Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 32 (2012) 4353–4361

www.elsevier.com/locate/jeurceramsoc

Phase transitions and electrical characterizations of $(K_{0.5}Na_{0.5})_{2x}(Sr_{0.6}Ba_{0.4})_{5-x}Nb_{10}O_{30}$ (KNSBN) ceramics with 'unfilled' and 'filled' tetragonal tungsten–bronze (TTB) crystal structure

Y.B. Yao [a,b,d,e], C.L. Mak [a,*], B. Ploss [c,f]

[a] *Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong*
[b] *Advanced Nanofabrication, Imaging and Characterization Core Lab, King Abdullah University of Science and Technology, Thuwal, Jeddah, Saudi Arabia*
[c] *Department of SciTec, University of Applied Sciences Jena, Carl-Zeiss-Promenade 2, 07743 Jena, Germany*

Received 1 June 2012; received in revised form 20 July 2012; accepted 25 July 2012
Available online 14 August 2012

Abstract

Alkali-doped strontium barium niobate $(K_{0.5}Na_{0.5})_{2x}(Sr_{0.6}Ba_{0.4})_{5-x}Nb_{10}O_{30}$ (KNSBN) ceramics has been prepared by a conventional solid-state reaction method. The alkali-dopant concentration x has been varied from 0.24 to 1.15 so that the crystal structure was transformed from 'unfilled' to 'filled' tetragonal tungsten–bronze (TTB) structure. Apart from the change in the structural properties, the effects of the alkali-dopants on the phase transition as well as ferroelectric, piezoelectric and pyroelectric properties have also been investigated. Phase transitions have been studied in the temperature range of −200 °C to 350 °C. The origins of these phase transitions are discussed. The addition of the alkali-dopants enhances the ferroelectric, piezoelectric and pyroelectric properties of the KNSBN ceramics. Alkali-doping also favors abnormal grain growth and thus results in a porous microstructure, which might contribute to the enhancement of the pyroelectric performance.

Keywords: Strontium barium niobate; Doping; Pyroelectricity; Porosity

1. Introduction

Environmental-friendly lead-free ferroelectric materials have received intense attentions in recent years. Among various lead-free ferroelectric materials, ferroelectrics with tetragonal tungsten–bronze (TTB) structure show great promise in pyroelectric,[1] piezoelectric,[2] non-linear optic[3] and high-frequency dielectric applications.[4] The TB structure consists of a complex array of distorted BO_6 octahedra sharing corners in such a way that three types of inter-sites (A_1, A_2 and C) are available for different cations with a general formula of $(A_1)_4(A_2)_2C_4(B_1)_2(B_2)_8O_{30}$ or $(A_1)_4(A_2)_2(B_1)_2(B_2)_8O_{30}$, in which A_1, A_2, C, and B are 15-, 12-, 9-, and 6-fold coordinated sites.[5] The first formula represents the so-called 'stuffed' TB structure, in which all of the A, C, and B sites are occupied. The second formula represents either 'filled' (all 6 A sites are occupied) or 'unfilled' (only 5 out of 6 of the A sites are occupied) structures. Various ferroelectric and ferroelastic materials have been identified by substituting different cations into A-site (Sr, Ba, Pb, Ca, K, Na, Li, Mn, Cu, Cr, rare-earth etc.), C-site (Li) and/or B-site (Nb, Ta, Ti).[1–22] It has been shown that ferroelectric material is more stable in the 'filled' TTB structure as compared to the 'unfilled' TTB structure.[18] This stable structure usually has a higher Curie temperature. Besides that, ferroelectric crystals possessing 'filled' TTB structure do not suffer optical damage for reasonable high power level at room temperature.[2,6]

Potassium sodium strontium barium niobate (KNSBN) possesses a TTB structure that can be tuned from 'unfilled' structure to 'filled' structure, by adjusting the alkali-dopant concentration. KNSBN has good mechanical properties, high Curie temperature, and large pyroelectric, piezoelectric, and electro-optic coefficients.[5,6,13,16,18,19] Previous studies on KNSBN were confined to the two extreme compositions, i.e. either 'unfilled' $(K_{0.5}Na_{0.5})(Sr_xBa_{1-x})_{4.5}Nb_{10}O_{30}$ ((K, Na):(Sr,

* Corresponding author. Tel.: +852 2766 5669; fax: +852 2333 7629.
E-mail addresses: yingbang.yao@kaust.sa (Y.B. Yao), apaclmak@polyu.edu.hk (C.L. Mak), bernd.ploss@fh-jena.de (B. Ploss).
[d] Tel.: +852 2766 5669; fax: +852 2333 7629.
[e] Tel.: +966 2 8082431; fax: +966 2 8021174.
[f] Tel.: +49 3641 205 353; fax: +49 3641 205 351.

0955-2219/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jeurceramsoc.2012.07.034