Materials Letters 84 (2012) 16–19

Contents lists available at SciVerse ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Weak ferroelectricity of potassium niobate $K_4Nb_6O_{17}$ single crystal grown by pulling down technique

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ARTICLE INFO

Article history:
Received 23 April 2012
Accepted 9 June 2012
Available online 23 June 2012

Keywords:
Fiber crystal
Dielectric constant
Thermal analysis
Ferroelectrics
Piezoelectrics

ABSTRACT

Although potassium niobate $K_4Nb_6O_{17}$ single crystal is easy to absorb moisture due to the intercalation of water molecules in the crystal, single crystals can be grown in fiber shape using an original pulling down method. $K_4Nb_6O_{17}$ single crystals are easy to break down in plate shape by cleavage which is in turn affected by moisture. The dielectric constant and electric polarization measurements show that $K_4Nb_6O_{17}$ single crystal is with weak ferroelectricity.

1. Introduction

Potassium niobate $KNbO_3$ single crystal (KN) is well known for its ferroelectric and piezoelectric properties [1–4]. Bulk KN can be grown from the melt in spite of its incongruent melting and twice solid-state phase transformations [1]. During the KN crystal growth process, another crystal phase of $K_4Nb_6O_{17}$ was sometimes formed as a secondary phase caused by the potassium evaporation in the KN melt [5]. The $K_4Nb_6O_{17}$ crystal has also been studied from the viewpoint of crystal structure [6,7] and crystal growth [8,9]. The $K_4Nb_6O_{17}$ crystal has an orthorhombic structure of which its lattice parameters are $a=0.7816$, $b=3.312$ and $c=0.6480$ nm, and with space group $P2_1nb$ (33) [7]. There is a disadvantage with the $K_4Nb_6O_{17}$ crystal; it is easy to absorb moisture (hydrated) to become $K_4Nb_6O_{17}\cdot 3H_2O$ [7,10]. From the viewpoint of electric properties, the $K_4Nb_6O_{17}$ crystal was reported as a ferroelectric nonlinear material [4], but its electric properties have not been subjected to much study so far.

When the electric properties of KN crystal are measured, we are afraid to measure those of $K_4Nb_6O_{17}$ crystal at the same time. So it is necessary to know electric properties of $K_4Nb_6O_{17}$ crystal in order to know those of KN single crystal clearly. Of course, many defects will be expected in the $K_4Nb_6O_{17}$ crystal. We believe single crystals have less defects than ceramics.

In the present work, the growth of potassium niobate $K_4Nb_6O_{17}$ single crystals, and characterization on the electric properties, such as dielectric constants, ferroelectric polarization (P–E) behavior, and a ferroelectric domain, will be reported.

2. Experimental procedures

A floating zone pulling down (Fz-PD) crystal growth method [11] was employed using a Pt tube with 4 mm diameter as the melt feeder for the starting materials. A keen slant cut Pt wire with 0.5 mm in diameter was used instead of seed crystal. This system was installed with conventional double ellipsoidal mirror halogen lamps and Pt tube. The potassium oxide and niobium oxide were stoichiometrically mixed as starting materials. Crystals were grown in Ar gas flow condition. The Pt wire's pulling-down rate was 10 mm/h without rotation. Schematics of crystal growth method were shown in our previous paper [12]. By using the conventional double ellipsoidal mirror furnace, the crystals with big enough size for properties characterization can be grown.

For the characterization of these samples, cleavage crystals were used as described later. Sample size was approximately $2\times2\times0.2$ mm^3. The characterizations were carried out by X-ray diffraction (XRD) (Rigaku RINT2500) and Thermogravimetric–Differential thermal analysis (TG–DTA) using Shimadzu (DTG-60H). Ag paste was used for electrode fabrication. Dielectric constant and loss were measured from 10 to 100 kHz by heating up to 500 °C and cooling down process using an Agilent LCR meter (4984A). The ferroelectric hysteresis P–E loop was measured at room temperature in silicone oil using an aixACCT (Easy Check 300) ferroelectric tester and a Matsusada high-voltage amplifier. Ferroelectric domain was observed using a SII Piezo-response Force Microscope (PFM: Nanocute).

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http://dx.doi.org/10.1016/j.matlet.2012.06.052

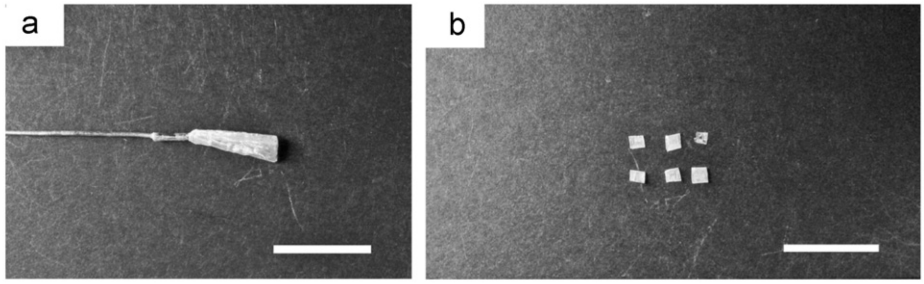

Fig. 1. $K_4Nb_6O_{17}$ crystals grown by the Fz-PD method: (a) As-grown crystal and (b) cleavage crystals. Scale: 10 mm.

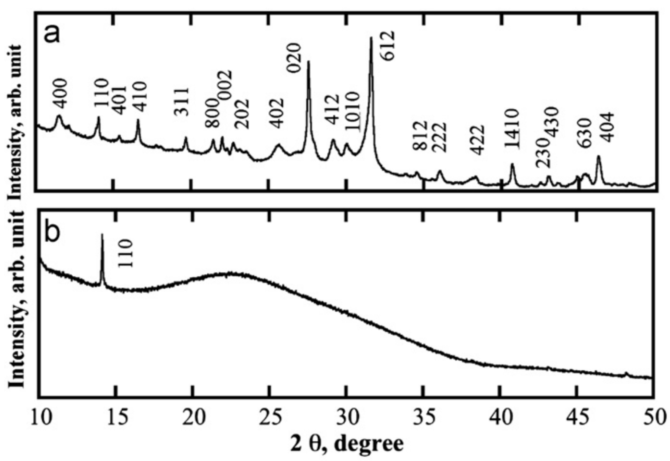

Fig. 2. X-ray diffraction pattern of $K_4Nb_6O_{17}$ crystal: (a) Crystal powder and (b) cleavage plane.

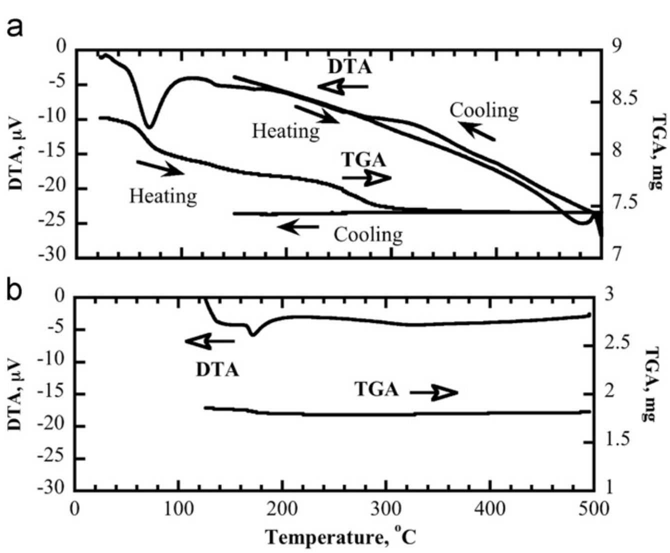

Fig. 3. TG–DTA curves during heating and cooling: (a) first measurement at heating and cooling and (b) second measurement at heating.

3. Results and discussion

$K_4Nb_6O_{17}$ crystals were grown as shown in Fig. 1(a). Single-phase crystals were obtained with 1–2 mm in diameter and 5–10 mm in length, in fiber-shape. Crystal's grown direction was basically in the *c*-axis (the shortest axis in the orthorhombic system). The grown crystals are reasonably stable in dry condition. However, they were broken down to small pieces when

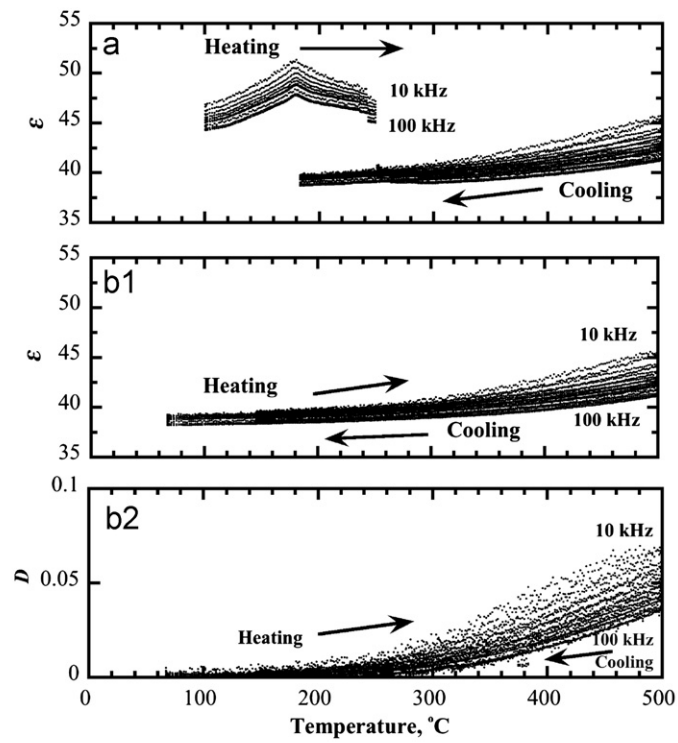

Fig. 4. Temperature dependence of dielectric constant, ε, at heating and cooling from 10 to 100 kHz: (a) first measurement, (b1) second measurement and (b2) that of dielectric loss, *D*, at second measurement.

cut under conventional water-cooling cutting equipment, i.e., a grown crystal is easy to break down by cleavage in moisture as shown in Fig. 1(b). When cleaved crystal was observed under cross nicols, twin image was observed. We expect many other lattice defects in the $K_4Nb_6O_{17}$ crystal, but we do not care such defects so much in the present work because it is important to know the electric properties.

The powder XRD pattern on the $K_4Nb_6O_{17}$ crystal was obtained after milling. The powder single-phase XRD is shown in Fig. 2(a). Here, the index is based on Ref. [7]. All the peaks can be indexed as the $K_4Nb_6O_{17}$ phase. The reason of large background signal at low angle is due to the X-ray detector of D/teX by Rigaku. The moisture absorption effect was not observed in the XRD measurement of $K_4Nb_6O_{17}$ crystal. Fig. 2(b) shows the XRD pattern on the cleavage plane of $K_4Nb_6O_{17}$ crystal in Fig. 1(b). The cleavage plane is determined to be (1 1 0) plane. This plane is not coinciding with a habitual plane of flux growth of (0 1 0) plane [8].

The TG–DTA curves are shown in Fig. 3. Fig. 3(a) shows the first measurement during heating and cooling. Fig. 3(b) shows the second measurement during heating just after the first measurement. Three