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High power density in a piezoelectric energy harvesting ceramic by optimizing the sintering temperature of nanocrystalline powders

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ABSTRACT

Piezoelectric energy harvesting is the research hotspot in the field of new energy, and its core is to prepare piezoelectric ceramics with high transduction coefficient ($d_{33} \times g_{33}$) and large mechanical quality factor (Q_m) as well. In addition, the miniaturization of the piezoelectric energy harvester also requires the material to have a submicron fine grain structure. In this work, submicron-structured ternary system, MnO_2-doped $Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Zr_{0.5}Ti_{0.5})O_3$ was constructed by pressureless sintering of nanocrystalline powders, which has been synthesized for the first time by high-energy ball milling route thereby evading the calcination stage. The microstructure and the energy harvesting characteristics were tailored through changing the sintering temperature. It was found that 1000 °C sintered fine-grained specimen (mean grain size ~0.95 μm) showed the maximum $d_{33} \times g_{33}$ value of 9627×10^{-15} m^2/N, meanwhile Q_m was as large as 774, which was almost seven times larger than pure counterpart. In the mode of the cantilever-type energy harvester, a high power density of 1.5 μW/mm^3 were obtained for 1000 °C sintered specimen at a low resonance frequency of 90 Hz and acceleration of 10 m/s^2, which were further increased to 29.2 μW/mm^3 when the acceleration increased to 50 m/s^2, showing the potential applications as a next generation high power multilayer energy harvester.

1. Introduction

Recently, there has been tremendous progress in harvesting environmental energy, in which mechanical vibration energy can be found everywhere [1–3], e.g., running engines, highways, human activity, bridges. Apparently, it is a useful, desired, and a workable energy source. Based on the piezoelectric effect, piezoelectric ceramics can harvest the vibration energy in the environment to generate electricity. To meet the application requirements of piezoelectric energy harvesters, piezoelectric materials need to have a high transduction coefficient ($d_{33} \times g_{33}$) and at the same time, also need to have a high mechanical quality factor (Q_m). The latter is critical to boosting the power characteristics of the piezoelectric energy harvesters, especially in the case of strong field excitation. Currently, most of the energy harvesting materials are concentrated on the lead zirconate-titanate (PZT) family because of high efficiency and is also a straightforward procedure [4–6]. Moreover, in order to meet the demand of multi-layering and miniaturization of piezoelectric energy harvester, it is urgent to developing fine-grained PZT based piezoelectric ceramics, that is, the grain size needs to enter the sub-micron scale. PZN-PZT is a well-known ternary PZT based system, which has been heavily reported in literatures for developing energy harvesting materials [7–9]. With the aim to improve Q_m of the material, transition metal ions are introduced into the ternary system for doping modification [10–12]. Among all doping ions, manganese ions show the most prominent in enhancing Q_m [13,14]. The literature results revealed that manganese ions played the acceptor role and made the properties hard, i.e. domain wall motion is pinned by the oxygen vacancy resulting in improved piezoelectric properties with high Q_m as well as low loss. But it should be pointed out that the previous studies usually use high-temperature calcined powder to sinter the ceramic, resulting in a large grain size of the ceramic body, generally in the order of micron scale. Unfortunately, the coarse grained structure hinders the miniaturization of the piezoelectric energy harvester.

In this work, as an extension to the study on the high power energy harvesting material, submicron-structured MnO_2-doped PZN-PZT ceramics have been built by pressureless sintering of nanocrystalline powder, which was obtained by mechanosynthesis. Through changing sintering temperature, the grain sizes have been modulated in a wide range and its effect on the microstructure and piezoelectric properties have been investigated in detail. In addition, the power generation performances of optimal material were evaluated in the mode of the cantilever-type energy har-

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vester in a wide acceleration range between 10 m/s^2 and 50 m/s^2. Extremely high power density and fine grain structure make this ternary system very suitable for use as a multi-layer high-power piezoelectric energy harvesting material.

2. Experimental

The general formula of the materials was 0.5 wt.% MnO_2-doped $0.2Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.8Pb(Zr_{0.5}Ti_{0.5})O_3$ (PZN-PZT+MnO_2). This composition was near morphotropic phase boundary (MPB), as estimated by previous work [15]. Reagent-grade oxide powders, such as, Pb_3O_4, ZrO_2, TiO_2, ZnO, Nb_2O_5 and MnO_2, were used as starting reagents and before batching, the raw chemicals were baked at 100 °C for 12 h to control water content and permit accurate control of the stoichiometric batching. Firstly, the powders were weighed and mixed by an ordinary planetary mill with zirconia balls as media at a low speed of 400 rpm for 10 h. Then the mixtures were treated by high-energy ball milling equipment (Fritsch Pulverisette 7, Fritsch GmbH, Idar-Oberstein, Germany). A 45 ml tungsten carbide vial with 658 units of 3 mm sized tungsten carbide balls were used as a milling medium. The high energy milling time was set between 0 and 150 min at a constant high speed of 800 rpm and a ball-to-powder weight ratio of 20:1. The nanocrystalline particles with perovskite structure can be directly obtained after milling 90 min without the calcination stage. And then, the resulted nanoparticles were pressed into disks of 11.5 mm in diameter at around 800 MPa. With the aim to investigate the size effect on energy harvesting properties, MnO_2-doped PZN-PZT ceramics with different grain sizes have been built by sintering green discs at 50 °C temperature intervals between 850 and 1050 °C for 120 min in a sealed alumina crucible. For comparison, the undoped counterparts were prepared with the same process route.

Specimen density was measured by Archimedes method. The phase development of the powders and sintered specimens were examined in a 2θ range from 20° to 60° by x-ray diffraction (D8 Advance; Bruker, Karlsruhe, Germany) using Cu–Kα radiation. The morphology and size of mechanically synthesized nanocrystals were characterized by high-resolution transmission electron microscopy (Tecnai F20; FEI, Hillsboro, OR, USA). The micromorphology development of sintered specimens was detected on a thermally etched cross section by a scanning electron microscope (S4800; Hitachi, Tokyo, Japan) and the grain size distribution was calculated with the Smile View software package.

To measure the electrical properties, silver paste was coated on both sides of the sintered pellets and then fired at 560 °C for 30 min to form electrodes. Prior to the testing of piezoelectric properties, the specimens were poled in a silicone oil bath at 120 °C by applying a DC field of 30 kV/cm for 30 min and then aged for 24 h. The detailed testing methods for piezoelectric properties were described elsewhere [16]. The power generation characteristics of piezoelectric ceramics are evaluated in cantilever mode. Fig. 1(a) and (b) schematically illustrates the measurement setup and test circuit of cantilever-type energy harvester. For the fabrication of cantilever beam piezoelectric energy harvester, the sintered ceramics were attached to stainless steel substrates using epoxy (353ND; Epoxy Technology, Billerica, MA) and the lead lines were connected between the top and bottom electrodes to load resistance. The continuous vibration was applied using a mini smart shaker with integrated power amplifier (Model K2007E01; The ModalShop Inc, Cincinnati, USA), and the vibration acceleration of cantilever beam was measured by piezoelectric accelerometer (Model 3211A, Dytran Instrument Inc, California, USA) and charge amplifier (MI2004, Econ Technologies Co., Ltd, China). The output voltage of the harvester was measured by a digitizing oscilloscope (TDO3062B, Tong Hui Electronic Co., Ltd, China).

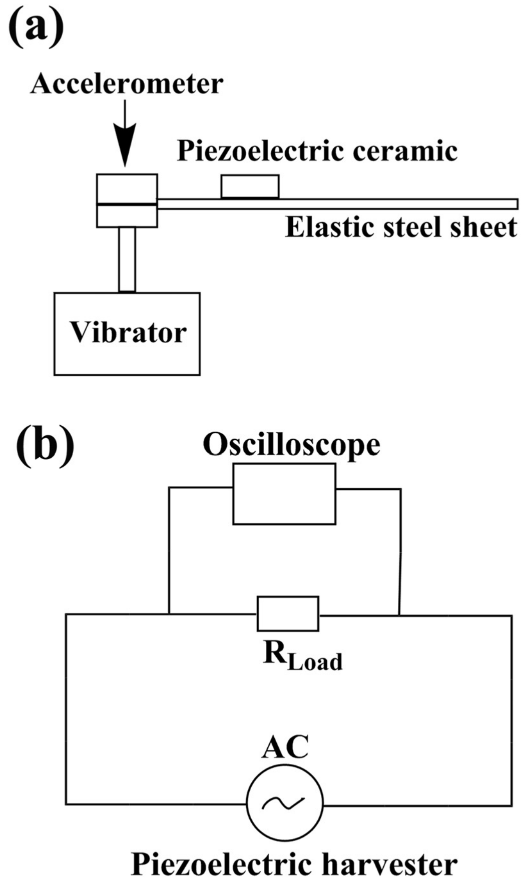

Fig. 1. The measurement setup (a) and test circuit (b) of cantilever-type energy harvester.

3. Results and discussions

Fig. 2 shows the XRD patterns of the mixed powders milled for 0–150 min by high-energy ball technique. In the initial state without milling, the diffraction peaks correspond to the individual raw materials, such as Pb_3O_4, ZrO_2, TiO_2, ZnO and Nb_2O_5. Due to the

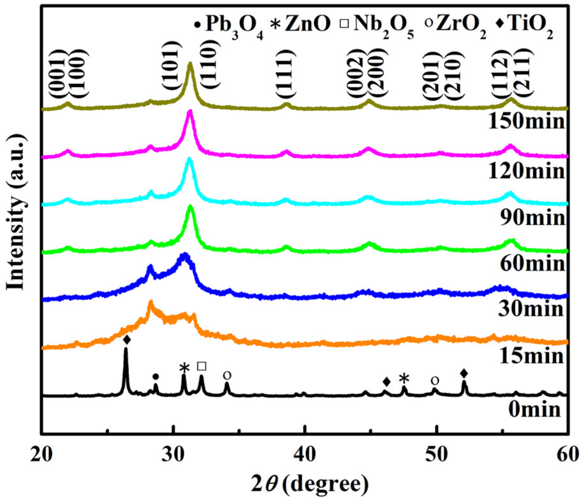

Fig. 2. XRD patterns of the mixed powders after various high-energy milling time (from 0 to 150 min).

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