TSL and fractional glow study of Ge-doped α-quartz.

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Abstract. Crystalline α-quartz doped with 0.1wt% and 0.9wt% germanium was studied using TSL and FGT equipment. Sample was chosen because previously it is known that Ge in quartz is efficient trap for electrons, therefore it could be used for detection of hypothetic self-trapped hole in α-quartz. However previous investigations of ODMR and TSL shows that in α-quartz the hole is still mobile and trapping occurs only on defect states. The activation energies for both TSL peaks are found by fractional glow and Hoogenstraaten method. The TSL distribution changes depending on Ge concentration and also on irradiation type. The TSL peaks below 70K in quartz doped with Ge could belong to hole trapped on Ge.

1. Introduction
The Ge center in α-quartz is described by several researchers [1 – 8] and the thermostimulated luminescence (TSL) was also observed [7, 8]. However the formation of the excited states responsible for TSL is not clear. On the one hand is known that in Ge doped α-quartz efficient electron trapping takes place at low temperatures [4, 5]. On the other hand, there must be traps for holes also since TSL was observed. However the evidence is that the hole in α-quartz remains mobile even at low temperatures and could be trapped only on defects [6, 7]. Since only one kind of dopant namely Ge is incorporated, it is not known if it is responsible for trapping electrons or holes. Additional information for understanding these processes is needed. Therefore we modified our equipment so that two different thermostimulated methods – classical TSL and fractioned glow technique (FGT) – could be used and, additionally, the luminescence spectra of glow peaks could be monitored. The testing of the modified equipment showed that the TSL peaks of Ge-doped α-quartz can be well reproduced and are very close to those described in [7] Additionally, the thermal activation energies were extracted from FGT results. These experimental data were used for clearing up some details of thermostimulated recombination in Ge doped α-quartz.

2. Samples and methods

2.1. Samples
The investigated samples were 0.1 wt.% and 0.9 wt.% Ge-doped synthetic crystalline α-quartz, grown by hydrothermal method. To achieve good thermal contact, samples were polished and pressed between two copper plates with holes in the centre for irradiation and luminescence measurement. The temperature was measured by a transducer diode fastened to these copper plates.

2.2. Equipment
The TSL measurement equipment consists of sample irradiation source, temperature control and luminescence measurement units. For the sample irradiation at low temperature two different sources

were used: the X-ray tube with W target operating at 40 kV, 10 mA and 7.9 eV F_2 laser (PSX-100-2) with pulse energy 0.5 mJ and pulse duration 5 ns. The luminescence spectra were recorded with spectrometer (Andor Shamrock B303-I) coupled with a CCD camera (Andor DU- 401A-BV) at exit port. The 150 lines per inch grating covered 295-865 nm spectral range in one measurement. This allowed measuring both TSL intensity and spectral distribution at each temperature point. For temperature control, the closed-cycle helium cryostat (Sumitomo HC-4) with temperature controlling unit (Lakeshore 331) was used. The temperature control range was 8-300K. All controlling devices, as well as data acquiring devices were connected to a PC and controlled using various TSL/FGT programs (ISSP UL).

2.3. TSL and FGT methods
For TSL measurements, the classic TSL method was applied: irradiation at low temperature followed by heating with a constant heating rate and monitoring of luminescence in dependence of temperature. For determination of activation energies 2 methods were used – initial rise method [9] and Hoogenstraaten method [10]. For the first method, only a fraction of a total glow is required, which leads to a non-linear temperature change, while the second method is based on the peak shifts resulting from different heating rates in classic TSL.

3. Results and discussion

First of all, the classic TSL was measured and the result obtained was compared with that found in [7]. Two TSL glow-curve peaks were observed at 51K and 75K (β=0.1 K/s, X-ray), which coincide well with the previous observations [7]. In addition, we measured TSL glow-curve when the sample was excited with UV laser. Results are shown in Fig.1. Excitation with UV laser resulted in a peak shift to higher temperatures, and the shift of a first peak is greater, than that of the second, so this process can not be related to a heating rate difference (remained constant) or temperature inaccuracy of any kind. Also, when exciting with UV laser with longer wavelength (266 nm), the second peak is lower in comparison to the first, compared to the case of the 157 nm excitation. Under X-ray irradiation at 8 K the luminescence intensity increases and reaches saturation after 20 min. To verify the impact of irradiation dose, an experiment with two different irradiation doses were made (5 min and 60 min). The irradiation time increased the TSL intensity; however the irradiation time/dose neither had an impact on peak positions nor on the peak ratio Fig.2. (inserted graph).
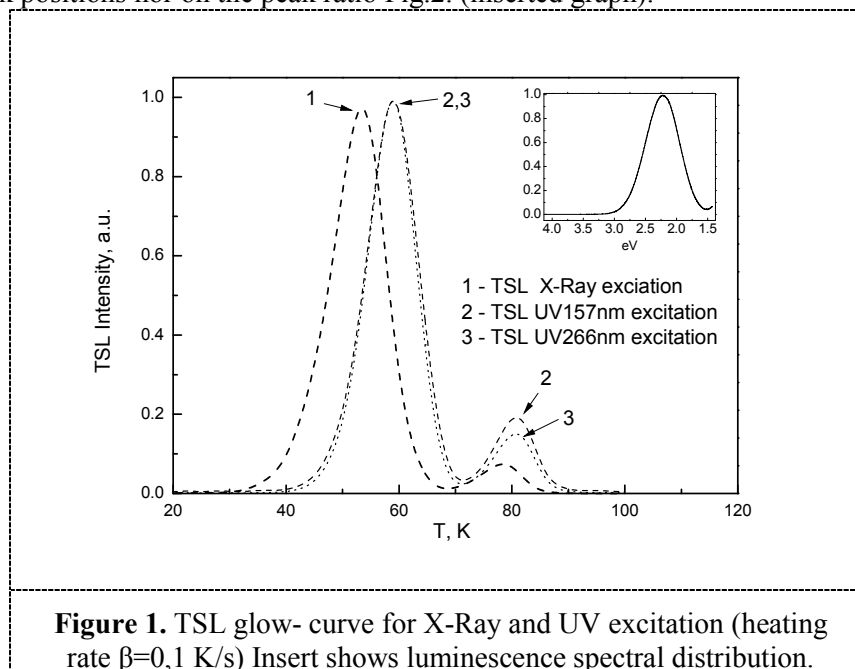

Figure 1. TSL glow- curve for X-Ray and UV excitation (heating rate β=0,1 K/s) Insert shows luminescence spectral distribution.

The luminescence spectra for all excitations are the same (Fig1. insert). Moreover, the photoluminescence and cathodoluminescence spectra measured at 8 K are the similar too, indicating that the recombination center in all cases is the same, however, the traps differ. Previously the TSL peaks were associated with Ge luminescence center which corresponds to self-trapped exciton (STE) on Ge and is found in Ge-doped samples. We verified that the luminescence spectral properties are the same in two samples with different Ge concentrations, however TSL spectra slightly differs, especially the intensity and position of second TSL peak.
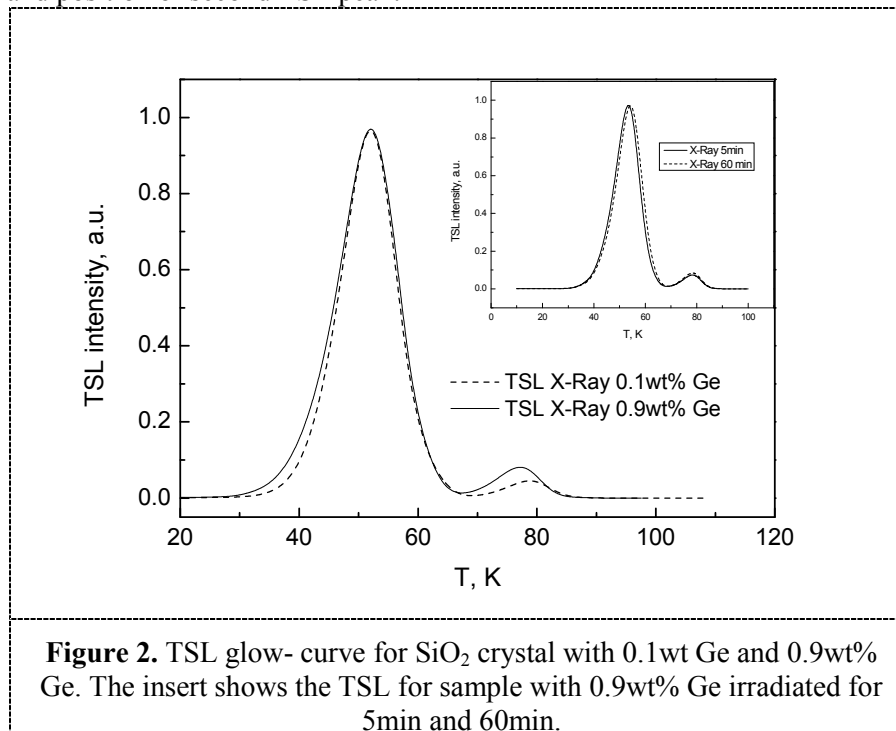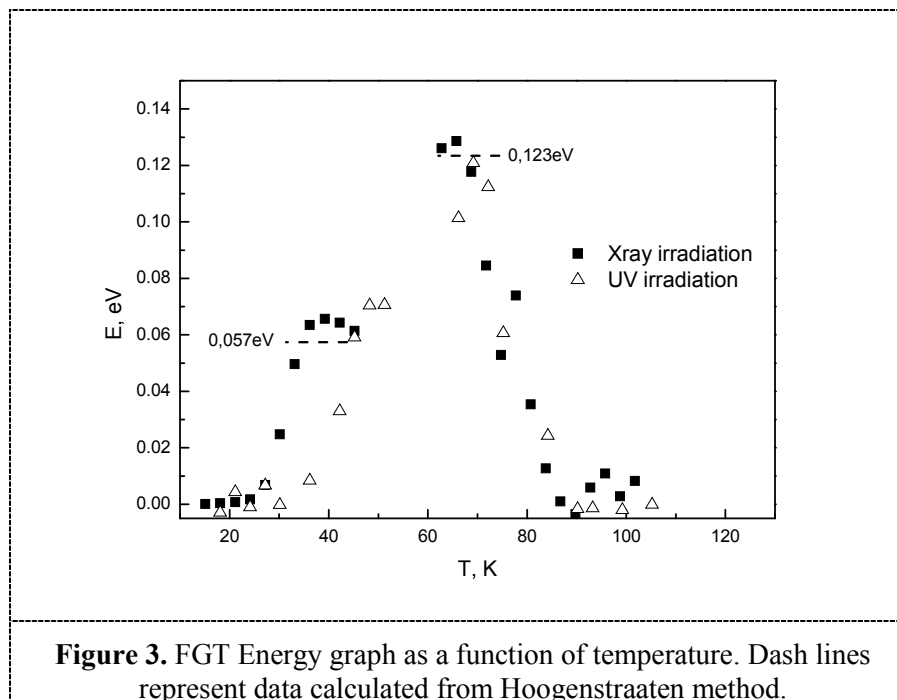

Figure 2. TSL glow- curve for SiO_2 crystal with 0.1wt Ge and 0.9wt% Ge. The insert shows the TSL for sample with 0.9wt% Ge irradiated for 5min and 60min.

As expected, the luminescence intensity increased with increase of the Ge doping concentration. The first TSL peak was similar for both samples; however, the second was slightly different (Fig.2). The ratio between the intensities of the first and second TSL peaks (after X-ray irradiation) for sample with 0.1wt% Ge was 25, but for sample with 0.9 wt% Ge the ratio was 11. With the decrease of Ge concentration the second peak decreases. The TSL peaks obtained under UV irradiation shows opposite dependence. The second TSL peak is even more intense and the respective intensity ratios were found 5 for 0.9 wt% Ge and 1.8 for 0.1wt% Ge samples. Not only the peak intensity ratio changes, also the TSL peak positions of UV irradiated samples slightly changed. This indicates that the mechanics behind this is more complex than previously assumed and not only STE but also hole traps are involved.

The FGT method was used to determine the activation energies for both peaks. The activation energy 0.065 eV (0.07eV under UV irradiation) was found for TSL peak at 50 K and this energy is close for both kinds of excitation. The activation energy for 75 K peak was 0.13 eV for X-ray excited sample and slightly lower for UV excited sample (Fig.3). Additionally TSL spectra with six different heating speeds were recorded and the Hoogenstraaten method was used to calculate the activation energies for both peaks. The calculated activation energy values 0.057eV and 0.123eV are slightly lower to these found by FGT method (Fig.3). This could indicated that the peak are not completely first order, but Hoogenstraaten method is applicable for first order TSL peaks. The TSL measurements for UV irradiated samples shows peak shift to larger energies, however the FGT energies under UV irradiation for second peak shows even lower calculated energies.

Figure 3. FGT Energy graph as a function of temperature. Dash lines represent data calculated from Hoogenstraaten method.

4. Conclusions

Two TSL peaks were detected in the range 8 – 100 K in crystalline SiO$_2$ doped with germanium having intensity roughly proportional to the Ge concentration. It is found that the peak positions are changed for different kind of excitation. For the case of X-ray excitation the peaks are situated at 50K and 75 K. For excitation with 157 nm excimer laser they are situated at 60 K and 80 K. The difference is explained as trap structure modification. Activation energies were determined for both excitation types. The activation energies found by FGT and Hoogenstraaten method were close; the small differences could be explained that Hoogenstraaten method is applicable for first order TSL peaks.

5. Acknowledgments

6. References

[1]   Trukhin A N 1992 *J.Non-Cryst. Solids* **149** 32-45
[2]   Trukhin A and Poumellec B 2004 *Sol. St. Commun.* **129** 285-289
[3]   Trukhin A N Boukenter A Ouerdane Y Girard S 2011 *J.Non-Cryst. Solids* **357** 3288-3291
[4]   Halperin A and Ralph I E 1964 *J. Chem. Phys.* **39,1** 63-73
[5]   Weil I A 1975 *Radiation Effects* **26,1** 261-265
[6]   Hayes W and Jenkin J T 1985 *J. Phys. C: Solid State Physics* **18** L849-L853
[7]   Trukhin A N 1986 *Sov. Solid State Physics* **28** 1460 – 1464
[8]   Godmanis I Truhins A 1981 *LPSR ZA Vēstis Fiz.Teh.zin.* **6** 26-29
[9]   Chen R and McKeever S W S 1997 *Theory of Thermoluminescence and Related Phenomena* 110-112
[10]   Hoogenstraaten W 1958 *Philips Res. Rept.* **13** 515