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Oxygen Partial Pressure Dependent Electrical Conductivity of $LiNb_{1-x}Ta_xO_3$ Solid Solutions

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Summary:
The electrical conductivity is investigated for piezoelectric single crystals of congruent lithium niobite ($LiNbO_3$, LN), lithium tantalate ($LiTaO_3$, LT), and their solid solutions ($LiNb_{1-x}Ta_xO_3$, LNT) at varying oxygen partial pressure in the range of 0.2-10^{-15} bar at a constant temperature of 900 °C. These crystals have been grown by the Czochralski and micro-pulling down method. At sufficiently low oxygen partial pressure, the LN sample demonstrates about two orders of magnitude larger electrical conductivity than LT. Such an outcome indicates a dominant n-type conductivity in the former. Moreover, the increase of the Nb/Ta ratio shows a tendency to decrease conductivity for LNT.

Keywords: piezoelectric single crystal, lithium niobate-tantalate solid solutions, electrical conductivity, high temperature

Background, Motivation, and Objective

High temperatures sensors and actuators enable a wide range of advanced technological applications in aerospace, automobile, energy conversion, and beyond [1,2]. Considering materials potentially suited for the above-mentioned devices, piezoelectric single crystals with large electromechanical coupling factors, high melting/phase transition temperatures, and cost-effective growth methods are essential [3,4]. However, state-of-the-art material such as quartz (α-SiO_2) is thermally unstable, showing a phase transition (α→β) at around 570 °C. In contrast, the family of langasite crystal displays no phase transformation up to the melting point (~1400 °C), but they possess a relatively low piezoelectric coefficient [2]. The ferroelectric lithium niobate (LN) and lithium tantalate (LT) have attracted significant interest because of their excellent dielectric, electro-optic, electro-acoustic, photoelectric, and piezoelectric properties [5]. Nevertheless, the high-temperature performance of these materials is restricted by thermo-chemical instability of LN and low curie temperature of LT. Meanwhile, few publications [6,7] and our preliminary work indicate that the properties of $LiNb_{1-x}Ta_xO_3$ (LNT) solid solutions can be tailored which includes refractive index, electroacoustic and electrooptic properties, melting point and curie temperature. In the current work, we investigate the oxygen partial pressure (pO_2) dependent high-temperature electrical properties of LN and LT crystals prepared by two different methods. Additionally, such experiments are also performed with LNT with different Nb/Ta ratios.

Description of the Method

The crystals investigated in this experiment were produced by the Czocharalski (CZ) and micro-pulling down (μ-PD) technique at the Institute of Microelectronics Technology and High Purity Materials (Russia) and at the Leibniz Institute for Crystal Growth (Berlin), respectively. The CZ crystals were then cut into a disc-shaped dimension (diameter 10 mm and thickness 1 mm) with a Z-cut orientation and polished. The μ-PD crystals were grown along Z-axis with about 15 mm in length and 1 mm in diameter. The samples were partially coated with Pt paste via screen printing and thermally treated at 1000 °C for 30 min. The electrical properties were measured by electrochemical AC impedance spectroscopy (Solartron 1260, UK) in a wide frequency range (10^6-10^0 Hz) under an alternative of bias of 100 mV at 900 °C and changing oxygen partial pressure (10^0-10^{-15} bar). The data were fitted using an equivalent circuit model consisting of a bulk resistor connected in parallel with a constant phase element. The conductivity was estimated using the equation, $\sigma = L/RA$ where R is the bulk resistance, A the electrode area, and L the sample thickness.

Results

The bulk electrical conductivity of LN and LT samples is represented in Fig. 1 as a function of pO_2 at 900 °C. As can be seen, the sample manufactured by the µ-PD method shows a higher electrical conductivity than the CZ sample. Such an outcome is expected due to a relatively high impurity content caused by rapid cooling during the µ-PD process. The latter prevents segregation and, thereby, lowering of impurity concentrations as expected for CZ growth. Further, LN possesses noticeably larger conductivity than LT, especially at low pO_2. For LT, the conductivity remains pO_2 independent down to 10^{-9} bar and increases slightly for increasingly reducing atmosphere. In contrast, a strong pO_2 dependent conductivity is observed for LN below about 10^{-3} bar, suggesting the LN system has a lower reduction enthalpy than LT. In general, the enhancement of the conductivity is typical for a mixed ionic-electronic conductor which exhibits an increasing electronic (n-type) conductivity as the pO_2 reduces [4,8].

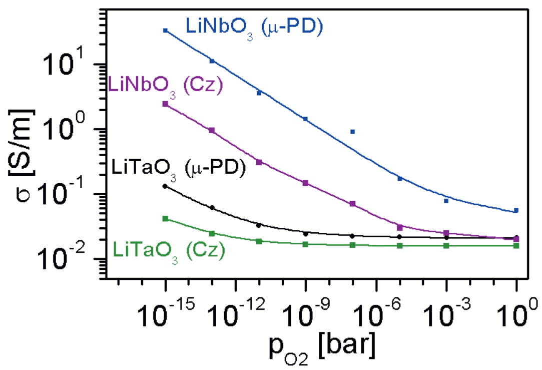

Fig. 1. Bulk electrical conductivity of LN and LT crystals grown by Czocharalski and micro-pulling down technique for varying oxygen partial pressure, measured at 900 °C.

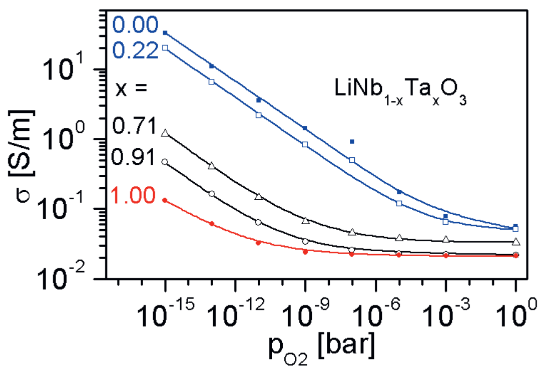

Fig. 2. Bulk electrical conductivity of LNT compounds with different Nb/Ta ratios prepared via micro-pulling down technique as a function of oxygen partial pressure, measured at 900 °C.

Fig. 2 illustrates the pO_2-dependent bulk electrical conductivity of LNT for different Nb/Ta ratios. The Nb-rich composition shows an identical reduction tendency to pure LN. The electrical conductivity is progressively dropped with increasing Nb/Ta ratio, and expectedly, the Ta-rich sample shows largely suppression of reduction like LT.

Conclusions

In summary, the electrical conductivity of LN, LT, and LNT solid solution was examined at a constant temperature of 900 °C with regards to different oxygen partial pressures. The outcome reveals a significant rise in conductivity for the LN sample than the LT at a low-oxygen partial pressure. The electrical conductivity can be tuned by the Nb/Ta ratio.

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