THERMOLUMINESCENT SPECTRUM CHANGES OF NATURAL QUARTZES DEPENDENT ON ANNEALING TREATMENT AND ALUMINUM-CONTENTS

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Abstract - Both of fused and annealed natural quartzes were spectroscopically analyzed by using the IPDA (intensified photodiode array) on-line spectrometric system for measuring 3-dimensional thermoluminescence (TL) glow-curves. A remarkable change of TL property from red to blue occurred after the transformation to fused quartz glass. The TL properties were also searched after thermally annealing treatment for 100 h at 1100 °C. Apparently different changes of TL-colorations were found to occur even within a Z-cut slice from a single quartz crystal; the original blue-TL quartz segments with higher Al-contents than about 100 ppm are readily changeable into red-TL color after the thermal annealing, presumably in cooperation with other impurities. Accordingly, the existence of Al-O-Al and/or Al-O-Si bond in natural quartz has been tentatively considered to play an important role of red-TL color at high temperature.

Key words - thermoluminescence, on-line spectroscopy, quartz sands, quartz crystal, glass, annealing, aluminum

The thermoluminescence color image (TLCI) technique, developed by the authors[1-4], has yielded meaningful results, in which a noticeable finding was of two different color images, distinguishable readily to red- and blue-TL emitting grains. These findings have brought some fruitful results in revealing the petrogenesis, mineralization process and the microcomposition of quartzes of different origins as well as in the establishment of the reliable quartz inclusion TL-dating using red-region TL measurements[5-7]. For the purpose of clarifying the causes of different TL colorations, an 3-dimensional on-line TL spectroscopic analysis, has been also developed by using image intensified unit (IPDA system) coupled to photodiode array reader because of known weak TL emission. Some annealed quartz pieces cut from a quartz crystal showed interesting color changes from blue- to red-TL. These results have been implied to be intimately correlated to the different coloration of TL with the content of Al-impurity

EXPERIMENTAL

1. TLCI and three dimensional TL spectrometry

The irradiated sample (normally 8.7 kGy) was placed on a heater controlled at a linear rate of 1 °C/sec. The TLCI was taken at any desired temperature interval by programming on a personal computer[1-3]. The color films were the commercially available high-sensitive film (ASA-1600)[4]. In more quantitative TL spectrometric analysis, an IPDA (abbreviated from Intensified Photo-Diode Array) on-line spectrophotometric system for the observation of 3-dimensional TL glow-curves (say, TL intensity, wave length and measuring time (or temperature)) has been developed. This IPDA system consisting of two main units, a heater control unit and a photon detection one, will be described in more detail elsewhere.

2. Determination of Al-contents by INAA

Natural quartz grains of about 50 mg and the slice piece samples of about 5-10 mg were sealed in the polyethylene bags. The neutron irradiation was performed at a thermal column pneumatic transfer tube in Kyoto University Research Reactor. In this facility, the purest thermal neutron was provided as the following neutron bombardment conditions; the ratio of thermal neutrons to

fast ones amounts up to 1000. Therefore, the formation of ^{28}Al due to $^{28}\text{Si}(n,p)^{28}\text{Al}$ reaction by fast neutrons was suppressed to be negligible small. After 5-8 min irradiation, the γ -rays of activated samples were measured for 200 sec with a pure Ge detector having 150 cc effective volume (ORTEC) connected to multi-channel analyzer (SEIKO EG&G, NAIG) within 3 min.

RESULTS AND DISCUSSION

1. TL properties from natural quartzes

The 3-dimensional glow-curves from three kinds of typical original quartz samples selected from different origins are presented in Fig.1-(a)-(c). It is evident in (a) derived from volcanic ash origin, that an intense broad emission band appears at high temperature (nearly at 330 °C) in the range of long-wavelength, corresponding to red color region. The maximum point is of 615 nm nearly at 330 °C. On the other hand, the hydrothermal quartz (b) shows a broad emission band in blue color region about 486 nm, nearly at 220 °C. From the quartz (c) of pegmatite origin, an intense band and a weak one in the range of blue region, appear around 200 °C, 320 °C respectively, together with a small band in red color region nearly at 608 nm at higher temperature. All these 3-dimensional glow-curves are in good agreement with the TLCI results[2].

Fig.1 Typical 3-dimensional TL glow-curves from original natural quartzes.

The samples from (a) Tazawa lake quartz (volcanic ash origin), (b) Madagascar quartz (hydrothermal origin) and (c) Ishikawa quartz (pegmatite origin) are used. Each sample was exposed to total dose of 8.7 kGy with X-ray for 200 sec.

The fused quartz glasses were also prepared from the same three natural quartz grains by heating beyond 1500 °C to melt completely the quartz. The fused glass from originally red-TL quartz grains showed mostly blue and partially yellow-green coloration. Both TL patterns of fused glasses from Madagascar (hydrothermal) and Ishikawa (pegmatite) quartzes certainly

2. Changes of TL properties on annealing treatment

As mentioned above, it was suggested that the annealing treatment (below 1500 °C) of quartzes should cause any changes of crystal structure affected to TL properties. Fig.2-(a),(b),(c), show the results of 3-dimensional glow-curves after annealing treatment (100 h at 1100 °C) on three typical quartz grains, same as used in Fig.1-(a). (b). (c)

Fig.2 Changes of 3-dimensional TL glow-curves after annealing treatment for 100 h at 1100 °C.

The samples from (a) Tazawa lake quartz, (b) Madagascar quartz and (c) Ishikawa quartz are used. Each sample was exposed with X-ray for 200 sec.

Tazawa lake sands (a) after the annealing treatment demonstrate mostly an intense broad peak in the blue region in addition to the weak original red TL as expected from their fused silica. On the other hand, annealed Madagascar quartz sample (b) displays unexpectedly two different colorations, namely bearing blue- and strong red-TL broad peaks nearly at 486 and 615 nm, respectively, at 320-330 °C along with apparent increase of TL intensity. Annealed Ishikawa quartz (c) shows similar tendency to the hydrothermal quartz; TL intensity remarkably increases up to about several to several-tenth folds and two intense broad bands, having peaks around at 486 and 615 nm, emerge at 320-330 °C. It is noteworthy that the original quartz grains having blue TL coloration cause unexpected change of TL colorations towards red region together with remarkable enhancement of TL intensity after annealing treatment.

On the basis of these results, some pieces of Madagascar Z-cut slices were utilized for further studies. Fig.3-(a), (b) show 3-dimensional glow-curves from Madagascar Z-cut pieces after annealing treatments. Fig.3-(a) containing lower Al-contents (48 ppm), shows a noticeable increment of TL intensity over the whole blue color region peaked nearly at 486 nm around 320-330 °C, whereas Fig.3-(b), containing higher Al-contents (109 ppm), emerges predominantly intense band in red color region (615 nm) at higher temperature around 320-330 °C.

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Fig.3 Comparison of 3-dimensional TL glow-curves from Madagascar Z-cut quartz pieces after annealing treatment. Aluminum content of sample (a) No.14 and (b) No.10 are determined to be 48 and 109 ppm, respectively, by INAA.

In the TLCL observation, some annealed segments of Z-cut slice displayed distinct increment of blue-TL intensity, while others alternatively displayed red TL coloration as mentioned above, despite of originally blue TL emission of unannealed pieces over the whole TL measuring temperature. It also implies that the conversion of blue one into red coloration occurs when the relatively weak blue emission appears in the original quartz pieces. Combining some of TLCL results with Al-contents, it is plausible that Z-cut pieces containing greater than about 100 ppm of Al-impurity are changeable from original blue one into red TL coloration after annealing treatment. These results are well consistent with the fact that all of the naturally occurring red TL quartz grains, which were assumed to be formed as high quartz or β quartz, always contained higher than 100 ppm of Al-impurity.

Combining the report by Speit et al.[8] with the present results, it is reasonable assumption that Al-O-Al centers should exist in quartz samples containing Al-impurities greater than 100 ppm. These centers also offer blue TL-centers in the original quartzes from hydrothermal origin. They might have weak blue TL properties rather than the Al-O-Si bonds, which are considered to become main blue TL centers after irradiation. Thus, the blue TL-intensity might be negatively correlated with the aluminium concentrations. However once these centers of Al-O-Al are suffered by annealing treatment, they can be readily dissociated to their bonding structure because of their large distortion in comparison with the ordinal Si-O-Si and Al-O-Si bonds. The newly appeared bond structure in the vicinity of Al-O-Al-O is considered to operate as red TL centers. Thus, the changes of TL coloration could be tentatively explained without any contradictions before and after the thermal annealing treatments, together with the different TL colorations in the natural quartzes from distinct origins.

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