Journal of Alloys and Compounds 616 (2014) 293–299

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

Dense $KSr_2Nb_5O_{15}$ ceramics with uniform grain size prepared by molten salt synthesis

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ARTICLE INFO

Article history:
Received 5 June 2014
Received in revised form 17 July 2014
Accepted 18 July 2014
Available online 27 July 2014

Keywords:
$KSr_2Nb_5O_{15}$
Lead-free ceramics
Grain size
Molten salt synthesis

ABSTRACT

Dense $KSr_2Nb_5O_{15}$ (KSN) ceramics with various grain-size distributions were prepared by the conventional solid-state sintering under different conditions, e.g. one-step and two-step techniques. Bi_2O_3 (2 mol%) was added as sintering aid. KSN powder crystals prepared by the molten salt synthesis was used as raw materials. Varying temperature from 1250 °C to 1350 °C at one-step sintering technique were found to enhance abnormal grain growth. For two-step sintering technique, presintering at 1250 °C followed by higher sintering temperature of 1350 °C controlled abnormal grain growth and obtained a dense KSN ceramics with uniform grain size (an average grain size of 3 μm). The effect of KSN powder crystals on promoting densification and presintering technology on controlling abnormal grain growth were discussed. The correlation of microstructure with dielectric properties was investigated.

1. Introduction

To date, the lead-free piezoelectric materials that have been extensively studied belong to the perovskite (such as $BaTiO_3$ [1,2], $K_{0.5}Na_{0.5}NbO_3$ [3] and (Na, Bi)TiO_3 [4–7]) and bismuth-layered (e.g. $Bi_4Ti_3O_{12}$) structures [8]. Besides these two families, piezoelectricity has also been identified in the ferroelectric tungsten bronze family. And tungsten bronze (TB) compounds are of particular interest recently since they exhibit excellent dielectric, electrooptic, piezoelectric, ferroelectric and pyroelectric properties [9,10].

(K, Sr)Nb_5O_{15} with tetragonal tungsten bronze (TTB) crystal structure is a kind of solid solution of $SrNb_2O_6$ and $KNbO_3$ when the $SrNb_2O_6$ content is between 59 and 78 mol% [11]. The compound $KSr_2Nb_5O_{15}$ (abbreviated as KSN) is very attractive candidate for lead-free ferroelectric and piezoelectric devices because of enhanced electrical properties [12–14], comparable with $Sr_{1-x}Ba_xNb_2O_6$ (SBN) solid solution. Additionally, KSN single crystal shows a room-temperature electro-optic effect nearly an order of magnitude greater than that of $LiNbO_3$ [11].

The applications of texture engineering in lead-free ceramics are of considerable interest due to the potential improvement of properties [15–18]. Recently, textured KSN ceramics can be obtained by various methods [19–21]. However, these investigations concerning texturing of the KSN material in the [001] focused on the promotion of the texture degree. Little attention was paid on densification of the textured KSN ceramics. It was surprisingly found that there were very limited numbers of studies reported in the literature on randomly oriented KSN ceramics [22]. KSN is a uniaxial ferroelectric material, the lattice constants are a = 1.247 and c = 0.394 nm [23]. These structural features point to a highly anisotropic material, which caused cracking and abnormal grain growth (AGG) in KSN ceramics. Our previous studies [24,25] suggested that cracking problem can be addressed with adding Bi_2O_3 and density of the KSN ceramics can be effectively improved by using KSN powder crystal as raw material. KSN powder crystals were fabricated by molten salt synthesis (MSS) [26–30]. Because compositional homogeneity of raw material, leading to few liquid phases during high temperature, appropriate sintering technique should been developed to control the occurrence of AGG in KSN ceramics. Therefore, it was expected to prepare dense KSN ceramics with uniform grain size when the KSN powder prepared by MSS was used as raw material. And it was economic and time-saving to check out the sintering technique of dense ceramics without AGG before fabrication of the textured KSN ceramics.

In this paper, KSN powder crystals, prepared by MSS, were used as raw material. 2 mol% Bi_2O_3 was used as a sintering aid. The

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http://dx.doi.org/10.1016/j.jallcom.2014.07.155
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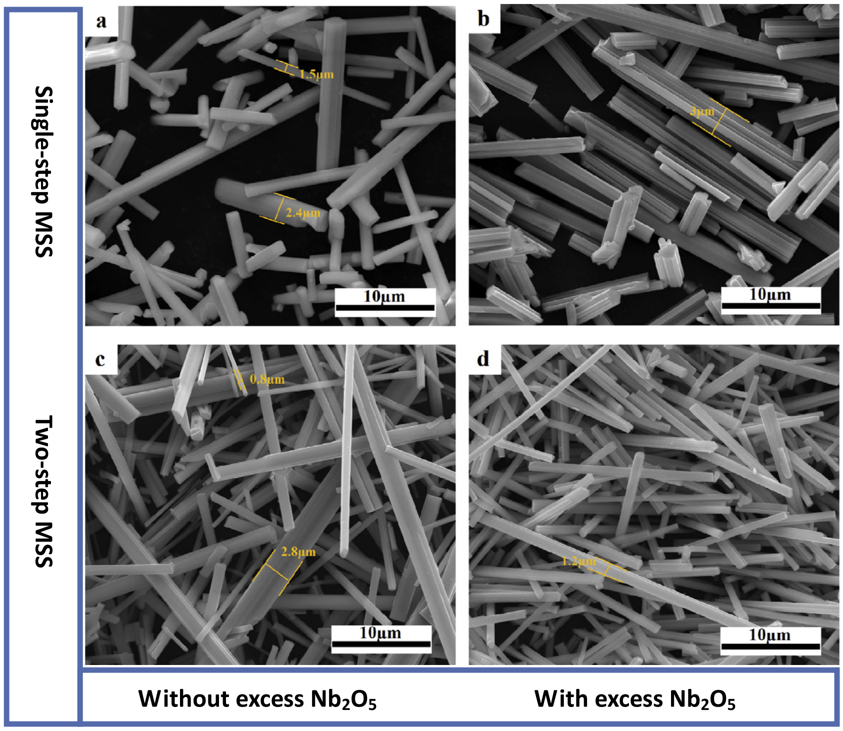

Fig. 1. Morphology of the KSN particles fabricated by molten salt synthesis at various seed and excess Nb_2O_5 content: (a) 0 wt% seed and excess 0 wt% Nb_2O_5, (b) 0 wt% seed and excess 100 wt% Nb_2O_5, (c) 10 wt% seed and excess 0 wt% Nb_2O_5 and (d) 10 wt% seed and excess 60 wt% Nb_2O_5, respectively.

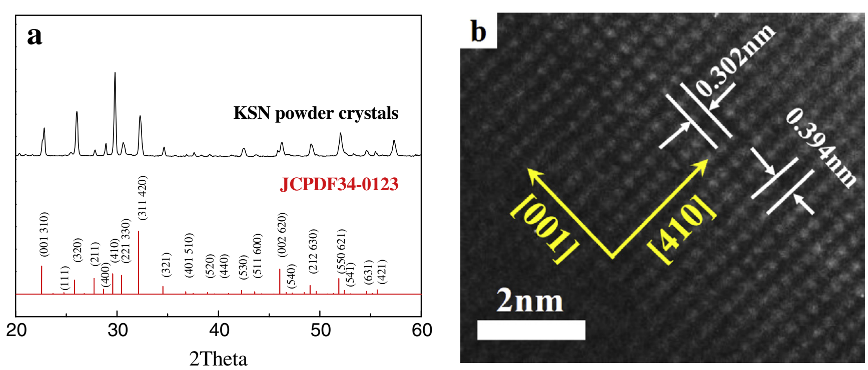

Fig. 2. XRD pattern of the KSN powder crystals (a) and HRTEM image of a KSN particle lateral surface (b) fabricated by molten salt synthesis.

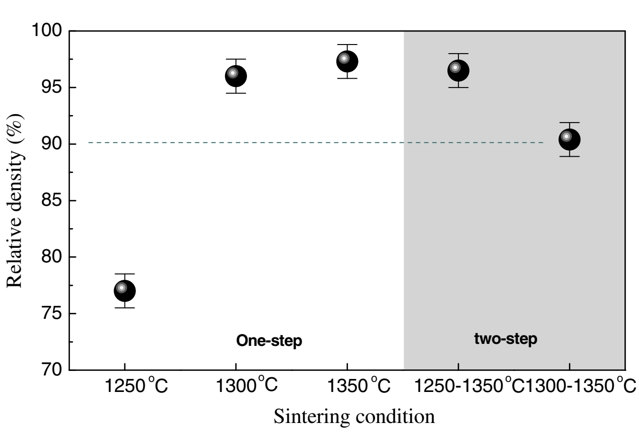

Fig. 3. Relative densities of the KSN ceramics at different sintering techniques.

effect of sintering technique (one-step and two-step) on density and microstructure development as well as electrical properties of the KSN ceramics were investigated detailedly.

2. Experimental procedures

Prior to $KSr_2Nb_5O_{15}$ (KSN) ceramics preparing, KSN powder crystals were fabricated by a molten salt synthesis (MSS) method. The single-step and two-step MSS methods combined with excess Nb_2O_5 were utilized to synthesize KSN particles. Details of the preparation of the particles were reported by our group in previous articles [26,27]. In the MSS method, the stoichiometric mixtures ($SrCO_3$, Nb_2O_5, KCl and seed) were mixed by ball milling with zirconia balls as grinding media in ethanol for 24 h. The mixture was placed into an Al_2O_3 crucible. The crucible was covered with a flat Al_2O_3 lid to minimize KCl evaporation, then heated to 1150 °C at a rate of 5 °C/min, held for 6 h and cooled to ambient temperature at a rate of 2 °C/min. After heat treatment, the products were separated from the mass of solidified salt by washing several times in hot deionized water to ensure complete removal of the redundant KCl salt.

KSN powder crystal and 2 mol% Bi_2O_3 additive were mixed by ball milling with zirconia balls as grinding media in ethanol for 24 h. After drying, the mixture was granulated with PVA as a binder and then pressed into pellets (φ12 mm × 1.3 mm).