

Study of the Dielectric Relation and the Doping Effect on Conductivity in Lithium Tantalate

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Ceramics $\text{Li}_{0.98-x}\text{Ta}_{1.004-x/5}\text{Ni}_x\text{O}_3$ (LTN) samples have been prepared, for $x \in \{0; 0.01; 0.02; 0.05; 0.08; 0.15; 0.2\}$. Ac impedance measurements were carried out in the frequency range 1Hz-1MHz and from 300°C to 900°C. The influence of Ni doping on dc conductivity was depicted. Through the ac impedance, dielectric constant was deduced and two dielectric relaxations have been clearly identified at high temperature. The low frequency relaxation is attributed to the space charges, and the high frequency one to ferroelectric dipoles. Systematic fits have been done using the Cole-Cole model. It's appears for identified relaxations, that at the temperature close to T_c , the dispersion step $\Delta\epsilon$ is maximum ; the relaxation time τ is thermally activated and also present an extremum at T_c . The influence of Ni doping on these relaxations, specially the relaxation of the space charges was examined.

Keywords : Impedance spectroscopy, dc conductivity, relaxation, space charge

I. INTRODUCTION

Lithium tantalate (LT) has in recent years been the object of intensive study, because of its large optic non-linearities and corresponding device potential in fields of electrooptic modulation, parametric oscillator, harmonic generator, etc...

LT compound is ferroelectric at room temperature. It's uniaxial at all temperature, with only a single structural phase transition para-ferroelectric at about 660°C, the precise value depending on the Li/Ta ratio [1] and which is close to a second order one.

Although LT does not have the perovskite structure, his ferroelectric structure belongs to the space group R3c and can be considered as a superstructure of the $\alpha\text{-Al}_2\text{O}_3$ corundum structure with Li^+ and Ta^{5+} cations along the c-axis [2].

According to Abrahams and Keve [3], ferroelectricity in this compound is due to the displacements of both the Ta and Li ions within the octahedric sites.

LT is well-known to be narrow range non stœchiometric compound, the solid solubility range extends from about 46 to 50.4% mole Li_2O at room temperature[4]. The Curie temperature T_c decrease linearly with decreasing Li_2O concentration [1], [5], and with varying the doped oxide concentration [6], [7], [8].

Different defect models were proposed to account for the non-stœchiometry. Jebbari et al [9] studied the vacancy model in LT and found that the Li-sites vacancy model seems more probable than the Nb-sites vacancy model. The oxygen vacancy

model was eliminated because he cannot describe the density variation in function of the composition [7].

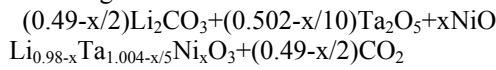
Several studies have reported on the change in electrical conductivity of the Lithium tantalate solid solutions[10], [11], [12], [13], [14]. By complex impedance spectroscopy Huanosta et al [11] studied the variation of the conductivity as function of the stœchiometry in $\text{Li}_{1-5x}\text{Ta}_{1+x}\text{O}_3$ compounds. The LT non-stœchiometric samples present different kind of intrinsic defects to maintain the charge neutrality and therefore can be easily doped by the extrinsic cations , in this way various studies have been performed [15], [6], [16]. Ravez et al [15] studied the relaxor ferroelectric ceramics $\text{Li}_{1-x}\text{Ca}_x(\text{Ta}_{1-x}\text{Zr}_x)\text{O}_3$ ($x=0.15$ and $x=0.20$), they identified a ferroelectric relaxation and determined his relaxation parameters . The relaxation frequency f_r is minimum and the dispersion step is maximum at T_c . When x increase a higher conductivity associated with a lower activation energy and a decrease of the magnitude of f_r at T_c are observed, while the unit cell volume become larger, T_c lower and the transition more diffuse. Joo et al [16] studied the crystallographic and dielectric properties of LiTaO_3 -based non-stœchiometric solid solutions substituted by trivalent ions $(\text{Li}_{1-x}\text{M}^{3+}_{x/3})\text{TaO}_3$, $\text{M}=\text{Al}, \text{Cr}, \text{Fe}, \text{In}$ and $x \leq 0.20$. They showed that all phases obtained are ferroelectric at room temperature, the Curie temperature T_c decreases when the composition deviates from LiTaO_3 . T_c has been related to the size of the M^{3+} cations and to the axial ratio c/a . Torii et al [6] studied the evolution of T_c as a function of doping in $(\text{Li}_{1-x}\text{M}^{2+}_{x/2}\text{Ta}_{x/2})\text{TaO}_3$ with $\text{M}=\text{Zn}, \text{Ni}, \text{Mg}, \text{Ca}$. They

showed that the change of the Curie temperature was found to be closely related with the c/a ratio of the hexagonal cell. The determination of complex impedances and dielectric permittivities allows one to access to conductivity and dielectric constant and eventually to couple them.

In the present paper we study the modification of the electric properties particularly the dc conductivity with Ni doping and the influence of doping in the dielectric properties

II. EXPERIMENTAL

The samples used in our studies were prepared starting from Li_2CO_3 carbonate, Ta_2O_5 and NiO oxides. The mentioned reagents weighted and mixed in the required amounts according to the following chemical reaction.



Then they were fired in three steps of 10 hours; first at 600°C, 800°C and 1000°C. The obtained powder was crushed in the agate mortar and pelletized as disks of 13mm of diameter and about 1mm thickness. The pellets were then pressed under 2500 bars pressure, and finally sintered at 1200-1300°C for 4 hours.

Silver electrodes were deposited on the pellet surface by painting. The painted pellets were placed in a furnace at 600°C for 2 hours.

Ceramics were characterised by X-ray diffraction with a Philips PW 1729 diffractometer using the $\text{Cu K}\alpha$ wave-length, the spectre obtained were pure.

Ac impedance measurements were carried out using an impedance analyser "Solartron 1260" in the frequency range 1Hz-1MHz and from 300°C to 900°C.

All the prepared compositions were analysed in the Service Central d'Analyse of CNRS at Vernaison. The formulae obtained are reported in Table 1. The number of vacancies was calculated by subtraction of the amount of cation sites, considering a main substitution mechanism $5\text{Li}^+ + \text{Ta}^{5+} \leftrightarrow 5\text{Ni}^{2+}$. The errors in the formulae obtained were estimated to be about 0.8% for Li, 0.1% for Ta, and 0.5% for Ni.

%Ni	Experimental formulae
Proposed formulae	
0	$\text{Li}_{0.98}\text{Ta}_{1.004}\text{O}_3$
$[\text{Li}_{0.98}\text{Ta}_{0.004}\square_{0.016}][\text{Ta}]\text{O}_3$	
1	$\text{Li}_{0.97}\text{Ta}_{1.002}\text{Ni}_{0.01}\text{O}_3$
$[\text{Li}_{0.97}\text{Ta}_{0.002}\text{Ni}_{0.01}\square_{0.018}][\text{Ta}]\text{O}_3$	
2	$\text{Li}_{0.96}\text{Ta}\text{Ni}_{0.02}\text{O}_3$
$[\text{Li}_{0.96}\text{Ni}_{0.02}\square_{0.02}][\text{Ta}]\text{O}_3$	
5	$\text{Li}_{0.93}\text{Ta}_{0.994}\text{Ni}_{0.05}\text{O}_3$
$[\text{Li}_{0.93}\text{Ni}_{0.044}\square_{0.026}][\text{Ta}_{0.994}\text{Ni}_{0.006}]\text{O}_3$	

8	$\text{Li}_{0.9}\text{Ta}_{0.988}\text{Ni}_{0.08}\text{O}_3$
$[\text{Li}_{0.9}\text{Ni}_{0.068}\square_{0.032}][\text{Ta}_{0.988}\text{Ni}_{0.012}]\text{O}_3$	
15	$\text{Li}_{0.83}\text{Ta}_{0.974}\text{Ni}_{0.15}\text{O}_3$
$[\text{Li}_{0.83}\text{Ni}_{0.124}\square_{0.046}][\text{Ta}_{0.974}\text{Ni}_{0.026}]\text{O}_3$	
20	$\text{Li}_{0.78}\text{Ta}_{0.964}\text{Ni}_{0.2}\text{O}_3$
$[\text{Li}_{0.78}\text{Ni}_{0.164}\square_{0.056}][\text{Ta}_{0.964}\text{Ni}_{0.036}]\text{O}_3$	

Table 1. Chemical formulae obtained by analysis and proposed formulae according to Iyi et al model [17], where [.] represents the cations sites and \square denotes the vacancies.

III. ELECTRICAL STUDY

It was found that is most convenient to plot the Impedance diagram results at each temperature in the complex plan plot Z'' vs Z' ; typical result is shown in Fig. 1.

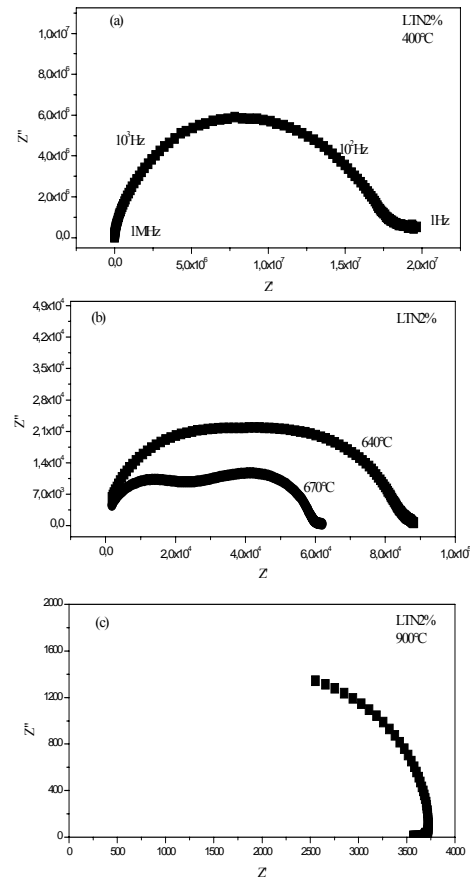


FIG. 1 : Impedance diagram of 2%Ni doped LT measured at fixed temperatures

At the temperature well below the Curie temperature ($\sim 660^\circ\text{C}$), the impedance data for $\text{Li}_{0.98-x}\text{Ta}_{1.004-x/5}\text{Ni}_x\text{O}_3$ take the form of single arc and appears to pass through the origin as shown in Fig1-a, this arc represents the bulk response of our

sample. The low frequency effect such as a spike, could be attributed to polarisation at the electrode-sample interfaces involving that conduction are ionic and charge carriers are probably the Li ions because of its relative feeble mass. However evidence for such polarisation behaviour, associated with ionic conduction is found in the materials which contain vacancies as our cases.

In the region of the Curie temperature, Fig.1-b ; data is regarded as comprising two semi-circles. The additional semi-circle is due to the polarisation mechanisms such as charge storage in the spontaneous polarisation processes responsible for the ferroelectricity [11].

At the higher temperature the arcs are incomplete at the high frequencies as shown in Fig.1-c, this is due to the lack of data caused by the frequency limit of the "Solartron1260".

The value of dc resistance R is given by the low frequency intercept of the semi-circle on the real Z' axis. The impedance data for $\text{Li}_{0.98-x}\text{Ta}_{1.004-x/5}\text{Ni}_x\text{O}_3$ were analysed in this way and values of dc resistance are determined.

In order to examine the influence of Ni doping on dc conductivity of our samples we have represented at fixed temperatures its evolution with Ni content in Fig.2. Three domains of variation of dc conductivity appear, separated by two critical concentration of Ni: $x=0,02$ and $x=0,15$.

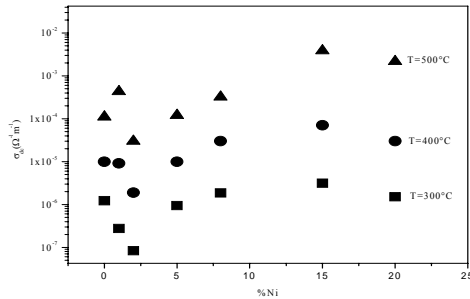


FIG. 2 : Evolution of dc conductivity with Ni content at fixed temperature

For $x \leq 0,02$; assuming that for this range of doping, the Ta ions in excess occupy the Li-sites [18]; the O-octaedra of elementary cell containing Ta ions in Li-sites would smaller than that the O-octaedra filled by the Li ions ($R_{\text{Ta}} = 0.64 \text{ \AA} < R_{\text{Li}} = 0.76 \text{ \AA}$). This deranges the structure and complicates the motion of Li ions; consequently we obtain the decrease of dc conductivity. For $0,02 \leq x \leq 0,15$; dc conductivity increases with Ni content. Indeed, there are no Ta ions in Li-sites [18], the number of vacancies increases with the introduction of Ni, also Li and Ni ions have approximately the same ionic radius ($R_{\text{Ni}} = 0.69 \text{ \AA}$); the motion of both Li and Ni ions contributes simultaneously to conduction, and increases the dc conductivity. When the Ni concentration reaches to

$x=0,15$; an insulating behaviour arises and dc conductivity decreases. So, we think that for high concentration of defects, the charge density at the grain boundaries and at the electrode-sample interface becomes so elevated that the blocking effect of these interfaces takes away the thermal diffusion of charge carriers.

IV. DIELECTRIC STUDY

In Fig.3 we have represented the temperature dependence of the dielectric permittivity for two compositions.

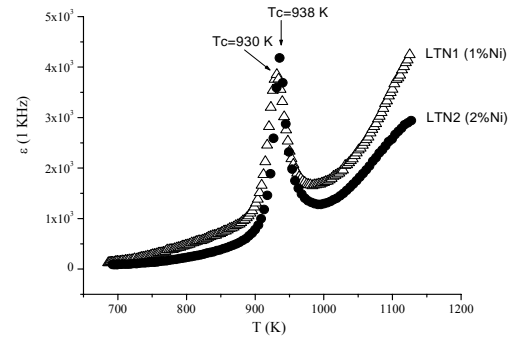


FIG. 3 : The temperature dependence of the dielectric permittivity for two compositions.

These curves present an extremum at the ferro-paraelectric temperature transition T_c . For high temperatures we observe the increase of the permittivity, this is due to the ionic conductivity component of the permittivity.

From the electrical response of our samples through the ac impedance, we have deduced their dielectric response. We have represented the frequency dependence of the real part of the dielectric constant in Fig.4. In the range of frequencies (1Hz-1MHz), and for all Ni compositions, two dielectric relaxations were clearly identified at high temperature.

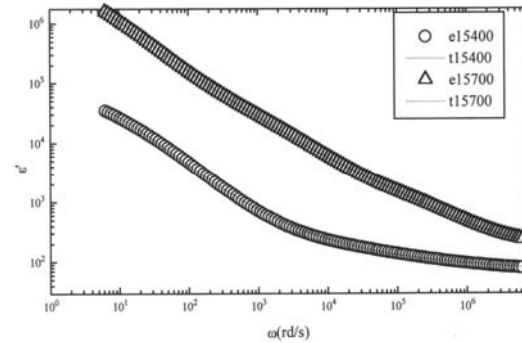


FIG. 4 : The frequency dependence of the dielectric constant of the data for 15%Ni, The solid line represents the fit , circle and triangle are the

experimental data presented respectively at 400°C and 700°C

Regarding typical domain of associated frequencies, we have attributed the high frequency relaxation to the ferroelectric dipole such as the movement of the Li^+ ions [19]; and the low frequency relaxation is due to the localisation of the free charges at the metal-dielectric interface and eventually at the grain boundaries. Indeed free carriers are stored at the metal-dielectric interface and at the grain boundary leading to a space charge, this effect is well known in number of dielectric materials [20]; the application of an electric field breaks the symmetry of this space charge and the macro-dipole is thus created.

In order to identify physical mechanisms associated to these relaxations, we have realised fitting curves using the following formula:

$$\varepsilon'(\omega) = \sum_{i=1,2} \left\langle \varepsilon_{\infty_i} + \frac{\Delta\varepsilon_i \left[1 + (\omega\tau_i)^{1-\alpha_i} \sin\left(\frac{\alpha_i\pi}{2}\right) \right]}{1 + 2(\omega\tau_i)^{1-\alpha_i} \sin\left(\frac{\alpha_i\pi}{2}\right) + (\omega\tau_i)^{2(1-\alpha_i)}} \right\rangle$$

Which represents the real part of the response as sum of the two dielectric relaxations according to the Cole-Cole model ($i=1$ points to the relaxation of the space charge, and $i=2$ to the relaxation of the ferroelectric dipole). Fig.4 shows for instance the fitting curves for two compositions.

From these fittings, the relaxation parameters have been determined, typical temperature dependence of these parameters are presented in Fig.5&6. It appears for identified relaxations that at the temperature close to T_c , the dispersion step $\Delta\varepsilon_i = \varepsilon_{s_i} - \varepsilon_{\infty_i}$; $i=1,2$; is maximum involving that the relaxor force is maximum.

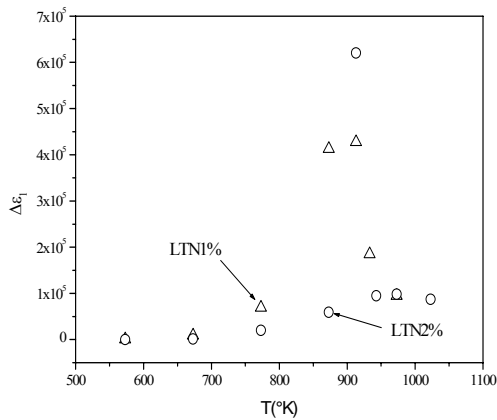


FIG. 5 : Evolution of the dispersion step of the relaxation of the space charge with the temperature for two studied concentrations of Ni.

The relaxation time of the relaxation of the ferroelectric dipole is thermally activated and also presents an extremum at T_c as consequence of the ferroelectric soft mode vibration of the Li^+ ions [19], which can oscillate from one side to another of an octahedral face.

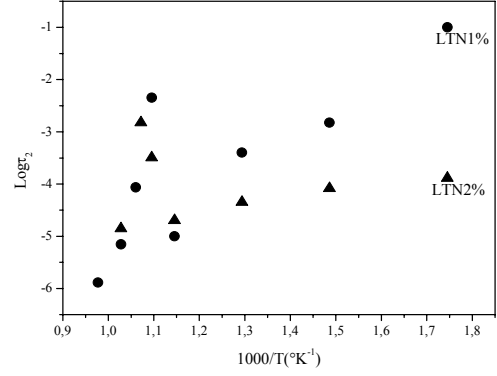


FIG. 6 : Evolution of the relaxation time of the dipole with the inverse of temperature for two studied concentrations of Ni.

In order to examine the influence of Ni doping on dielectric properties particularly the dielectric relaxation associated to space charges, we have represented at fixed temperature ($T=700^\circ\text{C}$) the evolution of its relaxation time with doping in Fig.7.

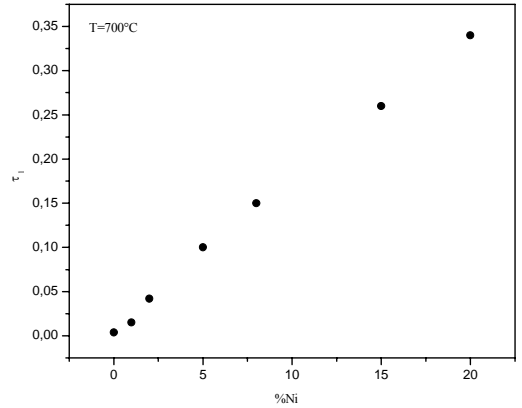


FIG. 7 : Evolution of the relaxation time of the space charge with Ni content at fixed temperature.

It appears that Ni introduction slows down linearly this relaxation; also at this temperature, dc conductivity increases linearly with Ni content as depicted in Fig.8. Indeed, the ions experience the combined influence of the field which tends to accumulate the charges at interfaces, and thermal diffusion which tends to oppose this accumulation. So we think that the Ni introduction increases linearly the charge density at the metal-dielectric

interface and eventually at the grain boundaries, through the dc conductivity; this reinforces the macro-dipole and renders its reorientation more difficult and therefore slower.

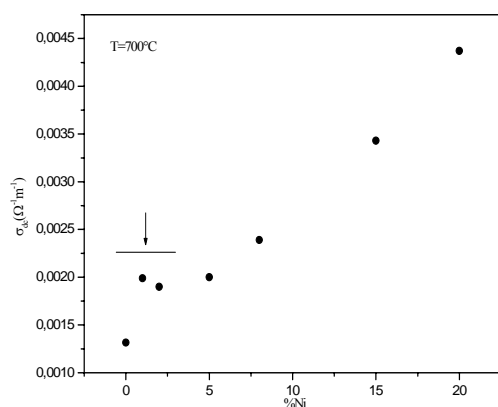


FIG. 8 : Evolution of dc conductivity with Ni content at fixed temperature

One notices that the evolution of dc conductivity with Ni content at $T=700^{\circ}\text{C}$ is not rigorously linear; in the small concentration of Ni ($x \leq 0.02$), we have a considerable deviation from a linear law as a consequence of the substitution of the Li ions by the Ta ions and related phenomena discussed earlier in the electrical study paragraph.

V. CONCLUSION

In the region of the ferroelectric Curie temperature, complex impedance plot shows evidence for an additional semi-circle associated with the capacitance of the ferroelectric polarisation processes. According to the substitution mechanism described by Iyi[17], for $\%Ni \leq 2\%$, Ta ions in excess and Ni ions occupy the vacants Li ions sites; dc conductivity decrease with Ni content. Beyond 2%, Ni ions occupy simultaneously the vacants Li and Ta ions sites, dc conductivity increases with Ni content, until at 15%, we have the decrease of dc conductivity. Two dielectric relaxations have been clearly identified at high temperature. The low frequency relaxation is attributed to the space charge and the high frequency one to ferroelectric dipole. Systematic fits have been done. It appears for identified relaxation that the relaxation time is thermally activated and presents an extremum at T_c ; also at T_c the relaxor force is maximum. At $T=700^{\circ}\text{C}$, the Ni doping slows down the relaxation of the space charge.

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