

Dopants, defects & domains – Dielectric spectroscopy in LiNbO₃

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Even though the perovskite structure type is often considered to be prototypical for ferroelectric materials, other corner-linked oxygen-octahedral structures are sometimes superior both for the study of fundamental physical properties and the exploitation of these properties in applications. A prime example is the pseudo-ilmenite-structured lithium niobate (LiNbO₃, LN). Due to its unique piezoelectric, pyroelectric, acoustic, electro-optic and photorefractive properties it has been the subject of intensive studies for many years and has found applications in photorefractive devices, holographic memories, optical frequency converters, etc [1]. There are several remarkable aspects that set LiNbO₃ apart from perovskite-structured ferroelectrics: first, it is a uniaxial non-ferroelastic ferroelectric, and only 180° domain wall configurations are possible. Second, it is most often employed in the form of single crystals, in contrast to materials such as lead-based perovskite-structured piezoelectric ceramics, which are more often polycrystalline. The material is usually grown from the melt using the Czochralski technique. Third, its properties are even more defect-dominated than those of most other ferroelectrics. Crystals are most often grown at the congruent melting point, which leads to a high deficiency in Li-ions. In congruently melting LN (c-LN), the concentration of lithium and niobium ions is $[Li]/[Li+Nb] = 48.6\%$. Antisite Nb_{Li} is known to be the most prominent defect. It is generally assumed to be compensated by the creation of either lithium or niobium vacancies, V_{Li} or V_{Nb} [2, 3]. Numerous studies have been performed to elucidate the effect of a large number of dopants in LN. Donor dopants such as iron (Fe) or copper (Cu) increase the photorefractive effect, while magnesium (Mg) reduces the optical damage threshold [1].

Particularly for the last case, the exact defect structure is still under discussion despite numerous publications on the subject. According to a recent study by Yatsenko et al., Mg-doping most probably leads to the formation of defect complexes (4Mg_{Li} + 4V_{Li}) [4]. Additionally, there is strong evidence that the local defect structure is decisively influenced by the ferroelectric domain structure, high external electric fields and thermal treatment at moderate temperatures below 200°C [5, 6]. In this context, dielectric spectroscopy is a promising tool to study the interaction between electric fields, intrinsic as well as dopant-induced defects and domain walls at various temperatures. However, these types of measurements have so far been mostly limited to undoped lithium niobate. Only singular measurements show that dielectric relaxation processes can be observed in doped LN, while undoped LN appears to be relaxation-free [7,8].

This presentation will focus on three different types of crystals: single-domain magnesium-doped c-LN, single-domain nominally undoped c-LN and periodically poled (polydomain) nominally undoped c-LN (c-PPLN). The real and imaginary part of the dielectric permittivity in the frequency range between 1 Hz and 1 MHz are measured at various temperatures between -100°C and +200°C. The Mg-doped samples show a very pronounced dielectric relaxation around 100 Hz (see Fig. 1) that irreversibly vanishes when the sample is heated above 140°C. It is suggested to originate from free Mg-donor defects that appear when the Mg_{Li}-V_{Li} defect complexes are destroyed by high-temperature poling. Annealing above 140°C allows the Li-ions to migrate back to their original positions, re-forming the defect complexes and quenching the dielectric relaxation. This interpretation is supported by measurements of the thermally stimulated depolarization current (TSDC) that show an anomalous depolarization current around 140°C during the first heating that is no longer seen in subsequent heating cycles. Similarly, the electrical conductivity is shown to increase drastically in that temperature range; the observed activation energy of ~1eV confirms that the charge transport is due either to lithium vacancies or hydrogen ions.

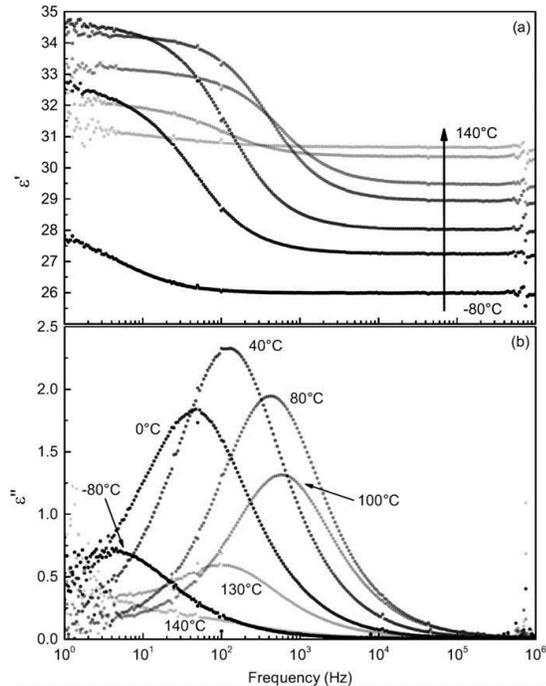


Figure 1 Real (a) and imaginary part (b) of permittivity of c-LN:Mg (5%) at different temperatures.

The behavior is rather different in the nominally undoped single domain c-LN and c-PPLN. Most undoped single-domain samples do not show any dielectric relaxation in the observed frequency range. A relaxation is observed occasionally in nominally undoped single domain c-LN around 10^4 Hz, i.e. at frequencies two orders of magnitude higher than in c-LN:Mg. This type of relaxation is also observed in all the c-PPLN samples examined. Apparently, the samples that are nominally undoped and single-domain still contain some type of defect, either in the form of unintended impurities or domain walls. It is interesting to note that the relaxation at 10^4 Hz again vanishes upon heating beyond 140°C in the single-domain c-LN, but is stable in the c-PPLN. It is tentatively attributed to ionic defects that have been left in an energetically unfavorable position by the high-temperature poling process in the single-domain sample, but are attached to and stabilized by the ferroelectric domain walls in the c-PPLN. The results are discussed with respect to the possibilities of defect- and domain-engineering in LiNbO_3 in particular and uniaxial ferroelectrics in general.

Acknowledgements: This work was supported by the ‘Fonds National de la Recherche’ (FNR) Luxembourg (Projects CO-FERMAT & S-MOD PV)

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