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Impedance spectroscopy analysis of pure and Ni-doped lithium tantalate

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Abstract

Ceramics of $LiTaO_3$ with different Li/Ta ratios and $Li_{0.98-x}Ta_{1.004-x/5}Ni_xO_3$ solid solutions with $0 \leqslant x \leqslant 0.20$ are studied by impedance spectroscopy in the 1 Hz–1 MHz frequency range and the 500–1200 K temperature range. The evolution of the dielectric properties and the Curie temperature are studied as a function of the Li/Ta ratio and of the Ni content. The ionic conductivity is determined for all compositions from Cole–Cole diagrams and the evolution vs temperature is studied as a function of the Li/Ta ratio and of the Ni content. The results are discussed and related to the substitution mechanism. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Defects; Dielectric properties; Impedance spectroscopy; Ionic conductivity; $LiTaO_3$

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1. Introduction

Lithium niobate and lithium tantalate have been the subject of extensive studies for more than 20 years due to their properties in electro-optics, electro-acoustics and nonlinear optics. Properties may be modified by doping: for example doping with MgO improves optical properties of $LiNbO_3$ crystals.[1] The structure of ferroelectric $LiTaO_3$ (LT) as well as that of $LiNbO_3$ (LN) belongs to space group R3c and can be considered as a superstructure of the α-Al_2O_3 corundum structure, with Li^+ and Ta^{5+} cations along the *c*-axis.[2] LT and LN are well-known to be narrow-range nonstoichiometric compounds; in LT, the solid solubility range extends from about 46 to 50.4% mol Li_2O at room temperature.[3] The Curie temperature T_C decreases linearly with decreasing Li_2O concentration.[4,5] Different defect models were proposed to account for the non-stoichiometry. The oxygen vacancy model was eliminated[6,7] and among the cation site vacancy models, the Li-site vacancy model[1,6,8] seems more probable than the Nb-site vacancy model.[9–11] Different works were published on LN or LT doped with different cations.[7,8,12] Torii et al.[8] studied the evolution of T_C, as a function of doping in $(Li_{1-x}M_{x/2})TaO_3$ (M = Zn, Ni, Mg, Ca) solid solutions. They showed that T_C increases with the c/a ratio of the hexagonal cell parameters. Iyi et al.[1] studied the Mg-doping effect on the structure of LN and Malovichko et al.[13] investigated K and Mg-doped LN. Paul et al.[3] reported on Ni- and Co-doped LN and LT. Substitution mechanisms have been the subject of controversy and depend upon the Li/Nb (Li/Ta) ratio of the pure LN or LT, the chosen type of substitution and the nature of the doping cations.[1,3,6,7,9]

Other properties which are the subject of investigations are (i) the dielectric permittivity and (ii) the ionic conductivity generally assigned to lithium diffusion, at least in non-stoichiometric compounds.[5,14–16] By complex impedance spectroscopy, Huanosta et al.[14] studied the variation of the conductivity as a function of the stoichiometry in $Li_{1-5x}Ta_{1+x}O_3$ compounds. With the same technique, Ming et al.[17] studied the dielectric dispersion of a $LiTaO_3$ single crystal at low frequencies and deduced a relation which is a generalisation of the Cole and Cole relation[18] between the complex permittivity ϵ^* and the measuring frequency ω, which takes into account the response of the lattice and of the

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charge carriers. 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 of LT with different stoichiometries and those of a slightly non-stoichiometric LT (%mol $Li_2O = 0.49$) when it is substituted by Ni^{2+} cations up to 20% mol Ni in relation with the substitution mechanism when the Ni content increases.

2. Experimental

Ni-doped LT samples were prepared from Li_2CO_3, Ta_2O_5 and NiO powders in stoichiometric quantities corresponding to the following equation:

$$(0.49 - x/2)\ Li_2CO_3 + (0.502 - x/10)\ Ta_2O_5 + x\ NiO \rightarrow\ Li_{0.98-x}\ Ta_{1.004-x/5}\ Ni_xO_3 + (0.49 - x/2)\ CO_2$$

considering a main substitution mechanism 5 Li + Ta$\Longleftrightarrow$5 Ni. The nickel contents are $x = 0$, 0.01, 0.02, 0.03, 0.05, 0.08, 0.15 and 0.20. All these compositions are in agreement with the stability domain of the phase determined by Paul et al.[3]

LT samples with a general formula $Li_{1-x}Ta_{1+x/5}O_3$ with $-0.1 < x < 0.1$ were also prepared.

Lithium carbonate and tantalum and nickel oxides are mixed by attrition with ZrO_2 balls in isopropanol in the 1/3 balls, 1/3 isopropanol and 1/3 solid phase ratio and shaken for 12 h. After the sedimentation, the suspension was dried in a rotovapor and calcined at 1100 K for 10 h. Powders were then isostatically pressed at 2500 bars to give pellets of 13 mm in diameter and 1 mm in thickness and were sintered at 1500 K for 4 h with a heating rate of 100 K/h. 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. The errors in the formulae obtained were estimated to be about 0.8% for Li, 0.1% for Ta and 0.5% for Ni.

A single crystal was prepared by CRISMATEC by the Czochralski method; the measured Curie temperature of 845 K is consistent with a composition described by a Li/Ta ratio of 0.935. A sample was cut as a disk, the diameter being perpendicular to the polar axis.

Ceramics were characterized by X-ray diffraction with a Philips PW 1729 diffractometer using the CuK_α wavelength.

Ag electrodes were deposited on opposing faces of the ceramics and the single crystal and fired at 1000 K for 2 h in order to perform electrical studies. Two types of electrical measurements were carried out as a function of temperature in an atmosphere of normal lab air: (i) the evolution of the dielectric permittivity ϵ' and (ii) the evolution of the conductivity σ by complex impedance spectroscopy. The dielectric permittivity was studied between 600 and 1200 K with a heating rate of 2 K/min. A preliminary measurement is necessary to insure the reproducibility of results and the stability of the samples. For conductivity studies, isothermal measurements were carried out between 600 and 1200 K with temperature steps of 50 or 100 K except in the T_C range where steps were reduced to 20 K. The instrumentation comprised a Solartron-1260 Impedance Gain Phase Analyzer controlled by a PC computer. The range of measuring frequencies was 1 Hz–1 MHz for ceramic samples and 1 Hz–13 MHz for the single crystal. Applied voltages were always 0.5 V (rms). Ceramic pellets or single crystal sample were put between the Pt electrode rods of a Al_2O_3 sample-holder running in an electric furnace. A Pt(Rh10%)/Pt thermocouple located near the sample is connected to a Keithley 2000 electrometer to measure temperatures; reported temperatures are estimated as accurate to ±2 K.

Table 1
Chemical formulae obtained by analysis and proposed formulae according to Iyi et al. model[1]

	Experimental formulae	Proposed formulae
Li/Ta		
1.12	$Li_{1.10}Ta_{0.98}O_3$	$[Li_{0.08}Li][Ta_{0.98}Li_{0.02}]O_3$
1.05	$Li_{1.05}Ta_{0.992}O_3$	$[Li_{0.042}Li][Ta_{0.992}Li_{0.008}]O_3$
1	$LiTaO_3$	$[Li][Ta]O_3$
0.976	$Li_{0.98}Ta_{1.004}O_3$	$[Li_{0.98}Ta_{0.004}\square_{0.018}][Ta]O_3$
0.95	$Li_{0.958}Ta_{1.008}O_3$	$[Li_{0.958}Ta_{0.008}\square_{0.034}][Ta]O_3$
0.88	$Li_{0.90}Ta_{1.02}O_3$	$[Li_{0.90}Ta_{0.02}\square_{0.08}][Ta]O_3$
Ni%		
0	$Li_{0.977}Ta_{1.005}O_3$	$[Li_{0.977}Ta_{0.005}\square_{0.018}][Ta]O_3$
1	$Li_{0.972}Ta_{1.0015}Ni_{0.010}O_3$	$[Li_{0.972}Ta_{0.0015}Ni_{0.010}\square_{0.0165}][Ta]O_3$
2	$Li_{0.955}Ta_{1.001}Ni_{0.020}O_3$	$[Li_{0.955}Ta_{0.001}Ni_{0.020}\square_{0.024}][Ta]O_3$
3	$Li_{0.942}Ta_{0.999}Ni_{0.03}O_3$	$[Li_{0.942}Ni_{0.029}\square_{0.029}][Ta_{0.999}Ni_{0.001}]O_3$
5	$Li_{0.912}Ta_{0.998}Ni_{0.05}O_3$	$[Li_{0.912}Ni_{0.048}\square_{0.040}][Ta_{0.998}Ni_{0.002}]O_3$
8	$Li_{0.897}Ta_{0.988}Ni_{0.08}O_3$	$[Li_{0.897}Ni_{0.068}\square_{0.035}][Ta_{0.988}Ni_{0.012}]O_3$
15	$Li_{0.836}Ta_{0.973}Ni_{0.15}O_3$	$[Li_{0.836}Ni_{0.123}\square_{0.041}][Ta_{0.973}Ni_{0.027}]O_3$
20	$Li_{0.780}Ta_{0.964}Ni_{0.20}O_3$	$[Li_{0.780}Ni_{0.164}\square_{0.056}][Ta_{0.964}Ni_{0.036}]O_3$

3. Results and discussion

Ceramics were characterized by X-ray diffraction and scanning electron microscopy. They exhibit the structure of pure $LiTaO_3$[9] and a uniform grain size of about 2 μm.

3.1. Cell parameters

The cell parameters were determined from X-ray patterns recorded at a scanning speed of 1/4° 2θ/min and were refined by least square method calculations. They are reported in Table 2. In pure LT, when the Li/Ta ratio decreases, cell parameters and volume increase whereas the *c*/*a* ratio decreases. In doped LT, when the Ni content increases, the *a* dimension slightly decreases whereas the *c* dimension, the cell volume and the *c*/*a* ratio increase (Fig. 1).

3.2. Dielectric measurements

Fig. 2 shows the temperature dependence of ϵ' for the different compositions at 1 kHz frequency measurement. The following features are observed:

- T_C increases with the Ni content as shown in Fig. 3. There is a sharp increase of T_C between $x=0$ and $x=0.025$ and a weaker increase for $x>0.025$;
- the shape of the dielectric peak varies with the composition. For $x=0$, the peak is quite large (FWHM ~40 K), it sharpens when x increases up to 0.02 (FWHM ~17.5 K) then it broadens for $x>0.02$ (FWHM ~37.5 K for $x=0.08$);
- the value of the dielectric constant at T_C is ~2500 in pure LT; it increases with the Ni content (as an example, $\epsilon'_{\max}$ ~8000 for $x=0.03$);
- the conductivity component of the permittivity increases with the Ni content above 1000 K.

In Fig. 4, the relative inverse dielectric susceptibility was plotted as a function of temperature for $x=0$ and $x=0.02$ compositions. The two curves are quite similar but for 2%Ni-doped LT, the Curie–Weiss law $1/\epsilon'=(T-T_C)/C$ is practically obeyed (at 1 kHz, the Curie constant $C=1.4\times10^5$ in good agreement with Tomeno

Table 2
Values of crystal parameters, Curie temperatures, FWHM of the dielectric peaks and activation energies for the different compositions studied

	a (Å)	*c* (Å)	*c*/*a*	Volume (Å)^3	T_C (K)	ϵ' (T) FWHM	E_a (eV)
Li/*Ta*							
1.12	5.1505	13.765	2.6726	316.24	658	17.8	1.02
1.05	5.1513	13.766	2.6723	316.35	652	17.9	1.04
1.00	5.1520	13.767	2.6722	316.46	644	22.4	1.16
0.976	5.1523	13.768	2.6721	316.51	633	39	1.14
0.95	5.1535	13.770	2.6720	316.72	588	69	0.91
0.88	5.1569	13.776	2.6713	317.27	510	–	0.86
%Ni							
0	5.1523	13.768	2.6721	316.51	633	39	1.14
1	5.1512	13.771	2.6734	316.47	658	30	0.94
2	5.1511	13.776	2.6744	316.55	663	21.3	1.12
3	5.1508	13.779	2.6751	316.59	680	22.3	0.93
5	5.1500	13.786	2.6769	316.62	684	23.4	0.97
8	5.1502	13.797	2.6789	316.93	688	34	0.88
15	5.1495	13.804	2.6806	317.00	696	–	0.81
20	5.1489	13.810	2.6821	317.16	705	–	0.95

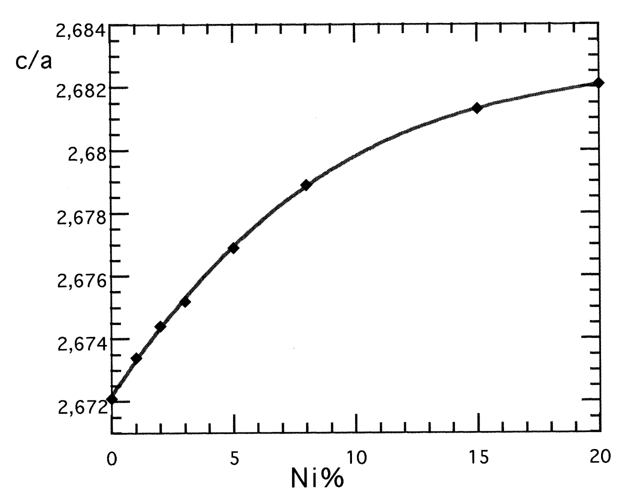

Fig. 1. *c*/*a* Ratio vs Ni% in the $Li_{0.98-x}Ta_{1.004-x/5}Ni_xO_3$ solid solution system.

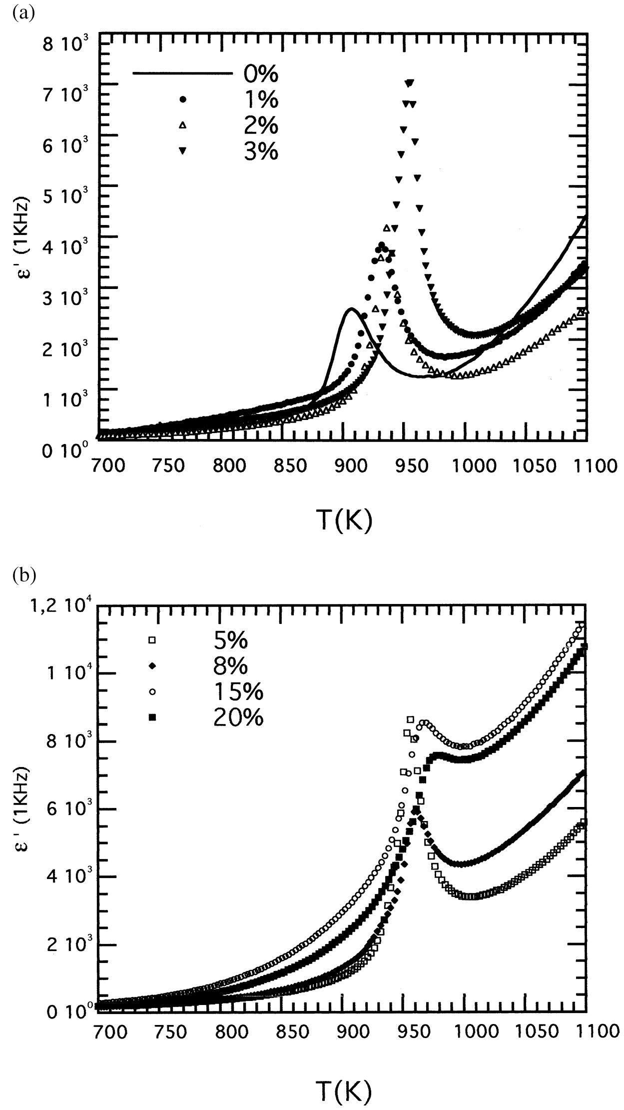

Fig. 2. Dielectric permittivity vs temperature for (a) pure LT and LT doped with 1, 2 and 3% Ni; (b) LT doped with 5, 8, 15 and 20% Ni (Li/Ta = 0.98).

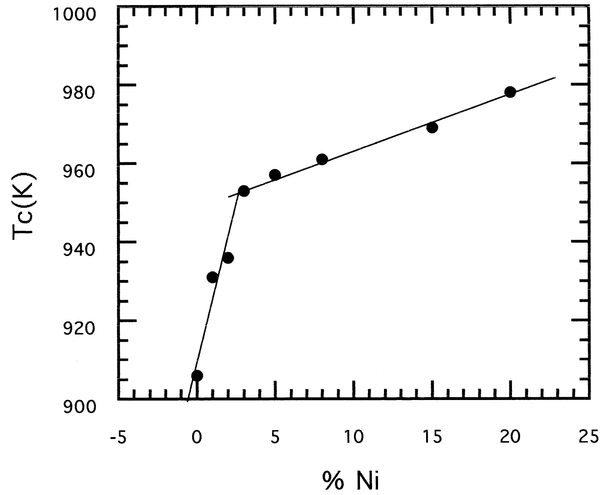

Fig. 3. Curie temperature as a function of Ni content in the $Li_{0.98-x}Ta_{1.004-x/5}Ni_xO_3$ series.

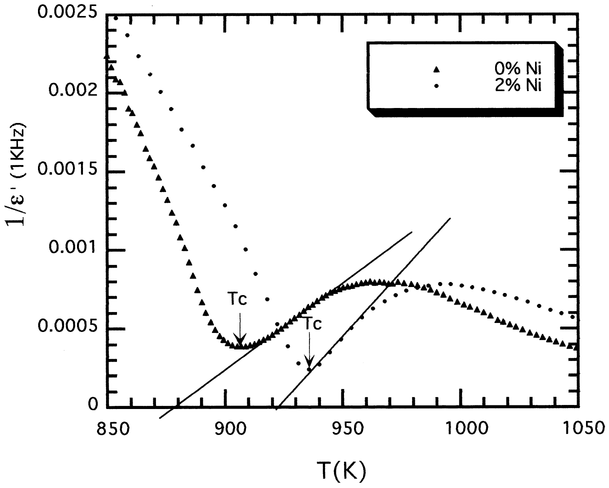

Fig. 4. Inverse dielectric permittivity at 1 kHz frequency measurement as a function of temperature for 0 and 2% Ni in the $Li_{0.98-x}Ta_{1.004-x/5}Ni_xO_3$ series.

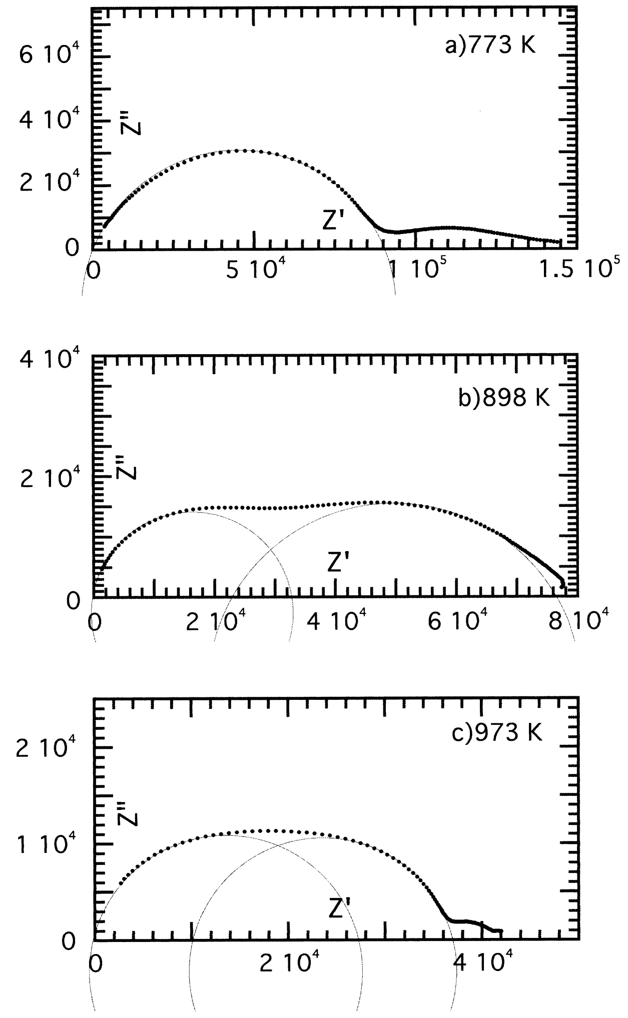

Fig. 5. Impedance spectra of pure LT (Li/Ta = 0.98) measured at (a) 773 K; (b) 898 K; (c) 973 K (Z' and Z'' in ohms).

and Matsumura)[16] whereas, for pure LT, a small deviation from linearity is observed about 20–30 K above T_C. Deviations from linearity are also observed in Ni-doped oxides with $x \geqslant 0.03$. These observations are in agreement with the $\epsilon'(T)$ behaviour.

In Table 2 are reported the values of T_C and of the dielectric peak FWHM for all the Ni-doped compositions as well as those observed for LT with different Li/Ta ratios.

A relationship is observed between the c/a ratio and T_C in the two series: T_C increases when the c/a ratio increases. This behaviour has already been observed by different authors.[8,19] According to Safarayan[20] the thermal expansion of the crystal could be the reason for a phase transition. This author suggests that the value of T_C depends on the position of the Li^+ ion along the c axis in the elementary crystal cell. On the other hand, Elouadi and Mouahid[19] mentioned the change of the c axis equilibrium position when a doping cation replaces Li^+ or Nb^{5+}. When the vacancy content and the Ni content vary, the relative position of cations in the crystal cell is modified. Thus the c/a ratio of the hexagonal cell is connected with the cooperative displacements of the cations along the c axis which are responsible for the ferroelectricity at T_C.

The anomaly observed for $x \approx 0.02$ in the evolution of T_C and in the shape of the dielectric peak may be related to a modification of the mechanism of substitution of nickel cations in the lattice when the NiO content is greater than about 2.5%. Taking into account the model described by Iyi et al.,[1] the prepared pure LT should have the chemical formula $(Li_{0.977}Ta_{0.005}\square_{0.018})$ Ta O_3. When Ni cations are inserted in the lattice, it is thus probable that they are preferentially located on the lithium sites and replace the tantalum atoms. From the formulae given in Table 1, it is seen that this is obtained for a Ni content comprised between 2 and 3%. For higher Ni contents, Ni cations should be located on both Li and Ta sites. For example, for $x = 0.05$ the formula should be: $(Li_{0.912}Ni_{0.048}\square_{0.040})$ $(Ta_{0.998}Ni_{0.002})$ O_3.

It can be noted that the disorder is minimised when the tantalum lies alone on the B-site of the structure and the A-site is occupied by Li^+, Ni^{2+} and vacancies, i.e. for $0.02 < x < 0.03$. This is in good agreement with the dielectric behaviour, disorder tending to a broadening of the dielectric peak and to a deviation from the Curie–Weiss law.

3.3. ac Impedance studies

It is usual to plot the results of the complex impedance measurements for each temperature as $Z'' = f(Z')$ diagrams. Some results are given for pure LT ceramic, 8%Ni-doped LT ceramic and for the single crystal in Figs. 5–7 respectively. For temperatures below T_C, experimental results give a semicircle inclinated of an angle $\beta \approx 20°$ with the Z' axis. To a first approximation, the corresponding equivalent circuit is a parallel RC element. The value of R is given by the low frequency intercept of the semi-circle on the Z' axis. The value of C is given by the relation $2\pi fRC = 1$, f being the frequency of the maximum of the semi-circle. For the data in Fig. 5a, C is evaluated to be 30 pF. It corresponds to the bulk response. The small semicircle observed at low

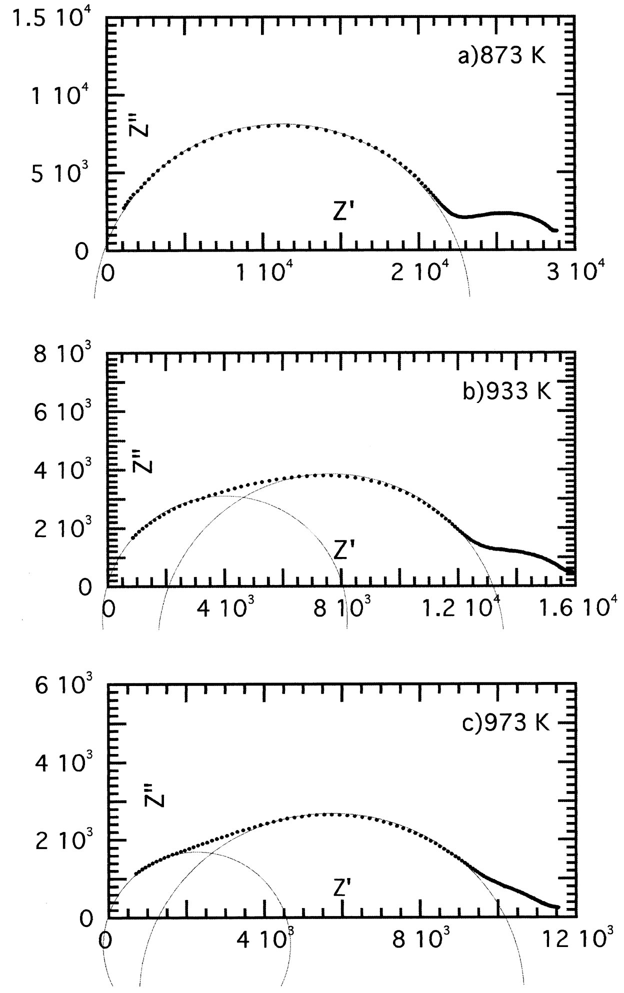

Fig. 6. Impedance spectra of 8%Ni doped LT measured at (a) 873 K; (b) 933 K; (c) 973 K (Z' and Z'' in ohms).

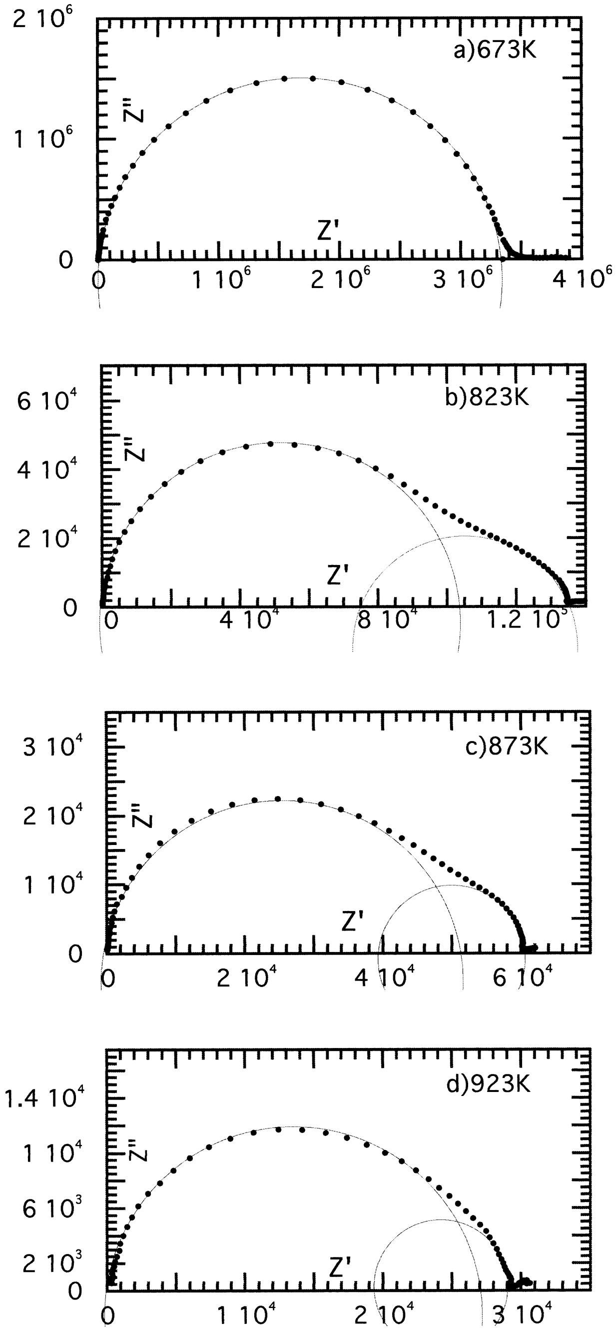

Fig. 7. Impedance spectra of LT single crystal (Li/Ta = 0.935) measured at (a) 673 K; (b) 823 K; (c) 873 K; (d) 923 K (Z' and Z'' in ohms).

frequencies is due to the component of the electrode–electrolyte interface;[21] this contribution would arise if the charge carriers are mobile ions or electrons. The corresponding C value is 1.2 μF and thus in the range of typical double-layer capacitances (1–10 μF). Approaching the T_C range (~925 K in pure LT ceramic), another semicircle appears (see Fig. 5b and c) which disappears slowly at temperatures above T_C. The same phenomenon is observed in Fig. 6 for the Ni-doped ceramic and in Fig. 7 for the single crystal. Our results are in good agreement with those published by different authors: Huanosta and West[14] in LT ceramics with Li/Ta ratio of 1 and 0.786, Ming et al.[17] in LT single crystal with Li/Ta ratio of 0.976. Different authors assigned the semicircle which appears in the T_C range to the spontaneous polarization processes.[14,15,17,22] In this assumption, the first semicircle should be assigned to dielectric relaxation due to permanent dipole orientations or other motions which do not involve long-range displacements of mobile charge carriers. According to Cho et al.[22] this dipole orientation obeys the dispersion relations of Debye. The second semicircle should be assigned to the conductivity relaxation or carrier response associated with long-range migrations of ions.

Huanosta and West[14] proposed an equivalent circuit which contains two elements R_d and C_d that represent charge storage in the spontaneous polarisation processes. Such dielectric processes are likely to be in parallel with the electronic resistance of the sample R_i and also in parallel with the bulk capacitance C_b. The magnitude of the two component resistances may be extracted from the intercepts on the real Z' axis, as shown in Fig. 8 and the value of the capacitance C_d may be extracted from the position of the maximum of the low-frequency semicircle, as shown. The low-frequency intercept again corresponds to R_i, the dc resistance of the sample. Electrode polarisation associated with the blocking of charge transport at the electrode–electrolyte interface is usually represented by a capacitance C_{dl} in series with the other circuit elements; it gives rise ideally to a vertical spike at low frequencies and more generally to an inclined spike or semicircle. Sinclair and West[15] and Cho et al.[20] proposed very similar equivalent circuits. Using the equivalent circuit of Fig. 8 we obtained R values for the different compositions and from R_i we deduced the conductivity evolution vs temperature.

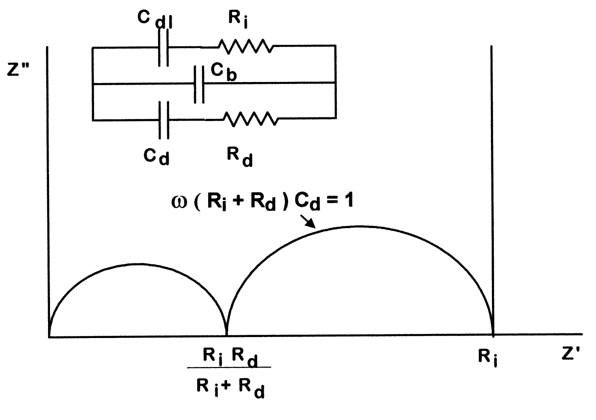

Fig. 8. Equivalent circuit and schematic ac impedance plot used (according to Ref. 14).

The expression of the conductivity is $\sigma = \sigma_0 \exp(-\Delta E_\sigma / kT)$ in which σ_0 is the pre-exponential factor, ΔE_σ is the activation energy and k the Boltzmann constant. By a linear fit and the calculation of the slope of the curve $[\ln\sigma] = \ln\sigma_o - (\Delta E_\sigma/1000.k)[1000/T]$ we obtained σ_o and ΔE_σ. Figs. 9 and 10 show the evolution of $\log\sigma$ as a function of $1000/T$ in the 830–1250 K range for Ni-doped LT compositions and pure LT with different Li/Ta, ratio respectively. Straight lines are obtained and no anomaly, such as a slope change, is manifested at T_C. Thus, the conduction mechanism seems to be the same in both ferro and paraelectric phases. In Fig. 9, it is observed that all straight lines for doped samples are practically parallel, with a slope slightly different from that of the pure sample. The conductivity increases more slowly with temperature in the doped compounds than in the pure one. On the other hand, the conductivity increases with the Ni content except for the 2% Ni-doped compound for which the conductivity is smaller than that observed for the 0 and 1% Ni-doped compounds. This observation can be related to the evolution of the permittivity as a function of temperature (Figs. 3 and 4) where the value of about 2.5%Ni-doping was considered as a threshold beyond which there are no longer tantalum cations on the lithium site. Thus, the introduction of Ni on the Li-site induces a decreasing of the Ta content and of the conductivity until there are no longer Ta on the Li-site. After this threshold which corresponds to a Ni content of about 2.5%, the conductivity increases with the Ni content due to the increasing of the vacancies. In Fig. 10, it is observed that non-stoichiometric LT exhibits a higher conduction than the stoichiometric one in agreement with Huanosta[14] results. In addition, we show that non stoichiometric LT with Li/Ta ratio > 1 exhibits a higher conductivity than non stoichiometric LT with Li/Ta ratio < 1. Thus, the conductivity is higher in compositions with no vacancies and excess of Li than in compositions with a noticeable cation vacancy content (8% for a Li/Ta ratio of 0.88).

All the activation energies are reported in Table 2. For LT with a Li/Ta ratio close to unity, they are about 1.1 eV in good agreement with Huanosta and West.[14] They decrease in Ni-doped compositions and in non stoichiometric LT. These values are characteristic for ionic conduction due to the Li^+ cations. In doped LT and LT with Li/Ta < 1, the diffusion of Li^+ cations increases with the vacancy content. In LT with excess of Li, the diffusion of Li^+ cations is enhanced.

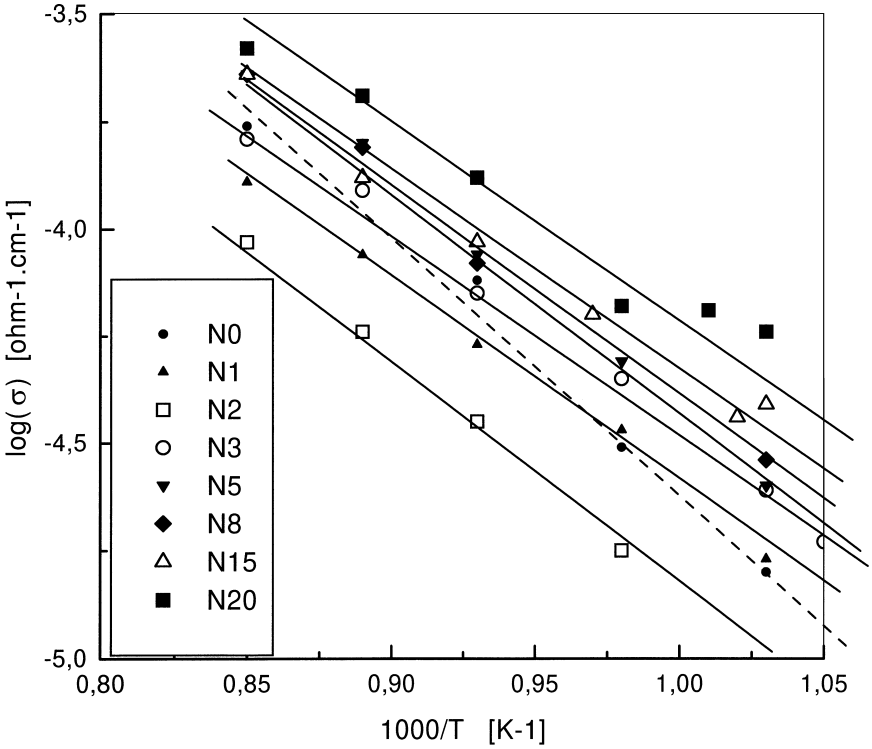

Fig. 9. Conductivity Arrhenius plots for different Ni-doped LT.

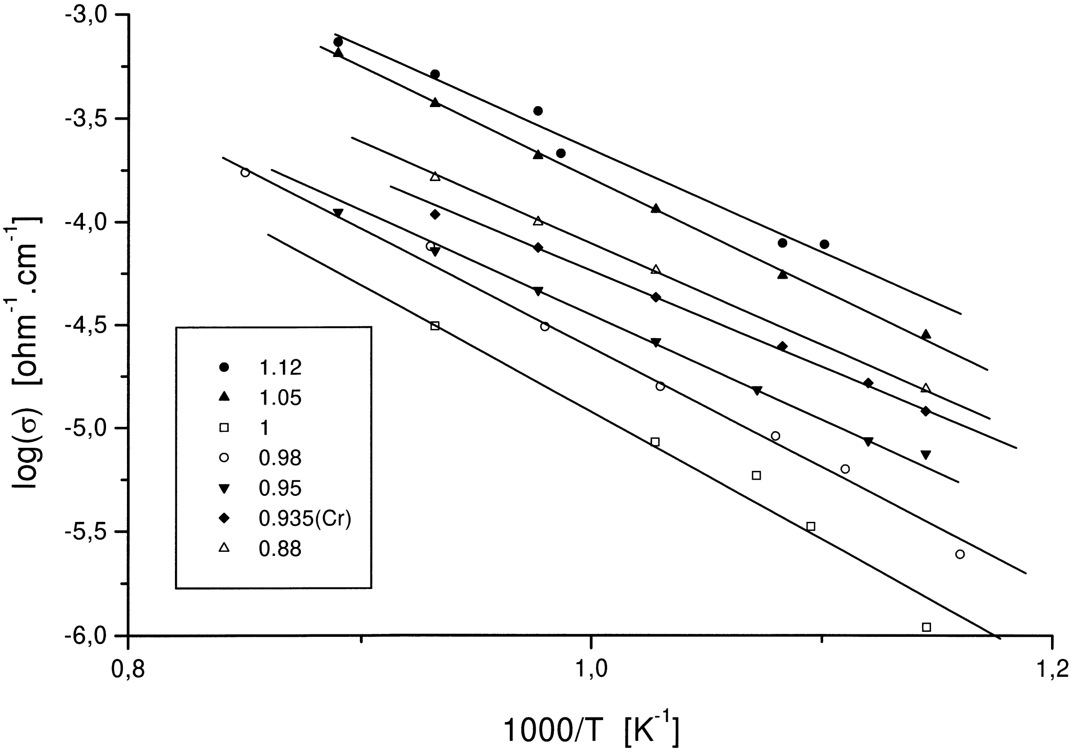

Fig. 10. Conductivity Arrhenius plots for different pure LT.

4. Conclusion

The ac impedance spectroscopy is a powerful technique for characterizing the doping influence and the defects in oxides such as $LiTaO_3$. In the $Li_{0.98-x}$ $Ta_{1.004-x/5}$ Ni_xO_3 series, the dielectric properties are very sensitive with respect to the Ni doping, even at low content, by the values of ϵ'_{max}, the Curie temperatures and the broadness of the dielectric peaks. The conductivity measurements show that the conduction mechanism exhibits the same activation energy in both ferroelectric and paraelectric phases. In pure stoichiometric LT (Li/Ta = 1) the conductivity is about $3\times10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. It increases when the Li/Ta ratio decreases i.e. when the vacancy content increases but it increases more when the Li/Ta ratio increases beyond 1. The variation of the conductivity as a function of the Ni content in the Ni-doped series is in agreement with the dielectric results. The dielectric peak is sharper and the conductivity is lower for $x \sim 0.025$. According to the substitution mechanism described by Iyi,[1] this value of x corresponds to the Ta-site fully occupied by Ta^{5+} cations and to the Li-site occupied by Li^{+} cations, Ni^{2+} cations and vacancies. Our electric measurements are also in good agreement with the proposed occupation of Li and Ta sites in the substitution mechanism $5\ \mathrm{Li} + \mathrm{Ta} \Longleftrightarrow 5\ \mathrm{Ni}$.

References

1. Iyi, N., Kitamura, K., Yajima, Y., Kimura, S., Furukawa, Y. and Sato, M., *J. of Solid State Chem.*, 1995, **118**, 148.
2. Abrahams, S. C. and Bernstein, L. J., *Phys. Chem. Solids*, 1967, **28**, 1685.
3. Paul, M., Tabuchi, M. and West, A. R., *Chem. Mater.*, 1997, **9**, 3206.
4. Ballman, A. A., Levinstein, H. J., Capio, C. D. and Brown, H., *J. Amer. Ceram. Soc.*, 1967, **50**, 657.
5. Fujino, Y., Tsuya, H. and Sugibuchi, K., *Ferroelectrics*, 1971, **2**, 113.
6. Iyi, N., Kitamura, K., Izumi, F., Yamamoto, J. K., Hayashi, T., Asano, H. and Kimura, S., *J. of Solid State Chem.*, 1992, **101**, 340.
7. Allemann, J. A., Xia, Y., Morriss, R. E., Wilkinson, A. P., Eckert, H., Speck, J. S., Levi, C. G., Lange, F. F. and Anderson, S., *J. Mater. Res.*, 1996, **11**, 2376.
8. Torii, Y., Sekiya, T., Yamamoto, T., Koyabachi, K. and Abe, Y., *Mater. Res. Bull*, 1983, **18**, 1569.
9. Abrahams, S. C. and Marsh, P., *Acta Cryst.*, 1986, **B42**, 61.
10. Schirmer, O. F., Thiemann, O. and Wöhlecke, M., *J. Phys. Chem. Solids*, 1991, **52**, 185.
11. Donnerberg, H., *J. of Solid State Chem.*, 1996, **123**, 208.
12. Joo, G. T., Ravez, J. and Hagenmuller, P., *Revue de Chimie Minérale*, 1985, **22**, 8.
13. Malovichko, G., Cercelier, O., Estienne, J. and Grachev, V., *J. Phys. Chem. Solids*, 1995, **56**, 1285.
14. Huanosta, A. and West, A. R., *J. Appl Phys*, 1987, **61**, 5386.
15. Sinclair, D. C. and West, A. R., *Phys. Rev. B*, 1989, **39**, 13486.
16. Tomeno, I. and Matsumura, S., *Phys. Rev. B*, 1988, **38**, 606.
17. Ming, D., Reau, J. M., Ravez, J., Gitae, J. and Hagenmuller, P., *J. Solid State Chem.*, 1995, **116**, 185.
18. Cole, K. S. and Cole, R. H., *J. Chem. Phys*, 1941, **9**, 341.
19. Elouadi, B. and Mouahid, F. E., *Mat. Res. Bull*, 1988, **23**, 241.
20. Safarayan, F. P., *Physics Letters A*, 1999, **255**, 191.
21. Bauerle, J. E., *J. Phys. Chem. Solids*, 1969, **30**, 2657.
22. Cho, J., Kim, J. and Kim, H., *Materials Letters*, 1997, **31**, 105.