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Dielectric Relaxation Process and Pyroelectric Currents in $LiNbO_3$: Fe Single Crystals

By

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The study of the dielectric function and the pyroelectric coefficient of $LiNbO_3$: Fe single crystals over a wide range of Fe concentrations and heat treatment reveals the presence of a low frequency relaxation process strictly associated to the variation of the pyroelectric currents in these materials. The investigation of these properties is very important in view of recent holographic storage applications of this kind of material.

Die Untersuchung der dielektrischen Funktion und des pyroelektrischen Koeffizienten von $LiNbO_3$: Fe-Einkristallen über einen weiten Fe-Konzentrationsbereich und bei Temperung ergeben einen niederfrequenten Relaxationsprozeß, der streng mit der Änderung der pyroelektrischen Ströme in diesen Materialien verknüpft ist. Die Untersuchung dieser Eigenschaften ist im Hinblick auf neuere Holographiespeicheranwendungen dieser Art von Materialien sehr wesentlich.

1. Introduction

$LiNbO_3$: Fe is a ferroelectric material with important optoelectronic and non-linear optical properties [1].

Laser induced changes in the index of refraction are responsible for holographic storage in this kind of material. During the hologram writing process electronic space charge fields are generated by non-uniform illumination, which modulate the refractive index via the electro-optic effect. During read-out the crystal is illuminated homogeneously and the space charge fields are partly compensated.

The storage of holograms in this kind of material is associated to photoexcitation of free electrons (from the Fe ions) out of the occupied traps and their subsequent recapture by empty traps. It has been assumed that the occupied traps are provided by Fe^{+2} and the empty traps by Fe^{+3} ions [2, 3], therefore, the study of this kind of dopant play an important role in developing favourable properties for optical applications.

The purpose of this paper is the study of complex dielectric function and pyroelectric coefficient of various Fe concentrations in $LiNbO_3$ subject to oxidation and reduction processes.

2. Experimental

The $LiNbO_3$: Fe and $LiNbO_3$ crystals were grown in air by the Czochralski method. Iron was added to the melt as Fe_2O_3. The impurity concentration in the crystals was measured

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in the liquid phase. The samples used were crystals with dimensions of 10 × 10 × 1 mm^3. The dielectric measurements were made using a capacitance bridge (General Radio model 1615-A) in conjunction with a lock-in amplifier (EG & G model 5208). Low-temperature measurements were done in a liquid-nitrogen cryostat. All the measurements were done with the capacitor plates perpendicular to the *c*-axis of the crystal.

Oxidation or reduction of impurity ions was achieved by subsequent heat treatment at 900 °C in air or pure argon atmosphere from 6 to 15 h [4, 5]. Reduction of Fe^{+3} to Fe^{+2} in $LiNbO_3$: Fe occurs when the crystal is annealed in atmospheres with low oxygen pressure.

$$2\,Fe^{+3} + O^{-2} \rightarrow 2\,Fe^{+2} + 1/2\,O_2\uparrow .$$

The pyroelectric coefficient was determined at constant stress using the dynamic technique of Lang and Steckel [6]. In this method the sample is shunted by a calibrated resistor, usually of 10^9 to 10^{10} Ω resistance. The voltage produced in the sample, while its temperature is changed slowly and uniformly, is measured by a high-impedance electrometer. Under these conditions, it can be shown that the voltage produced is related to the pyroelectric coefficient by the following equation:

$$U = PAR\,\frac{\mathrm{d}T}{\mathrm{d}t}\,, \tag{1a}$$

where U is the voltage, P the pyroelectric coefficient, A the electrode area, R the resistance of the shunt, and $\mathrm{d}T/\mathrm{d}t$ the time derivative of the temperature.

3. Results and Discussion

In Fig. 1 we have the real and imaginary parts of the dielectric function of sample No. 5 ($LiNbO_3$: Fe, x = 0.289 mol% Fe), which is the sample with the highest iron content. For this sort of samples we observed two main peaks. The first one is around 30 kHz and the second at 92 kHz with satellites.

This kind of behaviour was observed only in highly doped samples. The intensity of these resonances decreases rapidly with decreasing Fe concentration [7]. This is the reason why the resonances were not observed for samples with lower iron concentration (including pure $LiNbO_3$). This behaviour indicates that the Fe ions are responsible for the resonances.

In Fig. 2 (curves a and c) and Fig. 3a, b we have the same group of peaks as in Fig. 1 in a more appropriate scale. In these figures the points are the experimental data and the continuous line is a theoretical fitting that will be discussed in this paper.

One important characteristic of these resonances is that after a heat treatment in the presence of air or argon (oxidation or reduction) there is a tendency to disappear for all the resonances. In Fig. 2, curves b and d we observe what happens to the imaginary and real parts of the dielectric function shown in curves a and c, after a heat treatment (2 h at 600 °C in air) of the sample.

The main peak has a bigger linewidth ($\Delta\omega_1$ = 0.23 to 1.17 kHz) and is shifted in frequency. At the same time the first resonance around 30 kHz disappears completely with this annealing. If the period or the temperature of annealing is further increasing, no more resonances were detected (at least with our present experimental sensitivity).

In trying to understand the high loss behaviour observed in these samples the pyroelectric coefficient was measured around room temperature. In Fig. 4, curve c we have the coefficient for a pure crystal. If one starts increasing the Fe concentration, there is a clear tendency to decrease the pyroelectric current. A lower coefficient was detected for more concentrated samples, Fig. 4, curve a (x = 0.289 mol% Fe).

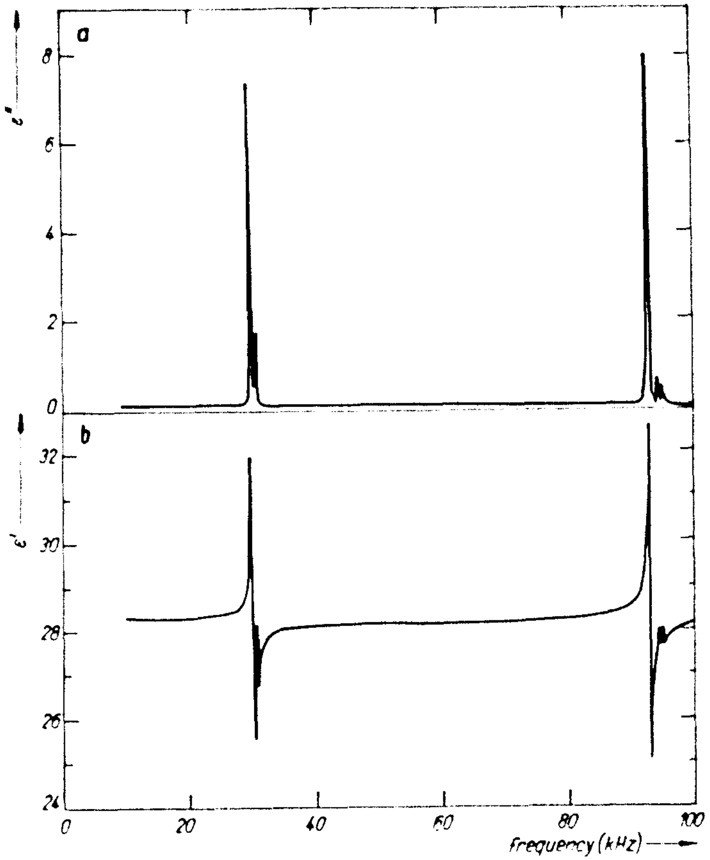

Fig. 1. b) Real and a) imaginary parts of the dielectric function of the sample with x = 0.289 mol% Fe. (The experimental points are connected by a continuous line)

On taking the same sample (No. 5) Fig. 5, curve a and submitting it to oxidation processes (in air) such as, 2 h at 600 °C and 4 h at 900 °C the coefficient will be just as shown in Fig. 5, curves b and d, respectively. Taking the same sample (Fig. 5, curve a) and applying a reduction (in argon) process we have a coefficient like that of curve c (6 h at 900 °C). This is a clear indication that the heat treatment increases the value of pyroelectric coefficient of the more concentrated sample.

We have to remember the existence of Fe^{+2} and Fe^{+3} in $LiNbO_3$ and at the same time that the ratio Fe^{+2}/Fe^{+3} could be changed by reduction or oxidation during heat treatment [5].

In our case the resonances are more pronounced in more doped samples and disappear for less doped and pure $LiNbO_3$. At the same time the pyroelectric coefficient is getting lower for these highly doped samples, Fig. 4. After the appropriate annealing (oxidation or reduction) all the resonances are destroyed and the pyroelectric coefficient increases up to values of the order of that for pure $LiNbO_3$, Fig. 5.

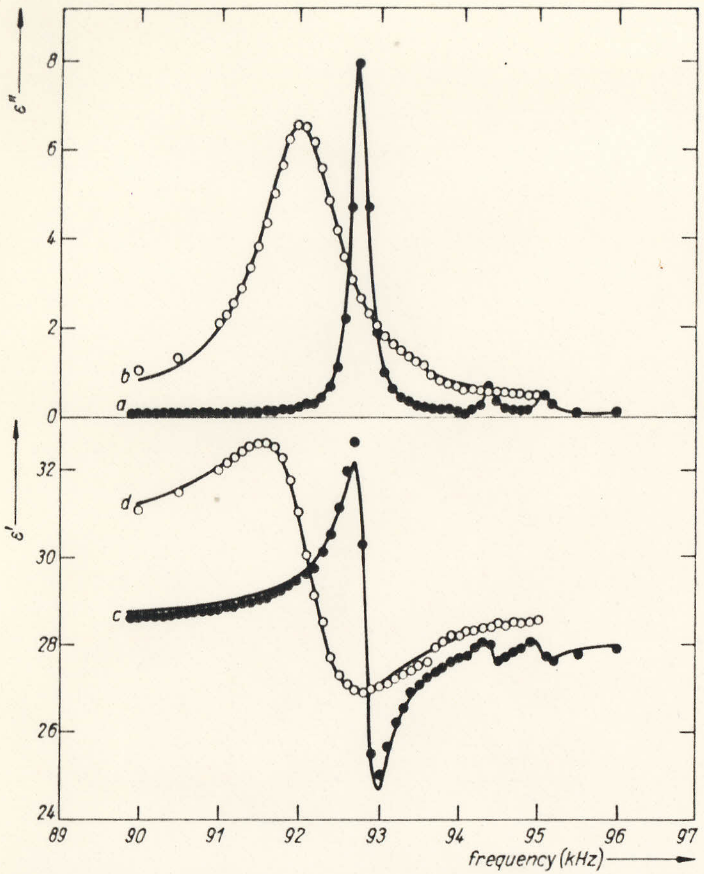

Fig. 2. Dielectric functions. Points are experimental results and the continuous line is the fitting of the theoretical functions. The relevant fitting parameters are (a) and (c) resonance frequencies $\omega_1 = 92.78$ kHz, $\omega_2 = 94.41$ kHz, and $\omega_3 = 95.1$ kHz and linewidths $\Delta\omega_1 = 0.23$ kHz; $\Delta\omega_2 = 0.14$ kHz, and $\Delta\omega_3 = 0.178$ kHz, respectively. For (b) and (d) $\omega = 92.14$ kHz and $\Delta\omega = 1.17$ kHz, respectively ($x = 0.289$ mol%, $T = 294$ K)

The low-energy and long-time relaxation associated with these resonances ($1/\Delta\omega \approx 5$ to 10 ms) suggest the existence of clusters of Fe^{+3} and Fe^{+2} in these samples. These clusters could be formed by a certain number of ions that relax very slowly as a unity with the ac field. Looking at Fig. 1 we could say that we have two main kinds of clusters in this sample. Resonance measurements in different samples of the same Fe concentration showed that the intensity relation between the two main peaks changes. This is an indication that the two populations of clusters could change from sample to sample depending only on the Fe diffusion during the sample preparation.

In less concentrated samples the tendency to form these clusters is much lower. This is clear from experiment since the resonance signals decrease rapidly with decreasing iron concentration.

After a heating treatment these structures are destroyed and Fe ions will be homogeneously distributed over the crystal. The low-frequency relaxation associated with these structures will disappear.

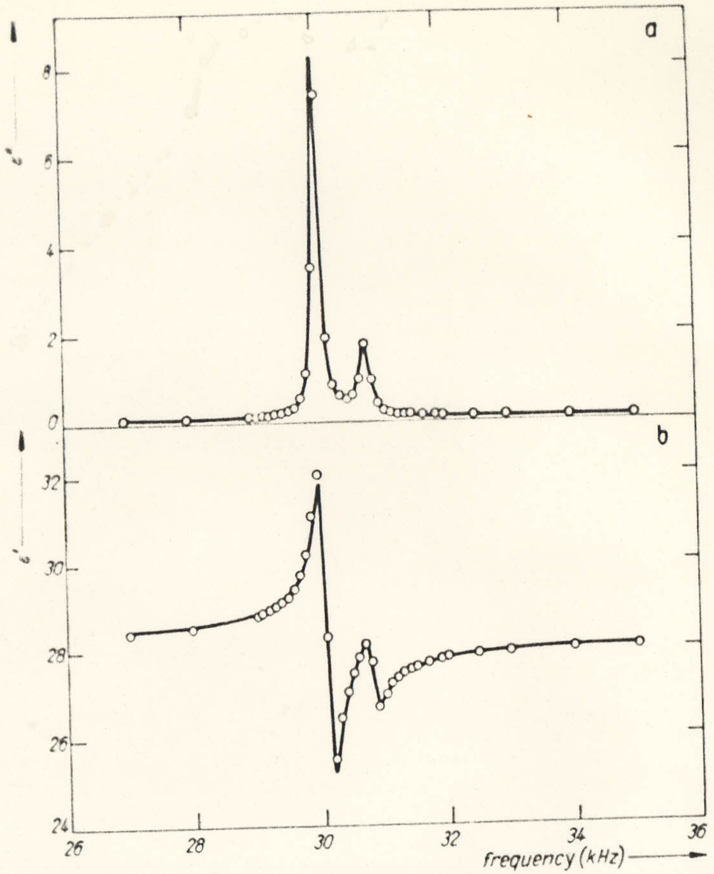

Fig. 3. Dielectric functions. Points are experimental data and the continuous line is the fitting of the theoretical function. Fitting parameters are $\omega_1 = 30.07$ kHz, $\omega_2 = 30.79$ kHz, $\Delta\omega_1 = 0.13$ kHz, and $\Delta\omega_2 = 0.19$ kHz ($x = 0.289$ mol%, $T = 294$ K)

We have to emphasize that the existence of these structures can change the crystal symmetry and consequently the clear decrease of the pyroelectric coefficient, Fig. 4. After the heat treatment, Fe has a homogeneous distribution and the pyroelectric coefficient increases again, Fig. 5.

We can conclude that a relaxation process is very clear from these measurements and could be analyzed by the classic treatment of the resonance absorption and dispersion of the dielectric function [7]:

$$\varepsilon^* = n^{*2} = A + \frac{B}{\Delta\omega + i\alpha}, \tag{1b}$$

$$A = 1 + \sum_s \frac{N_s e^2/m_s}{\omega_s^2}; \qquad s \neq r, \tag{2}$$

$$B = \frac{N_r e^2/\varepsilon_0 m_r}{2\omega_r}. \tag{3}$$

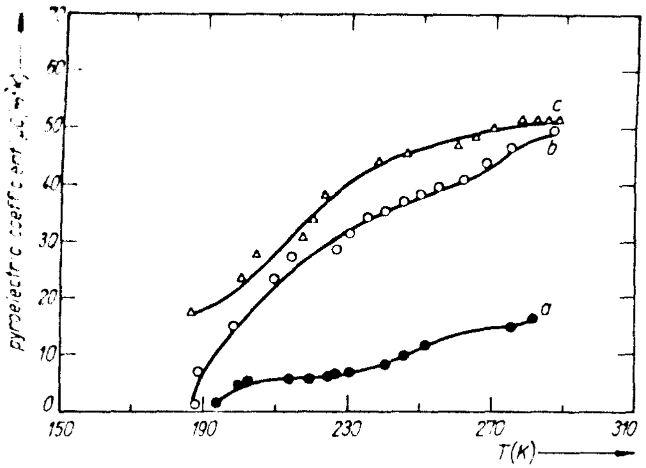

Fig. 4. Pyroelectric coefficient for the samples without heat treatment. (a) $x = 0.289$ mol% Fe. (b) $x = 0.08$ mol% Fe. (c) pure. (continuous line is a guide to the eye)

where ε^* is the complex dielectric constant, n^* the complex index of refraction of the medium, α the half-width of the spectral line, $\Delta\omega$ the deviation from resonance ($\Delta\omega = \omega_r - \omega$), $\alpha = \Delta\omega/2$, N is the number of oscillators, e the electron charge, ε_0 the electric permittivity, m the oscillator mass, and ω the vibration frequency.

The frequency dependence of the real part of the dielectric function is

$$\varepsilon' = n^2(1 - k^2) = A + \frac{B\,\Delta\omega}{(\Delta\omega)^2 + \alpha^2} \tag{4}$$

which is the dispersion characteristic of a dielectric medium near resonance.

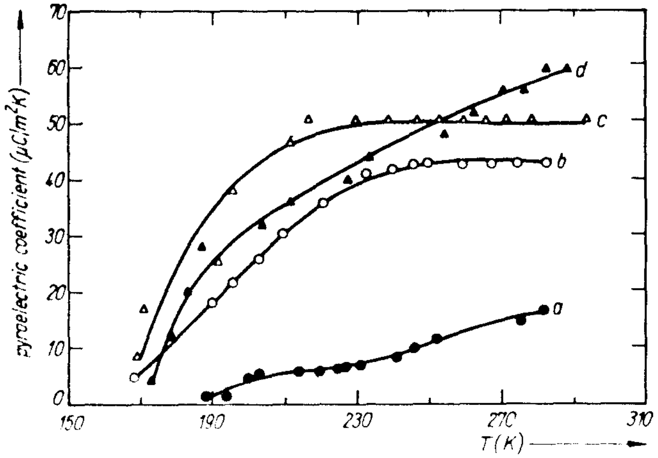

Fig. 5. Pyroelectric coefficient for the sample with $x = 0.289$ mol% of Fe subject to heating process (oxidation (in air) or reduction (in argon)): (a) without heat treatment, (b) 2 h at 600 °C (oxidation), (c) 6 h at 900 °C (reduction), and (d) 4 h at 900 °C (oxidation). (continuous line is a guide to the eye)

The absorption characteristic of the dielectric near resonance is

$$\varepsilon'' = 2n^2k = \frac{B\alpha}{(\Delta\omega)^2 + \alpha^2}. \tag{5}$$

The fittings of Fig. 2 and 3 were done with (4) and (5).

4. Conclusions

The study of the dielectric function and the pyroelectric coefficient of LiNbO$_3$:Fe single crystals over a wide range of Fe concentrations and heat treatment revealed the presence of a well-defined low-frequency relaxation process in highly doped LiNbO$_3$ associated to the formation of clusters of impurities in the crystal. The existence of these resonances is strictly associated with the pyroelectric currents and depends on annealing process and Fe concentration. The experimental dielectric function is well fitted by a low-frequency relaxation process.

The study of these impurities in LiNbO$_3$ is very important for a complete understanding of this kind of material in view of recent holographic storage applications.

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