Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 34 (2014) 4193–4200

www.elsevier.com/locate/jeurceramsoc

Influence of sintering conditions on piezoelectric properties of $KNbO_3$ ceramics

Dae-Hyeon Kim [a,1], Mi-Ri Joung [a,1], In-Tae Seo [a,1], Joon Hur [b,1], Jong-Hyun Kim [b,1], Bo-Yun Kim [b,1], Hwack-Joo Lee [c,2], Sahn Nahm [a,b,d,*]

[a] Department of Materials Science and Engineering, Korea University, 1-5 Ga, Anam-dong, Seongbuk-gu, Seoul 136-701, Republic of Korea

[b] Department of Information Technology-Nano Science, KU-KIST Graduate School of Converging Science and Technology, Korea University, 1-5 Ga, Anam-dong, Seongbuk-gu, Seoul 136-701, Republic of Korea

[c] New Materials Evaluation Center, Korea Research Institute of Standard and Science Daeduk Science Town, Taejon 305-600, Republic of Korea

[d] Electronic Materials Center, KIST 39-1 Hawolkok-dong, Seongbuk-gu, Seoul 137-791, Republic of Korea

Received 4 February 2014; received in revised form 18 June 2014; accepted 25 June 2014

Available online 4 August 2014

Abstract

A homogeneous $KNbO_3$ (KN) phase was formed in specimens that were sintered at 1020 °C and 1040 °C, without formation of the K_2O-deficient secondary phase, indicating that the amount of evaporation of K_2O during sintering was very small. However, the KN liquid phase was formed during sintering and assisted the densification of the KN ceramics. A dense microstructure was developed in the specimen sintered at 1020 °C for 6 h and abnormal grain growth occurred in this specimen. A similar microstructure was observed in the specimens sintered at 1040 °C for 1.0 h. The dielectric and piezoelectric properties of the KN ceramics were considerably influenced by the relative density. The KN ceramics sintered at 1020 °C for 6 h, which showed a large relative density that was 95% of the theoretical density, exhibited promising electrical properties: $\varepsilon^T_{33}/\varepsilon_o$ of 540, d_{33} of 109 pC/N, k_p of 0.29, and Q_m of 197.

Keywords: $KNbO_3$; Lead-free piezoelectric ceramics; Liquid phase sintering

1. Introduction

Piezoelectric devices such as sensors, ultrasonic motors, transformers, and actuators have received considerable attention because of their wide range of applications. [1–3] Lead–zirconate–titanate ($Pb(Zr,Ti)O_3$ or PZT)-based ceramics have been used for these devices because of their outstanding piezoelectric properties.[2] However, PZT-based ceramics contain more than 60 wt% of PbO, which causes serious environmental problems. Therefore, since the beginning of this century, there has been an increasing number of investigations on lead-free piezoelectric ceramics such as $BaTiO_3$, $(Bi_{1/2}Na_{1/2})TiO_3$, and $(Na_{0.5}K_{0.5})NbO_3$ (NKN).[3–6] In particular, NKN-based ceramics have attracted much interest because of their high piezoelectric properties and high Curie temperature (T_c).[7,8] However, NKN ceramics decompose easily in water, and Na_2O (or K_2O) evaporates during sintering at high temperatures (>1000 °C).[9] Therefore, it is very difficult to obtain dense NKN ceramics with homogeneous composition and reliable piezoelectric properties. In order to overcome this problem and improve the piezoelectric properties, many investigations have been conducted on NKN-based solid solutions.[9–15] In particular $(1-x)NKN-xLi(Nb, Ta, Sb)$ solid solutions have been studied extensively because

* Corresponding author at: Department of Materials Science and Engineering, Korea University, 1-5 Ga, Anam-dong, Seongbuk-gu, Seoul 136-701, Republic of Korea. Tel.: +82 2 3290 3279; fax: +82 2 928 3584.

E-mail addresses: daehyeon86@korea.ac.kr (D.-H. Kim), miri0805@korea.ac.kr (M.-R. Joung), tjdlsxo2000@korea.ac.kr (I.-T. Seo), 2007170023@korea.ac.kr (J. Hur), cristal9100@korea.ac.kr (J.-H. Kim), adorothy@korea.ac.kr (B.-Y. Kim), hjlee@kriss.re.kr (H.-J. Lee), snahm@korea.ac.kr (S. Nahm).

[1] Tel.: +82 2 3290 3701; fax: +82 2 928 3584.

[2] Tel.: +82 042 868 5449; fax: +82 042 868 5252.

http://dx.doi.org/10.1016/j.jeurceramsoc.2014.06.028

0955-2219/

of their promising piezoelectric properties.[3,16–18] The low-temperature sintering of NKN-based ceramics have been also studied to prevent the evaporation of Na_2O (or K_2O) during sintering.[9–11]

The $KNbO_3$ (KN) ceramic was also considered as a candidate for lead-free piezoelectric ceramics because the KN single crystal exhibited good piezoelectric properties and high T_c.[19,20] However, densification of the KN ceramics using the conventional solid-state method was very difficult because of the evaporation of K_2O and formation of unwanted secondary phases.[2,21] Therefore, special synthesis methods such as hot pressing,[22] sintering under an O_2 atmosphere,[21] and the addition of sintering aids[23,24] were used to obtain dense and homogeneous KN ceramics. Two time calcination method with a cold isostatic press was also used to obtain dense KN ceramics via the conventional solid-state process.[25,26] However, the sintering temperature used in this method was 1050 °C, which is very close to the melting temperature of KN ceramics (1058 °C).[27] Therefore, it is very difficult to apply these process conditions for the fabrication of the piezoelectric devices using KN ceramics, and a reduced sintering temperature of KN ceramics is required for practical applications. In this work, the sintering mechanism of KN ceramics was investigated in detail, and dense KN ceramics exhibiting promising electrical properties were obtained at relatively low sintering temperatures.

2. Experimental procedures

Using conventional solid-state synthesis, KN ceramics were prepared. The oxide compounds of K_2CO_3, and Nb_2O_5 (>99%, all from High Purity Chemicals, Saitama, Japan) were mixed with zirconia balls in a plastic jar for 24 h and then dried. The dried powders were calcined at 600 °C for 4 h and then heated at 1000 °C for 4 h.[25,26] The average particle size of the calcined powders was calculated using the Brunauer–Emmett–Teller (BET) specific surface area measured by Tristar 3000 (Micromeritics Co., Ltd., USA). Shrinkage of the specimens was measured using a thermal dilatometer (Dilatometer; DIL402C, Netzsch, Germany) under heating conditions, which were identical to the sintering conditions. The calcined KN powders were re-milled, dried, and pressed into discs under a pressure of 100 kgf/cm^2 and sintered at 1020 and 1040 °C for various periods of time. The specimens were heated to the sintering temperature at a rate of 5.0°/min and were slowly cooled in the furnace after sintering. The thickness and diameter of each specimen were 1.0 and 14.0 mm, respectively. Mass loss in the specimens with the heating temperature was measured using thermogravimetric analysis (TGA; TA Instruments, SDT Q-600, United States). The structural properties of the specimens were examined by X-ray diffraction (XRD; Rigaku D/max-RC, Tokyo, Japan). Scanning electron microscopy (SEM; Hitachi S-4300, Osaka, Japan) and field-emission transmission electron microscopy (FE-TEM; Tecnai F20, FEI, The Netherlands) were used to investigate the microstructure of the KN ceramics. Densities of the sintered specimens were measured using a water-immersion technique. A silver electrode was printed on the lapped surfaces, and the specimens were polled in silicone oil at 120 °C by applying a DC field of 4–5 kV/mm for 60 min. The polarization versus electric field (P–E) behavior was determined using a modified Sawyer–Tower circuit. The piezoelectric and dielectric properties and electromechanical coupling factor were determined using a d_{33} meter (Micro-Epsilon Channel Product DT-3300, Raleigh, NC, USA) and an impedance analyzer (Agilent Technologies HP 4294A, Santa Clara, CA, USA), all according to IEEE standards.

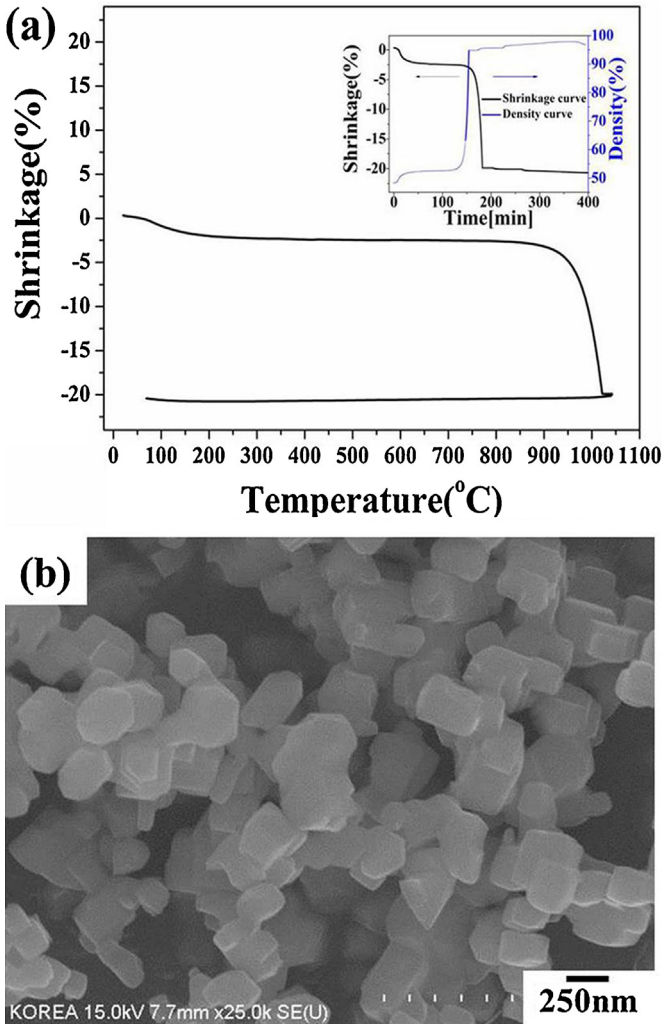

Fig. 1. (a) Shrinkage curve for a KN specimen; the inset shows the shrinkage and densification curves in terms of time. (b) SEM image of calcined KN powders.

3. Results and discussion

Fig. 1a shows a shrinkage curve for a specimen obtained from the thermal dilatometer under heating conditions, which were identical to the sintering conditions of the KN ceramics. The inset shows the shrinkage and densification curves for the specimen in terms of time.[28] Shrinkage of the specimen began at approximately 950 °C and finished at around 1020 °C. The final shrinkage of specimen was about 20%. Fig. 1b shows the SEM image of calcined KN powders; the average particle size was found to be approximately 0.25 μm. BET measurements