Measurements of radiation induced defects in quartz material by Dielectric Relaxation Spectroscopy

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***Abstract*— this paper presents the continuation of the results obtained in the R&D study initiated by the Centre National d'Etudes Spatiales (CNES) and presented during the last Frequency Control Symposium in 2006. This concerns more particularly the characterization of the defects in quartz material by using the Dielectric Relaxation Spectroscopy technique. Five different kinds (4 synthetic and one natural) of quartz material have been investigated. DRS measurements have been performed before and after three different irradiation doses (100krad, 1Mrad and 10Mrad). The irradiation exposure yields in all cases the defects in the materials more instable. No dose level effect has been established. An annealing process (450°C during 24hours) after irradiation cures to the damages produced in the quartz material by the irradiation dose.**

I. INTRODUCTION

For several years, defects induced by irradiation in quartz crystals are studied to solve the problem of frequency stability of piezoelectric devices in space environment (essentially proton radiation). To reproduce this space environment, the authors have compared the effects of gamma and proton radiations. [1-3]. They concluded that the effects of gamma and proton radiations are equivalent in terms of piezoelectric performances. The mechanism responsible for the frequency variations is due to ionisation effects enhanced by the impurity content in the quartz crystals. To characterize the chemical defects of the material a lot of techniques of investigation have usually been used like infrared absorption, thermal luminescence or thermal acoustic losses coupled to a chemical analysis of material like Inductive Coupled Plasma. It is well known that the principal defects in the as-grown cultured quartz are:

- the substitutional aluminium associated with an interstitial monovalent cation (Li^+, Na^+ or K^+) to form an Al-M^+ center.
- and –OH groups formed during the hydrothermal crystal growth process.

All the authors agreed on the mechanism of interaction between radiation and the material. When a resonator is irradiated with protons or gamma radiations electron-holes pairs are created in the material. These defects interact with the initial impurities modifying the local arrangement of the crystalline structure. The monovalent cation of the Al-M^+ centers is replaced by H^+ to form Al-OH^- or Al-hole centers. The large acoustic loss peak near 50K has been attributed to the effect of the irradiation of the Al-Na^+ center [4]. The migration of the free monovalent cations through the crystalline z-channels modifies the elastic modulus of the material implying frequency shifts of the piezoelectric resonator [5]. In fact, the [AlO_4] tetrahedron is distorted creating two different crystallographic sites currently named α and β [6-8]. By using low-temperature dielectric relaxation technique authors [9, 10] have measured the effect of the annealing on these two Al-Na peaks. The role of aluminium content has also been investigated by using the Electron Spin Resonance technique [11].

This paper relates the measurements of radiation induced defects in quartz material by using the Dielectric Relaxation Spectroscopy technique.

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II. DRS MEASUREMENTS – RESULTS AND DISCUSSION

A. Experimental

1) Materials

Five different kinds of quartz material have been chosen: one Natural quartz quality (noted N) and synthetic quartz issued from four producers including the French one, GEMMA. From our knowledge all these materials are as grown quality, and no sweeping process has been performed on these materials. Samples with the SC orientation have been cut in each material. The plates are plane and polished.

2) DRS technique

The ionic displacements are evaluated by measuring the temperature evolution of the imaginary part of dielectric permittivity ε”, with a Broadband Dielectric Spectrometer Novocontrol (figure 1), for an applied ac electric field at fixed frequency (f=0.02Hz). The quartz samples are inserted between two PTFE blocking electrodes.

Figure 1. Novocontrol Alpha Dielectric Analyser

3) Irradiation source

Radiation effects responsible of frequency shift on space USO are essentially caused by proton radiations present in the Van Allen belt round the earth. Based on previous works, showing that gammas elsewhere protons induced effects on piezoelectric properties of quartz material are similar, gammas ^{60}Co radiations have been chosen to reproduce the space proton radiation. On another hand, a pre-irradiation of quartz resonators with a dose level of 20 to 30krad reduces the frequency shift on board [12]. In our study, to enhance the phenomena in quartz material, we decided to apply three high levels of radiation doses (100kard, 1Mrad and 10Mrad).

B. Results and discussion

1) Before irradiation

The dielectric losses ε”(T) have been measured on the five quartz materials before any irradiation (figure 2). The peaks observed before 200°C correspond to the relaxation phenomenon of the impurities in the material. Indeed, in this temperature range, previous works have demonstrated that this energy (0,6 to 1,3eV) causes the relaxation of the alkali ions in the quartz material [13, 14]. Higher is the temperature of the relaxation peak more stable are the defects in the material. The chemical defects in the natural quartz quality relax easier than those of synthetics quartz. They are less trapped in the natural quartz material. We can separate these two classes of quartz quality with an arbitrary reference of relaxation temperature fixed at 100°C:

- before 100°C: the defects relax easily and the quartz quality is a natural like quality
- after 100°C, the chemical defects become more stable and the behaviour is that of a synthetic like quality.

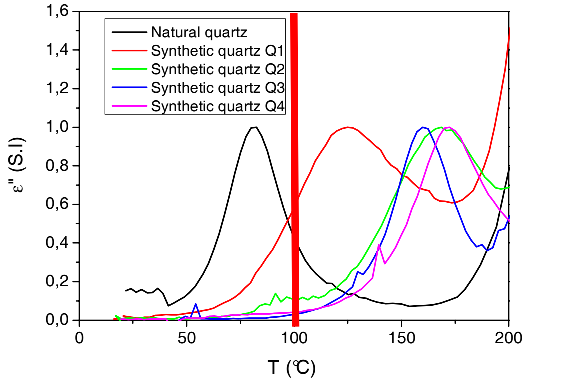
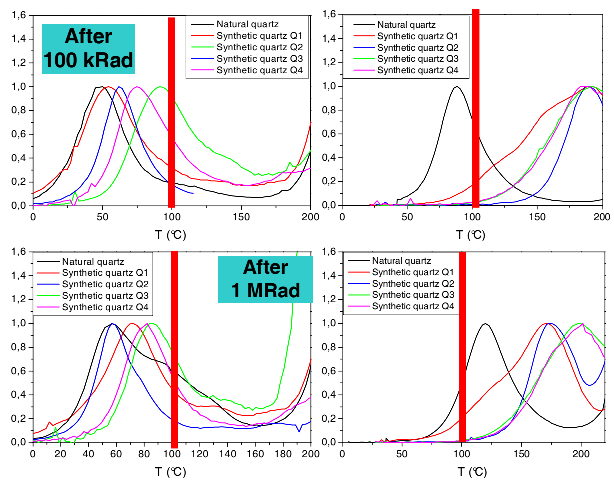
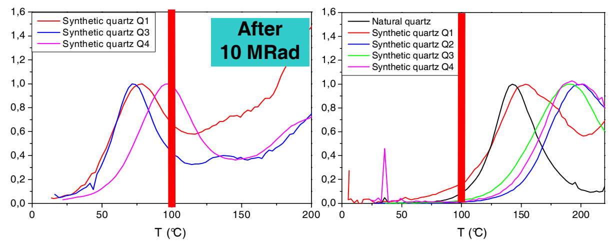


Figure 2. Relaxation peaks before irradiations

2) After irradiations and annealing treatment

In all cases, whatever the dose and the quartz origin, the irradiations destabilize the chemical defects. The temperatures of all the relaxation peaks become inferior to 100°C. The natural quartz quality reminds the worst but for the synthetic quartz qualities, the chemical defects are drastically destabilized.





(a) (b)

Figure 3. Relaxation peaks after irradiations (a) and after annealing treatment (b)

Annealing at high temperature is often used to relax the strain in the materials. This technique is also used to produce the migration of impurities (sweeping treatment). In this case, the temperature plays the rule of stabilizing agent by favouring the recombination of the chemical defects created by the irradiation. It could produce the migration of monovalent cations towards the electronic-hole centres created by irradiation in order to compensate the charge defect. Nevertheless, annealing at 450°C during 24 hours is a good process to make the chemical defects in quartz more stable. The temperature of the maximum (Tmax) of the relaxation peak becomes even higher than the Tmax of the relaxation peak before irradiation (figure 4). This behaviour is the same for all irradiation doses greater than 100krad.

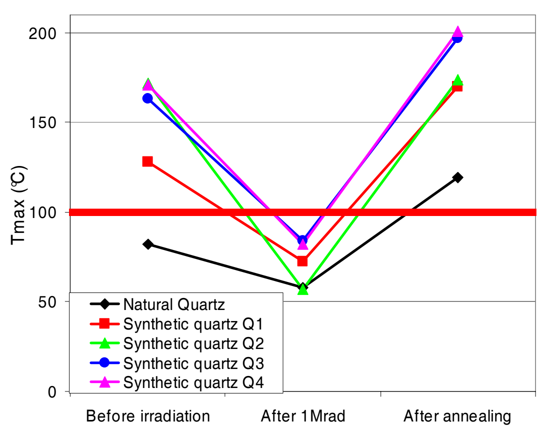


Figure 4. Evolution of the Tmax of the relaxation peak for an irradiation dose of 1MRad.

These results demonstrate that chemical defects in quartz (Al-substituting, alkali ions or hydroxyl groups) are potential source of instability of quartz material when it is submitted to space radiations.

III. CONCLUSION

The Dielectric Relaxation Spectroscopy is a powerful technique to investigate the irradiation effects in quartz material. The results show that an irradiation dose greater than 100krad is a saturation level for the excitation of the chemical defects in the material. From an application point of view, this paper proves that a pre-irradiation with a dose greater than 100kRad following by an annealing treatment can improve the stability of the defects in quartz material. For instance, these defects are not clearly identified but we suggest that they depend strongly on the presence of alkali ions. These two operations could consist of a pre-conditioning process for the quartz-resonators for space applications. Another way of improvement is to use swept material for which the alkali ions are nearly all removed. This study has to be undertaken from different swept quartz materials (air-swept, vacuum-swept or H_2-swept quartz qualities). However, the best way of improvement would be to optimize the crystal growth conditions to control very accurately the chemical defects creation. Remove all the Al impurities would be a very important optimization of the material. The swept quartz quality produced by the French producer GEMMA is already of a very good quality while the Al content is no more than 3ppm and the total alkali content is no greater than 1ppm.

IV. ACKNOWLEDGMENT

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