Available online at www.sciencedirect.com

SciVerse ScienceDirect

Journal of the European Ceramic Society 34 (2014) 23–28

www.elsevier.com/locate/jeurceramsoc

Effects of Li_2CO_3 and Sm_2O_3 additives on low-temperature sintering and piezoelectric properties of PZN-PZT ceramics

G.F. Fan[a,b], M.B. Shi[a,b], W.Z. Lu[a,b,*], Y.Q. Wang[a,b], Fei Liang[a,b]

[a] School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, PR China
[b] Key Lab of Functional Materials For Electronic Information, MOE, Huazhong University of Science and Technology, Wuhan 430074, PR China

Received 26 March 2013; received in revised form 20 July 2013; accepted 29 July 2013
Available online 27 August 2013

Abstract

To assist the development of applications for multilayer piezoelectric devices, the low-temperature sintering piezoelectric ceramics of $0.3Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.7Pb(Zr_{0.49}Ti_{0.51})O_3$ with Li_2CO_3 and Sm_2O_3 additives were fabricated by a conventional solid-state reaction, and their structural and piezoelectric properties were studied. With the addition of Li_2CO_3, the minimum sintering temperature of $0.3Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.7Pb(Zr_{0.49}Ti_{0.51})O_3$ piezoelectric ceramics was reduced from 1125 °C to 950 °C through the formation of a liquid phase and its piezoelectric properties showed almost no degradation. When the sintering temperature was below 950 °C, however, the piezoelectric properties degraded obviously. The additional Sm_2O_3 resulted in a significant improvement in the piezoelectric properties of $0.3Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.7Pb(Zr_{0.49}Ti_{0.51})O_3$ ceramic with added Li_2CO_3. When sintered at 900 °C, the optimized properties of the $0.3Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.7Pb(Zr_{0.49}Ti_{0.51})O_3$ piezoelectric ceramic with 0.3 wt% Li_2CO_3 and 0.3 wt% Sm_2O_3 were obtained as $d_{33} = 483$ pC/N, $k_{31} = 0.376$, $Q_m = 73$, $\varepsilon_r = 2524$, $\tan\delta = 0.0178$.

Keywords: Piezoelectric property; Low-temperature sintering; Sintering aid

1. Introduction

The piezoelectric ceramic materials of $Pb(Zr, Ti)O_3$ (PZT) have been widely used in various electronic devices such as actuators and capacitors because of their excellent piezoelectric properties. $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) is a typical relaxor ferroelectric with extremely high dielectric constant and relatively low sintering temperature. However, single-phase PZN is difficult to synthesize by the conventional ceramic process because of the formation of the pyrochlore phase,[1] meaning that some other perovskite materials such as lead titanate $PbTiO_3$, barium titanate $BaTiO_3$, or lead zircon-ate titanate $Pb(Zr, Ti)O_3$ (PZT) powders have to be added to stabilize the PZN.[2–4] It is well known that $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) is shows exceptionally high dielectric and piezoelectric properties, with a composition close to a morphotropic phase boundary (MPB) (Zr:Ti 52:48), the boundary between the tetragonal and the rhombohedral phases.[5] Moreover, a certain composition of $0.3Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.7Pb(Zr_{0.49}Ti_{0.51})O_3$ (0.3PZN-0.7PZT) system is modified as "soft" piezoelectric ceramics, which exhibit excellent piezoelectric properties with high electromechanical coupling factor and low mechanical quality factor and is suitable for the applications of large strain actuators in the non resonant condition. However, the sintering temperature for full densification of 0.3PZN-0.7PZT is above 1125 °C, which is considerably high for multilayer piezoelectric applications.

In recent years, multilayer piezoelectric ceramic devices have been developed rapidly with their advantages of low voltage and small size. And, for internally electroded PZT based multilayer piezoelectric ceramic devices, Ag/Pd alloy is generally used as the internal electrode to suppress the migration of Ag into the ceramics at high temperature.[6] It is necessary to lower the sintering temperature for multilayer piezoelectric ceramic in order to co-fire them with less expensive metal electrodes such as pure Ag or high Ag/low Pd.[7] Therefore, the low temperature sintering technology is indispensable for improving price competitiveness in manufacturing multilayer piezoelectric ceramic devices.[8] Furthermore, low temperature sintering can provide advantages such as reducing energy consumption,

* Corresponding author. Tel.: +86 27 87542594; fax: +86 27 87543134.
E-mail addresses: lwz@mail.hust.edu.cn, shimengbo1988@163.com (W.Z. Lu).

0955-2219/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jeurceramsoc.2013.07.028

and the reduction of PbO volatilization. To lower the sintering temperature of piezoelectric ceramics, many researchers have reported PZT-based piezoelectric ceramics with low sintering temperature by using low-melting point oxides and compounds as sintering aids, including CuO, Li_2CO_3, $LiBiO_2$, $Pb_5Ge_3O_{11}$, MnO, ZnO, Gd_2O_3, Y_2O_3, PbO, etc.,[9–13] which can form a liquid phase to assist the lowering of sintering temperature.[14] In the past, Li_2CO_3 is an important additive to lower the sintering temperature of ceramics. Yu-Dong Hou has observed that the addition of Li_2CO_3 to 0.5PZN-0.5PZT lowered the sintering temperature from 1100 °C to 950 °C, but the piezoelectric constant d_{33} and the Curie temperature T_c of the ceramics are only 278 pC/N and 250 °C respectively, which are too low for the applications of piezoelectric actuators and transformers.[15] On the other hand, the effects of Sm_2O_3 additive on the sintering temperature and piezoelectric properties of 0.3PZN-0.7PZT have been rarely reported.

Hence, in this study, in order to lower the sintering temperature of 0.3PZN-0.7PZT piezoelectric ceramics and maintain its high piezoelectric properties for multilayer piezoelectric ceramic devices, the effects of Li_2CO_3 and Sm_2O_3 additives on sintering temperature, microstructure, Curie temperature and piezoelectric properties of 0.3PZN-0.7PZT piezoelectric ceramics are investigated.

2. Experimental

The specimens were manufactured using a conventional mixed oxide process. The general formula of the researched materials was $0.3Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.7PbZr_{0.49}Ti_{0.51}O_3 + x$ wt% $Li_2CO_3 + y$ wt% Sm_2O_3, where $x = 0$, 0.1, 0.3, 0.5, 0.7 and $y = 0$, 0.05, 0.1, 0.2, 0.3, 0.5, respectively. Reagent grade oxide powders of Pb_3O_4, TiO_2, ZrO_2, ZnO and Nb_2O_5 used as starting materials were weighted by mole ratio and the powders were mixed by ball milling with partially stabilized zirconia balls as media in deionized water for 3 h. After drying, the mixture was calcined at 850 °C for 2 h. Thereafter, Li_2CO_3 and Sm_2O_3 were added to the calcined powder and ball-milled again. After drying, the resultant powders were mixed with the polyvinyl alcohol binder for granulation, and uniaxially pressed into disks of 15 mm diameter and rectangular plates. The green specimens were sintered at 900–1200 °C for 3 h. To measure the electrical properties, the sintered ceramics were polished, electroded with silver paste on both surfaces, and then poled in a silicone oil bath under a dc electric field of 4 kV/mm for 15 min at 120 °C.

The microstructure and crystal structure of specimens were analyzed through scanning electron microscopy (FEI-Sirion2000, Philips, Netherlands) and X-ray diffraction (Rigaku Dmax-rC, Japan) using Cu $K\alpha$ radiation. The piezoelectric constant d_{33} was determined using a quasi-static d_{33} meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, China), and its measurement frequency was 50 Hz. The electromechanical coupling coefficients k_{31}, k_p, and the electromechanical quality factor Q_m (The longitudinal mode) were calculated from the resonance and anti-resonance frequencies measured by a precision impedance analyzer (Agilent 4192A, USA-CA).

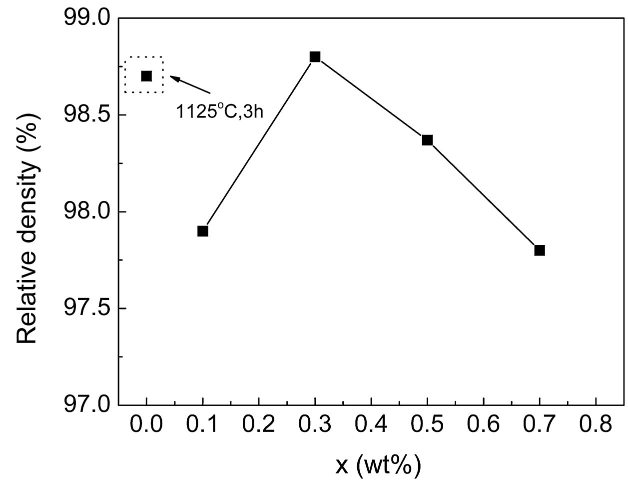

Fig. 1. The relative density of 0.3PZN-0.7PZT specimens with different amounts of Li_2CO_3 sintered at 950 °C for 3 h. (The dotted box refers to the relative density of undoped 0.3PZN-0.7PZT ceramics sintered at 1125 °C for 3 h.)

Ferroelectric properties were examined using a ferroelectric testing system (ZX-1, HUST, China). The dielectric properties were measured by a capacitance meter (TH2613, Changzhou Tonghui Electronics Co., Ltd., China). The temperature dependences of the dielectric constants were measured by the capacitance meter and an automatic temperature controller.

3. Results and discussions

3.1. Effects of Li_2CO_3 additive on piezoelectric properties of 0.3PZN-0.7PZT ceramics

Fig. 1 shows the relative density of 0.3PZN-0.7PZT specimens with different amounts of Li_2CO_3 additive sintered at 950 °C for 3 h. The relative density of the 0.3PZN-0.7PZT ceramics increases with increasing amount of Li_2CO_3, and reaches a maximum value 98.8% at 0.3 wt% Li_2CO_3 additive, then decreases rapidly. In the graph, the data point in the dotted box refers to the relative density of undoped 0.3PZN-0.7PZT ceramics sintered at 1125 °C for 3 h, showing that it is close to the relative density of 0.3PZN-0.7PZT ceramics with 0.3 wt% Li_2CO_3 sintered at 950 °C. The result shows that with the appropriate amount of Li_2CO_3, the sintering temperature has been reduced to 950 °C from 1125 °C and the sinterability of 0.3PZN-0.7PZT powders improved greatly. This improvement of the density may be related to the formation of the liquid phase which is proposed by Yu-Dong Hou and Li-Min Chang.[15] In the early and middle stages of sintering process, Li_2CO_3 additives with a low melting point of 723 °C forms a liquid phase, which wets and covers the surface of grains, and facilitates the dissolution and migration of the substances. Accordingly, densification is promoted by capillary action of the liquid phase. Normally, the liquid phase sintering accelerated the growth of grain.

Fig. 2 shows the electromechanical coupling coefficient k_{31}, the piezoelectric constant d_{33} and the mechanical quality factor Q_m of the 0.3PZN-0.7PZTceramics as functions of the amount of Li_2CO_3 addition sintered at 950 °C. As can be seen, both