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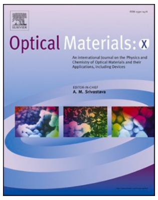

Luminescence of copper-doped α-quartz crystal after oxygen treatment

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ABSTRACT

Treatment of copper-doped natural α-quartz in oxygen atmosphere at 1200 °C leads to changes in luminescence properties. The luminescence center of AlO_4^--Cu^+ is modified. The intensity is low in the annealed sample and increases after X-ray irradiation at 293 K. Annealing of the irradiated sample leads to a strong peak of thermally stimulated luminescence (TSL) at ~500 K. Its spectral composition is mainly due to the AlO_4^--Cu^+ center. Irradiation of the sample treated with oxygen at 77 K gives a new TSL peak at ~180 K and a peak at 244 K existing in the untreated sample. Both peaks were attributed to Cu^o centers released from different sites and recombined with a hole in AlO_4 having additional oxygen. The introduction of copper ions into quartz removes alkali metal ions and eliminates the corresponding luminescence, but after treatment in oxygen, luminescence with similar parameters is restored at low temperatures. In this case, only the glow of the AlO_4^--Cu^+ center is observed in the recombination luminescence (TSL and afterglow). Therefore, modification of the AlO_4^--Cu^+ center with oxygen imparts to this center properties similar to the complex center AlO_4^- (K, Na or Li ion) with monovalent aluminum ions, although the alkali ions are replaced by copper ions. The oxygen-treated sample exhibits an increased efficiency of energy transfer by excitons to the luminescence center, measured as excitation spectra in the region of fundamental absorption of silicon dioxide. The X-ray excitation of the self-trapped exciton luminescence does not depend on oxygen treatment. Also, the spectra of intrinsic optical reflection and Raman scattering do not change compared to the untreated sample. The obtained result is interpreted as a modification of the defect by high-temperature treatment in oxygen.

1. Introduction

Silicon dioxide in general and SiO_2 crystal with α-quartz structure in particular are resistant to various treatments such as radiation and chemical, so the search for a treatment that effectively affects the properties of silicon dioxide is currently relevant. In this work, it was found that oxygen treatment at 1200C for a long period of time (98 h) affects the optical properties of the impurity defect on the one hand and affects the ability to migrate exciton on the other. I hope to conduct a future study of such a treatment on other crystals with a-quartz structure such as GeO_2, as well as $AlPO_4$ and $GaPO_4$. It would also be interesting to study such a treatment on the properties of silicon dioxide and germanium dioxide with rutile structure.

Natural crystalline α-quartz can be doped using the high-temperature electrolysis method with noble ions such as copper, silver, and the less studied gold, by exchanging impurity alkali ions [1] as charge compensators for aluminum impurity defects. Luminescence of noble ions in crystalline quartz has been studied [2]. The luminescence center contains noble ions, Cu^+ or Ag^+, for which absorption and luminescence are well described by intra-ion transitions $d^{10} \Leftrightarrow d^9s$ and $d^{10} => d^9p$. In the initial sample before electrolysis, another luminescence center existed and is described as a complex [AlO_4^--Me^+] (where Me is an alkali ion), where charge transfer transitions were responsible for absorption – luminescence [2]. This center exhibits intensive blue photoluminescence excited at low temperatures (77 K) in the range above 6 eV [2]. Subsequent investigations [2] have revealed that this is due to triplet-singlet transitions with a high value of time constant (~2 ms) and at low temperatures showing peculiarities of decay kinetics similar to the self-trapped exciton [2]. The structure of the defect responsible for both types of centers (noble ion and alkali ion) is the same. The difference lies in the ability of a hole to transition from oxygen to a noble ion, which then undergoes an intra-ion electronic transition. This transition is absent with alkali metal ions due to their high second ionization potential.

It was presumed that treatment in oxygen would induce modifications in defects. The treatment was carried out at a high temperature of 1200 °C for duration of 98 h in an oxygen atmosphere in a container evacuated to high vacuum (10^{-5}torr) before filling with pure oxygen. A

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sample of crystalline natural quartz activated with copper underwent this treatment, and despite the heating process (with a possible influence of the α-β transition at 573 °C), the sample remained in good optical condition; only a single non-linear crack appeared.

2. Experiment

A series of measurements were carried out using optical research equipment. Luminescence spectra were obtained with excitation by an X-ray source (W anticathode, 35 kV, 15 mA); a windowless homemade vacuum ultraviolet source using a high-frequency (~500 MHz) discharge in a hydrogen flow; and a deuterium CW discharge source (Hamamatsu L10366 VUV Light Source Units with MgF_2 window) through a vacuum monochromator (0.5 m concave grating 1200 l/mm). Excimer lasers (ArF, 193 nm, and F_2, 157 nm) with pulses of approximately 5 ns duration were employed for PL spectra and it decay kinetics measurement. The entire system, comprising the monochromator and windowless source, enabled the excitation of sample luminescence for photons above 7.5 eV. For photons below 7.5 eV, a monochromator was used in conjunction with a source featuring a magnesium fluoride window. However, this latter system was impractical for exciting luminescence with photons above 8.3 eV. The complete luminescence excitation spectrum was measured on these two systems and matched in the region of 7.5–8 eV. Luminescence detection was performed through a grating monochromator (MCD2) or an optical filter using a PM (Hamamatsu R11715-01, Cooled PMT). Decay kinetics were recorded using the PicoScope 2208. IR measurements were realized on FTIR Vertex 80v.

3. Results

The Photoluminescence (PL) and Photoluminescence Excitation (PLE) spectra of the oxygen-treated sample were compared with those of the non-treated sample (similar, but different) both activated with copper, as shown in Fig. 1. At room temperature, the PL spectra exhibit a similar band at 370 nm, typical for quartz crystals containing copper [2]. However, differences are observed in the PLE spectra. In the oxygen-treated sample, the PLE bands in the optical transparency region of quartz (below 8.7 eV) are weaker than in the untreated sample. In contrast, in the intrinsic absorption region (above 8.7 eV), the PLE bands are more intense, displaying a deeper modulation of intensity concerning the penetration depth of the exciting light. This modulation occurs due to the transfer of energy by elementary electronic excitations (excitons, electron-hole pairs) to the luminescence center, competing with non-radiative annihilation in the near-surface region [2].

Additionally, the PLE bands in the optical transparency region are sensitive to whether the sample is annealed or irradiated. In the annealed sample (actually, the initial measurements were conducted on x-ray excited luminescence spectra, and PLE of the virgin, non-irradiated sample was not measured), the PLE band in the transparency range is weaker than in the irradiated sample. The luminescence is attributed to the AlO_4^--Cu^+ center, indicating that the irradiation-annealing procedure alters the properties of this center. Comparison of PLE spectra between the oxygen-treated and non-treated samples in the intrinsic range reveals a prominent band at 9.8 eV in the treated sample. This observation suggests that oxygen treatment leads to an increase in energy transfer ability. The energy transfer ability is a product of the electronic excitation's energy migration ability and the efficiency of their interaction with defects. The efficiency of energy transfer shows only a slight increase with heating, as measured in PLE spectra up to 450 K.

Previous studies show that energy migration in quartz occurs via a relaxed exciton, whose ability to transfer energy increases exponentially with increasing temperature [3]. However, in the case of a sample treated with oxygen, the temperature dependence is weaker than in an untreated sample. Therefore, the increase in the efficiency of energy transfer corresponds to the increase in the efficiency of interaction of quasiparticles with the luminescence center.

The optical absorption spectrum of crystalline quartz activated with copper and treated with oxygen at 1200 °C is depicted in Fig. 2. A spectrum from Ref. [2], representing the copper-doped sample non-treated with oxygen, is included for comparison. Notably, the absorption band in the 5 eV range completely disappears in the oxygen-treated sample. This particular absorption is attributed to the $d^{10} => d^9s$ transition of the Cu^+ ion in the non-treated sample. The alteration in electronic structure due to oxygen treatment is suggested to create a bond between the Cu^+ ion and additional oxygen in some state. However, the observed luminescence band supports the $d^{10} \leq d^9s$ transition of the Cu^+ ion. Inset of Fig. 2 shows IR absorption related to OH groups in copper doped α-quartz before (similar but not exactly the same crystal) and after treatment in oxygen. It is seen that main effect is disappearance of a band at about 3482 cm^{-1}. This band was attributed

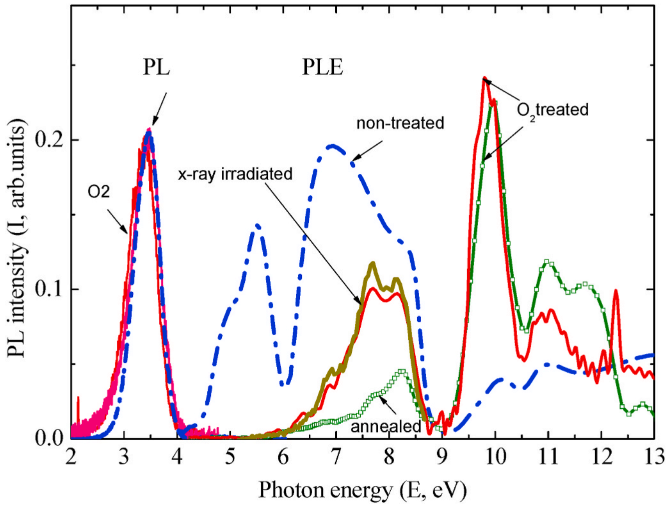

Fig. 1. Comparison of Photoluminescence (PL) and Photoexcitation (PLE) spectra for two samples of crystalline quartz activated with copper. One sample is treated with oxygen, and another non-treated sample (reference from Ref. [2]). PL measurements were conducted using an ArF excimer laser. The "annealed" curve corresponds to measurements on the treated sample up to 680 K, and the "x-ray irradiated" curves represent 5 and 15 min of x-ray irradiation.

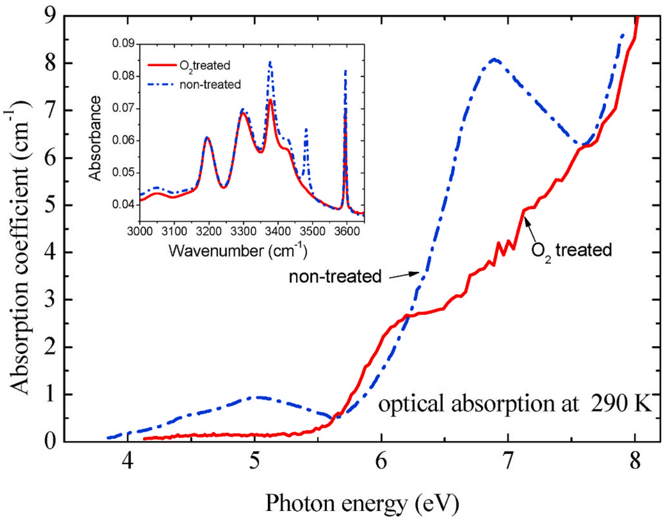

Fig. 2. Optical absorption spectra of crystalline quartz activated with copper, both treated with oxygen at 1200 °C and non-treated (reference from Ref. [2]). Inset shows IR absorption related to OH groups in copper doped α-quartz before (similar but not exactly the same crystal) and after treatment in oxygen.

to Li–OH absorption [4]. Others IR band can be accounted, having in mind possible difference in compared samples, are not strongly affected. The same can be said on the range of intrinsic IR absorption (omitted for shortness).

Two different types of luminescence were observed at different temperatures, as shown in Fig. 3, for copper-doped crystalline quartz treated with oxygen at 1200 °C, when excited by photons from an ArF excimer laser (193 nm). One type of luminescence is associated with the $\mathrm{AlO_4^-}$-$\mathrm{Cu^+}$ center, showing a band at 370 nm detectable at room temperature. The other luminescence at 400 nm increases in intensity as the sample is cooled to 100 K. Similar observations were made when excited by an F_2 excimer laser (157 nm), although with noisier PL curves due to the lower power of this laser. The PL decay curves are shown in Fig. 4, with excitation achieved using pulses from both of the above excimer lasers. At low temperatures, the time constant falls into the millisecond range, which suggests that oxygen treatment produces luminescence similar to that observed in the sample before copper was introduced [2]. At room temperature, the time constant is in the microsecond range (56 μs), which is typical for the $\mathrm{AlO_4^-}$-$\mathrm{Cu^+}$ center [2]. It is noteworthy that in the sample with copper introduced before oxygen treatment, PL with a time constant in the millisecond range is practically not detected and over the entire range of temperatures studied, a band of the $\mathrm{AlO_4^-}$-$\mathrm{Cu^+}$ center with a time constant of about 60 μs is observed, decreasing in the region of thermal quenching above 400 K.

The X-ray excited luminescence spectra of the studied sample treated with oxygen are shown in Fig. 5. Initially, when X-rays were irradiated at room temperatures of the annealed sample, a short-term increase in luminescence was observed, which indicates the recreation of $\mathrm{AlO_4^-}$-$\mathrm{Cu^+}$ centers. Long-term irradiation leads to a decrease, which indicates the destruction of the luminescent ability under the action of irradiation (insert in Fig. 5). At room temperature, the main band corresponds to the $\mathrm{AlO_4^-}$-$\mathrm{Cu^+}$ center, similar to the case of ArF excitation (Fig. 1). At low temperatures, the main band in the X-ray excited luminescence spectrum is the luminescence of self-trapped excitons (STE), and the band of the $\mathrm{AlO_4^-}$-$\mathrm{Cu^+}$ center appears as a shoulder that practically disappears upon irradiation. At low temperatures, the blue band observed under ArF excitation is covered by a strong STE luminescence band in the case of X-ray excitation. When x-ray excitation is turned off, an afterglow is observed, as depicted in Fig. 6. The afterglow primarily features the band of the $\mathrm{AlO_4^-}$-$\mathrm{Cu^+}$ center, with weak intensity at 80 K and much higher intensity at 290 K. The afterglow decay kinetics, as shown in the inset of Fig. 6, are exponential over almost the entire region with a time constant of 3740 s. This behavior does not exhibit the usual hyperbolic pattern associated with bimolecular recombination processes, indicating that recombination is monomolecular. The initial part of the afterglow appears to involve a more complex process. Therefore, recombination occurs with the participation of Cu related defect.

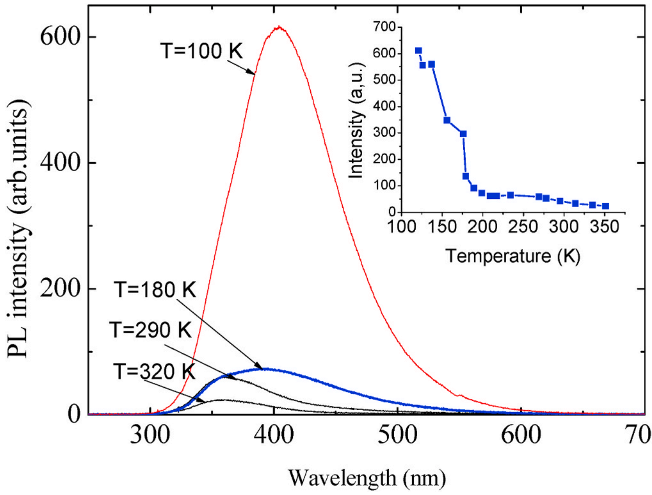

Fig. 3. Photoluminescence (PL) spectra of crystalline quartz activated with copper and treated with oxygen at 1200 °C. The sample was cooled from 320 K to 100 K, revealing an increase in the blue band with cooling. Excitation was performed using an ArF excimer laser. Similar effects were observed with an F_2 laser (157 nm). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

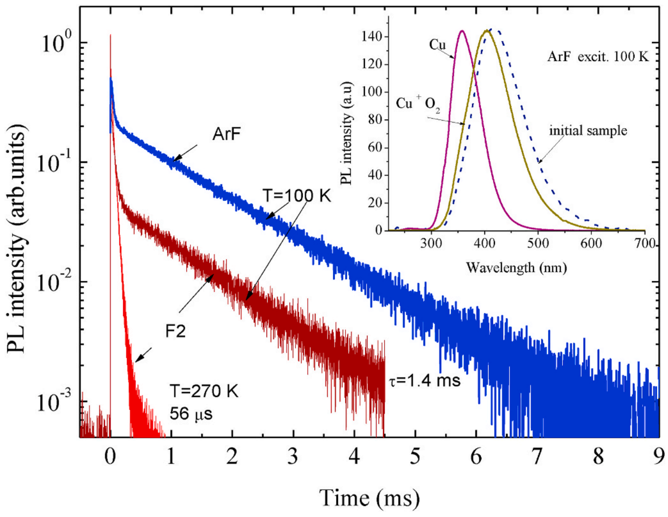

Fig. 4. PL decay kinetics curves of the studied sample. Excitation was achieved with pulses from excimer lasers. The insert compares PL spectra of the sample before copper introduction (initial), after copper introduction (Cu), and after copper-treated with oxygen (Cu $^+$ O_2).

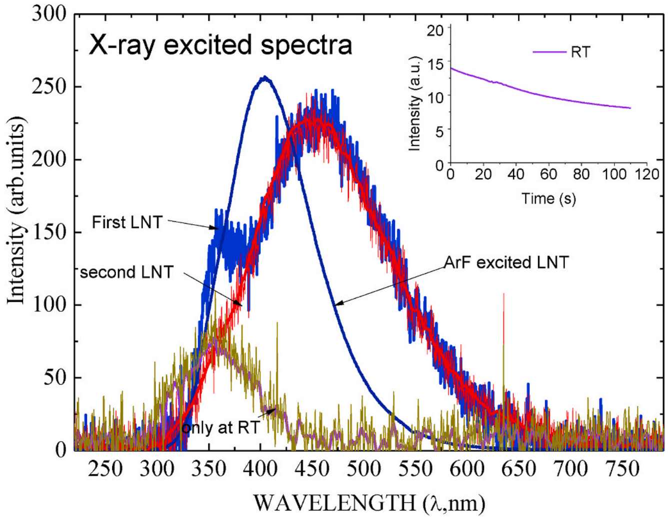

Fig. 5. X-ray excited luminescence spectra at 80 K and 290 K of crystalline quartz activated with copper and treated with oxygen at 1200 °C. The main luminescence band at 80 K is due to a self-trapped exciton with a small shoulder of the $\mathrm{Cu^+}$ band, diminishing during irradiation. An ArF laser-excited PL spectrum is presented for comparison. The inset shows luminescence intensity changes during x-ray excitation.

The STE luminescence does not manifest in the afterglow [2]. It is noteworthy; the blue band observed under photoexcitation at low temperatures in oxygen treated samples is not detected in the afterglow. Hence, the main electron-hole recombination processes seem to excite only the band of the $\mathrm{AlO_4^-}$-$\mathrm{Cu^+}$ center. A similar situation is observed in thermally stimulated luminescence (TSL). The case for the temperature range 100–340 K is shown in Fig. 7. In TSL, the main band is near 370 nm, which is related to the $\mathrm{AlO_4^-}$-$\mathrm{Cu^+}$ center, but there are some

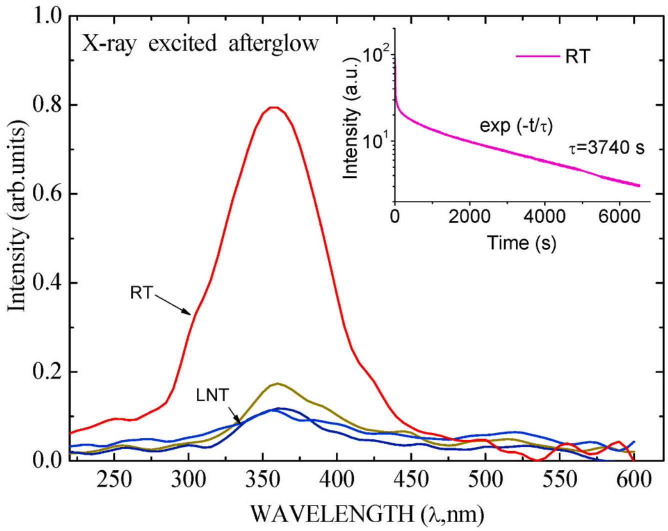

Fig. 6. Afterglow of X-ray excited crystalline quartz activated with copper and treated with oxygen at 1200 °C. LNT – 80 K, RT – 293 K. Inset – afterglow curve when x-ray irradiation is stopped.

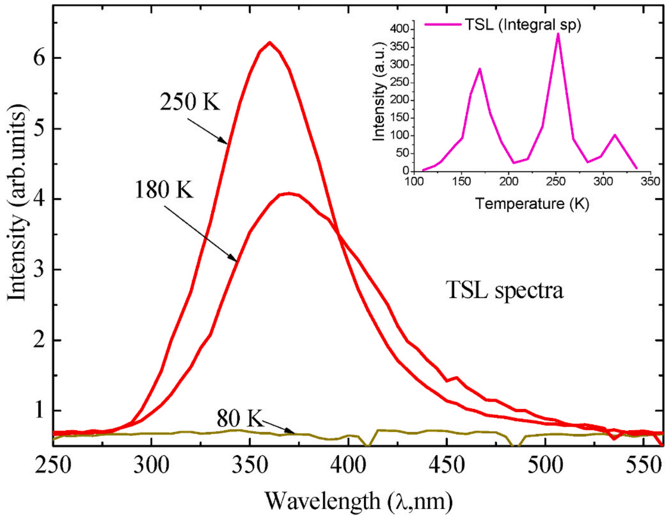

Fig. 7. Thermally stimulated luminescence (TSL) of X-ray excited at 80 K crystalline quartz activated with copper and treated with oxygen at 1200 °C. The main part of the figure displays TSL spectra at different temperatures from 100 K to 310 K, showing that the principal luminescence band belongs to Cu^+ center. The insert is the TSL curve showing intensities at band maxima.

peculiarities. The TSL band in the range near 180 K is broader and shifted to a higher wavelength (370 nm) relative to the TSL band in the range 250 K, which is at 350 nm. The presence of the band at 180 K can be explained by an additive effect of the blue band. The TSL peak at ~250 K was observed earlier [2] in crystalline quartz activated with copper and was explained by the thermal liberation of a Cu^o center induced by radiation at low temperatures. Liberated Cu^o migrates to an aluminum tetrahedron, captures a hole, recombines with it, and provides luminescence of the AlO_4^--Cu^+ center. The appearance of the peak at 180 K in the oxygen-treated sample could also be explained as Cu^o center in a different position, possibly related to a defect created by treatment in oxygen.

The TSL peak at 180 K is also observed in the oxygen-treated sample after irradiation with photons from an ArF laser, as shown in Fig. 8. In this case, the TSL band is situated at 360 nm, and the influence of the blue band is weaker than in the case of X-ray irradiation.

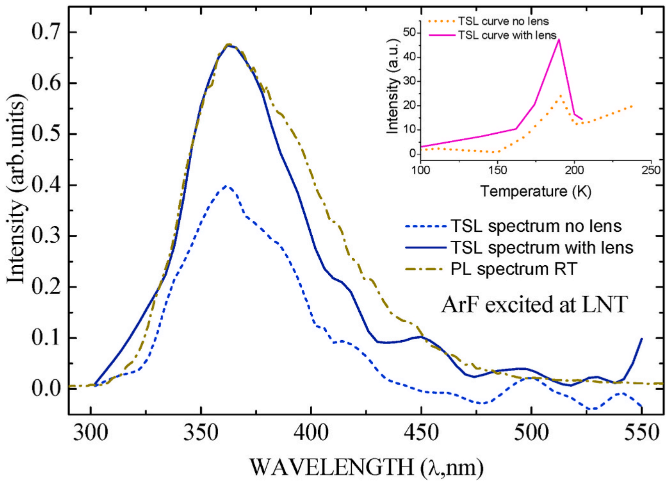

Fig. 8. TSL spectra of crystalline quartz activated with copper treated with oxygen at 1200 °C, ArF-excited. Insert: intensity of corresponding TSL at different temperatures. The spectra show mainly AlO_4^--Cu^+ luminescence, as observed from the comparison with PL spectrum measured at RT. A lens was used to focusing laser light.

The case for the temperature range 300–680 K is presented in Fig. 9, where the spectrum of TSL at ~500 K is compared with that of PL of the treated and non-treated samples. The highest temperature was used for annealing the irradiated sample. The inset shows a comparison of TSL in the three samples: the original sample before introducing copper (labeled - Al), the copper-doped sample (labeled - Cu^+), and the copper-doped sample treated in oxygen (labeled - Cu^+-O_2). It is evident that the TSL of the oxygen-treated sample is a kind of broadened TSL curve of the original natural quartz sample.

The PLE spectra at 90 K for the oxygen-treated sample are similar to the known luminescence of natural quartz (not treated) [2] and correspond to an aluminum-related center. Thus, despite the exchange of alkali ions for copper ions, blue luminescence similar to the non-treated sample is observed. Assuming that alkali ions are completely removed from the sample, renewal could be possible by using copper in a manner similar to alkali ions. This implies that charge transfer transitions in excitation and luminescence also occur with copper when the hole cannot be transferred at low temperatures to Cu^o due to some specific

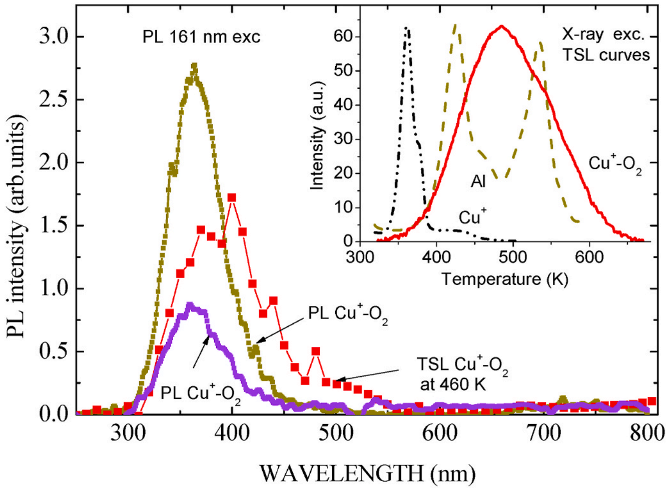

Fig. 9. TSL spectra of crystalline quartz activated with copper treated with oxygen compared with PL spectra of treated and non-treated copper-doped samples. Inset shows a comparison of TSL in the three samples: original before copper introduction (labeled - Al), copper-doped sample (Cu^+), and copper-doped sample treated in oxygen (Cu^+-O_2).

position. At room temperatures, only the pure AlO$_4^-$-Cu$^+$ center luminescence is observed.

4. Discussion

The prolonged high-temperature treatment of crystalline quartz in oxygen for 98 h resulted in significant changes in properties. To ensure that these changes were limited to impurity defects, fundamental parameters such as the reflectance spectrum in the intrinsic region and Raman spectra were measured. The processing did not induce any alterations in these fundamental spectra, leading to the conclusion that the changes introduced by the treatment were confined to impurity defects.

It was hypothesized that oxygen diffuses into quartz in a molecular state and localizes near aluminum tetrahedra. This molecular oxygen may act as a screen between the tetrahedron and the Cu$^+$ compensator, potentially forming bonds with it. The interaction with oxygen could also alter charge trapping and release dynamics during irradiation.

In Fig. 4, the insert compares the PL spectra of three samples at 100 K excited by a 193 nm ArF excimer laser: the initial sample before copper introduction, after copper introduction, and after the copper-doped sample's treatment in oxygen. It is observed that the luminescence of the initial sample is significantly diminished after copper introduction but is renewed after treatment in oxygen, albeit with a slightly different PL band. The decay kinetics at 100 K are slow and practically indistinguishable for both the initial sample and the oxygen-treated sample. In the latter sample, at room temperature, decay with a time constant corresponding to the AlO$_4^-$-Cu$^+$ center persists.

Assuming that, after electrolysis in copper electrodes, all alkali ions leave the sample, the renewal of the luminescence center is possible if copper ions start playing a role similar to alkali ions in the luminescence center [AlO$_4^-$-Me$^+$].

The luminescence of the [AlO$_4^o$—Me^o] center is associated with charge transfer transitions from the oxygen ion to the alkali ion, forming a structure like [AlO$_4^o$—Me^o] in the excited state. The hole on the aluminum-oxygen tetrahedron cannot be transferred to the alkali atom due to the high second ionization potential. This differs from the case of a noble ion, where the hole from the aluminum-oxygen tetrahedron can be transferred to the noble ion, resulting in the excited center [AlO$_4^o$ -Cu^o] and luminescence with intra-ion transition.

During oxygen treatment, the defect in the sample is transformed. At low temperatures, the transient Cu^o created by excitation is in a position screened by additional diffuse oxygen, which does not allow Cu^o to accept a hole. Radiative transitions are carried out by recombination of an electron from Cu^o with a hole on the aluminum tetrahedron similar to the case of an alkali atom in an excited state. So far, the search for Cu^o by the EPR method has not been successful. Previously Cu^o in α-quartz was studied by EPR in Ref. [5] and there it was obtained that Cu^{++} was not created by irradiation, perhaps due to higher efficiency of the hole to be trapped on aluminum tetrahedron [6]. Probably due to the influence of additional oxygen, Cu^o cannot be detected. However, the presence of Cu^o is confirmed by the existence of TSL peaks similar to those in samples not subjected to oxygen treatment. In this case, the TSL always shows the PL band of the Cu$^+$ center.

Now we will discuss the processes observed at room temperature and thermally stimulated luminescence (TSL) at 500 K. Annealing at 500 K of the irradiated sample at room temperature leads to a decrease in the efficiency of intra-center excitation of the Cu $^+$ center. This may be a restoration of the original situation after oxygen treatment at 1200 °C. Under X-ray irradiation, oxygen, which plays the role of a screen between the aluminum tetrahedron and Cu$^+$, captures a hole and relaxes, diminishing the role of screening. What kind of oxygen plays role of screening is not yet understood. It is need further investigations. This leads to an increase in the efficiency of intra-center excitation. However, the situation is not exactly the same as for the luminescence center before treatment with oxygen, as the efficiency of intra-center excitation is still lower than for the initial copper-doped quartz presented in Fig. 1.

The light sum storage for the TSL peak at 500 K may involve other processes, and a possible explanation could be similar to that for the high-temperature peak discussed in Ref. [7]. The monomolecular decay kinetics (inset in Fig. 6) indicate that the recombining parts are located close to each other, but the corresponding traps are very deep, leading to a high-temperature TSL peak. The thermal emission peak can be associated with the migration of Cu^o.

On the other hand, when oxygen-modified defects interact with electronic excitations, the presence of additional oxygen nearby increases the efficiency of interaction with electronic excitations. This enhancement is reflected in the increased band at 9.8 eV. This presence of additional oxygen may influence the efficiency of charge trapping and release during irradiation.

5. Summary

Treatment of copper-doped natural α-quartz in oxygen atmosphere at 1200 °C causes changes in the luminescence properties compared to the original sample. The spectral parameters of impurity defects are changed, but the spectra related to fundamental absorption, such as the reflectance and Raman spectra, are not changed. The luminescence corresponding to intra-ionic transitions of Cu$^+$ retains the photoluminescence (PL) band, but the excitation spectra change significantly. The band corresponding to the d10⇔d9s transitions is practically invisible (also in the absorption at about 5.6 eV), and the bands above 6.2 eV (bands with charge transition and d10=>d9p) are weakened compared to the untreated sample. On the contrary, in the region of fundamental absorption the photoexcitation bands (PLE) are relatively more intense. This means that the luminescence center is modified so that the electron transitions for intra-center excitation are changed and the efficiency of energy transfer from the main substance to the defect is increased. The efficiency of interaction of the center with quasiparticles (excitons and electron-hole pairs) is probably increased. In addition to the luminescence associated with intra-ionic transitions, the treated sample also exhibits luminescence associated with charge transfer transitions at low temperatures, which is absent in the untreated sample but present in the samples before the introduction of copper by electrolysis. This is the so-called low-temperature luminescence center [AlO$_4^-$-Me$^+$]. The excited state of this center is associated with the transition of an electron from oxygen [AlO$_4^o$-Me^o], in which the hole from the oxygen cannot be transferred to the alkali metal atom. Since the alkali metal ions are removed by electrolysis and replaced by copper ions, the observation of analogous luminescence possible due to the participation of copper in charge transfer transitions during excitation and luminescence. Such a scenario is realized when the hole cannot be transferred to Cu^o due to the modification of the defect by treatment in oxygen.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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