Enhanced Piezoelectric and Ferroelectric Properties of (K,Na,Li)(Nb,Ta,Sb)O_3 Single Crystals by Defect Control

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Ferroelectric single crystals can be used in a wide range of sensors, actuators and transducers [1]. Moreover, they are invaluable to study the fundamental mechanisms governing the electromechanical response of ferroelectrics. Single crystals based on (K,Na)NbO_3 (KNN) have been extensively researched over the past 10 years, predominantly driven by the increasing environmental and health concerns of lead-based systems. Unfortunately, KNN-based crystals often exhibit high leakage currents, which prevent a detailed characterization of their electromechanical behavior. Their properties are therefore still considerably inferior to their lead-based counterparts and even to polycrystalline lead-free ceramics.

Here we present an approach for enhancing the electromechanical properties of (K,Na,Li)(Nb,Ta,Sb)O_3 single crystals by defect control through thermal annealing in oxygen atmosphere. The crystals were grown by the top-seeded solution growth method using a self-flux, as described elsewhere [2]. The chemical composition was investigated by electron probe micro-analysis (EPMA) and inductively coupled plasma optical emission spectroscopy (ICP-OES). The samples were annealed in pure oxygen at 900 °C for one week. The dielectric permittivity, polarization, strain, small- and large-signal piezoelectric coefficients were measured over a broad temperature range.

As compared to the non-annealed state, the annealed samples exhibited lower dielectric losses and a 3–5-fold increase in the electric-field-induced polarization and strain over the investigated temperature range. The room temperature remanent polarization of a poled sample was 24.9 $\mu C \cdot m^{-2}$, while the unipolar strain at 4 $kV \cdot mm^{-1}$ reached 0.20 %. The room-temperature small-signal d_{33} increased from 381 $pC \cdot N^{-1}$ for the non-annealed sample to 732 $pC \cdot N^{-1}$ for the annealed sample, which exceeds the previously-reported values for KNN-based single crystals and polycrystalline ceramics.

The reduced losses and enhanced electromechanical properties were found to be related to the decreased defect concentration. The defects are formed during the high-temperature growth process by several mechanisms, *e.g.*, volatilization of the A-site ions, oxygen vacancy formation, or reduction of the multi-valent B-site ions (Sb, Nb). During the oxygen annealing the oxygen vacancy concentration was decreased and Sb^{3+} was found to oxidize to Sb^{5+}. In addition, Nb^{4+} to Nb^{5+} oxidation is expected. The conductivity mechanisms were investigated by impedance spectroscopy and the corresponding activation energies were determined.

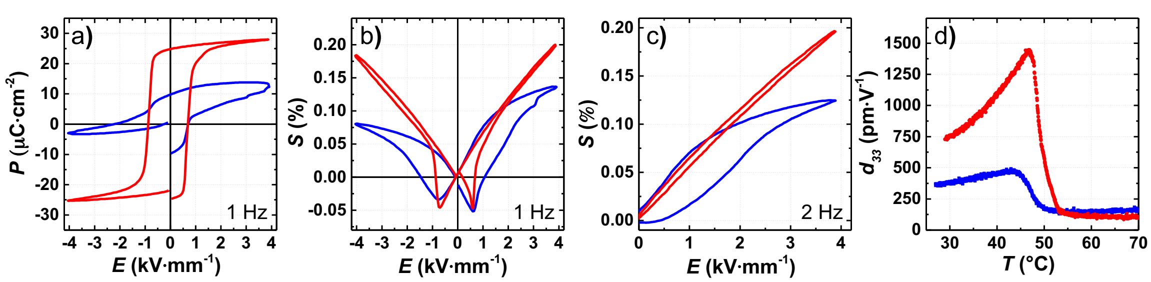

Figure 1. a,b) Bipolar polarization and strain, c) unipolar strain, and d) temperature-dependent small-signal d_{33} piezoelectric coefficient of the (K,Na,Li)(Nb,Ta,Sb)O_3 single crystals: before (blue) and after (red) thermal annealing in oxygen atmosphere.

[1] Zhang and Li, *J. Appl. Phys.* 111, 031301 (2012).
[2] Liu et al., *CrystEngComm* 18, 2081 (2016).