Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 28 (2008) 1657–1663
www.elsevier.com/locate/jeurceramsoc

Growth behaviour of potassium sodium niobate single crystals grown by solid-state crystal growth using $K_4CuNb_8O_{23}$ as a sintering aid

John G. Fisher [1], Andreja Benčan *, Jerneja Godnjavec, Marija Kosec

Department of Electronic Ceramics, Jožef Stefan Institute, Jamova 39, Ljubljana 1000, Slovenia

Received 28 June 2007; received in revised form 12 November 2007; accepted 25 November 2007
Available online 4 February 2008

Abstract

The effect of addition of 0, 0.5 and 2 mol% $K_4CuNb_8O_{23}$ liquid phase sintering aid on the growth of single crystals of $(K_{0.5}Na_{0.5})NbO_3$ by solid-state crystal growth (SSCG) was studied. Single crystal growth in the samples with 0 and 0.5 mol% $K_4CuNb_8O_{23}$ was initially rapid and then tailed off with annealing time, due to matrix grain growth which reduced the driving force for crystal growth. Addition of 0.5 mol% $K_4CuNb_8O_{23}$ caused a reduction in both single crystal and matrix grain growth rates. Addition of 2 mol% $K_4CuNb_8O_{23}$ caused matrix grain growth to stagnate, resulting in an almost constant driving force and constant crystal growth during annealing. Single crystals grown using 0 and 0.5 mol% $K_4CuNb_8O_{23}$ were stoichiometric, but single crystals grown with 2 mol% $K_4CuNb_8O_{23}$ were Na-rich. This was due to lowering of the solidus temperature by addition of $K_4CuNb_8O_{23}$.

Keywords: Single crystals; Grain growth; Interfaces; Niobates; Perovskites; (K, Na)NbO_3

1. Introduction

Due to the toxic nature of lead, there is a great interest in the development of lead-free piezoelectric ceramics. The mixed niobate system $(K_{1-x}Na_x)NbO_3$ and its derivatives are promising candidates for lead-free piezoelectric ceramics. The $(K_{1-x}Na_x)NbO_3$ system has a morphotropic phase boundary close to the $(K_{0.5}Na_{0.5})NbO_3$ composition, and ceramics of this composition display optimum piezoelectric properties in the system.[1,2] $(K_{0.5}Na_{0.5})NbO_3$ has moderate piezoelectrical properties[1–3] which can be improved by substitution with Li and Ta.[4,5]

Single crystals of several lead-free systems have excellent piezoelectric properties, especially when combined with crystallographic engineering.[6,7] It is expected that single crystals of $(K_{0.5}Na_{0.5})NbO_3$ would also have good piezoelectric properties. Single crystals of $(K_{1-x}Na_x)NbO_3$ have been grown by the flux method.[8–11] Difficulties were experienced by several workers in growing crystals with high K contents, but recently crystals with a composition of $(K_{0.47}Na_{0.53})NbO_3$ were grown using a KF/NaF flux.[11]

Single crystals of $(K_{0.5}Na_{0.5})NbO_3$ and Li/Ta-substituted $(K_{0.5}Na_{0.5})NbO_3$ have recently been grown by the solid-state crystal growth method.[12,13] In this method, a single crystal (called a seed crystal) is buried and then compacted in a ceramic powder. The sample is sintered and a single crystal of the ceramic composition grows epitaxially on the seed crystal. When the $(K_{0.5}Na_{0.5})NbO_3$ and Li/Ta-substituted $(K_{0.5}Na_{0.5})NbO_3$ single crystals were grown, $K_4CuNb_8O_{23}$ was added as a liquid phase sintering aid.[12,13] For single crystals of PMN-PT grown by SSCG, addition of up to a certain amount of PbO as a liquid phase sintering aid was found to promote single crystal growth, with further additions retarding crystal growth or having no effect.[14,15] It is expected that changing the amount of liquid phase sintering aid will also affect single crystal growth of $(K_{0.5}Na_{0.5})NbO_3$, but this has not yet been studied. In the present work, single crystals of $(K_{0.5}Na_{0.5})NbO_3$ have been grown using different amounts of $K_4CuNb_8O_{23}$ liquid phase sintering aid. The effect of sintering aid upon single crystal growth rate, grain growth in the matrix and chemical composition of the single crystal and the matrix grains has been investigated.

---

* Corresponding author. Tel.: +386 1 477 3256; fax: +386 1 477 3887.
E-mail address: andreja.bencan@ijs.si (A. Benčan).

[1] Current address: Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-Dong, Yusong-gu, Daejon 305-701, Republic of Korea.

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.11.010

2. Experimental

Powders of $(K_{0.5}Na_{0.5})NbO_3$ and $K_4CuNb_8O_{23}$ were prepared using the methods in Ref. 12. Both powders were examined by X-ray diffraction and found to be single phase. Different amounts of $K_4CuNb_8O_{23}$ were added to the $(K_{0.5}Na_{0.5})NbO_3$ powder, followed by planetary milling in acetone with ZrO_2 media for 1 h. Powders were made with additions of 0, 0.5 and 2 mol% $K_4CuNb_8O_{23}$.

$KTaO_3$ single crystals (FEE GmbH, Germany) oriented in the ⟨0 0 1⟩ direction were used as seed crystals. The ⟨0 0 1⟩ direction was used because crystals grown in this direction have planar growth fronts, making measurement of growth distance possible.[12] The single crystals were supplied as plates of dimensions 5 mm × 5 mm × 1 mm, with one face of each crystal polished to a 0.25 μm finish. Seed crystals were prepared by cutting each plate into quarters with a diamond wire saw, followed by ultrasonic cleaning in acetone. To make the samples, seed crystals of dimensions approximately 2 mm × 2 mm × 1 mm were again ultrasonically cleaned in acetone and then buried in 1 g of powder in an 8 mm diameter die. Samples were uniaxially pressed at 60 MPa, followed by cold isostatic pressing at 200 MPa. The samples were then hot pressed in air at 975 °C and 50 MPa for 2 h. Heating and cooling rates were 5 °C min^{-1}. Hot pressed samples were vertically sectioned into two halves using a diamond wire saw and ultrasonically cleaned in acetone.

To reduce alkali volatilization, for each crystal growth experiment, half of a hot pressed sample was wrapped in Pt foil and buried in packing powder in an alumina crucible with a lid. The packing powder was of the same composition as the sample. The crucible was then placed in another crucible with a lid and placed in a tube furnace which could sinter samples under vacuum or under a controlled atmosphere. Samples were annealed at 1100 °C for between 1 and 20 h. All heating and cooling rates were 5 °C min^{-1}. During heating from room temperature to 400 °C, the samples were degassed under vacuum to remove adsorbed water. All further heating, annealing and cooling steps were then carried out under flowing synthetic air which had been passed through a desiccating column filled with silica gel. The weight of each sample was measured before and after each crystal growth experiment. In all cases, weight loss was ≤0.5%. Separate Pt foils and crucibles were used for the samples without and with $K_4CuNb_8O_{23}$.

Samples were polished to a 0.25 μm finish and characterized using a scanning electron microscope (SEM, JEOL 5800, Tokyo, Japan) equipped with a LINK ISIS 300 energy-dispersive X-ray spectrometer (EDS). For microstructural characterization, samples were thermally etched at 1050 °C for 1 h and carbon coated. Single crystal growth distance was measured from SEM micrographs. For each single crystal, 100 measurements of the growth distance were made and the mean growth distance calculated. Errors may be introduced into the measurement of the single crystal growth distance because the plane of polish may not be parallel to the [0 0 1] growth direction of the single crystal. To compensate for these errors, the thickness of each seed crystal was measured with a micrometer before it was buried in the powder. The thickness of the seed crystal was then measured again after the crystal growth experiments from optical micrographs (Nikon Eclipse TS100). By determining the ratio of the seed thickness as measured by micrometer to the seed thickness measured from the micrographs, the true single crystal growth distance could be calculated. The mean equivalent spherical 2D matrix grain radius was calculated from SEM micrographs using image analysis software (UTHSCSA Image Tool, The University of Texas Health Science Centre in San Antonio, USA). For each sample, at least 300 matrix grains were analyzed.

For chemical analysis, samples were polished but not etched. Samples were carbon coated. Single crystals of $KNbO_3$ and $NaNbO_3$ were used as standards.[16,17] The samples were analyzed using an accelerating voltage of 20 keV, a spectrum acquisition time of 60 s, a 35° take off angle and a 0° specimen tilt.

3. Results

Fig. 1(a)–(c) shows SEM secondary electron images of polished and etched samples that had been annealed at 1100 °C for 10 h. In the sample with 0 mol% $K_4CuNb_8O_{23}$, a single crystal layer up to 200 μm thick has grown on the seed crystal (Fig. 1(a)). The boundary between the single crystal and the matrix grains is not regular, but varies by as much as 60 μm. In the sample with 0.5 mol% $K_4CuNb_8O_{23}$, the growth distance of the single crystal has been reduced to 110 μm and the boundary between the single crystal and the matrix is now regular (Fig. 1(b)). In the sample with 2 mol% $K_4CuNb_8O_{23}$, the growth distance of the single crystal increases to 225 μm and the boundary between the single crystal and the matrix remains regular (Fig. 1(c)). Fig. 1(d) is an SEM backscattered electron image of a polished sample with 2 mol% $K_4CuNb_8O_{23}$ after annealing for 10 h. A secondary phase is present inside the single crystal and between the matrix grains. EDS of this phase showed it to contain Na, K, Cu and Nb. This phase is the $K_4CuNb_8O_{23}$ sintering aid. The Na present in this phase comes from dissolved $(K_{0.5}Na_{0.5})NbO_3$.[12] In the samples with 0.5 mol% $K_4CuNb_8O_{23}$ this phase was present in the matrix but not in the single crystal. No secondary phases were visible in the samples with 0 mol% $K_4CuNb_8O_{23}$.

Fig. 2 shows SEM secondary electron images of the matrix grains from the samples in Fig. 1. Fig. 2(a) shows the matrix of the sample with 0 mol% $K_4CuNb_8O_{23}$. The matrix grains are coarse, with a wide grain size distribution. The grain boundaries appear faceted. Porosity is visible at the grain triple junctions. When 0.5 mol% $K_4CuNb_8O_{23}$ is added, the matrix grain size is reduced and the shape of the grains also becomes more faceted with rounded corners (Fig. 2(b)). Pores are trapped inside some of the larger grains. When 2 mol% of $K_4CuNb_8O_{23}$ is added, the matrix grain size is reduced still further (Fig. 2(c)). The matrix grain shape remains faceted with round corners.

Fig. 3 shows measurements of the growth distance of the single crystals versus annealing time. The values at an annealing time of 0 h are the growth distances of the as-hot-pressed samples before any subsequent annealing took place. The data points are the mean growth distance, and the error bars are the standard deviation of the growth distance. The error bars give an indi-