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Original research article

Growth and mechanical properties of near-stoichiometric $LiNbO_3$ crystal

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ABSTRACT

The near-stoichiometric $LiNbO_3$ crystal (SLN) with dimension of $\Phi 25 \times 45\,mm^3$ has been successfully grown from Li-rich solutions by the Czochralski method. The results of X-ray rocking curve measurement indicate that the as-grown SLN crystal has a relatively high crystallinity. The mechanical properties of SLN crystal were determined by nanoindentation method. The hardness and elastic modulus values obtained revealed higher values for (300) plane of SLN crystal (10.02 and 225.6 GPa) compared to the (600) plane of SLN crystal (7.09 and 202.8 GPa). Different hardness and elastic modulus values for different planes suggest anisotropic character of mechanical properties in SLN crystals. The distribution characteristic of residual stress in SLN crystal along the optical axis is analyzed by means of photoelasticity effect.

1. Introduction

Lithium niobate ($LiNbO_3$, LN) crystal has attracted a great deal of attention for its wide variety of applications in modern optic over a wide range extending from near UV to the far IR wavelength [1–3]. Due to ferroelectric, pyroelectric, and piezoelectric properties with large electro-optic, acousto-optic, and photoelastic coefficients as well as strong photorefractive and photovoltaic effects, LN crystal is widely used in acoustic wave (SAW) devices, optical waveguides, optical modulators, optical integrated circuits, holographic memory devices, and second-harmonic generators (SHG), etc. [4–7]. Crystal of LN are generally grown from congruent melt composition (congruent lithium niobate, CLN) by Czochralski method, which suffers from Li deficient (48.6 mol. % Li_2O). However, The CLN crystal contains a high concentration of intrinsic defects in the form of Nb anti-sites (Nb_{Li}^{5+}) and Li vacancies (V_{Li}^{-}) that limit its scope for optical applications [8–10]. LN crystal with near-stoichiometric composition (SLN), on the other hand, exhibits larger electro-optic and nonlinear optic effects, shorter absorption edge wavelength, and smaller electric field required for ferroelectric domain switching compared to the CLN crystal [11,12]. Hence SLN offers a better choice for optical device applications [13,14]. As the demand for SLN crystals with large size and high optical quality kept increasing, many crystal growth techniques were used to produce SLN crystal, such as double crucible Czochralski method, top seeded solution growth technique, etc [15,16]. In this paper, we describe the growth of near-stoichiometric $LiNbO_3$ crystals from Li-rich solution by the Czochralski method, along with the investigation of as-grown mechanical properties.

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Fig. 1. $LiNbO_3$ crystal was grown by the Czochralski method.

2. Experimental procedure

The ploycrystalline material for the crystal growth was synthesized by a solid-state reaction method. The chemicals used were Li_2CO_3 and Nb_2O_5 with purity of 99.99% in a molar ratio of Li_2CO_3 / Nb_2O_5 = 58/42. After mixing and grinding, the raw materials pressed into pieces. The mixture was put into a crucible, and heated in air to 750° for 10 h and 850° for 5 h with intermittent regrindings. Grinding and sintering are repeated in order to obtain chemically homogeneous starting material. The synthesized charge 1080 g is filled into the platinum crucible of 80 mm diameter and 60 mm height suitable for Czochralski growth. The charge is melted in a 2KHz frequency furnace in air with an active afterheater for desired temperature gradient. The pulling rate and rotation rate were set to 0.2–0.3 mm/h and 10–20 rpm, respectively. After growth, the crystal was removed from the melt and cooled at 20–30 °C/h to room temperature. Two (300) and (006) oriented wafers of a SLN crystal with typical dimensions of 5 mm × 20 mm × 2 mm were cut from the as-grown crystal and chemo-mechanically polished on both sides for measurements of high-solution X-ray diffraction and mechanical properties.

High-resolution X-ray diffraction spectra were measured on a Bruker D8-discover diffractometer with a 4-bounce Ge (220) monochromator for CuKα1 radiation (λ = 1.54056 Å). The step time and step increment were 1.0 s and 0.001°, respectively. The ω-scans of rocking curves were investigated for the (300) and (006) Bragg peaks from the polished SLN wafers. Mechanical properties of the SLN crystals were determined by nanoindentation using a Nano Indenter G 200 (Keysight, USA). A Berkovich diamond indenter tip with a rounding of 20 nm was used in this study. The load-displacement data obtained from the SLN crystals were used to determine hardness and Young's modulus using the Oliver - Pharr model [17,18]. The internal stress distribution was evaluated for both the SLN wafers by polarized surface stress meter PSV-413 manufactured by Suzhou PTC Optical Instrument Co., Ltd. in China.

3. Results and discussion

The SLN crystal with dimension of $\Phi 25 \times 45\ mm^3$, which was grown from Li-rich solution using Czochralski method, was transparent without any visible macroscopic defects, as shown in Fig. 1. Seed crystal was obtained by picking SLN grains from polycrystalline boules grown on a platinum wire. The seed crystal was oriented along z-axis direction. The novel seeding technique was applied to determine the saturation temperature quickly and to minimize the seed loss in the process of seeding [19]. The weight of the grown SLN crystals was limited to approximately 10% of the weight of the initial solution to avoid the composition deviation of the grown crystal. In order to improve SLN crystal quality and stabilize growth interface shapes, a lower pulling rate and dynamic adjustment of rotating rate during the process of SLN crystal growth were adopted. The grown SLN crystal was thermally annealed in a multi-temperature zone annealing furnace and the annealing time was about 120 h. The annealing temperature was set to 1150–1200 °C, near but lower than the Curie temperature. And the heating and cooling rates during annealing were set very slow to avoid additional residual thermal stress. Moreover, the grown crystals were annealed with slow heating and cooling rate to eliminate structural grain boundaries and reduce OH-concentration [20].

X-ray rocking curves measured on the (300) and (006) crystallographic planes were carried out and are illustrated in Fig. 2. The rocking curves from (300) and (006) plane of SLN crystal displayed a sharp and symmetric curve, which meant no