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Airflow deposition of oxide electroceramic films

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Abstract

Thick films of several oxide ceramic compositions based on lead zirconate titanate (PZT), barium titanate, and zinc oxide were fabricated by deposition from an airflow at room temperature. The as-deposited films showed green densities close to 80% theoretical for all compositions. Unfired, poled PZT-based films provided an audible acoustic response, and some PZT and $BaTiO_3$ compositions formed translucent layers. X-ray diffraction revealed no preferred crystallographic orientation of the particles in the films. High green densities and increased particle surface energies were thought to operate as drivers for significant reductions in sintering temperature, final grain size, and shrinkage. Films of PZT–PMN (lead magnesium niobate)-$Pb_5Ge_3O_{11}$, sintered at 750 °C, had a density of 99.5% theoretical, and relative permittivities greater than 2000. ZnO-based varistor films exhibited higher breakdown fields than equivalent bulk samples prepared by conventional routes.

Keywords: Airflow deposition; Films; Piezoelectric properties; PZT; Sensors

1. Introduction

Piezoelectric ceramics (in particular PZT) are commonly used as actuating/sensing elements in a range of electromechanical and acoustical applications. Until recently devices requiring thin piezoelectric elements have been based on machined PZT plates (50–200 μm) which are glued or bonded to an appropriate substrate.[1] There are compelling economic and technical arguments for eliminating the machining and handling of thin ceramic plates by developing a method to deposit PZT films directly onto the substrates. At film thicknesses of 5 μm, and less, methods such as chemical solution, physical vapour and chemical vapour deposition have been shown to be effective.[2,3] A technological gap remains, however, in the thickness range 5–100 μm, for which a processing solution is being actively sought.[4,5] At present the principal contenders are tape-casting, screen-printing and spray deposition.[6,7]

This paper describes a low-energy deposition process used for thick film fabrication, and examines the properties of several types of films produced by this method. Several oxide compositions have been deposited including PZT and $BaTiO_3$-based ferroelectrics, ZnO, and ZnO-based varistor compositions. From a technological viewpoint the method enables low temperature fabrication of high quality supported and self-supporting ceramic films, as well as complex structures such as monomorphs, bimorphs, multilayer stacks and compositionally graded elements.[8]

2. Experimental procedure

The basic technique for depositing a thick film from an airflow was described in Ref. 9. An air-particle flow was generated by a commercial jet-mill (Micron-Master 02-506) fed from a compressed air line at a pressure of 700 kPa. Precursor powders of PZT and $BaTiO_3$-based compositions were prepared by a conventional mixed oxide route. Lead germanate (PGO), used as a sintering aid for PZT–PMN (lead magnesium niobate) composition, was synthesized separately and subsequently mixed with the PZT–PMN powder in a ball mill. Likewise the multiple component ZnO-based compositions were also mixed in a ball mill. The initial particles sizes of the jet mill powder feedstock were in the range of ~5 to 500 μm. Deposition was performed at room temperature on nickel and tungsten carbide substrates. Neither the airflow nor the substrate was heated.

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Densities of the films and bulk samples were measured by using an Archimedean displacement technique in a water or carbon tetrachloride medium. Green film samples for dielectric measurements were electroded with an air-drying conductive silver paint, whereas sintered samples were electroded with fired-on silver. The permittivity and loss tangent were measured at a frequency of 1 kHz at room temperature with an Agilent 4294A impedance analyzer. Micrographs were obtained with a scanning electron microscope and an Olympus BX60M optical microscope. Sample shrinkage measurements during sintering were performed in situ using a Harrop TDA-H1-CP6X dilatometric analyzer. The dilatometer measurement cell was loaded with an atmosphere powder to prevent lead losses. Similarly the PZT-based samples were sintered in closed crucibles filled with an atmosphere powder to minimize the loss of lead during processing.

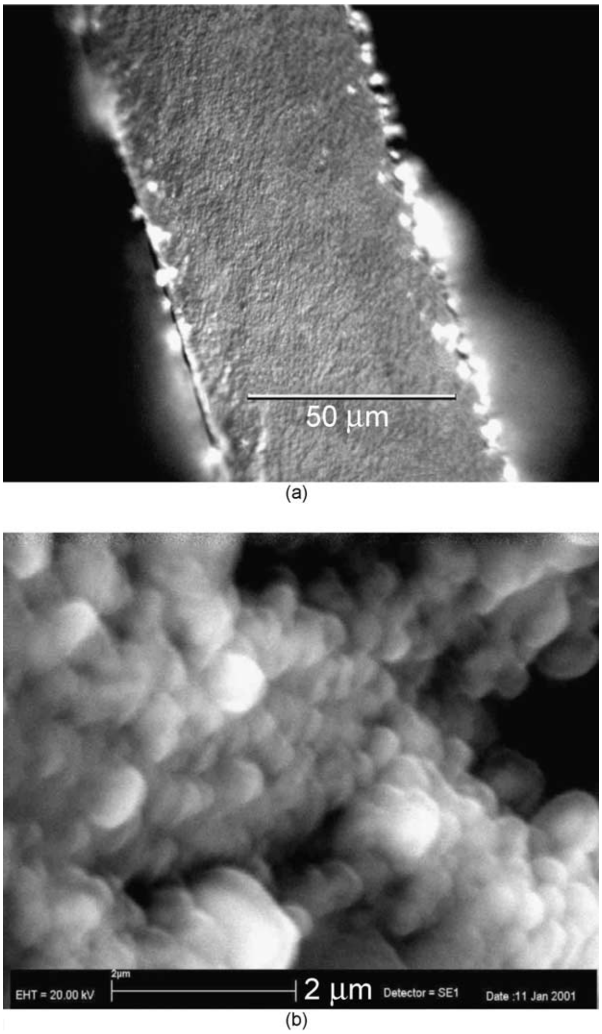

Fig. 1. Micrographs of the fracture surface of a PZT–PMN green film.

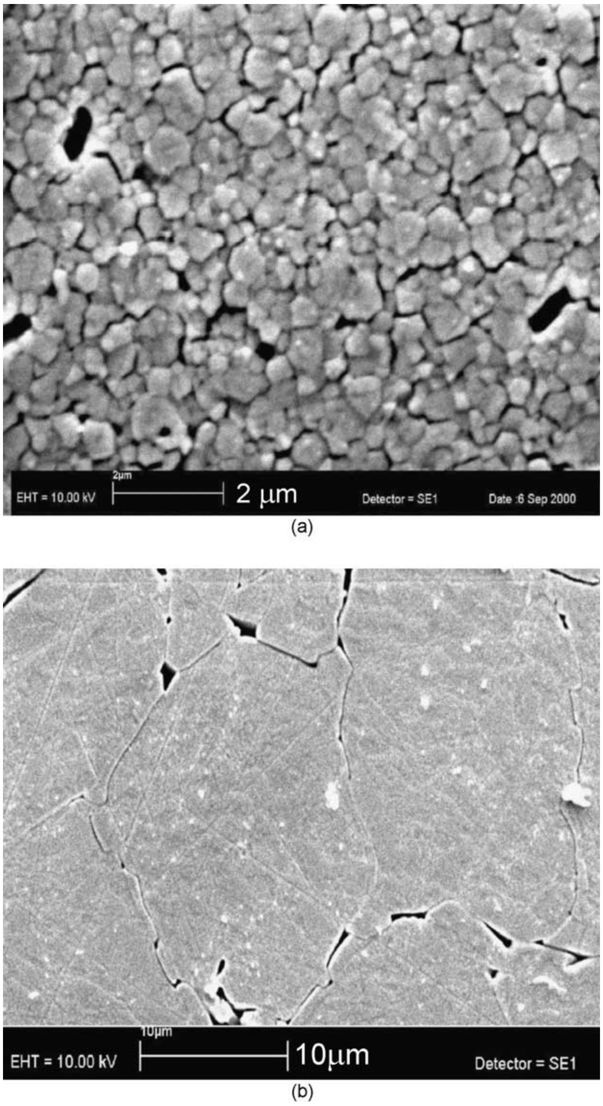

Fig. 2. Micrographs of polished and chemically-etched sections of PZT–PMN films sintered at 800 °C (a) and at 1250 °C (b).

Table 1
Properties of ferroelectric films sintered under various conditions

Composition	Sintering regime, temperature/time (°C/h)	Relative density	Relative permittivity[a]/tan δ
PZT–PMN	800/10	0.98–1.0	2000–2150/0.02
PZT–PMN	900/2	0.98–1.0	2000–2200/0.01
PZT–PMN	1000/2	0.98–1.0	2000–2200/0.01
PZT–PMN + 1%PGO	800/2	0.98–1.0	2000–2200/0.01
PZT-5	750/10	0.92–0.95	1000/0.025
PZT-5	1000/2	0.95	2200/0.01
$BaTiO_3 + CaTiO_3$	800/2	0.97–0.98	800/0.41
$BaTiO_3 + CaTiO_3$	900/2	0.97–0.98	1200/0.36
$BaTiO_3 + CaTiO_3$	1000/2	0.97–0.99	1200/0.23
$BaTiO_3 + CaTiO_3$	1200/2	0.97–0.99	1200/0.007

[a] Unpoled, at 1 kHz.

3. Results

Thick films of PZT–PMN, PZT-5, and $BaTiO_3$–$CaTiO_3$ with thicknesses from 5 to 200 μm were deposited onto a nickel substrate. It was found that the relative green densities for all as-deposited films were close to 80% theoretical, thereby exceeding the green density of isostatically pressed bulk samples (63–67% th.). A micrograph of a green PZT–PMN film (Fig. 1a) shows the high density and degree of uniformity of the film. Electron microscopy revealed that the film was composed of densely compacted, rounded submicron particles (Fig. 1b).

X-ray diffraction analysis of the green films indicated that there was no preferred crystallographic orientation of the particles in the films.

The green film specimens were sintered using various sintering regimes (Table 1). The results obtained from the density and dielectric measurements showed that full density of the materials could be achieved at much lower temperatures than typical for the corresponding bulk ceramics. The lead germanate sintering aid, used with the PZT–PMN composition, made possible lower temperature and more rapid sintering. Acceptable dielectric and piezoelectric properties for PZT–PMN + 1%PGO were observed after sintering for 2 h at 750 °C.

Further investigations revealed that the microstructure of those films sintered at low temperature was much finer than for bulk samples and films sintered at elevated temperatures. Fig. 2 shows PZT–PMN films sintered at 800 °C (a) and 1250 °C (b). The micrographs confirm that the extended range of sintering temperatures provides an opportunity for efficient grain size control from less than 1 μm up to 20–30 μm.

The effect of the sintering regime on the room temperature ferroelectric hysteresis of the sintered films indicated that the remanent polarization and coercive field increased with an increase in sintering temperature (Fig. 3). Electrical breakdown (at 50 Hz a.c.) of film samples was observed in the range of 120–170 kV/cm, which is also higher than observed for bulk ceramics of the same type.

Dilatometric data (Fig. 4), obtained from a constant heating rate experiment, suggested that the improved sinterability of the deposited films might be attributed to both a particle size reduction and an increase in available surface energy resulting from the process of jet milling. This conclusion was supported by a comparative study of sintering behaviour for different methods of powder preparation using bulk powder compacts.

As a point of comparison, bulk samples prepared from the powder recycled after the film deposition and sintered at the same conditions displayed lower density and poorer electrical properties than corresponding films.[9]

An examination of the microstructure of the green film indicated that the films comprised particles of less than 0.5 μm, whilst other measurements showed that the powder in the airflow contained a significant proportion of particles larger than 1 μm. This suggests that the

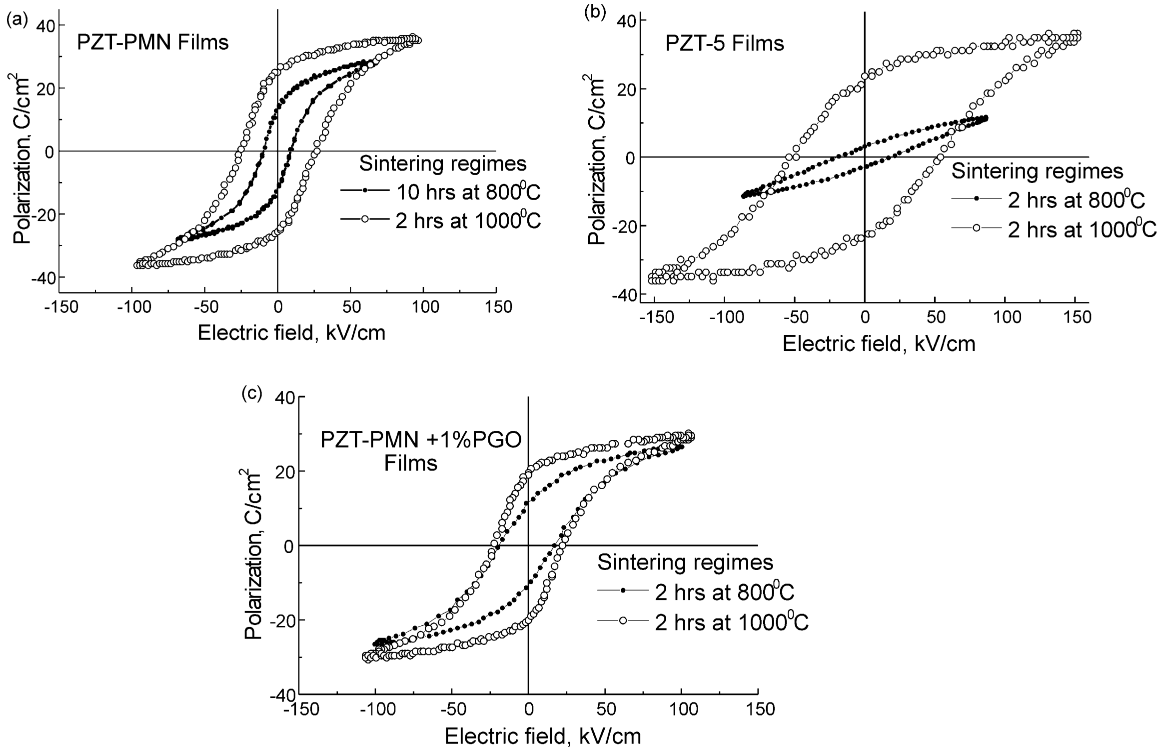

Fig. 3. Ferroelectric hysteresis of PZT–PMN (a), PZT-5 (b), and PZT–PMN + 1%PGO (c) films sintered at various temperatures.

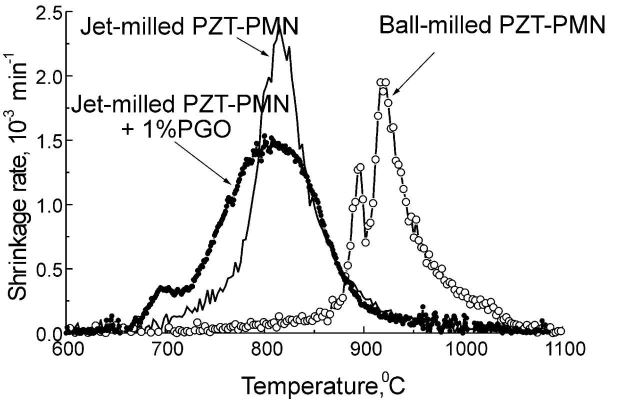

Fig. 4. Dilatometry data for jet-milled and ball-milled PZT–PMN powder compacts using a constant heating rate of 1.0 °C/min.

deposition process involves particle selection by size. It is believed that particle breakage in the jet mill exposes clean surfaces thus increasing the bonding potential of the particles. A film is built-up by directing the air-particle flow at an angle α ($0<\alpha<90$) to the substrate (Fig. 5).

Normal components of the particles' velocities V_n are responsible for particles bonding to the substrate. Tangential velocity components V_t perform a scouring function—removing outsize and poorly accommodated particles from the substrate. A proper balance can be achieved by adjustment of the flow velocity V and deposition angle α, which enables dense selective packing of submicron powder particles to be achieved.

Consistent with the very high green density of the films, the process makes it possible to deposit very dense oxide piezoelectric films which display an audible acoustic response, and translucent layers of up to 20–30 µm of PZT and $BaTiO_3$-based compositions.

Although deposition from a multiphase air-particle flow (e.g. a mixture of different oxides) can be subject to segregation of the components, homogeneous multiphase powder deposition was demonstrated using selected mixtures. Examples include a single-phase perovskite PZT–PMN composition with lead germanate, and a ZnO-based varistor composition containing six different oxides. Thick films prepared from PZT–PMN powder containing 1% of lead germanate as a sintering aid were sinterable at 750 °C. The films displayed electrical properties close to the properties of bulk samples prepared from the same powder. ZnO-based varistor films were deposited using a ball-milled mixture of six oxides.[10] An energy dispersive X-ray analysis of as-deposited and sintered films in the scanning electron microscope showed no significant changes in the concentrations of the oxides across the thickness of the films. The absence of segregation can be attributed to the similar densities and adhesion capabilities of the oxides. Varistors prepared from the deposited film had higher breakdown field than equivalent bulk varistors prepared from the powder recycled after deposition. This observation is consistent with a fine grain microstructure, and may be regarded as further proof of selective packing.

4. Conclusions

Airflow deposition provides a method for achieving the following:

- High-density oxide films with excellent green strength.
- Lower sintering temperatures.
- Lower shrinkage (no binders or other organics are required).
- Submicron-grain sizes and highly uniform microstructures.
- Improved mechanical properties.
- Relatively high deposition rates (~1 µm/min).
- Applicability to multilayer and functionally-graded structures.

The underlying reasons for these improvements relate to particle size selection and selective particle packing intrinsic to this process.

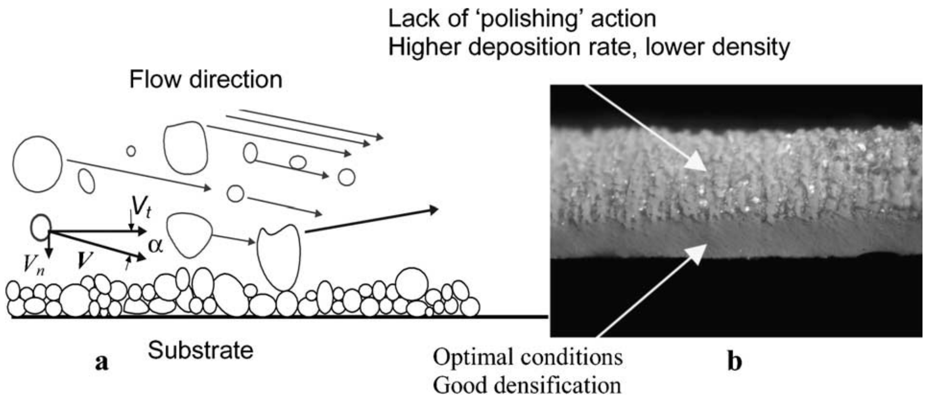

Fig. 5. Film deposition mechanism (a); a fracture of a green $BaTiO_3$–$CaTiO_3$ film (b).

Acknowledgements

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