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Microwave and conventional sintering of lead-free (K,Na) NbO_3-based piezoelectric ceramic multilayer actuators

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A comparative study of microwave and conventional sintering of lead-free Li-and Ta-modified (K,Na)NbO_3 (KNN) multilayer ceramic actuators (MLCAs) was completed. It was found that microwave sintering (MWS) could be successfully applied to the co-firing of KNN/AgPd MLCAs with a firing cycle that is ten times shorter and a firing temperature 150 °C lower (900 °C) than conventional furnace sintering (1050 °C) for sufficient densification. Furthermore, MWS-derived specimens showed electric field-induced strain comparable to those obtained using conventional sintering.

Key words: Lead-free piezoceramics, Multilayer actuators, Microwave sintering, Perovskite, Alkaline niobate.

Introduction

Piezoelectric materials that can interchangeably convert mechanical energy to electricity play important roles in solid-state sensors and actuators. Over the past several decades, lead zirconate titanate (PZT) has been the primary material used. Recent environmental concerns have accelerated research on new lead-free alternatives of PZT that contains more than 60 wt% Pb [1, 2]. Among lead-free ferroelectrics, (K,Na)NbO_3 (KNN) has attracted significant attention because of its excellent piezoelectric properties [1-7]. However, it is very difficult to obtain dense KNN ceramics via conventional ceramic processes due to the inherent volatility of both K and Na at the necessary sintering temperatures, as well as the cuboid shape of KNN grains. Such problems could be largely overcome by doping Li-compounds into KNN ceramics [3-5], leading to dense microstructures without requiring sophisticated processes such as hot pressing. Moreover, it has been demonstrated that multilayer ceramic actuators (MLCAs) can be successfully fabricated using Li- and Ta-modified KNN ceramics and AgPd inner electrodes with a high electric field-induced strain of 292 pm/V [8].

The application of microwave energy to the processing of materials including ceramics, metals, and their composites offers several advantages over conventional furnace sintering (CFS), such as smaller grained microstructures, improved product yield, energy savings, reduction in manufacturing cost, and synthesis of new materials [9-13]. It has been also reported that microwave sintering (MWS) can be applied to the co-firing of multilayer ceramic devices, in which ceramic and metal thick films are alternatively stacked, including $BaTiO_3$ multilayer ceramic capacitors [14, 15], ferrite chip inductors [16, 17], and integrated passive devices [18]. However, there has been little work on MWS of piezoelectric devices, in particular on lead-free piezoelectric ceramics and their multilayer devices. Therefore, in this study we investigated the MWS of Li- and Ta-modified KNN lead-free MLCAs. For comparison, the microstructure and piezoelectric properties of conventionally sintered specimens were also examined.

Experimental

Lead-free $(K_{0.47}Na_{0.51}Li_{0.02})(Nb_{0.8}Ta_{0.2})O_3$ (hereafter abbreviated as KNLNT) powders were synthesized using a conventional solid-state reaction route. Reagent grade powders of K_2CO_3 (99.0% purity), Na_2CO_3 (99.9%), Nb_2O_5 (99.95%), Li_2CO_3 (99.9%), and Ta_2O_5 (99.9%) were used as raw materials. The powders were weighed according to the chemical formula and then ball-milled for 24 hrs in anhydrous ethanol with zirconia balls. The slurry was dried and calcined at 850 °C for 2 hrs. We added 0.01 mol Li_2CO_3 as a sintering aid before forming.

We prepared KNLNT/AgPd (80/20) MLCAs with 12 piezoelectrically active layers. Piezoelectric ceramic sheets were obtained by tape casting a mixture of KNLNT powder, organic binders, a plasticizer and solvents. The green sheets were cut into pieces of 10×10 cm^2, on which AgPd thick films were screen-printed and then laminated. After soaking at 500 °C for 6 hrs in air to remove organic additives contained in the green sheets, the laminated composites were co-

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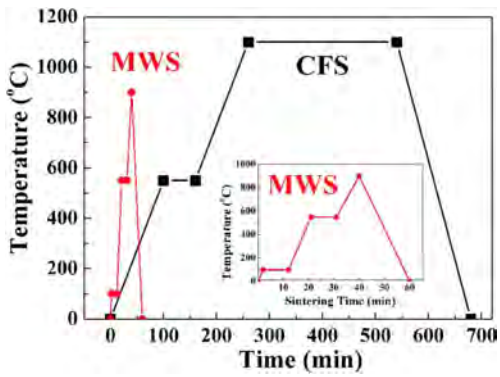

Fig. 1. Comparison of firing cycles between conventional furnace sintering (CFS) and microwave sintering (MWS).

fired via one of two different sintering approaches: conventional furnace sintering (CFS) at 950 - 1100 °C for 4 hrs, or microwave sintering (MWS) using a microwave heater (UMF-01, 2.45 GHz, Unicera, Korea). The firing cycles for the two sintering methods are compared in Fig. 1. The heating rate under MWS was 50 °C/min while the rate under CFS was 5 °C/min.

The surface morphology was analyzed with both an optical microscope (Olympus PMG3, Japan) and a field-emission scanning electron microscope (FE-SEM, JSM-65OFF, JEOL, Japan). After poling samples in a silicon oil bath under an electric field of 4 kV/mm for 30 min at 100 °C, electric field-induced strain (*S-E*) measurements were carried out using a linear variable differential transducer.

Results and discussion

Two different sintering approaches, CFS and MWS, were compared in terms of co-firing behavior, microstructure, crystal structure, and dielectric and electric field-induced strain properties of MLCAs. Fig. 2 presents photos of the MLCAs with 12 active layers prepared in this study. Firing shrinkage and density were measured, and the results are displayed in Fig. 3(a) as a function of co-firing temperature (T_s). Both firing approaches resulted in similar densification as a function of T_s, whereas MWS needed a T_s about 150 °C lower than CFS to attain the same level of shrinkage and density. This phenomenon is in consistent with previous works on MWS of other electroceramics such as PZT [11] and NiCuZn ferrite [16].

However, firing-induced deflection was generated by thermal shrinkage mismatch between the KNLNT ceramic and AgPd layers. The curvature (K) of the co-fired MLCAs was measured for at least 5 specimens according to a method found in previous literature on multilayered substrates [19], and the results are shown in Fig. 3(b). As seen in the figure, the firing-induced bending in co-fired specimens decreases as the firing temperature increases. The lowest curvature was obtained at 900 °C for MWS and at 1050 - 1100 °C for CFS. The

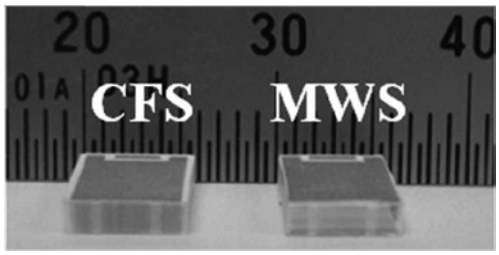

Fig. 2. Photos of KNLNT/AgPd MLCAs prepared using conventional sintering (CFS) and microwave sintering (MWS).

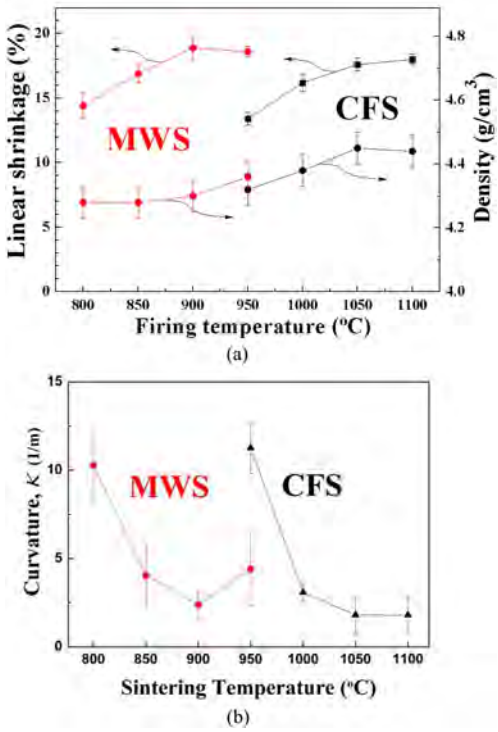

Fig. 3. Co-firing temperature dependence of (a) linear shrinkage and density and (b) firing-induced camber of KNLNT/AgPd MLCAs prepared using conventional sintering (CFS) and microwave sintering (MWS).

firing-induced deflection was more sensitive to the firing temperature for MWS than CFS, which might be due to local temperature nonuniformities [20] in the MWS specimen. The power absorbed per unit volume P (W/m^3) for MWS can be expressed as the following equation [21]:

$$P = \sigma |E|^2 = 2\pi f \varepsilon_0 \varepsilon_r \tan \delta |E|^2 \quad (1)$$

where E (V/m) is the magnitude of the internal field, σ the total effective conductivity (S/m), f the frequency (GHz), ε_0 the permittivity of free space ($\varepsilon_0 = 8.86 \times 10^{-12}$ F/m), and ε the dielectric permittivity. When microwave energy is in contact with materials having different dielectric properties, it will selectively couple with the higher loss tangent material. Therefore, it is naturally presumed that higher nonuniformities in temperature distribution may exist in composite specimens like

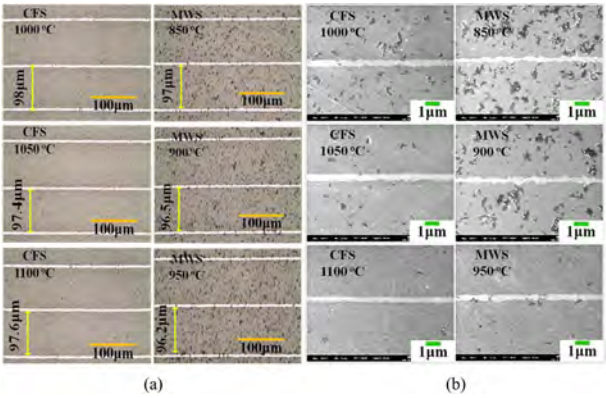

Fig. 4. Polished cross-sectional micrographs of a KNLNT/AgPd MLCA observed using (a) an optical microscope and (b) an SEM. The symbols CFS and MWS stand for conventional furnace sintering and microwave sintering, respectively. The number after the symbols denotes the firing temperature in °C.

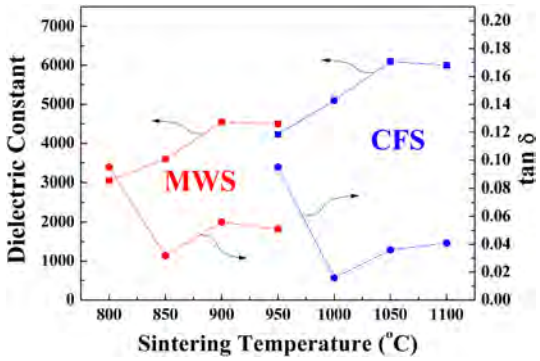

Fig. 5. Dielectric constant and loss tangent of KNLNT/AgPd MLCAs prepared using conventional sintering (CFS) and microwave sintering (MWS) for different firing temperatures.

MLCAs during MWS.

Fig. 4 shows the cross-sectional morphologies of KNLNT/AgPd MLCAs using both an optical and a scanning electron microscope. Based on the optical micrographs in Fig. 4(a), it can be seen that the piezoelectric layers of about 96-98 μm in thickness are uniformly laminated with AgPd layers with clear interfaces. However, many closed pores, appearing as dark spots, can be seen, especially on the higher magnification SEM micrographs in Fig. 4(b). MWS resulted in larger pores and resultantly higher porosity than CFS; the porosity rapidly decreased after elevating the firing temperature to 1100 °C for CFS and 950 °C for MWS. MWS led to rougher interfaces between the KNLNT and AgPd layers than CFS, which might be also attributed to local nonuniformities in the temperature distribution during MWS that may have been induced by heterogeneities in the absorption coefficients of microwave energy between different materials.

Fig. 5 shows the relative dielectric constant and loss tangent of a KNLNT MLCA as a function of firing temperature. Both sintering approaches showed similar firing temperature dependence of ε_r and tan δ. The ε_r

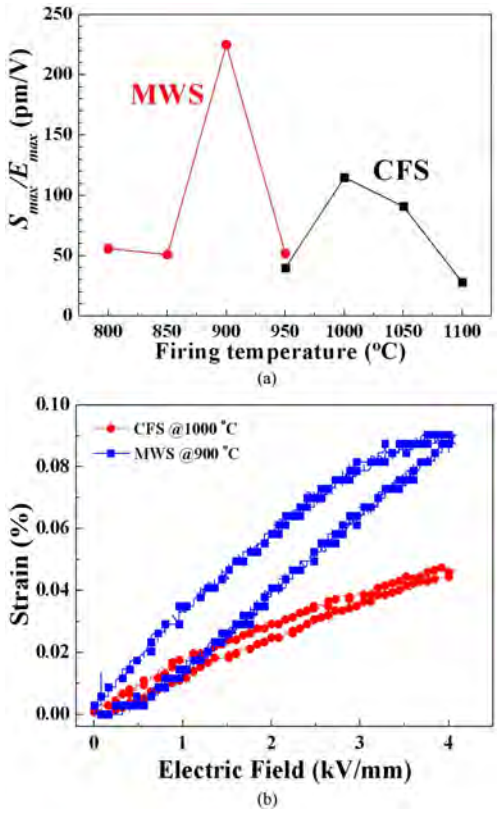

Fig. 6. Electric field-induced strain properties of MLCAs as a function of firing temperature for different sintering methods: (a) the normalized strain S_{max}/E_{max} and (b) typical unpipolar *S-E* loops.

peaked at 900 °C for MWS and 1050 °C for CFS, while tan δ reached a minimum at 850 °C for MWS and 1000 °C for CFS. Such trends seem to be related to the counteracting effects of enhanced densification and increased defects due to the evaporation of volatile elements with increased firing temperature.

The electric field-induced strain in a unipolar mode was measured for the specimens, and the results are given in Fig. 6. Unlike the dielectric properties of Fig. 5, the highest normalized strain (S_{max}/E_{max}) of 225 pm/V was obtained in a specimen prepared using MWS at 900 °C. This finding is very important, because this is the first report on the successful preparation of MWS-derived lead-free MLCAs. More work is still required for further optimization of the complex process variables.

Conclusions

Microwave sintering of lead-free KNN-based MLCAs was explored and compared with conventional sintering. We successfully demonstrated the preparation of lead-free KNN/AgPd multilayer actuators using microwave sintering. As previously reported for the MWS of other materials, we found that MWS of KNN-based MLCAs led to firing cycles almost ten times shorter and grained microstructures that were much smaller than for similar specimens obtained via CFS.

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