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Thermally stimulated luminescence and its related thermally stimulated currents in quartz

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Simultaneous measurements of the thermally stimulated luminescence (TSL) and thermally stimulated currents (TSC) were carried out on synthetic electronic-grade quartz crystals excited by x rays. Samples were cut from $+X$-growth and $+Z$-growth sections of plates perpendicular to the Y axis of the quartz crystals. The electric field was applied along the Y axis and in some measurements along the optical axis (the Z axis). The TSL peaks at 70, 136, 161, 181, 188, 192, 221, and 250–270 K measured with the field along the Y axis all exhibited related TSC peaks. These TSL peaks involve the thermal release of electrons from traps into the conduction band, and so the related TSC must be electronic. The TSL peaks at 76, 83, 92, and 109 K did not show any corresponding TSC, which implies that in these cases no electrons are released into the conduction band. It is proposed that they involve the release of trapped holes and are not observable in the TSC because of the very low drift mobility of holes. Two strong TSC peaks at 216 and 300 K were observed with the field along the optical axis. The strong anisotropy of these peaks suggest that they are ionic in character; namely, they involve the migration of Li^+ ions along the Z-axis channels. They seem to appear when electrons trapped near lithium ions are thermally released when the lithium ions become free to drift with the field along the Z channels.

INTRODUCTION

Thermally stimulated currents (TSC) can provide useful information on defects in crystals, especially when examined in correlation with thermally stimulated luminescence (TSL). Still very few articles on the TSC of quartz can be found in the literature. Bernhardt[1] in his investigation on the TSL of quartz also made some TSC measurements. He observed a TSC peak near 190 K which appears only after a double irradiation of the crystal.[2] Bernhardt, however, was not aware of the special conditions necessary for the production of the 190-K peak and it seems that he obtained it accidentally. This unawareness of the "peculiar" behavior of the 190-K peak may also have entailed wrong conclusions drawn by Bernhardt from the disappearance of the peak under other experimental conditions. Bernhardt's TSC curves also show additional peaks which he claims to be "due to other processes," not related to TSL.

Halperin *et al.*[3] have also carried out TSC measurements on quartz crystals, and have observed a few peaks which could be correlated with TSL peaks. The crystals examined by the latter authors were natural and were not cut from specific growth zones, and no conclusions were drawn regarding the nature of the electrical conductivity involved.

More investigators dealt with radiation-induced conductivity (RIC) of quartz. Hughes[4] measured the conductivity induced in quartz by very short x-ray pulses, and has observed strongly anisotropic delayed conductivity, which he assigned to interstitial alkali-metal ions (M^+). Nowick and co-workers[5] have carried out an extensive investigation on the RIC in quartz. They have stressed the ionic character of the RIC. However, more recently[6] they have observed that irradiation at 150 K gave larger RIC than irradiation at 200 K despite the strongly reduced migration of the M^+ ions at the lower temperature. This observation led them to the conclusion that the RIC was most readily explained in electronic rather than ionic terms.

Martini and co-workers[7,8] have examined the TSL, phosphorescence, and RIC induced in quartz by x or γ rays. They found a close relation between the decay of the phosphorescence and that of the RIC after x irradiation of the crystal at room temperature (RT). They have assigned the phosphorescence to electrons thermally released from traps related to the TSL peaks near 100 °C, emitting the phosphorescence on recombination at luminescence centers. Still, they claim that the RIC is ionic in nature. To explain the close relation with the phosphorescence, they propose that the M^+ ions released from the Al^{3+} impurities by RT irradiation are neutralized by electrons, coming out of the traps, and so they stop moving in an electric field.

The exact nature of the conductivity in quartz seems to remain unclear. In the present work we have carried out simultaneous measurements of the TSL and TSC in quartz with the hope that it will contribute to our understanding of the nature of the conductivity. Some of our measurements were taken with the electric field along the Z axis of the crystal and others with the field direction perpendicular to the optical axis (along the Y axis) which enabled us to distinguish between ionic conductivity and that electronic in nature. Our measurements also covered various radiation treatments. Thus double irradiation with warming to an intermediate temperature between the two irradiations formed the TSL peak at 190 K (Refs. 2 and 9) when we observed its analogous TSC peak. Similarly, RT irradiation followed by low-temperature irradiation under conditions favorable for the formation of TSL peaks at 136, 161, and 181 K (Ref. 10) enabled the observation of the TSC peaks analogous to these latter TSL peaks.

EXPERIMENTAL PROCEDURE

The crystals used in the present work were cut from a *Y*-grown bar of unswept Sawyer synthetic electronic-grade quartz. Samples were cut from the main growth sectors of the *Y* plates, namely $+X$ and $+Z$. Typical dimensions of the samples were 11×8 mm^2 and they varied between 1 and 2 mm in thickness. The main faces of all samples were perpendicular to the *Y* axis. The aluminum impurity content in the $+X$-growth section samples was about 30–40 ppm per silicon atom, and that of the *Z*-growth zone was much lower. Samples were polished to nearly optical flatness, then cleaned, and annealed for one hour at 530 °C, in order to remove effects of exposure to radiation in the history of the crystal, thus restoring it to nearly virgin conditions.

Two types of electrodes were used for the TSC measurements—silver paint or sputtered gold electrodes. The silver paint was applied either to the main faces, when the applied electric field was in the *Y* direction, or on a pair of small faces when the field was along the *Z* axis. The gold electrodes were sputtered, to about 2500-Å thickness, on the main faces only. The electrodes, when on the main faces, covered about one quarter of the faces in order to allow the TSL emission to reach the detector. Thin copper wires were indium soldered to the gold electrodes, or dipped into the silver-paint electrodes.

The samples were mounted in an Air Products Displex closed-cycle double-stage refrigeration system, which enabled measurements in the temperature range 10–350 K. They were fitted into a rectangular bore in the cold finger of the cryostat, and were surrounded by indium wires pressed to the sample by a copper cover screwed to the cold finger. This provided a good thermal contact between the sample and the cold finger of the Displex cryostat.

The cryostat was provided with Spectrosil fused-silica windows, a thin aluminum window (0.3 mm), a heater, platinum and germanium sensors, and a Chromel–gold + 0.07 at. % iron thermocouple. A precision temperature controller enabled to keep the crystal at any temperature in the above range. A motor-driven potentiometer was inserted into the variable-resistance arm of the bridge of the temperature controller, thus enabling, when using the platinum sensor, a nearly linear heating rate during the TSC-TSL measurements. The standard heating rate in these measurements was 10 K per min.

The electric field was supplied by a dc 275 V stabilized power supply. In some of the measurements we used dry-cell batteries with an output of 170 V. Shielded coaxial cables with BNC connectors were coupled to a metal grounded box attached to the Displex cryostat, and ceramic vacuum seals enabled to pass the high voltage to one electrode on the sample in the cryostat. The current through the samples was monitored by connecting the second electrode to a 610C Keithley electrometer, whose output was recorded on a chart recorder.

The TSL was measured simultaneously with the TSC. The emitted light was reflected by an aluminized mirror located behind the cryostat, and condensed by a quartz lens onto the photocathode of a cooled (-25 °C) EMI 9658R photomultiplier. The output of the photomultiplier was fed into a second 610-C electrometer and recorded on a separate chart recorder.

Samples were x rayed (55 kV peak, 18 mA) from a tungsten target through the thin aluminum window in the metal shroud of the cryostat. They were located about 6 cm away from the target and received about 3000 rad per second.

RESULTS

Curve 1 of Fig. 1 depicts the TSC (left ordinate scale) of a $+X$-growth-zone sample (sample $X2$) after excitation by x irradiation for 30 min on each side of the crystal plate at 15 K. The electrodes were gold sputtered, and the applied electric field was 1330 V/cm (275 V across the 2.06-mm thickness of the sample), and was applied along the *Y* axis. A very weak current (about 10^{-13} A) was observed in the temperature range below 100 K. At higher temperatures there appear TSC peaks at 205 K, above 260 K, and above 330 K, with peak currents between 10×10^{-13} and 15×10^{-13} A.

Curve 2 shows the TSC for the same sample but with the field along the *Z* axis. In this case the electrodes were silver painted on the pair of small faces perpendicular to the *Z* axis. The separation between the electrodes was 10.5 mm and with an applied voltage of 170 V (from dry cells) the average field was 160 V/cm. The sample was x irradiated in this case for 60 min on one side of the crystal only. Again the currents are very low below 100 K, even lower than in curve 1, presumably because of the lower electric field applied in this case. Two peaks appear now at higher temperatures, at 216 and 300 K. Their intensities are higher by about an order of magnitude compared to those in curve 1, and this in spite of the much lower applied field.

Curve 3 of Fig. 1 gives the TSL (right ordinate scale) of the same sample taken simultaneously with the TSC

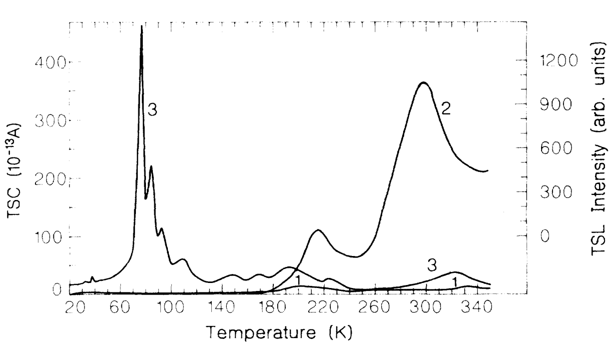

FIG. 1. TSC and TSL of an *X*-growth zone sample (sample *X*2), after 1 h of x irradiation at 15 K (see text). Curve 1: TSC with electric field (1330 V/cm) along *Y* direction; curve 2: TSC with electric field (160 V/cm) along *Z* direction; curve 3: TSL of same crystal.

shown in curve 2. It shows a variety of glow peaks typical to the nearly virgin crystal.[11] It is obvious that the TSL peaks below 120 K do not show any corresponding TSC peaks. On the other hand, at higher temperatures the TSC peaks in curve 1, namely those at 205, 260, and above 330 K seem to be related to the 192, 252, and 325 K TSL peaks correspondingly.[12] The high anisotropy of the TSC shown in curve 2 suggests that in contrast with the TSC shown in curve 1, which seems to be of electronic character, that shown in curve 2 is ionic.

It has been shown that double irradiation at low temperature with warming to about 200 K between the two irradiations produced a very strong TSL peak near 190 K.[9] This latter peak was found to be related to the $[SiO_4/Li^+]^0$ center, and it was proposed[2] that the emission occurs when electrons from the $[SiO_4/Li^+]^0$ centers are released thermally into the conduction band and recombine with holes at luminescence centers. If so, the 190 K TSL peak must show a related TSC peak. This is indeed the case, as shown in Fig. 2. The sample used was again $X2$ with sputtered gold electrodes on the main faces, so that the applied field (1330 V/cm) was along the Y axis. Curve 1 in Fig. 2 shows the TSC after the first x irradiation (30 min on each side of the sample) at 17 K. The TSC curve (left ordinate scale) is similar to that shown in Fig. 1, curve 1, but on a more sensitive ordinate scale (compare scales). One sees clearly on this scale the TSC below 100 K and the peak near 205 K. When reaching 220 K the sample has been cooled down and x irradiated for the second time at 17 K (31 min on one face and 34 min on the other one). Curve 2 shows the resulting TSC obtained during warming. There appears now a strong peak at 195 K and another one near 265 K. The latter is the same as in Fig. 1, curve 1, but somewhat stronger because of the double irradiation. Curve 3 shows the TSL obtained simultaneously with curve 2. It shows clearly the "190-K" peak (actually at 188 K). The relation between this latter peak and the TSC peak at 195 K is obvious.

Figure 3 is the same as Fig. 2, but for a Z-growth-zone sample (sample $Z2$). Again, curve 1 shows the TSC (left ordinate) after the first x irradiation (45 min) at 15 K, with the field along the Y axis. The low temperature TSC is this time somewhat higher compared to that in Fig. 2. At higher temperatures there appears again the TSC peak at 205 K. Warming has been stopped as before at 220 K when the sample was cooled down to 15 K and x irradiated for the second time for 45 min. Curves 2 and 3 show the TSC (left scale) and TSL (right ordinate scale) obtained on warming. There appear again the TSL at 188 and TSC at 195 K. This pair of peaks is now much weaker compared to that obtained for the $X2$ sample (Fig. 2), as expected for the $Z2$ sample with its lower aluminum content.[11] The TSC peak above 200 K in curve 1 looks complex and it may consist of two superimposed peaks, one corresponding to the 192 K TSL peak and the other corresponding to the 206-K peak (see curve 3) specific to Z-growth zone samples.[11]

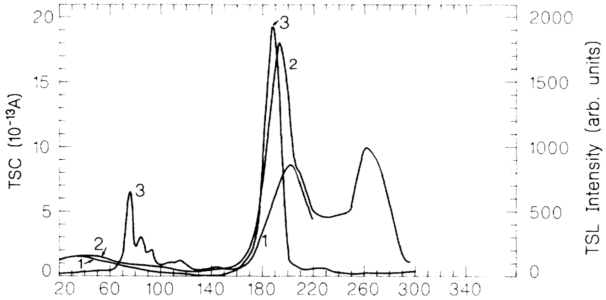

FIG. 2. TSC and TSL of sample $X2$ with field along Y direction. Curve 1: TSC after first x irradiation at 17 K, crystal warmed up to 220 K; curve 2: TSC after cooling from 220 K and second x irradiation at 15 K; curve 3: TSL measured simultaneously with curve 2.

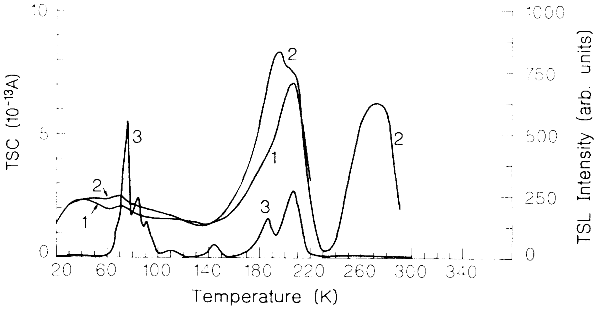

FIG. 3. Same as Fig. 2 but with a Z-growth zone sample (sample $Z2$).

Curves 1 and 2 show also a very weak TSC peak near 70 K, which seems to correspond to the TSL at this temperature observed in Z-growth zone samples.[11] It appears in curve 3 as a shoulder to the 76-K peak. Note also that the TSC peak at 270 K looks complex (compare with that in Fig. 2, curve 2).

Figure 4 illustrates the TSL (curve 2, right ordinate scale) and the TSC (curve 1, left scale) for a $+X$-growth-region sample (sample $X3$). In this case the crystal was first x irradiated for 105 min at RT, then cooled down and x irradiated again for 32 min at 15 K. This procedure was found to produce TSL peaks at 136, 161,

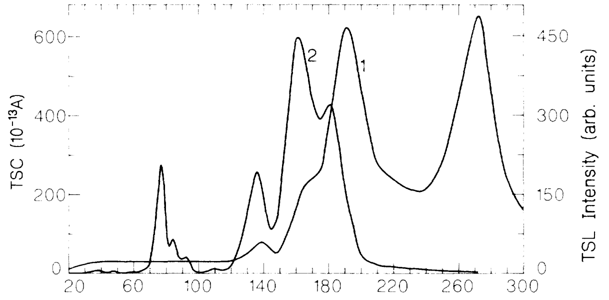

FIG. 4. TSC (curve 1) and TSL (curve 2) of sample $X3$ (X-growth zone) after 105 min of RT x irradiation followed by 60 min of x irradiation at 15 K.

and 181 K,[10] and indeed these peaks appear in the TSL (curve 2). The thickness of sample $X3$ was 1.23 mm and the electrodes were gold sputtered on the main faces perpendicular to the Y axis. With 270 V from the power supply the average applied field was 2240 V/cm. The TSC (curve 1) shows a peak near 140 K corresponding to the 136 K TSL peak. The TSC corresponding to the 161 K TSL appears at about 165 K as a shoulder to the stronger TSC peak above 190 K. This latter peak seems to combine the peak corresponding to the 181 K TSL and a component related to the TSL peak at 192 K (see curves 3 in Figs. 1 and 3). In addition there appears a TSC peak above 270 K broadened on the low-temperature side. As in curve 2 of Fig. 3, this indicates that the TSC in this temperature range contains two overlapping peaks.

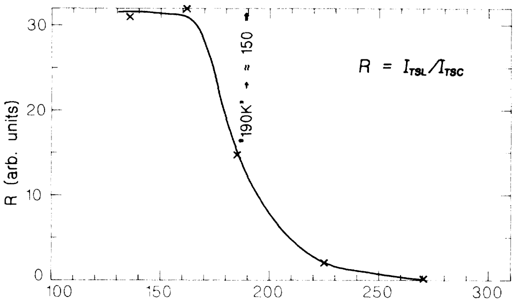

FIG. 5. Dependence on temperature of the ratio R of the intensities of the TSL peaks and their related TSC peaks. Solid line drawn to fit experimental R values (×).

DISCUSSION AND CONCLUSION

In the present work we show that quartz exhibits a variety of TSC peaks. Still, not all the TSL peaks show corresponding TSC peaks. The weak TSC at low temperatures appeared in all our measurements. It spreads continuously up to above 100 K (see, for example, Fig. 2). It seems to be related to the phosphorescence observed by us after low-temperature irradiation, which covered the same temperature range.[11]

The TSC peaks observed in the present work with the field along the Y axis (perpendicular to the Z axis) were found to have corresponding TSC peaks. Thus the peaks at 136, 161, 181, 188 ("190") and at 192 K show related TSC peaks, all at temperatures a few degrees higher compared to the TSL peaks as expected.[12] Even the TSL peak appearing mainly in Z-growth zone samples near 70 K shows a corresponding weak TSC peak (Fig. 3). It seems that the TSL peak at 221 K also has a related TSC peak blurred by the stronger peaks at lower and higher temperatures (see Fig. 2). All the above TSL peaks as well as the low-temperature phosphorescence emit at 380 nm (3.26 eV), an emission which was correlated with the thermal release of electrons from traps and their recombination with holes at luminescence centers. We conclude, therefore, that in all these cases the TSC is due to electrons thermally released from traps to the conduction band.

Our measurements also showed a complex TSC peak near 270 K (Figs. 3 and 4) with no apparent TSL. In fact, though weak there appear in this temperature range two TSL peaks at 252 and about 265 K [see Ref. 10, Fig. 1(a)]. The relative weakness of these TSL peaks compared to the corresponding TSC should be attributed to temperature quenching of the 380-nm emission in the range 200–300 K. Such quenching was in fact observed in radioluminescence measurements.[13,14] Taking ratios (R) of the TSL and TSC intensities ($R = I_{TSL}/I_{TSC}$) with the same arbitrary units for all temperatures, we obtain for R the curve shown in Fig. 5. In this figure the value of R is seen to be above 30 at 160 K and it drops to about 15 at 185 K. At 225 K its value is about 2 and it is only 0.06 at 270 K. The R values for all the above mentioned peaks, except for the one at 188 K (190 K) fit one quenching curve coming down sharply near 200 K. This deviates somewhat from the quenching curves reported for radioluminescence,[13,14] which should at least partly be attributed to the mobility of the electrons rising somewhat with temperature.[4] The 190-K peak gives an exceptional R value. Instead of a value of about 12 on the curve at this temperature, we obtained a value of about 150. This may be attributed to a higher luminescence efficiency, and a correspondingly lower conductivity due to the close proximity between the traps and the luminescence centers in this case as suggested previously.[9] It should be stressed that the TSL peaks at 250–270 K, and at least the 252 K one also emit at 380 nm,[11] and thus the related TSC is in this case also due to electrons thermally released into the conduction band. We see that practically all TSL peaks emitting at 380 nm exhibit related TSC peaks (for the weak TSL peaks at 115 and 145 K,[11] the TSC was not observable under our experimental conditions). The fact that the TSC is measurable over such a wide temperature range down to 15 K indicates that the electron mobility is not strongly temperature dependent. In fact Hughes,[4] discussing the drift mobility of excess electrons in semiconductors and insulators, stated that in several single crystals it was found to be roughly independent on temperature.

The TSL peaks in the range 76–110 K did not show any corresponding TSC. This eliminates the possibility that these peaks also involve thermal release of electrons into the conduction band. Would this be the case, one would expect the strong TSL peaks to produce TSC peaks much stronger than the weak background due to the phosphorescence in this temperature range. It is of interest to point out that the emission of the TSL peaks in the range 76–110 K is also different. The 76- and 83-K peaks were found to emit at 435 nm (3.22 eV), and those at 92 and 109 K at about 460 nm (2.70 eV).[11] We suggest that these TSL peaks involve the thermal release of positive holes and their successive recombination with trapped electrons. The lack of TSC peaks in this temperature range can then be readily explained by the very low mobility of holes compared to that of electrons.[15] The mobility of electrons at RT (in amorphous SiO_2) was found to be about 20 cm^2/V sec.[16,17] The values are however completely different for holes. In amorphous

SiO_2 their room temperature mobility was found to be about 10^{-5} $cm^2/V\,sec$, and it was found to come down to 10^{-7} $cm^2/V\,sec$ at 100 K. With such low mobilities one cannot expect the TSC due to holes to be observable, at least up to RT.

The TSC measured with the electric field along the Z axis was found in the present work to show two peaks, at 216 and about 300 K (Fig. 1, curve 2). These peaks were stronger by about an order of magnitude compared to the TSC peaks with the field along the Z axis, and this in spite of the electric field along the Z axis being weaker by nearly an order of magnitude, and the area of the contact electrodes being smaller. This high anisotropy suggests that the TSC at these peaks is ionic in character. The monovalent ions in our samples were mainly Li^+ and since Li^+ has a higher diffusion constant than Na^+ and K^+ we can assume that the ionic TSC is primarily due to Li^+. The shape of the peaks in Fig. 1, curve 2 suggests that they involve thermal release of trapped carriers. What is then the nature of the "traps" from which the lithium ions are thermally released? We propose that the two ionic TSC peaks at 216 and 300 K are related with the same traps responsible for the electronic TSC peaks at 205 and about 265 K, respectively (Fig. 1, curve 1). Why then the big temperature shift, and why is the intensity of the 300-K peak much higher compared to that of the 216-K peak while the 265-K peak is weaker than the 205 K one? These differences seem to arise from the difference between the temperature dependence of the mobility of the Li^+ compared to that of the electrons. As stated above, the electron mobility in quartz is almost temperature independent.[4] Things are completely different for the lithium ions. Their mobility was found to depend exponentially on temperature with an activation energy of 0.27 eV.[4] The mobility thus should rise by about 2 orders of magnitude between 200 and 300 K. This steep rise in mobility with temperature explains the high intensity of the 300-K peak compared to the 216 K one. It also explains the higher peak temperatures, which should obviously result from the steep rise in current with the rise in mobility. The mechanism for the production of the TSC peaks at 216 and 300 K is assumed to be as follows: The exact nature of the trapping defects is not known, but they can be described as $[X_i,Li^+]^0$ centers. In these centers a Li^+ close to an unspecified defect in the crystal gets trapped by an electron during the low-temperature x irradiation. For one of these X_i defects the electron is thermally released at 192 K, producing the 192 K TSL (Fig. 1, curve 3) and the electronic TSC peak at 205 K (curve 1). When the electron leaves the center, the lithium ion becomes free to drift with the electric field along the Z-axis channels, hence the 216-K ionic TSC peak. When reaching the temperature range 250–270 K electrons are released from other $[X_i,Li^+]^0$ centers producing in the way described above the set of TSL, electronic TSC, and ionic TSC at 300 K.

The above model, by which practically all the electron traps below RT in lithium containing quartz are of the type $[X_i,Li^+]^0$ was proposed by us previously.[10] In the earlier work, however, the model was limited to temperatures below 230 K. The present results indicate that it can be extended to include the TSL peaks in the range 250–270 K. This notion is supported also by the fact that hydrogen sweeping eliminates the TSL peak at 70 K and all peaks in the range 120–270 K.[2]

No ionic TSC was observed below 200 K. This should be attributed to the steep decrease in the mobility of the lithium ions as stated above. To summarize in the following we can say that the present work has revealed a variety of TSC peaks up to RT.

(a) The TSC measured along the Y axis is electronic and they are all related to TSL peaks emitting at 380 nm. In all these cases electrons are thermally released from various traps into the conduction band.

(b) No TSC due to positive holes can be observed below RT because of the very low mobility of the holes in this temperature range.

(c) Two ionic TSC peaks were observed at 216 and 300 K. These seem to be related to the TSL peaks at 192 and 250–270 K, respectively. The big temperature shift between the TSC and its related TSL is due to the steep rise in the mobility of the lithium ions with temperature. This is also why no ionic TSC is observed below 200 K.

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[1] Hj. Bernhardt, Cryst. Res. Technol. **19**, 133 (1984).

[2] A. Halperin, M. G. Jani, and L. E. Halliburton, Phys. Rev. B **34**, 5702 (1986).

[3] A. Halperin, A. A. Braner, and J. Shapira, J. Lumin. **1/2**, 385 (1970).

[4] R. C. Hughes, Radiat. Eff. **26**, 225 (1975).

[5] H. Jain and A. S. Nowick, J. Appl. Phys. **53**, 477 (1981); *ibid.* **53**, 485 (1981).

[6] E. R. Green, J. Toulose, J. Wacks, and A. S. Nowick, *Proceedings of the 38th Annual Frequency Control Symposium, 1984* (IEEE, Piscataway, New Jersey), p. 32, Document No. 84 CH2062-8.

[7] M. Martini, E. Sibilia, G. Spinolo, and A. Vedda, Nucl. Tracks **10**, 497 (1985).

[8] M. Martini, G. Spinolo, and A. Vedda, J. Appl. Phys. **60**, 1705 (1986).

[9] A. Halperin and S. Katz, J. Lumin. **31-32**, 129 (1984).

[10] A. Halperin and S. Katz (unpublished).

[11] S. Katz and A. Halperin (unpublished).

[12] Theoretical considerations show that under most experimental conditions the peak temperatures of the TSC should be higher compared to those of the corresponding TSL peaks; see, for example, R. Chen and Y. Kirsh, *Analysis of Thermally Stimulated Processes* (Pergamon, Oxford, 1981), pp. 45 and 46.

[13] P. J. Alonso, L. E. Halliburton, E. E. Kohnke, and R. B. Bossoli, J. Appl. Phys. **54**, 5369 (1983).

[14] W. Hohenau, Phys. Status Solidi A **88**, 267 (1985).

[15] R. C. Hughes, Phys. Rev. B **15**, 2021 (1977).

[16] W. B. Fowler, Semiconduct. Insul. **5**, 583 (1983).

[17] H. J. Fitting and J. U. Friemann, Phys. Status Solidi A **69**, 349 (1982).