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Dielectric characterization and ionic conductivity of α-$LiIO_3$ crystals related to the growth conditions

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Abstract

The dielectric response of α-$LiIO_3$ has been studied at room temperature between 20 Hz and 1 MHz with various types of electrodes and compared to the results in the literature. By changing the sample thickness, a relaxation of space charges is clearly identified and the bulk ionic conductivity is deduced from the admittance diagram. Finally a comparison is carried out between chromium doped and undoped crystals obtained from acid and neutral growth solutions. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Lithium iodate in the α form (α-$LiIO_3$) is a well-known optical material exhibiting a large transparency range and strong piezoelectric, photorefractive and non-linear effects. After having been used for second harmonic generation and frequency mixing, new applications in the fields of solid state laser technology and optical data storage have been proposed by incorporating iron-group ions and rare earth elements in these crystals.

Since optical properties of this non-ferroelectric material are strongly related to the quasi-one-dimensional ionic conduction, the response of Z-cut samples under low frequency electric fields has been widely studied by means of dielectric investigations, dielectric breakdown, synchrotron radiation and conventional X-ray diffraction experiments. Nevertheless there are many discrepancies in the literature: results depend not only on intrinsic parameters (acidity and inclusions of the growing solution, doping, etc.) but also on external ones such as the amplitude of the electric field, its time of application and the nature of the electrodes.

In this paper the dielectric behaviour is investigated by using the impedance spectroscopy technique with both metallic and ideally polarizable insulating electrodes (i.e. impermeable to electronic and ionic charge carriers) on crystals grown under different conditions with or without deliberate impurities. We have already shown the ability of α-$LiIO_3$ for guiding light when implanted with protons [1] and the aim of this study is to characterize the ionic conduction of crystal plates in order to develop possible waveguides production by proton exchange and/or ion diffusion methods. Therefore, the identity of the ionic charge carriers and the mechanism of direct conduction must be clearly identified.

2. Experimental details

Large α-$LiIO_3$ single crystals were grown by slow evaporation of slightly supersaturated aqueous solutions (the compound α-$LiIO_3$ was first obtained by the reaction of Li_2CO_3 and HIO_3 in stoichiometric amounts) at a constant temperature of 40°C in neutral ($pH = 6$) or acid ($pH = 2$) environment. Cr-doped crystals were grown by adding chromium nitrate in known amounts to the solution and setting the pH at 2. The Cr^{3+} has been found to replace a Li^+ [2,3] and/or I^{5+} [4] ions and charge compensation occurs through lithium vacancies.

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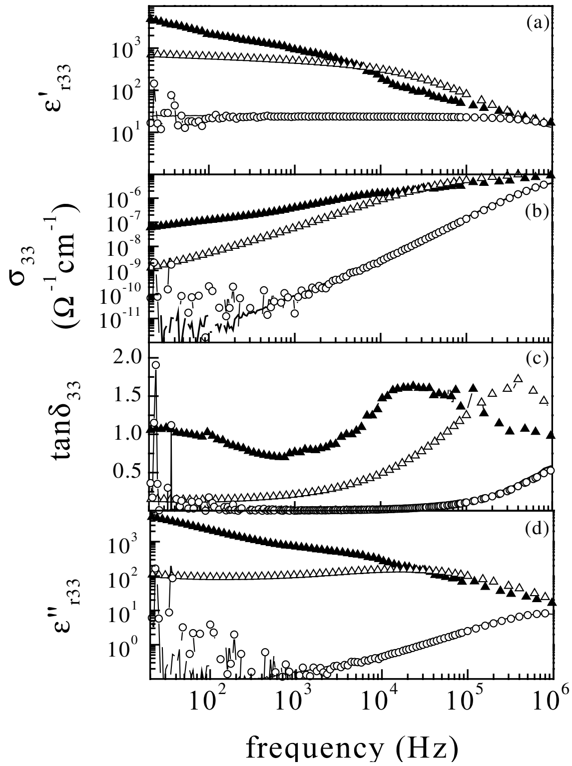


Fig. 1. Dielectric response of an acid α-$LiIO_3$ crystal ($e = 0.35$ mm) with different electrodes: (—) CM with rigid nickel electrodes, (○) NCM with a 20 μm air gap and rigid nickel electrodes, (▲) CM with wet silver paste, (△) CM with "dry" silver paste.

All the dielectric experiments reported here were carried out with Z-cut plates, cut from homogeneous crystals of good optical quality and polished with 1 μm diamond paste. The applied electric field is set in the range 10^{-2}–10^1 V cm^{-1} in order to be in the linear part of the current–voltage characteristic and to avoid time dependent decomposition (dry electrolysis), arising above a few kV cm^{-1} [5,6].

The experimental system, an HP4284A impedance analyser, allows the simultaneous determination of the real part of the dielectric permittivity ϵ'_{r33} and the dissipation factor tan δ for frequencies ranging from 20 Hz to 1 MHz. A 4-terminal pair measurement method is used as well as calibrations to eliminate stray admittance and residual impedance. The edge capacitance is also reduced by using a guarded electrode for both the Contacting Method (CM) (with either rigid metal electrodes of brass nickel-plated or thin film electrodes of metallic pastes) and the Non-Contacting Method (NCM) (here, for a constant distance between rigid electrodes, measurements are made with and without the material inserted so that contact capacitive effects due to the sample surface roughness are reduced).

3. Results

3.1. Determination of the best suited electrodes

A comparison of the different available methods given by experimental setup is illustrated by Fig. 1 where the frequency dependence of the real part of the permittivity ϵ'_{r33} (a), the a.c. conductivity σ_{33} (b), the dissipation factor tan δ_{33} (c) and the imaginary part of the permittivity ϵ''_{r33} (d) is presented for an acid type plate of thickness 0.35 mm.

The NCM and CM with rigid electrodes give identical responses whereas those obtained with silver paste clearly depend on the state of the paint ("wet or dry") and hide the previous ones in the whole frequency range investigated. At very low frequencies, the "wet" silver paint response shows a relaxation mechanism with characteristics of the Maxwell–Wagner effect [7,8] since electrodes are not completely free from solvent. A second relaxation peak, still silver paste state dependent, arises at higher frequencies but is not yet understood. Very high values of ϵ'_{r33} and ϵ''_{r33} are observed and could be related to the "ionic nature" and surface chemical composition of lithium iodate crystals [9], leading to the occurrence of electrochemical reactions. Indeed this surface decomposition has been observed by short circuit currents with deposited Ag, C and In electrodes and confirmed by X-ray photoelectronic spectroscopy [10].

This apparent dielectric response can be compared with spectra obtained with silver paste or sputtered gold films [11,12] and it gives admittance diagrams at room temperature similar to those given in Ref. [13] where deposited layers of Ag, Pd or Li were used as contacting electrodes.

Moreover, as many dielectric materials ($LiNbO_3$, etc.) have identical responses with both metallic pastes and rigid metal electrodes, it seems important to confirm that CM and NCM reveal properties of the material itself and not processes related to the nature of the electrodes. In this way, insulating plates like glass, teflon, mica and kapton were placed between the sample and rigid nickel electrodes because they are chemically inert and present a frequency independent response. Considering a series combination of ideal capacitors, the permittivity can be written:

$$\epsilon'_{r33} = \frac{e}{\epsilon_0 S\left(\frac{1}{C_{tot}} - \frac{2e_i}{S\epsilon_i}\right)} \tag{1}$$

where e ($2e_i$) is the thickness of the sample (insulating plates), ϵ_0 (ϵ_i) the permittivity of the vacuum (insulating material), S the surface of the guarded electrode and C_{tot} the total measured capacity. For an acid type crystal ($e = 1.74$ mm) we obtain a similar behaviour for ϵ'_{r33} with either the CM or the NCM with all ideally polarizable electrodes (Fig. 2).

Oscillations observed at low frequencies for the NCM are due to the small detected values inherent to the method

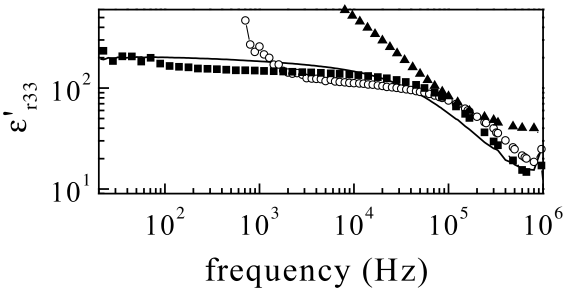
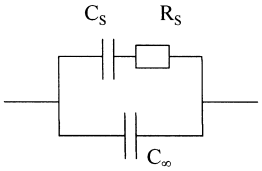


Fig. 2. ϵ'_{r33} dispersion of an acid α-$LiIO_3$ crystal ($e = 1.74$ mm) with different electrodes: (—) CM with rigid nickel electrodes, (○) NCM with a 60 μm air gap and rigid nickel electrodes, (■) NCM with two 70 μm insulating glass plates and rigid nickel electrodes, (▲) CM with wet silver paste.

which are in the limit of the impedance analyser measurement range.

3.2. Characterization of the dielectric response

The continuous decrease of ϵ'_{r33} and the appearance of a wide loss peak on ϵ''_{r33} (Fig. 3) correspond to a relaxation mechanism. From an electrical point of view, the response can be modelled by a series R_S–C_S circuit in parallel with a frequency-independent capacity C_∞ representing any physical process with a faster response. The resistance R_S is assigned to the macroscopic displacement of electric charges in the bulk and C_S to the space charge accumulation so that the complex admittance $Y(\omega)$ becomes:



$$Y(\omega) = i\omega C_\infty + \frac{i\omega C_S}{1 + i\omega R_S C_S}$$

$$= i\omega C_\infty + \frac{i\omega C_S + \omega^2 R_S^2 C_S^2 / R_S}{1 + \omega^2 R_S^2 C_S^2} \quad (2)$$

with

$$C_S = \frac{\epsilon_0 \epsilon_S S}{e},\ C_\infty = \frac{\epsilon_0 \epsilon_\infty S}{e},\ R_S = \frac{1}{\sigma_c}\frac{e}{S}$$

where ϵ_S (ϵ_∞) is the static (infinite) permittivity and σ_c the direct current conductivity.

The relaxation peak in a log–log scale (Fig. 3) is then fitted by the commonly used empirical law [7,p. 192]. For an acid α-$LiIO_3$ crystal of thickness 1.52 mm, linear fits below and above the relaxation frequency give, respectively, $m \approx 0.65$ and $n - 1 \approx -0.8$. Since the absolute slopes m and $(n - 1)$ are lower than 1 this relaxation of ionic conductivity deviates from an ideal Debye response [14,15].

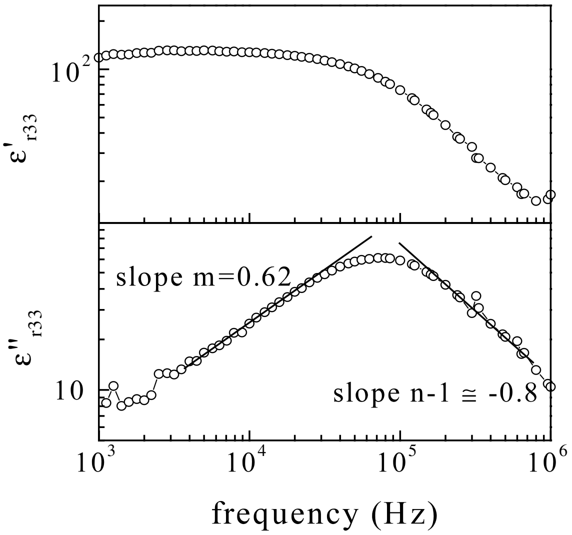


Fig. 3. Dielectric response of an acid α-$LiIO_3$ crystal ($e = 1.52$ mm): (○) NCM with a 30 μm air gap and rigid nickel electrodes.

Afterwards, several equivalent representations exist for analysis:

- Cole–Cole plots are well suited for true dipolar response since ϵ_S and ϵ_∞ directly appear as the extremities of a semicircle.
- The impedance diagram allows, especially in the field of electrochemistry when interphases of different conductivities are permeable to ions, to separate processes related to the bulk from those of the interfaces.
- Here, for completely blocking electrodes, the admittance diagram is used (Fig. 4) for the pH = 2 plate studied above. A vertical straight line corresponding to C_∞ and a semicircle associated with the relaxation mechanism are observed. The two parts are well described if the ratio $\epsilon_S/\epsilon_\infty$ is large [7] and according to Eq. (2) the high frequency limit of the real part of $Y(\omega)$ tends towards the direct conduction σ_c.

As often observed in experimental responses the circular arc is tilted by an angle α from the real axis and the explanation of this inclination is founded on the assumption of a weak dispersion of the local value of conductivity around the average value σ_c [16,p. 163]. So the experimental data are fitted with the circle of radius A centred in $(A\cos(\alpha), -A\sin(\alpha))$ from which we can deduce $\sigma_c = 2A\cos(\alpha) = (0.80 \pm 0.02)\ 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (Fig. 4).

Moreover the disturbances observed around 300 kHz are due to the piezoelectricity of α-$LiIO_3$. Being aware that the number of measurements per decade (≈ 20 pts) is low, these disturbances appear in Fig. 5 below 200 kHz for the sample of thickness 6.26 mm. They are not observed for the plate of thickness 0.35 mm, being probably above 1 MHz, because the thicker the sample is the lower the resonance

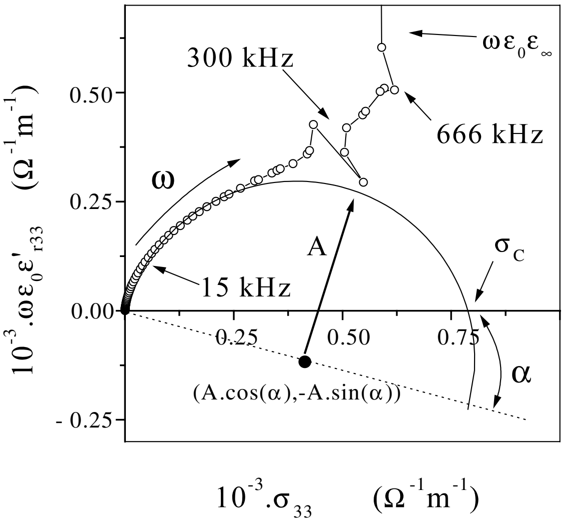


Fig. 4. Admittance diagram of an acid α-$LiIO_3$ crystal ($e = 1.52$ mm): (○) CM with rigid nickel electrodes, (—) ($A\cos(\alpha)$, $-A\sin(\alpha)$) circle of radius A.

frequency is. Moreover we have checked, by using the finite element modelling software ANSYS, that the frequency range around 300 kHz corresponds to the principal modes of vibrations for a parallelepiped of 1–2 mm in thickness.

3.3. Influence of sample thickness

For ionic conductors the displacement of electric charge carriers and their accumulation in the vicinity of the surface create a zone of space charges. In this zone, also called electrochemical double layer structure, the excess of charges induces a variation of the average electrostatic potential. The value of this potential which finally limits the accumulation of charges must not depend on the thickness of the sample.

So, the apparition of space charges was checked by measuring the capacity of samples with thickness varying between 0.35 and 6.26 mm, i.e. in a ratio 18. As the measured capacity remains constant for all plates, the apparent static permittivity increases with the thickness as it appears in Fig. 5 below the relaxation. For ϵ''_{r33}, we observe a shift of the relaxation peak towards the high frequencies when the thickness decreases. This remains coherent with the displacement of a same charge carrier of constant mobility for the acid type crystals.

On the admittance diagram represented in Fig. 6, the semicircle for the sample of thickness 6.26 mm (i.e. with the greatest apparent static permittivity) is more “traversed with increasing frequency before the vertical spur makes a significant contribution” [7,p. 72]. But for all the acid type plates, the direct conductivity deduced from the admittance diagram when the frequency tends towards the infinite is constant around $10^{-5}\,\Omega^{-1}\,cm^{-1}$ and this also confirms a relaxation of ionic conductivity due to the formation of space charges.

3.4. Influence of the growth conditions

Being assured to observe the dielectric properties of the material itself, a first comparison is made for crystals obtained with different growth conditions. The responses of a neutral type plate ($e = 1.03$ mm) and of a chromium doped sample (0.05 mol%, in a growing solution pH = 2,

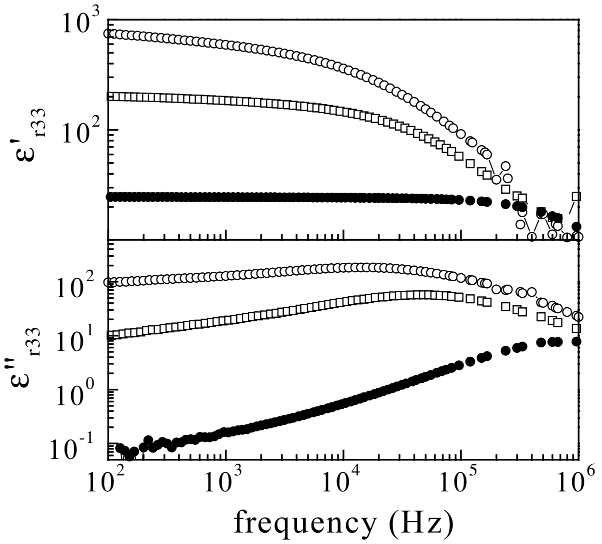


Fig. 5. Dielectric response of acid α-$LiIO_3$ crystals of various thicknesses: CM with rigid nickel electrodes. (○) $e = 6.26$ mm, (□) $e = 1.74$ mm, (●) $e = 0.35$ mm.

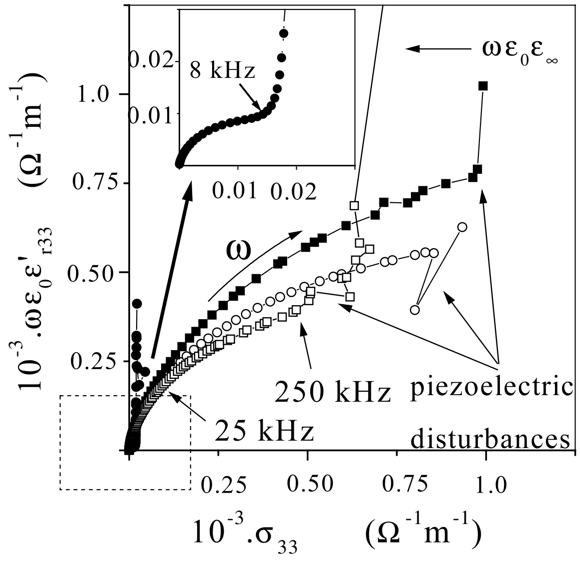


Fig. 6. Admittance diagram for different α-$LiIO_3$ crystals: CM with rigid nickel electrodes. (○) $e = 6.26$ mm, pH = 2, (□) $e = 1.74$ mm, pH = 2, (■) $e = 2.83$ mm, pH = 2, Cr^{3+} doped (0.05% mol.), (●) $e = 1.03$ mm, pH = 6.

$e = 2.83$ mm) are compared on the admittance diagram (Fig. 6).

If the static permittivity of doped crystals behaves, on dielectric spectra (not given here) like that of the acid type plates, the direct conductivity $\sigma_c = (1.70 \pm 0.02) \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ is practically doubled. Thus, the vacancies incorporated during the growth seem to present a determinant contribution to the conduction mechanism of the samples pH = 2.

More striking is the neutral α-$LiIO_3$ crystal behaviour which also presents a relaxation of ionic conductivity (inset of Fig. 6) but the absorption peak is shifted by a factor approximately 30 towards the low frequencies i.e. appears around 1 kHz. On the admittance diagram the direct ionic conductivity varies with the same ratio and is measured at $(0.019 \pm 0.001) \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$.

4. Conclusions

After having demonstrated dubious dielectric behaviour when some metallic pastes are applied on lithium iodate Z-cut plates, we have used impedance spectroscopy to perform fast non-destructive characterizations of crystals grown in different environments. With the use of chemically inert, ideally polarizable electrodes, the low frequency dielectric response observed is to be dominated by the formation of a zone of space charges. The true value of the direct conductivity, i.e. corresponding to macroscopic displacements of ionic charges in phase with the applied electric field, are then deduced from the admittance diagrams.

Identification, concentration and activation energies of the charge carriers are now investigated by studying thermal properties of the dielectric response. A vacancy mechanism seems to confirm the room temperature relaxation of space charges.

In addition, we have shown in the present study that, depending on the growth conditions, ionic conductivity can be already reduced at room temperature. Now, the strong increase of the ultraviolet photorefractive effect below 200 K [17,18] has been connected with the freezing of the ionic conduction. If they remain photoconductive, neutral α-$LiIO_3$ crystals could be of great interest for ultraviolet photorefraction.

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