn and U were grown by a flux method. Several zircons doped with P and REE (Dy, Tm, Eu and Sm) in addition to each one of the above elements were also grown. These zircons were irradiated with the thermal neutrons (neutron flux = 8×10^{13} n/cm²sec). After the irradiation, a unique type of photo-luminescence was detected in all of the Ca-, Ca-P-, B- and S-doped zircons. In the latter two zircons, a deep coloration of red-purple occurred. The zircons except for the above four did not change in the luminescence spectra and in coloration, even though the intense γ -ray radiation or nuclear fission took place in these crystals. This unique type of the luminescence may be caused from the luminescence center which was created by the charged particles such as α -particles or proton generated by Ca(n, α)Ar, B(n, α)Li and S(n, p)P nuclear reactions of doped elements. Although this luminescence center disappears after several months, it might be stabilized in the presence of REE in the zircons. This luminescence was the same type as detected in natural zircons (Type II).

Introduction

It has been already confirmed that there exist three types of photo-luminescence, so called type I, type II and type III in natural zircons (Shinno, 1986). The type I luminescence was caused by trace amounts of Dy, Eu, Sm and Tm in the zircons. The type III may be characterized by the luminescence centers of Ca, Sc and Mn with the sensitizer of P. Although the type III was also caused by the electron-hole center due to an U-P pair, the artificial center of the type III is found to diminish after several months.

The type II luminescence is somewhat different from the types I and III, and is not caused by the luminescence centers of ions and electron-hole (Shinno, 1986). The type II has characteristic nature that its intensity is nearly proportional to the geologic age of the zircon (Shinno and Hayashi, 1984). The luminescence can be bleached by heating or irradiation of UV-light, however, it was restored in the room temperature, and it was confirmed that the restoration speed of the luminescence was accelerated in

the dark room. The marked pleochroism of color and luminescence was observed in the zircons with strong type II luminescence (Shinno, 1986). All these properties of the type II luminescence have not been well understood yet.

Although the type II was successfully made in a Ca-doped zircon by the neutron irradiation (Shinno, 1986), this artificial center of the luminescence has been diminished after several months as observed in the type III. Therefore, more experiments to form the stable artificial type II luminescence are needed to clarify the properties of this luminescence.

Experimental

Single-crystals of zircons used in this study were grown by the flux method (Shinno, 1987). Trace amounts of Ca, Mn and U were doped in zircon to substitute for Zr. On the other hand, to substitute for four-coordinated Si, Al_2O_3 , S and H_3BO_3 reagents were separately added to the flux. Reagents used in the flux growth were given in Table 1. The contents of doped elements of Mn, Al, S and B in zircons could not be determined. However, U content was estimated by the fission track method. The distribution of fission tracks in the U-doped zircon was very inhomogeneous as shown in Fig. 1. The fission

TABLE 1. Reagents used in the flux growth of zircon single crystals and in the doping experiments.

Reagents	mol%	Assay	Remarks
<u>for zircon</u>			
ZrO ₂	3.0	99.99	Aldrich Chemical Co.
Li ₂ SiO ₃	3.0	99.5	Mitsuwa's Pure Chemicals
<u>for flux</u>			
Li ₂ MoO ₄	10.0	?	Katayama Chemical
MoO ₃	83.2	99.5	Nakarai Chemicals
<u>for doping (0.8 mol%)</u>			
H ₃ BO ₃		99.5	Wako Chemical Ind.
Al ₂ O ₃		?	Katayama Chemical
S		99.9999	Wako Chemical Ind.
CaCO ₃		99	Merk
Li ₃ PO ₄ 1/2H ₂ O		?	Katayama Chemical
MnC ₂ O ₄ 2H ₂ O		99.9	Wako Chemical
UO ₂ (NO ₃) ₂ 6H ₂ O		99	Mitsuwa's Pure Chemicals
MBA=KSDA			

track density on the part of crystal edges shows about 400 ppm of U (detectable also by EPMA), while the inner part of the prism-face is rather homogeneous and shows about 60ppm of U. Ca is soluble to zircon to the extent of percent (Shinno, 1986) and Ca content in the present sample was determined to be about 50ppm by EPMA.

(a)

(b)

FIG. 1. Photographs of (a) U-zircon crystal and (b) its fission tracks on muscovite detector; A, B, C and D corners in the photographs correspond to each other (prism size $AB \times AC$: 2×1.4 mm). The crystallographic c -axis of the zircon is parallel to the AC-edge. U-distribution: AB and CD edge parts = 416 ± 106 ppm, central part = 65 ± 6 ppm.

All zircons obtained were transparent single crystals and almost colorless except for the U-doped zircon* (* abbreviated to U-zircon) with a faint green color.

In addition to Ca and U, REE (here, four elements of Dy, Eu, Tm and Sm) and P were also doped to zircon. The P-doped zircons irrespective of other doped elements have the crystal shape similar to those of natural zircons with predominant prism faces.

All of the zircons were irradiated with thermal neutrons using the JRR2 or JRR4 Reactor of Japan Atomic Energy Research Institute, Tokai, Ibaraki, Japan. The thermal neutron flux was about $8 \times 10^{13} \text{ n/cm}^2 \text{ sec}$. The irradiation was done for 1 to 40 minutes.

The main types of nuclear reactions that occur due to the irradiation are shown in Table 2. The thermal neutron cross sections of the doped elements which were collected from the isotope table of the Japan Radioisotope Association are given in Table 3. It can be seen from the table 2 and 3 that Ca and B are capable of generating α -particles by the thermal neutron irradiation. If Ca and B were successfully doped to a zircon, the effect of α -radiation within the crystal would be detectable. The irradiation experiment for the crystal which contains a stable element such as Ca and B may have an greater advantage of controlling the number of α -disintegration in the crystal rather than the methods of bombarding α -particles from an outer α -sources or of doping radioactive isotopes with α -radiation. This attempt was successfully done.

Photo-luminescence measurements were performed using a microscope spectro-photometer according to Shinno (1986 and 1987). The microscope method has an advantage that a small piece of zircon crystal is enough to record the luminescence spectra. This will lower the radiation damages from the zircons activated by the neutrons.

TABLE 2. Doped elements and their main nuclear reactions in the synthetic zircons irradiated by the thermal neutrons.

Doped element	Type of decay	Nuclear reactions
non(pure) *	β , γ	$^{94}\text{Zr} (n, \gamma) ^{95}\text{Zr}$, $^{96}\text{Zr} (n, \gamma) ^{97}\text{Zr}$
B	α	$^{10}\text{B} (n, \alpha) ^7\text{Li}$, $^{11}\text{B} (n, \gamma) ^{12}\text{B}$
Al, U	β , γ	$^{27}\text{Al} (n, \gamma) ^{28}\text{Al}$, U (see below)
S	p , β	$^{32}\text{S} (n, p) ^{32}\text{P}$
Ca	α , β , γ , E C	$^{44}\text{Ca} (n, \gamma) ^{45}\text{Ca}$, $^{48}\text{Ca} (n, \alpha) ^{37}\text{Ar}$
Ca, P	α , β , γ , E C	ditto, $^{31}\text{P} (n, \gamma) ^{32}\text{P}$
Mn	β , γ	$^{55}\text{Mn} (n, \gamma) ^{56}\text{Mn}$
U	α , β	$^{235}\text{U} (n, f) f. p.$, $^{238}\text{U} (n, \gamma) ^{239}\text{U}$

* The type of decay and the reaction in the zircon are common in the above all zircons.

TABLE 3. Color and luminescence types of irradiated zircons.

Doped elem.	color	luminescence	cross section**
non(pure)	colorless	non	0.076
B	reddish purple *	type II	3813
Al, U	pale blue, no change	type III	0.21
S	reddish purple *	type II	0.3
Ca	colorless	type II	0.0025
Ca, P	colorless	type II	0.0025
Mn	pale brown, no change	type III	13.3
U	pale blue, no change	type III	577, 2.74

* Before the irradiation, B- and S-doped zircons are not colored and non-luminescent.

** Neutron cross sections are quoted from the isotope table (The Japan Radioisotope Assoc.), unit=barn

Results and discussion

A unique type of photo-luminescence was detected in all of the Ca-, Ca-P-, B- and S-doped zircons which were irradiated with thermal neutrons (Fig. 2). This photo-luminescence was identical to the type II luminescence observed in natural zircons (Shinno, 1986). It was demonstrated that the intensity of the luminescence was nearly proportional to the irradiation time of the thermal neutrons, that is to α -disintegration numbers in the zircons (Fig. 3). The color and luminescence types of synthetic zircons after the

FIG. 2. Artificial type II luminescences of B-, S- and Ca-P-zircons irradiated with thermal neutrons. The neutron flux is about 8×10^{13} n/cm² sec and 20-minute irradiation.

FIG. 3. Artificial type II luminescences of Ca-P-zircon irradiated with thermal neutrons (Neutron flux = 8×10^{13} n/cm²sec). The irradiation times are given in the figure. (1)-(4) spectra: the approximate electric field vector of the luminescence E is normal to the *c*-axis direction. When the *c*-axis rotated at an angle of 90 degrees around the excitation beam, the spectra became (5); E is parallel to the *c*-axis. The bands shifted their positions to higher wavelength.

irradiation are given in Table 3.

As the B- and S-zircons were almost colorless and non-luminescent before the irradiation as well as the pure zircon, the degree of doping these elements to the zircons may be very small. However, these zircons were colored deeply to red-purple after the irradiation. Examples of the absorption spectra of the irradiated B-zircon are given in Fig. 4. Although the anisotropic absorption was not caused extensively differing from that of natural zircons (Shinno, 1986), the B- and S-zircons showed clear reddish color in spite of the poor absorption. Judging from the absorption maximum of about 530nm in Fig. 4, the color of these zircons must not be reddish but yellowish green. These zircons may show the complementary color that corresponds to the absorption maximum. It is likely that even a small amount of B in the zircon is detectable by the coloration because of the largest neutron cross section of B (Table 3). On the other hand, it is thought that Li does not dissolve in zircon judging from that the pure zircon grown in the MoO₃-Li₂MoO₄ flux do not show any changes in color after the irradiation in spite of a large neutron cross section (945) of Li next to B.

Although the Ca- and Ca-P-zircons did not show color change after the irradiation, both zircons emitted the same type of strong luminescences (Figs. 2 and 3). Before the irradiation, these zircons had the type III luminescence with a simple broad emitting peak at 548 nm, where P simply acted as a sensitizer of the luminescence (Shinno, 1986).

FIG. 4. Absorption spectra of B-zircon oriented with C//E and C $\perp$ E. C = crystallographic c-axis, E = electric field vector of incident light.

After the irradiation, a unique luminescence with multiple bands, so called type II, was detected though very small neutron cross section of Ca. These bands changed their positions when the c-axis of the Ca-P-zircon rotated around the radiation beam under no polarizer (Fig. 3-(3) and -(5)). This unique luminescence and the changes of its band positions completely coincide with the type II of natural zircons (Shinno, 1986).

The type II luminescence was also detected in the B- and S-zircons as shown in Fig. 2, where the bands were not well resolved and had lower intensity than that of the Ca-P-zircon. The differences of the luminescence and coloration between the B- and S-zircons and the Ca-P-zircon may be attributed to the manner of replacement of doping elements, i.e. the former B and S may replace Si and the latter Ca replaces Zr in the zircon.

All of the type II luminescence formed by the irradiation disappeared after several months, although the color of the B- and S-zircons still remains unchanged for more than a year. The decay curve of the type II luminescence could not determine at the present study.

As shown in Table 2, it is found that α -particles and proton produced by the disintegration of doped elements are only in the Ca-P-, Ca-, B- and S-zircons, which can emit the type II luminescence after the irradiation of thermal neutrons. The other Al-, Mn- and U-zircons did not change in coloration and not emit any luminescences after the irradiation, even though various nuclear reactions occurred in these crystals. It is an important fact that the charged particles with energy of several MeV such as α -particle and proton can only produce the type II luminescence center. On the other hand, the prompt neutrons with several MeV accompanied with nuclear fission in the U-zircon and the thermal neutrons and γ -ray in Mn- and Al-zircons do not produce the center.

It was already reported that in ESR measurement of Ca- and Ca-P-zircons a unique signal of $g=2.0083$ (g is a factor of spectroscopic splitting in ESR) ascribed by only α -particles was detected (Shinno et al., 1986 and 1987). The intensities of this unique ESR signal and the type II luminescence were nearly proportional to the geologic age of the formation of natural zircons (Shinno & Hayashi, 1984; Taguchi et al., 1986). However, the dependence of these intensities on the number of α -disintegration in the zircons has not been measured precisely yet. The preliminary experiments were done to obtain this dependence. The type II luminescences of the Ca-P-zircons irradiated for 5, 10, 20 and 40 minutes are shown in Fig. 3. The Ca-P-zircon with the irradiation of 10 minutes contains nearly 1×10^5 of α -disintegration per mg at nuclear reaction $^{40}\text{Ca}(n, \alpha)^{37}\text{Ar}$. The linear relation between the type II luminescence intensity and α -disintegration (proportional to the irradiation time) was obtained, but the relation could not be obtained qualitatively for the gradual decay of the type II luminescence after the irradiation.

It was already confirmed that the restoration of the type II luminescence on thermally bleached zircons was accelerated in the dark room (Shinno, 1986). Therefore, the type II luminescence as well as Eu absorption in the silicate glass (Cohen and Smith, 1962) are very sensitive to UV-light. Natural zircons usually contain appreciable amounts of REE, which are usually of low photochemical oxidation-reduction potential and are usually trivalent state in the zircons (Shinno, 1986 and 1987). In the oxidation-reduction reaction: $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+} + e$, an europium (II) produced by the heating may easily transfer an electron to the luminescence center at the dark room.

To stabilize the type II luminescences, Ca-P-zircons doped with REE (Dy, Eu, Tm and Sm) were prepared and irradiated by thermal neutrons to produce the type II centers. The type II in the REE-Ca-P-zircon has been holding stably for more than one year after the irradiation.

ESR studies showed that there exist several Si-O radicals such as SiO_4^{3-} , SiO_3^{3-} and SiO_2^- in natural zircons (Marfunin, 1979). The Ca-P-zircons irradiated by the thermal neutrons may yield various radicals rather than γ -ray irradiation (Shinno et al., 1986 and 1987). It was already reported that the former irradiation produced three typical signals ($g=2.0010$, 2.0030 and 2.0083), while the latter produced the same two signals of the three. The unique signal for the former is $g=2.0083$ mentioned above. This signal was also observed in wollastonite glass and norbergite irradiated with thermal neutrons and disappeared for several months (unpublished). However, the type II luminescence just identical to that of natural zircons did occur in norbergite only (Shinno and Sugihara, 1988). These facts that the irradiation of α and p-particles with higher energy than thermal neutrons and γ -ray may produce SiO_2^- radical which is closely related to the type II luminescence and the $g=2.0083$ ESR signal. And the irradiation of thermal neutron and γ -ray may only produce SiO_4^{3-} and SiO_3^{3-} radicals which are

related to $g = 2.0010$ and 2.0030 signals and do not emit photo-luminescence.

To explain the origin of the type II luminescence of zircon, the electronic structure of various silicate radicals have been calculated by using environmental potential MPX α method (Inokuchi and Katsuki, 1987). However, it has not been found that any single radicals have energy levels emitting the type II luminescence.

These facts described above give rise a speculation that there may exist the equilibrium between the several radicals and REE (here, Eu as the representatives of REE) as follows:

The fact that natural zircons have usually the stable type II luminescence would be attributed to the equilibrium situation as shown above. And the luminescence with multiple bands may be emitted by the electron transfers between the energy levels of coexisting several radicals.

Acknowledgement—We thank Profs. M. Hayashi of Kyusyu University and S. Taguchi of Fukuoka University who gave us much information about natural zircons and the detection of fission tracks of U-zircon.

For the experiments of neutron irradiation, we are very indebted to the staffs of National Universitys' Laboratory for the common use of Japan Atomic Energy Research Institute. A part of the expense of this study was defrayed by the Scientific Grant-in-Aid from the Ministry of Education, Science and Culture of Japan.

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Received September 14, 1988; revised November 17, 1988.