

**IMPEDANCE, DIELECTRIC
SPECTROSCOPIES AND ^7Li NMR
SPECTROSCOPY AS TOOLS FOR THE
DETERMINATION OF THE Li^+ DYNAMICS IN
THE POLYCRYSTALLINE FAST IONIC
CONDUCTOR $\text{Li}_{3-x}\text{La}_{2/3-x}\text{TiO}_3$**

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Broadband dielectric spectroscopy and nuclear spin relaxation are used to characterize the dynamics of the lithium ions in the polycrystalline fast ionic conductor $\text{Li}_{3-x}\text{La}_{2/3-x}\text{TiO}_3$. This oxide is a purely ionic conductor of the perovskite-type ABO_3 ($\sigma_{\text{dc}} = 10^{-3} \text{ S cm}^{-1}$ at 25°C [1]). The space group P4/mmm best describes the crystallographic structure [2]. The dynamics of the Li^+ ion is studied by dielectric spectroscopy in the frequency range from 4 GHz – 1 Hz and by ^7Li NMR relaxation times measurements (T_1 , $T_{1\rho}$ and T_2) at 116 MHz and 62.5 kHz. These complementary techniques allowed us to describe the different motions of the moving ion in this oxide. A careful analysis of the NMR spectra has showed that dynamic effects govern the shape of the NMR spectra. The presence of two kinds of Li^+ ions with slightly differing environments is displayed in these experiments. Finally, an unusual behavior is observed around 200 K that is ascribed to a change in the dimensionality of the Li^+ motions when temperature increases.

Dielectric spectroscopy, performed in the temperature range from 200 K to 300 K, revealed the presence of several dielectric relaxations that can be ascribed to different motions of the Li^+ ions in the oxide corresponding to long-range and localized motions of the charge carriers (interfacial polarization and dipolar reorientation). A slow motion also probed by ^7Li NMR $T_{1\rho}$ and T_2 relaxation times and by dc-conductivity, corresponds to the hopping of the Li^+ ions from one A-cage of the perovskite structure to a next vacant cage through bottlenecks made of four oxygen ions. This leads to the long-range motion of the charge carriers and to the dc-conductivity. A fast motion, also probed by ^7Li NMR T_1 relaxation time, corresponds to a localized motion of the Li^+ ion between their off-centred positions in the A-cage. A change of the dimensionality of these motions from 2D to 3D occurs around 200 K. Between 200 K and 300 K, we think that a fractal dimensionality is observed. At low temperature ($T < 200 \text{ K}$), both the local and long-range Li^+ ions motions happen in the (a,b) planes of the crystallographic structure (2D motion). As temperature increases, Li^+ ions experience the entire volume of the A-cage to finally move on the three directions above 400 K (3D motion). This change is corroborated by the ratio of the activation energy in the two domains, (i.e., 1.5) observed in T_1 vs $1000/T$ plot as well as in dc-conductivity vs $1000/T$ plot and in the dielectric relaxations. It also agrees with the crystallographic structure of this oxide [2].

This work shows the complementarity of the dielectric, the impedance and the NMR spectroscopies in order to entirely describe the microscopic motion of

the Li^+ ions in this material. Furthermore, this work shows that, in this oxide, $T_{1\rho}$ and σ_{dc} can be compared since they are related to the same ionic motion and not T_1 and σ_{dc} , as it is generally the case.

References

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- [2] J.L.Fourquet, H.Duroy, M.P.Crosnier-Lopez, J; Solid State Chem. 127 (1996) 283.