INVESTIGATIONS ON IRRADIATION AND STRUCTURAL CHARACTERISTICS OF HIGH QUALITY CULTURED QUARTZ CRYSTALS USED IN SATELLITE COMMUNICATION

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Abstract

Quartz crystals are important components in frequency standards used in space communications. Radiation effects therefore become important because the crystals undergo a frequency change. Majority of frequency effects are known due to impurity related defect and their radiation induced modifications. Premium *Q* quartz from Sawyer Applied Research Products and Supreme *Q* quartz from Toyo Communications Company, Kawasaki, Japan are the grades of commercially available high Q quartz used for high precision application such as in satellite-borne frequency standards in communication systems. This paper reports our investigations on theroluminescence, cathodoluminescence and paramagnetic defects in such crystals.

1. Introduction

Crystalline quartz is one of those materials which have received attention of numerous investigators from different branches of science and engineering for a long time. It continues to be the material of current technological importance. As one of most abundant and purest minerals in the earth's crust coupled with its stable structure, thermoluminescence (TL) and electron spin resonance (ESR) in quartz crystals have long been used as for dating of rocks, radiation dosimetry and related issues.

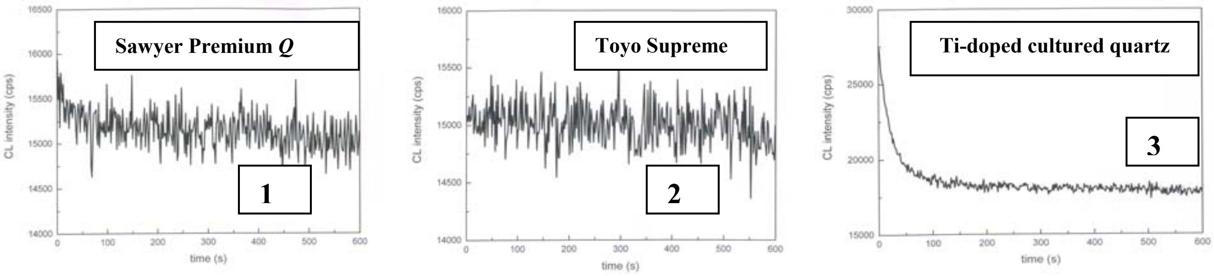
Premium *Q* quartz from Sawyer Applied Research Products and Supreme *Q* quartz from Toyo Communications Company, Kawasaki, Japan are the grades of commercially available high Q quartz used for high precision application such as in satellite-borne frequency standards in communication systems. These two grades of quartz crystals have been investigated extensively for their radiation induced modifications of point defects and associated frequency changes by Oklahoma group[1-4].These crystals have almost identical mechanical *Q* and aluminum concentration[3]. While the Premium *Q* grade material has all the aluminium charge compensated by Li^+ ion, the Supreme *Q* material is grown in NaOH or Na_2CO_3 rich solution with any Li salt so that almost all the aluminium becomes charge compensated by Na^+ ions[3]. Natural quartz is almost always used as a starting material in hydrothermal synthesis of high quality cultured quartz[5]. Therefore, some of the impurities in cultured quartz get transported from the source material, i.e. natural quartz. Other than Al^{3+}, Ge, Ti, and also Fe are among the other common impurities in quartz which replace the substitutional Si^{4+}.

When irradiated, the impurity-related point defects in quartz undergo a radiation-induced modification. Some of these defects exhibit many observable effects. There are still many complex and unresolved issues on the defect structures of impurity-related defect centers in quartz. The complexity arises due to several factors such as; mixed ionic and covalent character of Si-O bands, wide energy band gap which gives rise to several localized levels within the band gap which act as electron traps, presence of open channels along the growth directions where a variety of interstitial impurities can reside. When exposed to ionizing radiations, electron and hole pairs are generated which move across the band gap. In the course of their movement, when they recombine and if the recombination takes place near aluminum, the energy of recombination is transferred to the interstitial charge compensator which consequently moves away from the aluminum. As a result, a hole is trapped at the aluminum site in the non-bonding p-orbital of one of the four oxygen atoms surrounding the substitutional aluminum. Thus, $[AlO_4]^0$ –centers are formed. At the same time, protons from some of the still unidentified sites drifts towards aluminum to compensate the electron-excess charge of aluminum and form $[Al0_4/H^+]^0$. Thus, irradiation breaks up the $[AlO_4/M^+]^0$ centers into a mixture of $[AlO_4]^0$ and $[Al0_4/H^+]^0$. Upon thermal annealing, the emission of light occurs due to charge recombination at either aluminum centers or any other impurity. A number of TL peaks are thus observed in the temperature range 70-700 K.

The high purity cultured quartz crystals show a thermally stimulated luminescence (TSL) peaks at 110°C, and 325°C. The peak at 110°C is also known as optically stimulated luminescence (OSL) peak used for measuring radiation doses[6]. These two peaks arise from the same defect pairs and emit different luminescence but through different mechanisms. While the peak at 110°C is known to be due electron-hole recombination at the $[AlO_4]^0$-hole centers, the peak at 325°C is related to migration of alkali ions. Bahadur[7]has recently attributed a TSL peak at 200 °C in Ge-doped cultured quartz to the presence of Ge centers. The present work shows a glow-peak at 275 °C is due to presence of Ti in quartz crystals.

In the present work, we report our results on radiation effects on thermoluminescence (TL) and cathodoluminescence (CL) and ESR investigations on Premium Q/Supreme Q and Ti-doped cultured quartz crystals grown at Bell Laboratories, Murray Hill, NJ. While the low temperature (80 K) CL investigations have been found to exhibit nearly identical characteristics in terms of the spectra and decay in the intensity versus time characteristics, the room temperature CL and TL characteristics above room temperature have shown a difference. Irradiation at room temperature was done with a dose of 400 Gy and 10 kGy. The characteristics TL glow curves for Ge and Ti impurities have been looked for. The Premium Q material after irradiation with 400 Gy showed peaks at 110°C, 200°C and 275°C. While the peak at 110°C is the characteristic peak, the peak at 200°C is Ge-related[6] and the present work shows that the 275°C peak is related to presence of Ti in quartz. For TL investigations thermal images, the glow curves and the associated spectra were measured. CL spectral measurements were carried out on a JEOL JSM-5410LV scanning electron microscope (SEM) equipped with an Oxford Instruments MonoCL2 cathodoluminescence spectral analysis system. The techniques have been described in detail elsewhere[8]

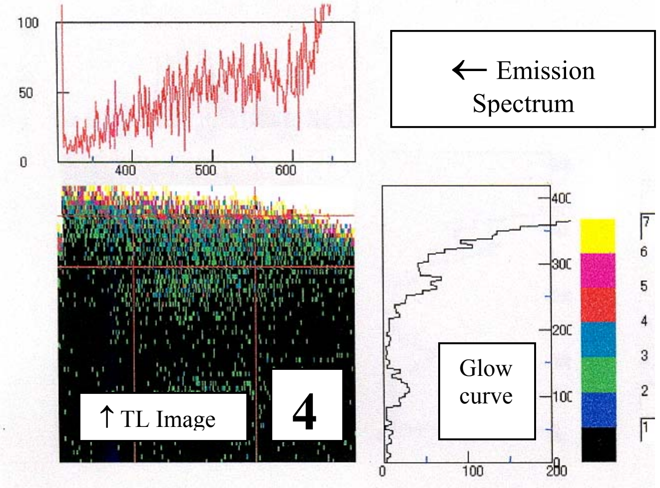
The CL images for Premium *Q* and Supreme *Q* materials were nearly identical in both the cases showing that the impurity distribution was uniform in both types of crystals. The blue band intensity (at ~ 425 cm) observed at room temperature in Premium *Q* sample was about 50 % more than in Supreme *Q* quartz. The CL intensity was observed upon room temperature irradiation as a function of continued irradiation (15 KeV, 20 mA) up to 10 minutes showed that for initial 100 sec, the decay was faster for Premium *Q* crystal than the Supreme *Q* material (Figures 1 and 2). This shows more Li ions at the aluminum sites. The sharp decay of the blue band emission spectrum in the case of Ti-doped crystal (Figure 3) shows that the defect responsible for contains more $Al\text{-}OH^-$ than either of the two other crystals. The Ti-doped crystal has about 20 ppm of Al in comparison with the Premium *Q*/Supreme *Q* materials which have Al of the order of 5 ppm. Also, since the Ti-doped crystal was a much faster grown material, it was found to have higher intensity of as-grown hydroxyl defects compared to the other two types of crystals.

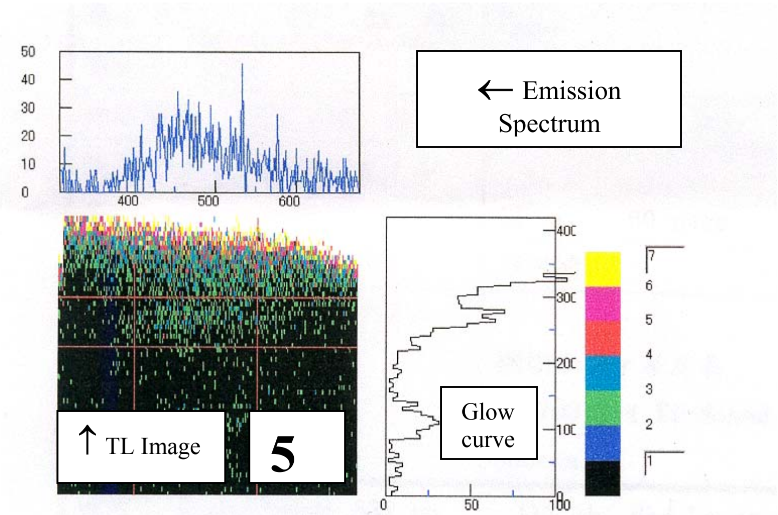


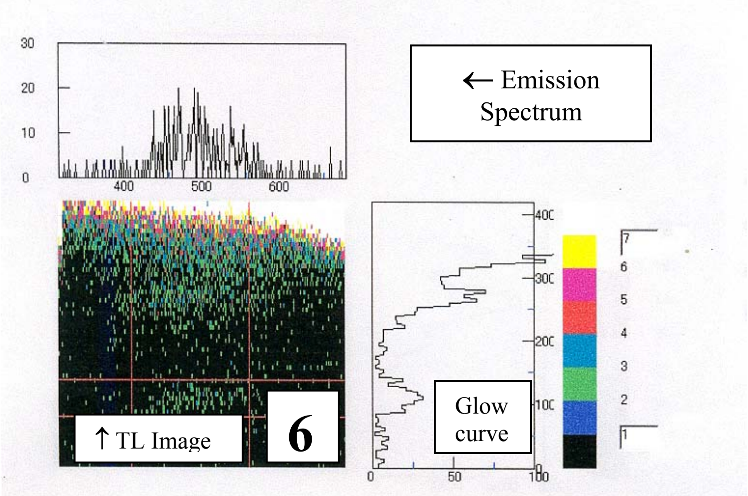
Figures 1-3: Irradiation versus time characteristics for the blue band emission of [1] Sawyer Premium Q quartz, [2] Toyo Supreme Q quartz and [3] Ti-doped cultured quartz

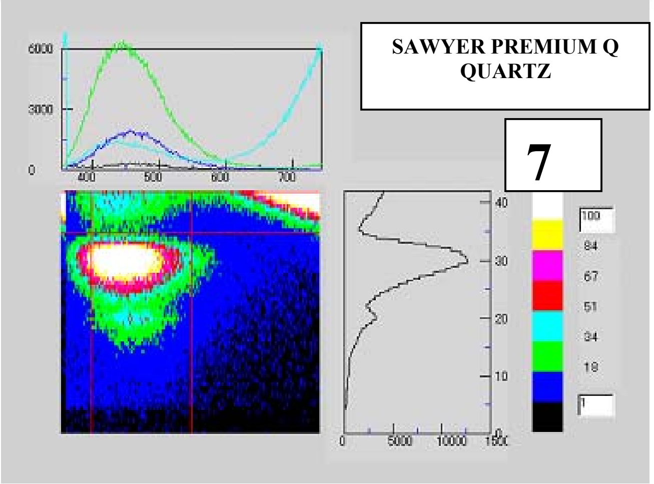
Figures 4-6 show a set of the thermal images, glow curve and emission spectra of the Ti-doped quartz grown at Bell Laboratories after it was irradiated with a dose of 400 Gy. Figure 7 represents such information for a Sawyer Premium *Q* and Figure 8 and 9 for the Toyo Supreme *Q* grades of quartz materials. The irradiation was done at 300 K using the ^{60}Co facility of Takasaki Research Institute of Japan Atomic Energy Research Institute.

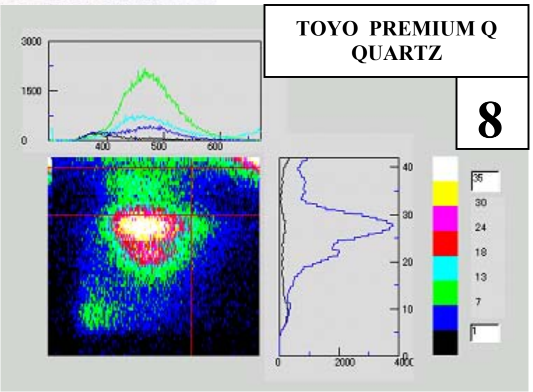
In conclusion, our present work on irradiation studies in Ti-doped, Premium *Q* and Supreme **Q** quartz suggest the following.











Figures 4-6: Thermal image, Glow curves and spectral emissions for a Ti-doped cultured quartz .

Figures 7-8: Thermal image, Glow curves and spectral emissions Sawyer Premium Q and Toyo Supreme Q cultured quartz crystals.

1. A TL glow peak at 275°C is due to the presence of Ti as an impurity in quartz as noticed in the Ti-doped cultured quartz. This peak has been observed by earlier investigators in natural quartz but no assignment was possible at that time due to the specific impurity.
2. Based on this observation, the study on Premium *Q* and Supreme *Q* quartz suggest that while both the crystals in addition to Al, have Ge and Ti as impurities present in much lower concentrations than Al. However, present results also suggest that while Ti is present in higher concentration in Supreme *Q* material than the Premium *Q* material. Since Brazilian or Arkansas quartz is used as the starting material for the growth of its most grades of Sawyer cultured quartz, it is probably possible that natural quartz, in the these terrains has more of Ge than in Japan which seem to have more Ti than in Brazil / US. Further work in this direction is necessary.
3. Dependence of CL spectral blue band as a function of irradiation dose at room temperature suggests that there are more Al-centers in Ti-doped quartz are compensated with Li ions than in either Premium *Q* or Supreme *Q* quartz. This is perhaps due to higher concentration of Al in the former.

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