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# Study of sodium tellurite glass using the thermally stimulated depolarization current technique (TSDC)

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ABSTRACT

In order to have a better understanding of the role of the structure and the defects involved in the polarization processes in an $85TeO_2$–$15Na_2O$ mol% glass, we used the thermally stimulated depolarization currents (TSDC technique). The TSDC of the non-irradiated sample presented a strong negative peak of current at the temperature of 340 K, preceded by a relatively weak positive peak at about 300 K, after different d.c. voltages of 1200, 1500 and 2000 V were applied. No response was obtained with 1000 V, but the peak intensity increased considerably for voltages above 1200 V. After γ-irradiation of 25 and 50 KGy doses, a depolarization of the negative peak was observed in the sample submitted to25 KGy, whereas for the sample irradiated with 50 KGy, six TSDC peaks appeared at regular intervals of 5 KGy, in the temperature range of 100 and 300 K.


## 1. Introduction

The tellurite glasses are largely chosen among the best materials for optical applications [1], due to their high refractive index between 1.8 and 2.3 ($\lambda = 589.9$ nm); low phonon energy of 600 to 850 $cm^{-1}$ surpassed only by fluoride and chalcogenide glasses [1]; low glass transition temperature Tg and due to its easy preparation at room temperature. Furthermore, these glasses were found to be excellent materials for hosting lasing ions. Because of their low phonon energy environment the non-radiative losses are minimized [2].

The thermally stimulated depolarization current (TSDC) technique, applied to the study of oxide glasses containing modifier cations, is sensitive to the chemical composition and to the electrical polarization conditions of the glasses. In the present case the dipole responsible for this effect is due to the pair of charges composed by a non-bridging oxygen $NBO^-$ and a near neighboring glass modifier cation which compensates the local charge. The corresponding TSDC peak is due to the electrical dipolar relaxation currents from the orientations which depend of the different positions occupied by the cation in the near neighborhood of the NBO.

After Hong and Day [3] the TSDC technique was applied for the study of charge-trapping mechanisms in chalcogenide glasses ($As_2Se_3$), polarization migration in aluminoborate glasses and the movement of $Na^+$ ions from the interfaces of $SiO_2$ films with Si or Al electrodes producing thermally stimulated ionic currents and the values of the trap depths and $Na^+$ mobility were measured. The TSDC had never been used previously to study alkali oxide glasses and the TSDC peaks are dependent on the chemical composition and the polarization conditions of the glass. They used the following glass compositions: 4 $Na_2O$–96 $SiO_2$, 25 $Na_2O$–75 $SiO_2$ and 30 PbO–70 $SiO_2$ (mol%). For the sample containing PbO only a single TSDC peak was observed and for the samples containing sodium two peaks were observed. For the 4 $Na_2O$–96 $SiO_2$ (mol%) sample the first peak consisted of the depolarization of the alkali ion orientations relative to the position of a NBO, as proposed by Charles [4,5] and by Hong and Day [3], this process occurs in two ways:

a) the alkaline ions jump from one NBO to another, by means of a mechanism not yet well understood, perhaps through a vacancy-interstice combination;
b) an alkali ion probably jumps to other nearest-neighboring sites around a single NBO.

Another mechanism may occur for glasses possessing two immiscible phases that have different electrical characteristics, so that some kind of polarization is expected at the phases interface.

In addition to the permanent dipoles involving an alkali cation, there are other possible permanent dipoles, as the $TeO_2$ itself, as currently discussed in the literature [6–8]. As the tellurite glass structural units are covalently bound throughout the glass network, it is expected that their dipoles are rigidly fixed and will not be able to change their orientation if an external electrical field is applied. Therefore, we have chosen to limit ourselves to concentrate the attention exclusively on the permanent dipoles involving a $NBO^-$ and a glass modifier cation and/or an oxygen vacancy $V_0^+$.

For the case of a set of nearest neighboring sites around a $NBO^-$, Agarwal and Day [9] proposed a model for the alkali ions in the

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presence of an applied electric field. The depth of the potential wells was classified as being essentially of three types: the deep wells whose depth is assumed to be the activation energy for dc conductivity, $E_{dc}$, assumed to be the stable alkali-ion sites; the shallow wells considered as the interstitial sites located around the NBO´s; and the conduction channels or pathways slightly shallower than the stable sites.

Radiation-induced changes of the TSDC in aluminoborate glass were reported recently by Da Rocha [10] showing interesting changes produced by dipole creation and/or annihilation effects.

## 2. Experimental

The glass samples were prepared by melt-quenching method using appropriately weighed high-purity compounds: $TeO_2$ (99.999%) and $Na_2CO_3$ (99.995%). The batch was held at the temperature of 850 °C at an electric furnace, in air, during 30 min in platinum crucible. The stoichiometry of the $C_1$ sample was (85 $TeO_2$–15 $Na_2O$) mol%.

The TSDC measurements were carried out with a setup built in the Laboratory of Dosimetry of the Physics Institute of the University of São Paulo.

The TSDC measurements were performed by polarizing the samples under the conditions given in Table 1 for 3 min, followed by cooling with liquid nitrogen (LN), reaching a temperature of about 100 K after an exponential decay. The applied tension was turned off after waiting for about 30 min, to allow sufficient mobility for the polarization to relax. The electrodes were then short-circuited by means of an electrometer, and the sample was heated at the rate of 0.1 K/s, initially maintained nearly constant with the progressive withdrawal of the LN and heated further with a heating cloth. The TSDC measurements were performed until reaching the temperature of ~360 K.

In Table 1 the experimental parameters are the following: the sample, applied tension (AT) measured between the electrodes, initial temperature under applied tension (TAT), turn-off temperature (TOT), irradiation or thermal treatment (I or TT) and the sample thickness of the TSDC measurements of $C_1$ sample.

The sample was γ-irradiated at room temperature using Panoramic $^{60}Co$ source at the conditions given in Table 2. The TSDC data include the set of measurements performed before and after sample irradiation.

The measured density of the $C_1$ sample, obtained by Archimedes method was $(4.9770 \pm 0.0005)$ g/cm$^3$.

**Table 1**
Experimental parameters for the TSDC measurements of the sample $C_1$.

| AT (V) | TAT (K) | TOT (K) | I ou TT | Thickness (mm) | Figure |
|---|---|---|---|---|---|
| 1000 | 288 | 104 | none | $(1.465 \pm 0.005)$ | 1 |
| 1200 | 292 | 103 | | | |
| 1500 | 297 | 105 | | | |
| 2000 | 300.4 | 104 | | | |
| 2000 | 300.4 | 104 | none | $(1.465 \pm 0.005)$ | 2 |
| 2000 | 295.2 | 101.5 | | | |
| 1500 | 296 | 105 | none | $(1.465 \pm 0.005)$ | 3 |
| 1500 | 300.8 | 110 | 25 KGy | | |
| 1500 | 297.7 | 97.3 | 50 KGy | | |
| 1500 | | | | | |

**Table 2**
Irradiation conditions of the sample $C_1$.

| Dose (KGy) | Dose rate (KGy/h) | Distance (cm) | Time of exposition (min) |
|---|---|---|---|
| 25 | 0.3622 | 5.0(0.1) | 4140 |
| 50 | 0.3622 | 5.0(0.1) | 8280 |

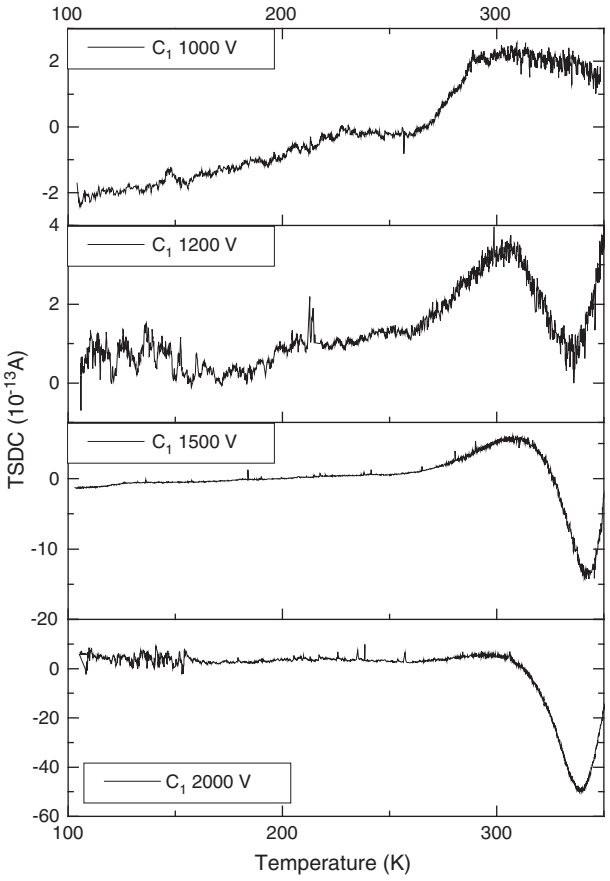


**Fig. 1.** Spectra of TSDC of sample $C_1$.

## 3. Results

The TSDC spectra of the non-irradiated $C_1$ sample are shown in Fig. 1. Increasing amplitudes of the inverted peaks of the sample polarized at room temperature with 1200, 1500 and 2000 V were observed, localized at 334, 343 and 340 K, respectively, and no response was obtained with 1000 V applied tension. When the polarizing temperature $T_p$ was changed from 300.4 K to 295.2 K with constant tension of 2000 V, the TSDC negative peak increased slightly, as shown in Fig. 2.

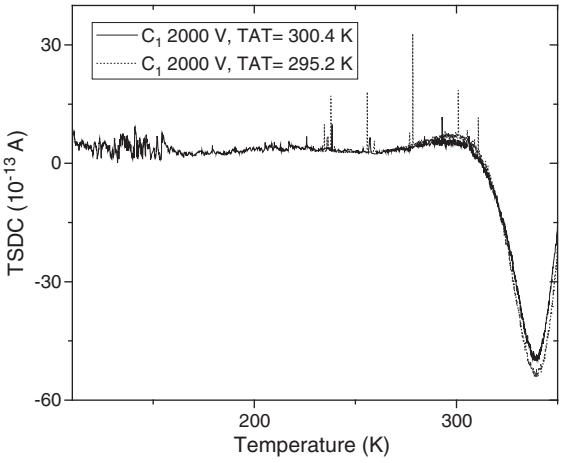


**Fig. 2.** Repeated TSDC spectra of the $C_1$ sample with constant applied tension of 2000 V to check eventual shift of negative peak. A small increase of the TSDC intensity was observed as TAT changed from 300.4 K to 295.2 K.

The TSDC study of the γ-irradiated $C_1$ sample was performed with exposure to γ-ray doses of 25 and 50 KGy. An initial decrease of the depolarization current was observed at 25 KGy when compared with non-irradiated sample. After irradiating at 50 KGy, a set of six positive peaks appeared at approximately regular intervals of 50 K, in the range of 100 to 300 K (see Fig. 3). The thermal bleaching effect of subsequent measurements of the $C_1$ sample initially irradiated at 50 KGy was performed (see Fig. 4). A better understanding of the thermal behavior of the defect states in the tellurite glass was obtained from a recent EPR study of the isochronal thermal decay of the $g_1$, $g_2$ and $g_3$ resonances recently attributed by Giehl et al. [11] to the tellurium oxygen hole center (TeOHC), to the non-bridging oxygen hole center (NBOHC), and to the tellurium electron center (TeEC), respectively as it is shown in Fig. 5.

The EPR measurements were taken at room temperature and the thermal treatment was performed at an electrical furnace with a given gradually increasing temperature step of 10 min. The peak-to-peak intensity of each resonance is plotted versus temperature in Fig. 6. It is observed a monotonical decrease for all the three resonances. The $g_2$ resonance was completely bleached at 120 °C and the $g_3$ resonance followed a similar behavior, but was not completely bleached at 120 °C and a tail was observed between 120 °C and 160 °C. The $g_1$ resonance decreased more slowly and was not completely eliminated at 160 °C.

## 4. Discussion

Sekiya et al. [12] reported that their Raman results indicated that in tellurite glasses containing increasing amount of $Na_2O$, up to 20% mole fraction, the continuous random network of $TeO_4$ trigonal bipyramids and $TeO_{3+1}$ polyhedra connected by the vertices, except one containing a NBO. Such a structural change associated with the formation of negative charged $NBO^-$, compensated by $Na^+$ glass modifier cations, reduces the glass matrix overall strength of covalent bonds, that results in decreased $T_g$ values.

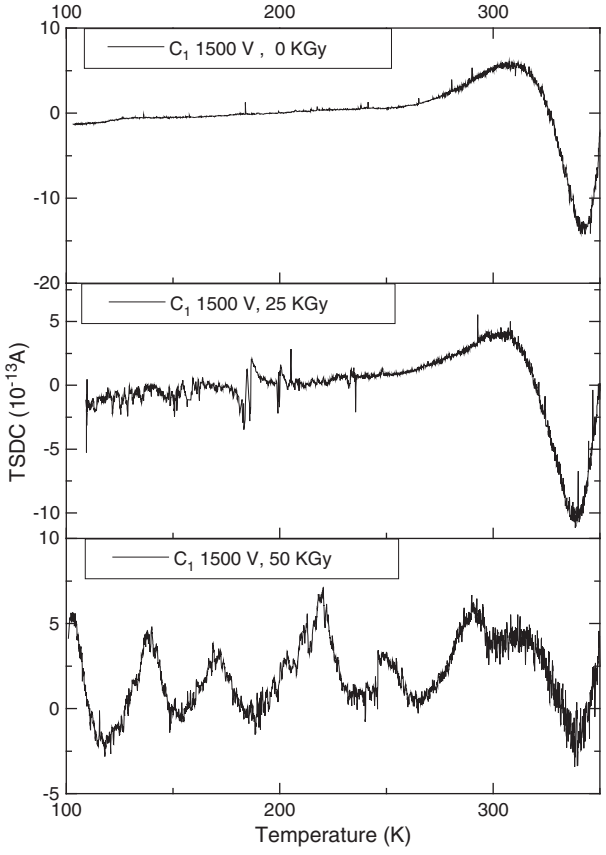


**Fig. 3.** TSDC spectra of the sample $C_1$ with doses 0, 25 and 50 KGy, respectively, with applied tension of 1500 V.

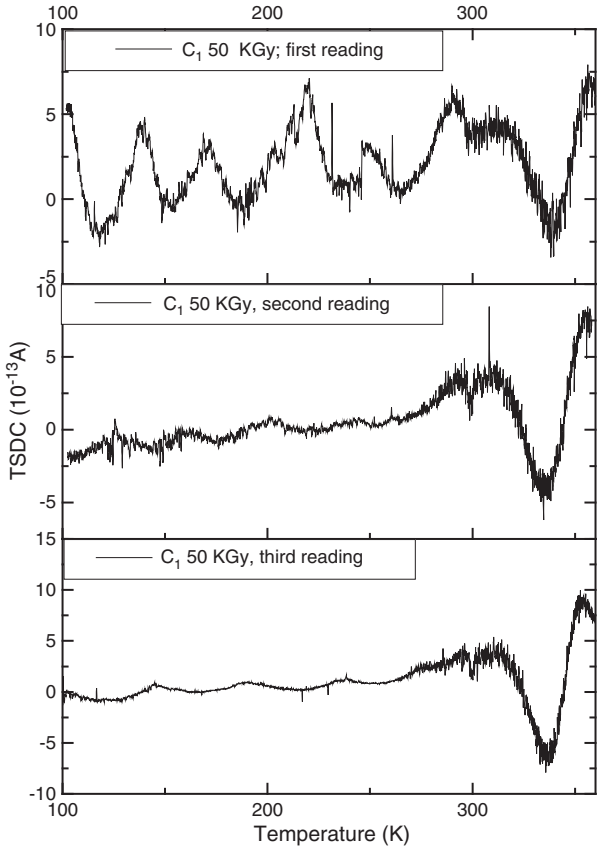


**Fig. 4.** TSDC Spectra of $C_1$ sample irradiated with 50 KGy (red: 2000 V, 300.4 K; black: 2000 V, 295.4 K).

### 4.1. Non-irradiated sample

The TSDC profile of the $C_1$ sample has shown a similar behavior observed by Hashimoto et al. [13] in polyethylene, where a strong negative peak is preceded by a relatively weak positive peak which increases with gradually higher polarization voltages. According to the authors, these TSDC peaks would be produced by two electron

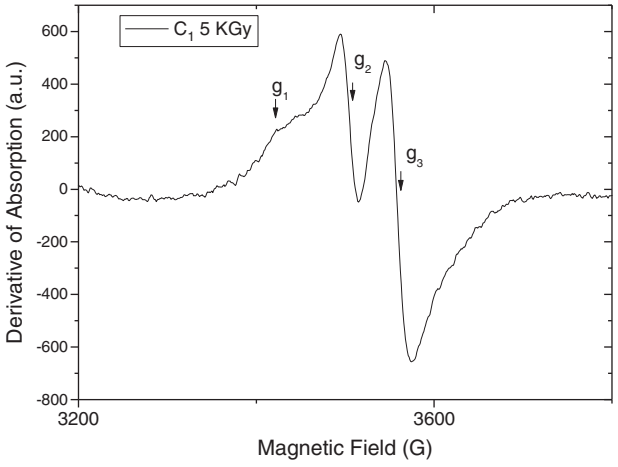


**Fig. 5.** Defect centers $C_1$ sample irradiated with 5 KGy [11].

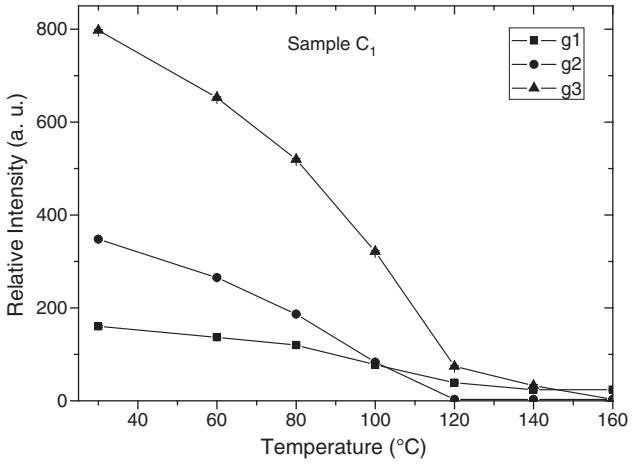


**Fig. 6.** Isochronal curve EPR intensity of sample $C_1$ γ-irradiated with dose of 1 KGy. The error bars are smaller than the experimental points. The straight lines are merely a guide for the eye.

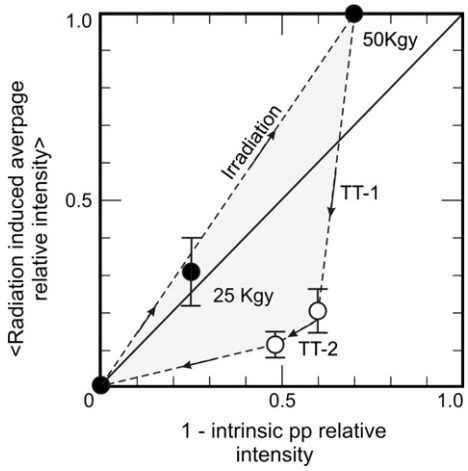


**Fig. 7.** Correlation plot between the radiation-induced average relative TSDC intensity of the positive peaks vs. the complement of the intrinsic peak to peak relative TSDC intensity of the non irradiated sample $C_1$. The solid diagonal ascendant straight line represents a hypothetical bi-reciprocal (one to one correspondence of a mutually interdependent relation) system. The dashed lines were drawn as a guide for the eye. The dark circles were determined from data taken on irradiation, and the open circles form effective thermal treatments (TSDC sans) TT-1 and TT-2, respectively. The errors bars were calculated from the error of the original average value, of the six peaks, and propagated to the relative value calculated dividing by the respective value of maximum dose (50 KGy).

trapping mechanisms involved with different processes of charge injection: 1) the positive peak is attributed to the release of homo-charges (ions or electrons injected by the electrode) and 2) the negative peak is due to hetero-charges (permanent dipoles or ions previously existing inside the material) which accumulate at the interface separating crystalline from amorphous phases, where the electrons formerly injected in the material were trapped by defects and/or impurities present in the bulk. Certainly this is not exactly the case of the material considered in the present study, which is amorphous, so that such interfaces do not exist. In the present case we attribute the TSDC intrinsic intensity (peak to peak of the non-irradiation sample) to the changes in the orientations of the ($NBO^-$, $V_O^+$) and/or ($NBO^-$,$Na^+$) dipoles on heating, after the previous sample polarization procedure. The small positive peak seen in Figs. 1 and 2 is interpreted as a small (negligible) amount of electrons (holes) injected by the electrode.

### 4.2. Irradiated sample

It is seen in Figs. 3 and 4 that on irradiation there is a decrease of the negative intrinsic peak which was originally observed in the non-irradiated sample, which is recovered by the heating of the successive readings, resulting in an apparently reversible process. Conversely, the growth of the six TSDC peaks, of approximately regular spacement of 50 K seems to occur at the expense of the previously existing peaks prior to irradiation, as confirmed by the partial correlation plot of the relative peak intensities, shown in Fig. 7.

In Fig. 7 the relative intensities (fractions of the maximum value) of the average values of the six positive γ-radiation induced peaks, defined as "radiation induced average relative intensity", are plotted versus the complement of the intrinsic peak to peak relative intensities of the negative TSDC at ~340 K, preceded by the relatively weak positive peak at ~300 K, here defined as "1 − intrinsic pp relative intensity". The comparative values of the ascendant irradiation path and the descendant path of effective thermal treatments, TT-1 and TT-2, equivalent to successive heating procedures of two TSDC readings, were compared to a straight ascendant diagonal (solid) line of a hypothetical one to one correspondence. This analysis led to the following immediate conclusions:

1) the first TSDC reading, equivalent to the first thermal treatment (TT-1) has eliminated ~80% of the radiation induced peak intensity, indicating that there is a fast initial thermal decay followed by a near slow one of thermal treatment TT-2, followed by a complete thermal bleaching;
2) if the correspondence between the growth mechanisms of the six TSDC peaks and the decrease of the pre-existing peak before irradiation would be bi-reciprocal (one to one correspondence of a mutually interdependent relation), it is expected that the ascendant path evolution on irradiation would be coincident with the descendant one under subsequent thermal treatments TT-1 and TT-2 on the same straight diagonal (solid) line of Fig. 7. This is not the case for the actual experimental points, indicating the presence of at least one additional species taking part in the reaction induced by irradiation, where creation and annihilation of dipoles take part in the TSDC measurements.

One of the possible mechanisms, contributing to the observed recombination behavior, can be postulated on the basis of the γ-ray ionizing and also radiolyzing radiation-induced defects. The radiolysis effect of the radiation produces the breaking of some NBO bonds, after the following reactions:

$$NBO^- \xrightarrow{radiolysis} V_0^+ + O^{2-}$$

$$NBOHC^0 \xrightarrow{radiolysis} V_0^+ + O^-$$

describing the production of oxygen vacancies $V_0^+$ and interstitial $O^-$ and/or $O^{2-}$ anions, at the expense of $NBO^-$. These ions, under favorable conditions, may combine among themselves producing $O_2^-$ or even $O_3^-$ such as found in early EPR work in single crystals heated in oxygen [14–16]. It is expected that the $O^-$ and $O^{2-}$ ions compensate the charges of the $V_0^+$.

It is shown in Fig. 4 that for each TSDC scan, as a consequence of heating, the six peaks created on irradiation are thermally bleached. It is reasonable to ascribe this bleaching to an inversion of the NBO radiolysis reaction, i.e., the gradual reconstruction of the covalent bond of the oxygen formerly withdrawn by the radiolysis effect of the sample irradiation. Thus, for each intermediate stage of this bond reconstruction can be the responsible for each of the six TSDC peaks observed after γ-irradiation. The thermal recovery of the intrinsic intensity can be then associated with the NBO recovery. Such NBO reconstructed bonds would be initially weak and elongated, relaxing gradually until reaching the original stable distances of $\alpha_x \sim 2{,}3$Å or $eq \sim 2{,}0$Å. During the course of this relaxation specific interactions of

the several related intermediate dipoles and the electric field applied during the TSDC measurements occurred, whose detailed mechanism is not yet understood.

The not bi-reciprocal result (Fig. 4) indicates the existence of another center which receives electrons from the $NBO^-$ centers, more stable than the products of the radiolysis effect described above. Reminding that the NBOs are mainly charge-compensated by the mobile $Na^+$ cations, rather by the positively charged oxygen vacancies $V_0^+$, it is reasonable to introduce the idea that the ionic bonds are broken by the γ-irradiation giving rise to the displacement of the $Na^+$ ion to a remote site far away from the $NBO^-$. The thermal treatments performed after γ-irradiation promote the $Na^+$ ion diffusion providing their recombination with the NBOs.

## 5. Conclusion

An intrinsic TSDC response was registered for the non irradiated sodium tellurite glass, composed by an inverted peak of current at about 340 K, preceded by a relatively weak positive maximum observed at ~300 K when a polarizing voltage ≥1200 V was applied. The TSDC intensities decreased by means of subsequent heat treatments, equivalent to successive heating procedures of two TSDC readings.

After 25 and 50 KGy γ-irradiation doses, the growth of a set of six positive TSDC peaks, regularly spaced by intervals of 5 K, was observed with a concomitant decrease of the depolarization of the intrinsic peak.

The subsequent effective thermal decay steps were performed; with additional TSDC readings showing a fast initial thermal decay followed by a slower one, indicating that the recombination between the irradiation radiolysis products do not have a simple mutually interdependent relation (one to one relation) thus having a more complex nature involved. One of the possible mechanisms contributing to the observed recombination behavior is attributed to radiolyzing radiation-induced defects by means of the NBO bond breaking, by producing the $(V_0^+,O^{2-})$ dipoles with allowed discrete distances, each one responsible for each of the six positive TSDC positive peaks. However, the lack of one to one relation between these components, indicates that there is at least one additional component taking part in the reaction. A reasonable hypothesis is that the γ-irradiation induces the separation of the $Na^+$ from the $NBO^-$. This process is reversible after thermal treatments.

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