Thermal-electric field induced luminescence under poling condition in soda-lime glass
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Abstract
The thermal-electric field luminescence induction under the poling conditions in soda lime glass is investigated. The blue-violet luminescence shows three main peaks at ~340 nm (3.56 eV), ~360 nm (3.77 eV), and ~380 nm (3.34 eV). The potential barrier associated to the ionic current (0.26 eV) and the luminescence (3.6 eV) agree respectively to the Sodium ionic current reported in the literature and to the observed signal. The luminescence thresholds are also observed with, a minimum electric field of ~3.5kV/cm or thermal energy ~31meV. The average ionic jump length of the ionic current and the luminescence also shown similar trend of threshold. At a thermal energy range of ~33-44 meV the ionic current length exhibit a boost and the luminescence jump length increases by a factor of 4.

Introduction
Meyers et al. experimentally showed the possibility of induction of second order nonlinearity (SON) in glass using a poling technique [1]. Further investigations have been relating this effect to the ionic current owing to impurities in the glass composition letting an asymmetrical charge distribution inside the material. Due to this asymmetry an intense electric field ($E_{DC}$) is established in the material, and a stable effective SON related to the third order nonlinearity - $\chi^{(3)} = \chi^{(3)} E_{DC}^2$ - is induced [2,3]. Nevertheless, despite the high alkali content the effective SON does not last long in soda-lime glasses under traditional poling conditions [4]. Recently an alternative procedure to poling this glass controlling the rate of the induced current was adopted and this drawback was overcome [5], and SON lasting up to seven months was observed.

Thus, owing the relevance of the induced ionic current to the poling process, this investigation aims to characterize the contribution of the luminescence observed during the poling procedure in the induced ionic current under the traditional poling procedure.

Experimental Setup
The experimental setup for thermal-electric filed procedure (TEFP) processes was reported elsewhere [1-5]. The present apparatus consists of a DC High voltage power supply (GLASSMAN) with the output voltage (0-5kV) and the short-circuit output current (0-25mA) independently set. The samples are hold in pressed-on stainless-steel electrodes and warmed up by temperature adjustable heating elements. The temperature is monitored via voltage of a thermocouple type $N$ acquired through a digital multimeter (AGILENT 34401). The dynamic of the induced current across the sample is observed via the voltage drop in the resistor $R$ measured and the digital multimeter (HP3457A). The electrical induced current and the electrodes temperature are acquired during each poling procedure and stored in a computer. The output power supply voltage and current are set and monitored via an Analog-Digital board in the same computer. The luminescences were detected by an S-20 photomultiplier tube and a SR-530 Stanford Research lock-in amplifier coupled to a microcomputer for data storage. When applicable the McPherson 0.67m, and resolution ~0.1nm, monochromator is used to the light dispersion. The samples with typical compositions 73%SiO$_2$- 13%Na$_2$O-9%CaO-4%MgO and small amount of other oxides are cut in pieces of about 25x40mm and 1mm thick.

Results and Discussions
The typical luminescence spectra in the 300-450 nm region is reported in figure 1. It was not detected any signal in the infrared region from 800 nm up to 2400 nm. This visible signal, collected setting the induced current to a fixed value of 300 µA, consists on main contributions at 3.77 eV, 3.56 eV, and 3.34 eV respectively. It was not observed substantial difference in the normalized luminescence spectra for currents fixed at values ranging from 54µA to 700µA. The temperature and electric field dependence of the signal has shown similar trend as the induced current. However, they show different activation energies. Due to this similarity, the luminescence and the induced ionic current were assumed an exponential dependence obeying the simple theory of ionic conduction in crystalline materials. The good agreement with the measured signal and current enable us
qualitatively apply this theory to amorphous materials as well. Thus, the current density expression described by ionic conduction is given by [6]:

\[ j = j_0 \exp\left[-(\phi - \alpha E)/kBT\right] \]  \hspace{1cm} (1)

where \( \phi \) is the height of the potential barrier, and \( \alpha (\alpha = eL/2) \) accounts for the distance between potential barriers \( L \) and the electrical charge \( e \). The order of magnitude of the activation energy of the luminescence and the ionic current are both summarized in the figure 2. These measurements were done directing the whole luminescence to the photomultiplier without dispersion. Assuming two linear fitting region to the luminescence data (solid circles), it is determined a potential barrier of \( \phi \sim 3.6 \text{ eV} \) which are in good agreement with the signals depicted in the figure 1. However, the potential barrier of the induced current (open squares) is \( \phi \sim 0.26 \text{ eV} \), letting an activation energy \( \sim 0.7 \text{ eV} \) for electric fields above 8 kV/cm. This figure is also in good agreement with the activation energy attributed to the ions of Na\(^+\) in the induced ionic current reported in the literature [7]. These results suggest the ionic current also have the contribution of ions trapped in deeper potential well. This contribution to the ionic current is \( j_{\text{ic}} = j_{\text{ic}} + j_{\text{ext}} \), thus the activation energy has also two contribution being one due to the DC contribution \( \sim 0.26 \text{ eV} \) and one assigned to an extraction activation energy \( \sim 3.6 \text{ eV} \) as reported in ref. [8].

![Figure 1: Typical thermal-electric field luminescence spectra of soda-lime glass.](image1)

![Figure 2: Activation energies of the luminescence (solid circle) and the induced ionic current (open square). The solid lines are only guide to the eyes.](image2)

As shown in the insert of figure 3, depending on the applied electric field strength the luminescence has a different start temperature. The dependence of the minimum thermal energy required to start the luminescence is depicted in Figure 3. A thermal energy above \( k_BT = 31 \text{ meV} \) is necessary to activate the signal independently of the electric field. It was not observed luminescence at room temperature \( (k_BT = 25 \text{ meV}) \) even for electric field as high as 50 kV/cm. Conversely, it is expected a minimum electric fields strengths of \( \sim 3.5 \text{ kV/cm} \) to generate the blue-violet luminescence. However, this luminescence onset does not follow the induced ionic current one. The luminescence shown the dependence depict in the figure 3 while the induced current shows a thermal energy linear dependence with the minimum electric field strength like \( k_BT = (46.3 - 1.15E) \text{ meV} \), where \( E \) is given in kV/cm.

The ionic average jump length, estimated through the density current parameter \( \alpha \), was also investigated for different electric fields. The insert of figure 4 depicts its typical trend for thermal energies above 32 meV, where three different slopes are observed. \( L1 \) and \( L2 \) are temperature dependent while the last part has a saturation-like behaviour with small changes with temperature. These results are summarised in the figure 4. Concerning the induced ionic current the first jump length (open squares) – \( L1 \) - increases linearly with the thermal energy in the
range 28-33 meV showing a monotonically behaviour above it. An increasing in the average jump length (solid circles) is observed at ~34 meV suggesting a new contribution to the current. This result reasonably agrees with the onset of the luminescence observed in the figure 2. The consistence of this observation is also observed considering the average jump length evaluated through the luminescence data (solid stars) in the figure 4. The lengths are 5-fold increased for thermal energy in the range ~34-43 meV matching the thermal energy of the onset of the luminescence.

Conclusions
In conclusion, it was investigated the contribution of the luminescence on the ionic current in the soda lime glass under poling condition. It was seen that the ionic current have the contribution of ions trapped in deeper potential well giving a contribution to the ionic current like $j_{\text{eff}} = j_{\text{DC}} + j_{\text{sc}}$. Suggesting that the activation energy has also two contributions being one due to the DC contribution (~0.26 eV) and one assigned to an extraction activation energy (~3.6 eV). The signal had shown a thermal energy or electric field strength threshold. Independently of the temperature it was not observed visible signal for electric field above 4.0 kV/cm, as well as, it was not observed the signal for electric field as high as 50 kV/cm at room temperature. Finally, the average jump length witnesses the signal contribution to the ionic current showing a substantial change in the potential barrier distance for temperature above the luminescence onset.

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References