



Pyroelectric Properties of PZT/PMNZTU Composite Thick Films

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Abstract. Lead zirconate titanate/uranium doped lead magnesium niobate—lead zirconate titanate (PZT/PMNZTU) composite thick films have been fabricated on silicon substrates at 710°C using a composite sol gel technique. A slurry, made up of PMNZTU powder and PZT sol, was spun onto a silicon substrate and fired to yield a porous skeletal ceramic structure. Subsequent sol infiltration and pyrolysis was used to modify the density of the films prior to final sintering at 710°C.

Pyroelectric and dielectric properties have been measured as a function of sol infiltration. The pyroelectric coefficients ($p_{\max} = 2.41 \times 10^{-4} \text{ Cm}^{-2} \text{ K}^{-1}$) of the composite thick films were found to be comparable to the tape cast and monolithic ceramics of similar composition (2.8 and $3.0 \times 10^{-4} \text{ Cm}^{-2} \text{ K}^{-1}$ respectively).

Maximum figures of merit ($F_V = 2.23 \times 10^{-2} \text{ m}^2 \text{ C}^{-1}$, $F_D = 0.89 \times 10^{-5} \text{ Pa}^{-1/2}$), calculated using the electrical properties of the thick films, can be compared with those of screen printed thick films ($F_V = 2.7\text{--}3.9 \times 10^{-2} \text{ m}^2 \text{ C}^{-1}$, $F_D = 0.8\text{--}1.1 \times 10^{-5} \text{ Pa}^{-1/2}$) processed at temperatures of ca 1100°C. The ability to directly integrate thick pyroelectric films onto substrates at temperatures as low as 710°C, while maintaining competitive figures-of-merit is of considerable interest for future device applications.

Keywords: sol gel, composite, thick film, PZT, pyroelectric

1. Introduction

Pyroelectric materials are of considerable interest for applications involving the detection of infra red (IR) radiation with wavelengths in the ranges 3–5 μm and 8–14 μm . IR radiation with wavelengths in these ranges is of interest as it is transmitted through the atmosphere with minimal absorption. Furthermore, the peak in the black body emission spectrum for objects at around 300 K lies in the 8–14 μm wavelength range. Detection of such radiation is therefore of interest for applications such as thermal imaging, intruder detection and fire detection [1].

To provide an indication of the effectiveness of a given material for pyroelectric applications it is useful

to define two figures of merit (FOM) [2].

$$F_V = \frac{p}{c' \varepsilon_o \varepsilon_r} \quad (1)$$

$$F_D = \frac{p}{c' (\varepsilon_o \varepsilon_r \tan \delta)^{1/2}} \quad (2)$$

where ε_o is the permittivity of free space and p , c' , ε_r , and $\tan \delta$ are the pyroelectric coefficient, the specific volume heat capacity, the relative permittivity, and the loss tangent of the materials respectively. These figures of merit describe the likely performances of the pyroelectric devices in terms of the physical properties of the materials. F_V is proportional to the device voltage responsivity and F_D to its specific detectivity (assuming that circuit noise is dominated by AC Johnson noise due to the AC conductance of the element). F_D is the most important FOM for devices operating in voltage mode with a low noise amplifier well matched to the pyroelectric element capacitance.

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The use of polycrystalline ceramic pyroelectric materials for the detection of IR radiation in such applications offers advantages over other systems such as photoconductive and photovoltaic systems [1]. Along with the ability to operate devices without cooling, ceramics are cheap to manufacture in large areas, they are mechanically and chemically more robust, have high Curie temperatures for greater stability, and their properties can be readily modified through doping to tailor them for specific applications.

The sensitivity of IR detection systems can be increased by employing thin sections of ceramic 10–20 μm thick [3]. Such thicknesses represent a compromise between increases sensitivity (thinner films) and higher signal to noise ratio and voltage output (thicker films) [4]. Hence, despite high FOMs exhibited by thin films, the advantages of better signal to noise ratios and higher voltage output mean that thick films are of significant interest for pyroelectric applications.

It is time consuming and expensive to machine monolithic ceramic components to such dimensions and the associated material wastage would be large. To produce films of such thicknesses, screen printing techniques have been used to deposit PZTZN [3] and PLZT [5, 6] materials onto refractory substrates. Following firing at 1100°C, these films exhibited room temperature pyroelectric coefficients in the range 1.2–1.5 $\times 10^{-4} \text{ Cm}^{-2} \text{ K}^{-1}$. These screen printed films exhibited typical figures of merit of $F_V = 2.7\text{--}3.9 \times 10^{-2} \text{ m}^2 \text{ C}^{-1}$, and $F_D = 0.8\text{--}1.1 \times 10^{-5} \text{ Pa}^{-1/2}$. The properties of these screen printed films were reported to be lower than those of bulk ceramics of comparable composition. This was attributed to effects associated with the clamping of the substrate, diffusion of impurities into the films and loss of lead at the high sintering temperatures. However, it was felt that the use of screen printed films was still of value as the increase in sensitivity compensated for the reduction in pyroelectric response [3].

Recently a solid solution of lead zirconate titanate and lead magnesium niobate (PMNZT), doped with manganese [7], chromium [8], antimony [8], or uranium [9], has been proposed as an attractive material for applications involving detection of IR radiation due to the high pyroelectric coefficient. Values of room temperature pyroelectric coefficients (p), F_V and F_D are given in Table 1.

Tape cast uranium doped PMNZT materials [10] have been shown to exhibit a room tempera-

Table 1. Reported pyroelectric properties of doped PMNZT monolithic ceramics.

	p ($\times 10^{-4}$ $\text{Cm}^{-2} \text{ K}^{-1}$)	F_V ($\times 10^{-2} \text{ m}^2 \text{ C}^{-1}$)	F_D ($\times 10^{-5} \text{ Pa}^{-1/2}$)
Mn doped	3.5	7.1	3.6
Cr doped	2.5	4.5	1.5
Sb doped	2.5	3.2	1.1
Ur doped	3.0	6.6	4.7

ture pyroelectric coefficient of approximately $2.8 \times 10^{-4} \text{ Cm}^{-2} \text{ K}^{-1}$ ($F_V = 5.2 \times 10^{-2} \text{ m}^2 \text{ C}^{-1}$, $F_D = 3.1 \times 10^{-5} \text{ Pa}^{-1/2}$) which compares favourably with that observed in monolithic ceramic components. It should be noted, however, that the tape cast material was not bonded to a rigid substrate and therefore would not be expected to exhibit the deleterious effects of substrate clamping. These PMNZT based materials were all processed at an upper temperature of between 1200 and 1300°C. The use of such high processing temperatures for the production of films 10–20 μm thick is not practical due to the loss of lead at elevated temperatures [3] and the damage to the underlying (required) support material [11]. When processing monolithic ceramic components at elevated temperatures lead loss is less of an issue as the ratio of surface (low lead levels) material to core material (optimum lead levels) is very small. However, as the thickness of the components is reduced this ratio becomes significant, to the point where a reduction in the properties of the surface layers will have a significant effect on the overall properties of the system. Such degradation of the surface layers may still occur even if lead rich atmospheres are used. To overcome this problem of lead deficiency, PMNZT type films were fabricated using a low temperature composite sol gel technique [12]. A ceramic producing sol and a ceramic powder are mixed together to produce a slurry which is then spun onto a substrate. Subsequent firing at much reduced temperatures (550–800°C) converts the sol to an oxide ceramic to form a thick film. Intermediate sol infiltration and pyrolysis can be used to vary the density of the films. To demonstrate the use of the composite sol gel technique for producing thick pyroelectric films it was decided to utilise a simplified sol composition ($\text{Pb}_{1.05}(\text{Zr}_{0.825}\text{Ti}_{0.175})\text{O}_3$) due to the difficulties associated with obtaining a perovskite PMNZTU material using the sol gel process. The composition of the PMNZTU powder was maintained at $\text{Pb}_{1.01}(\text{Zr}_{0.825}\text{Ti}_{0.175})_{0.9687}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.025}\text{U}_{0.0063}\text{O}_3$.

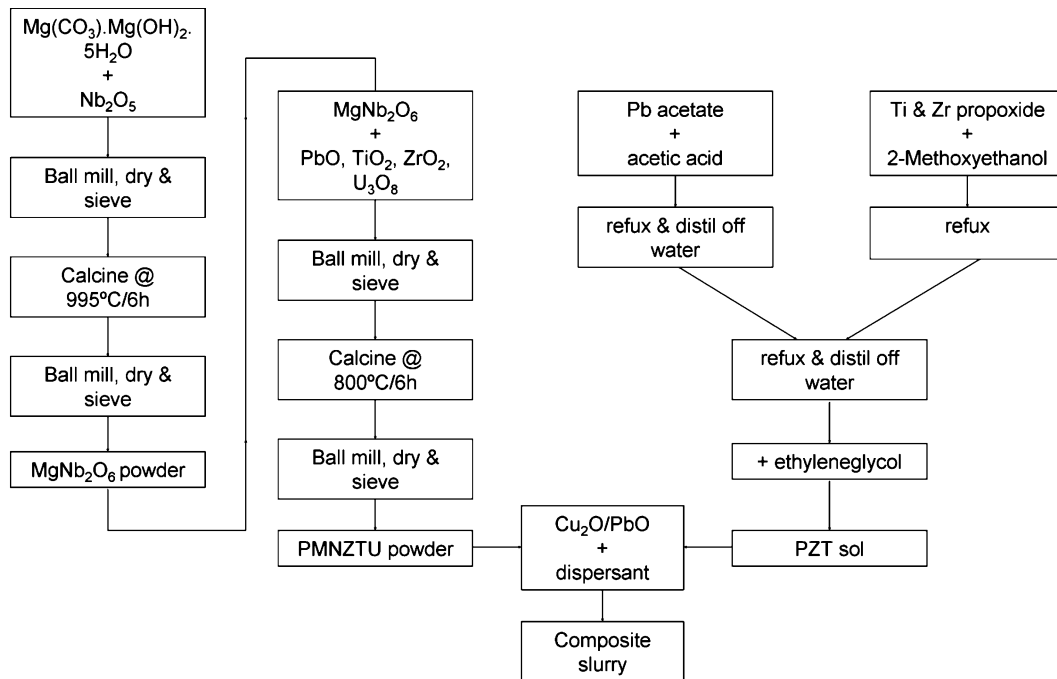


Fig. 1. Schematic of the PMNZTU mixed oxide and PZT sol gel processing routes.

2. Experimental

The PZT producing sol was produced using lead acetate trihydrate (Fisher), zirconium iso-propoxide (Aldridge) and titanium n-propoxide (Aldridge) as starting reagents. The PMNZTU powder was produced using a mixed oxide route. Figure 1 shows a schematic of the sol gel and PMNZTU powder preparation route.

The composite slurry was composed of 30 ml of sol, 45 g PMNZTU powder, 0.9 g dispersant (KR55, Kenrich Petrochemicals) and 2.24 g of $\text{Cu}_2\text{O}/\text{PbO}$ sintering aid [12]. The slurry was ball milled in a N_2 atmosphere (to prevent hydrolysis of the sol) for 24 hours prior to use to ensure a homogenous mixing.

Prior to the deposition of the ceramic film, a ZrO_2 diffusion barrier (to prevent the diffusion of lead into the underlying substrate) and back electrode were first deposited onto the silicon substrate. The diffusion barrier was deposited by spinning a solution of zirconium iso-propoxide in ethanol onto the silicon wafer. The solution was dried and pyrolysed at 450°C . In total 3 layers were deposited prior to crystallising the film at 700°C . Following the deposition of the 40 nm ZrO_2 layer, 8 nm of titanium and 200 nm platinum were deposited using RF and DC magnetron sputtering.

The ceramic films were deposited by coating the wafer with the composite slurry and spinning the wafer at 2000 rpm for 30 seconds. The slurry was then dried at 200°C and pyrolysed at 450°C . The resultant porous structure was infiltrated with pure sol, dried and pyrolysed. This sol infiltration/pyrolysis was conducted 1, 2, or 4 times. Once the required number of sol infiltration/pyrolysis stages had been completed further composite layers were then deposited (each infiltrated and pyrolysed the appropriate number of times). 4 composite layers were deposited to achieve a final film thickness of approximately $10\ \mu\text{m}$. The films were then subjected to a final sintering regime at 710°C in air to develop the perovskite structure and to enhance the density of the film.

To allow the electrical characteristics of the films to be assessed circular Cr/Au top electrodes were deposited by evaporation. The samples were poled at 130°C for 5 minutes using a field of $8\text{V}/\mu\text{m}$. The field was maintained until the sample had cooled to below 100°C . Dielectric properties were measured after poling using a Wayne Kerr precision component analyser (6235B) at 30 Hz (close to the expected frequency of operation) and 1 kHz. The pyroelectric current response for each sample was measured by varying the

temperature of the sample by $\pm 2.5^\circ\text{C}$ about a mean temperature of 25°C . The samples were isolated from surrounding thermal fluctuations by conducting the tests in a vacuum chamber. The resultant pyroelectric currents were measured using a Kiethley 6517 electrometer and used to calculate the pyroelectric coefficient using Eq. (3).

$$I = A p \frac{dT}{dt} \quad (3)$$

Where A is the area of the electrode, dT/dt the rate of change of temperature with respect to time and I the measured pyroelectric current.

3. Results and Discussion

Figure 2 shows the variation in relative permittivity and loss (at 30 Hz) as a function of the number of sol infiltration/pyrolysis stages. The relative permittivity can be seen to decrease slightly as the number of sol infiltrations is increased. With a high number of sol infiltrations (4) the relative permittivity is shown to increase slightly.

The values of relative permittivity observed in the thick films were greater than those observed in the tape cast [10] and monolithic PMNZTU ceramics [9] which were in the range 230–300 depending on the process-

ing temperature. It is unlikely that the increase in relative permittivity would be a result of the sol gel derived PZT phase. Bulk PZT of comparable composition is expected to have a value of relative permittivity of approximately 350 [13] which is comparable to that of the expected value for PMNZTU. Sol gel materials also tend to exhibit lower values of relative permittivity when compared to bulk ceramics. Furthermore, the fact that the relative permittivity decreased slightly with the additional sol infiltrations further indicates that the high relative permittivity is not associated with presence of the sol gel phase. Examination of Fig. 2 shows that the relative permittivity was already enhanced (despite the high level of porosity) prior sol gel infiltration. This indicates that the cause of the high relative permittivity is either due to the PMNZTU power used or the $\text{Cu}_2\text{O}/\text{PbO}$ sintering aid.

The addition of a low dielectric insulating second phase (i.e. the sintering aid) into a dielectric material would be expected to result in a reduction in relative permittivity. However, if a conducting material were to be introduced, then the relative permittivity would increase [14]. Studies on PZT ceramics incorporating conducting silver particles [14] showed that the relative permittivity increased with increasing silver content. At the same time, the dielectric loss was shown to remain approximately constant. The presence of conducting (or semiconducting) phases (as a result of the presence of the sintering aid) could, therefore, account

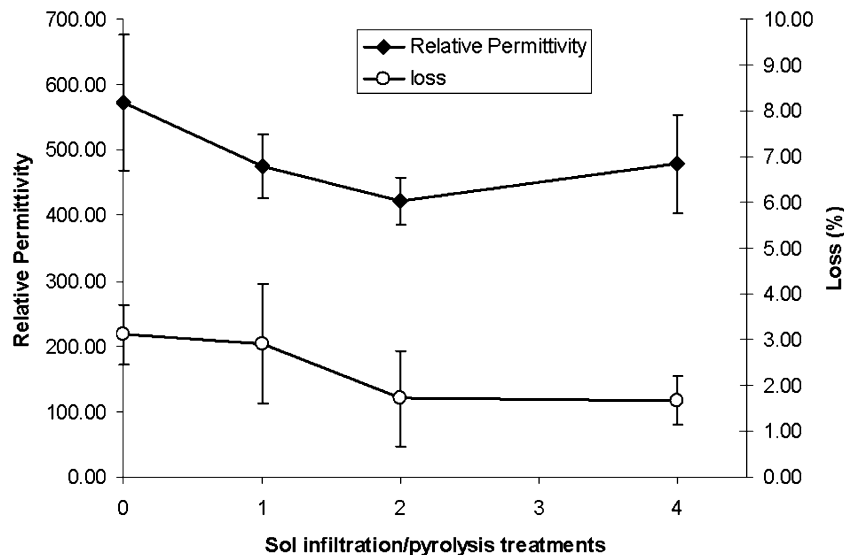


Fig. 2. Variation in value of relative permittivity (at 30 Hz) as a function of the number of sol infiltration/pyrolysis treatments.

for the increased relative permittivity of the system. However, comparison can be made with previous work [12] which showed that the addition of the sintering aid (to a morphotropic phase boundary (MPB) composition PZT) only increased the relative permittivity of the films to 370. This is below that exhibited by the films in this study. Furthermore, it is also below the value quoted for the PZT (1200) used in the previous study. The fact that films made using high (1200) permittivity powder only exhibited a relative permittivity of 370 seems to indicate that it is unlikely that a film made using low (300) permittivity powder would exhibit a relative permittivity in excess of 400. This observation eliminates the postulate that the Cu₂O/PbO sintering aid is responsible for the increase in relative permittivity.

An alternative explanation could be due to the PMNZTU powder itself. It is not possible to determine the dielectric properties of the individual powder particles and the values quoted for bulk ceramics have been obtained from samples sintered at between 1200 and 1300°C. It would be expected that the powder used in this study would have a similar relative permittivity to that of the monolithic and tape cast materials, to which it was identical. If anything, crystallographic grain damage, caused to the PMNZTU grains during manufacture (milling) of the powder, might be expected to decrease the relative permittivity of the powder due to the increased difficulty in domain wall motion. However, the high temperatures of bulk ceramic processing would be expected to lead to a certain degree of atomic homogenisation and compositional change (particularly in the level of lead) that is not present in the powder. Hence, it is quite probable that the state of the PMNZTU powder following processing at 710°C would be significantly different from that of the same powder following processing at between 1200 and 1300°C. Local regions of lead magnesium niobate (PMN) or near-MPB composition PZT could, in theory, lead to significant increases in relative permittivity and/or loss. Increasing levels of sol gel phase may be able to lead to a degree of atomic homogenisation (due to its high reactivity) and could account for the initial decrease in relative permittivity. Such homogenisation could also explain the reduction in dielectric loss observed if high loss phases (such as PMN) were transformed into low loss phases or reduced in volume. The subsequent increase in dielectric constant at high sol infiltration levels is a result of the increased density. This is in agreement with the observation that

Table 2. Pyroelectric coefficients and figures of merit for the PZT/PMNZTU composite thick films.

Infiltrations	p ($\times 10^{-4}$ Cm ⁻² K ⁻¹)	F_V ($\times 10^{-2}$ m ² C ⁻¹)	F_D ($\times 10^{-5}$ Pa ^{-1/2})
0	0.7	0.57	+0.09 -0.08
1	0.8	0.76	+0.09 -0.07
2	2.24	2.39	+0.22 -0.19
4	2.41	2.27	+0.43 -0.31

the loss does not change between 2 and 4 infiltration treatments.

The pyroelectric coefficient of the composite sol gel films can be seen to increase as the level of sol infiltration/pyrolysis increases (Table 2). The maximum pyroelectric coefficients observed are comparable with those observed in the bulk and tape cast materials. The increase in pyroelectric coefficient is thought to be due to the increase in the amount of active material present following the infiltration of the structure.

The figures of merit (F_V and F_D) for each of the films are given in Table 2. They are lower than those for the tape cast and monolithic PMNZTU ceramics due to the higher values of relative permittivity and loss. However, they are comparable to the values previously reported for thick films. It should be noted that in calculating the FOMs the specific volume heat capacity of the films was assumed to be comparable to that of the monolithic material (i.e. 2.5×10^6 Jm⁻³ K⁻¹). Due to the porous nature of the films this value could be expected to be lower in the thick films, which would result in an increase in the FOMs.

Both relative permittivity and loss were shown to decrease with increasing frequency ($\epsilon \sim 470@30$ Hz; $460@1$ kHz; loss $\sim 1.5%@30$ Hz; $0.8%@1$ kHz). Figure 3 shows the resultant variation in the F_V and F_D FOM as a function of frequency for a film with 4 infiltration treatments. Slight increases in FOM could, therefore, be obtained by increasing the operating frequency of such devices.

Further enhancements in the FOMs of these thick films should be possible if the relative permittivity can be reduced. Studies of the dielectric behaviour of other thick films produced in a similar manner have shown that the relative permittivity of the thick films is less than that of the parent powder due to the constraining

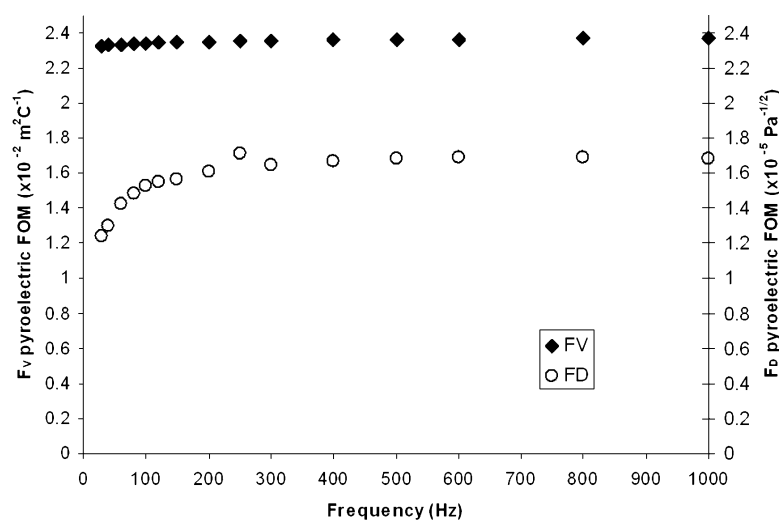


Fig. 3. Variation in FOM (F_V and F_D) as a function of frequency for a composite films with 4 infiltration/pyrolysis treatments.

actions of the rigid substrate [5, 12] indicating improvements in the FOMs should be possible.

4. Conclusions

A series of PZT/PMNZTU composite thick films were fabricated at 710°C using a composite sol gel technique. Pyroelectric coefficients comparable to those of bulk and tape cast components were observed despite the considerable reduction in upper processing temperature. The relative permittivity of the high density composite films was slightly higher than that of the bulk and tape cast materials. It is not clearly understood what caused the increase in relative permittivity. Possible causes of this increase could be attributed to the formation of conductive second phases due to the presence of the sintering aid, or enhancement of the relative permittivity of the PMNZTU powder due to chemical inhomogeneity following low temperature processing. Irrespective of the cause, the higher value of relative permittivity meant that a lower figure of merit was obtained for the composite thick film. Studies to determine the exact cause of the rise in relative permittivity could lead to a significant reduction in its value and hence an increase in the figure of merit of the composite films. Despite the lower FOMs, the increase in sensitivity associated with the use of thick films and the low processing temperatures make this deposition technique an attractive one for manufacturing pyroelectric sensor.

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