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Liquid-phase sintering of PZT ceramics

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Abstract

Lead zirconate titanate (abbreviated as PZT) ceramics are of considerable commercial importance for a host of piezoelectric and pyroelectric applications. Conventionally, many PZT ceramics are sintered at temperatures above 1250°C. Such extreme temperatures are undesirable due to the increased energy consumption, limitation of electrode material and evaporation of volatile components. A liquid-phase sintering aid incorporating Cu_2O and PbO is presented which demonstrates a reduction in the required sintering temperature of these ceramics. This new aid is described with particular reference to a commercial PZT, termed Pz26, used industrially for its optimised piezoelectric properties. Pz26 has a composition near the morphotropic phase boundary and possesses a tetragonal crystalline structure. Typically this material is sintered between 1260 and 1300°C for 1 h to achieve the required densification. With the inclusion of sintering aid, sintered densities comparable to those obtained by conventional sintering are achieved at only 800°C. The optimum weight percentage of sintering aid varies for different ceramic materials, particle sizes, morphology and the desired sintering temperature. However, with standard "mixed-oxide" produced Pz26 powder and with a median particle size in the range 1.6–1.7 μm, a value of 5 wt.% allows sintering at 800°C, according to densification, dielectric and piezoelectric measurements ($\epsilon = 873$, $\tan\delta = 1.13$ %, $k_p = 43.1\%$). When finer grained powder is used ($d_{0.5} = 1.1$ μm), improved properties ($\epsilon = 960$, $\tan\delta = 1.04\%$, $k_p = 51.7\%$) are obtained for an addition of 3 wt.% sintering aid and a sintering temperature of 850°C.

Keywords: PZT; Perovskites; Sintering; Dielectric properties; Cu_2O–PbO

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1. Introduction

High-temperature sintering (> 1200°C) of commercial lead zirconate titanate, ($PbZr_xTi_{1-x}O_3$, PZT) ceramics increases manufacturing costs for many reasons. On large-scale productions, energy consumption can be substantial. Material compatibility with temperatures above 1000°C also demands the utilisation of expensive electrode materials such as platinum, again increasing costs of many multilayer devices. In addition at these elevated temperatures, problems occur in the manufacturing process due to the volatility of PbO. An uncontrolled loss of Pb results in deteriorated or variable electrical properties and is furthermore an environmental concern. All these factors have been common knowledge throughout the respective industry and research institutes for many years and consequently much effort has been focussed on realising different procedures for reducing the required sintering temperature of different materials. The use of liquid-phase sintering aids is just one mechanism used for lowering the sintering temperature.

Liquid-phase sintering is basically the incorporation of additives into a "green" unsintered ceramic to aid densification and thus reduce the required sintering temperature. The theoretical explanation of this process was comprehensively reported over 40 years ago by Kingery,[1] and since this time numerous additives, usually taking the form of metal oxides, have been suggested for different ceramic compositions. Typically a specific weight percentage of additional metal oxides are incorporated into the ferroelectric powder which when pressed makes up the "green" unfired ceramic. The additional oxides mixed together are chosen to have a eutectic significantly below the conventional firing temperature of the respective ceramic. This results in the formation of a liquid phase at an early stage of firing. If successfully maintained, the required density of the original ceramic material may be obtained at tempera-

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tures much lower than that required by conventional solid-state sintering. This acceleration of densification occurs due to a "wetting" action of the powder particles by this liquid phase. Creating curved liquid-meniscus surfaces on the particles, capillary forces act and hence draw the particles together. Simultaneously, the wetting agent acts as a lubricant to allow reorientation of the particles into a more compact, dense structure. Combining these two influencing factors, a good liquid-phase additive can stimulate early densification and hence reduce required sintering temperatures by several hundred degrees. Often a valuable effect can be observed with only a small weight percentage of sintering aid added.

Practical success and application of this technique is limited as the oxide additives will generally form an unwanted second phase in the final sintered ceramic. Subsequently this second phase will reduce the electrical characteristics of the end ceramic device. To obtain an optimised ceramic process, a compromise must, therefore, be found between the accelerated densification and the detrimental effect of this associated impurity. In practice, this results in using lower levels of sintering aid than that required to induce full densification through liquid phase sintering alone. Instead a reduced amount is used and the final sintered product achieves full densification through a combination of both liquid-phase and solid-state sintering. It is also understood that no one liquid-phase aid will be adaptable to all ceramic compositions and furthermore, the effect of the liquid-phase aid will vary substantially with starting material properties, i.e. both particle size and morphology. Efforts for inventing new aids are, therefore, directed to those ceramic materials that are most frequently utilised in electromechanical devices.

PZT is one of the most well known ferroelectric materials in the ceramic industry. Since Jaffe et al. [2] demonstrated the unusually high piezoelectric characteristics of poled PZT ceramics with composition near the morphotropic phase boundary, which separates the rhombohedral and tetragonal phases, these ceramics have been exploited for many electromechanical devices. PZT is already widely used in a number of electronic applications due to their exceptionally high piezoelectric and pyroelectric responses. Combined, PZT devices have a current worldwide market of several billion dollars. The end applications are varied and depend in part on the region of the phase diagram used. For some of the most common commercial devices, including stress sensors,[3] actuators[4] and pyroelectric IR detectors,[5] there is a clear interest in lowering the sintering temperature. It is for this reason that the new liquid-phase sintering aid reported is optimised for PZT and more specifically on a commercial composition with typical *hard* properties near the morphotropic phase boundary (termed Pz26). With conventional ceramic processing the sintering temperature of Pz26 is generally within the range 1250–1300°C.

The ability to lower the sintering temperature of PZT through the addition of numerous metal oxide additives has been reported on several occasions [6–8] with examples referenced utilising additives such as MnO_2, a combination of Li_2CO_3 and Na_2CO_3/Bi_2O_3, and finally a mixture of PbF_2 and NaF respectively. Using these known additives, acceptable sintered densities can be achieved at temperatures just above 900°C. Second phases after sintering are reported, although in some cases the liquid-phase additives are incorporated into the perovskite PZT lattice resulting in a modification of the crystal structure. This again can be an unwanted phenomenon, as electrical properties may be deteriorated.

The novel sintering[9] aid now reported consists of only 2 chemicals — PbO and Cu_2O and typically provides acceptable densification at 800°C, considerably lower than those previously reported. The combination of metal oxides Cu_2O:PbO in a ratio 1:4 gives a eutectic with a melting point of around 680°C, as is depicted in Fig. 1. Such a low melting point creates a working liquid phase at a highly favourable temperature for use as a densification aid. The eutectic is also broad in contrast to many others. In practice this allows slight deviations from the optimum PbO:Cu_2O levels, which one may anticipate on large-scale manufacture to have a much less detrimental effect on the formation of the liquid-phase.

2. Experimental preparation

The effect of this new sintering aid was characterised by sintering Pz26 ceramic pellets at different temperatures. As a preliminary investigation, the density variation

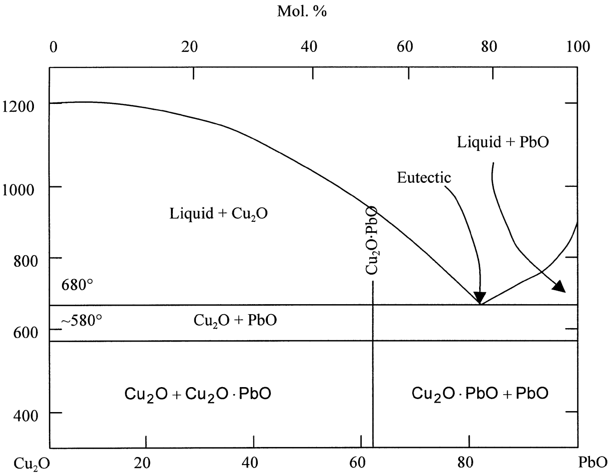

Fig. 1. Solid solution system Cu_2O–PbO.

was monitored by examining linear shrinkage obtained using 0 and 5 wt.% sintering aid within the temperature range 850°–1250°C. In order to prepare pellets containing sintering aid, molar proportions required by the eutectic depicted in the phase diagram in Fig. 1, were weighed such that when added to the Pz26 powder, they comprised of 5 wt.%. All powders were then mixed with acetone and PVA binder in a plastic container. The mixture was then ball milled for 12 h using yttria-stabilised zirconia pellets. After milling, the slurry was decanted and allowed to dry whilst continuously being stirred. After drying was complete the resultant powder was ground using a pestle and mortar and then sieved through a 180 μm sieve. Around 8 g of powder was then pressed (typically 80.6 MPa) to create each pellet. In each case, ceramic pellets were pressed in 3 cm dies. All pellets were then debound to remove organic content and then sintered in an upturned alumina crucible where the lid and edge are lapped such that an approximate sealed container is formed. For all pellets, 3°C/min ramp-up and 2°C/min ramp-down rates were used. For those pellets containing sintering aid, the maximum sintering temperature was held for 45 min, while for those not containing sintering aid the hold time was increased to 3 h. After sintering, a standard micrometer was used to measure the diameter of the sintered pellets giving an indication of the effective densification obtained. The results from this preliminary experiment were highly promising and indicated a need for greater characterisation.

For a more comprehensive study of the sintering aid, ceramic test samples were prepared with 3, 5 and 7 wt.% addition. Further experimentation also included widening the range of sintering temperatures down to 700°C. Finally, to examine the effect of the grain size of the powder, both batches with standard grain size ($d_{0.5} = 1.7$ μm) and more fine-grained batches ($d_{0.5} = 1.1$ μm) were prepared. Ceramic preparation procedures for this more comprehensive study were for the main carried out as described above; however, ball-milling was carried out in water as an alternative to acetone. This change in processing had previously been found to have an insignificant effect on the final ceramic and for bulk production was considered a preferable option.

After ceramic preparation a standard poling procedure was undertaken. Silver electrodes were first screen-printed on each ceramic pellet and then each was immersed in an oil bath at 130°C. A maximum voltage of 2.5 kV/mm was then applied, ramping slowly to this value over a 2-min period. The voltage was then held for a 15-min period before the field was removed.

Dielectric properties were then measured on a standard Hewlett-Packard HP4278A capacitance meter at 1 kHz. Piezoelectric resonance measurements were taken using a Hewlett-Packard HP4194A impedance/gain-phase analyser and d_{33} using a Berlincourt-type instrument.

3. Results and discussion

3.1. Electron microscopy and X-ray diffraction studies

3.1.1. Sintering aid location and PZT crystallinity

After the densification process, liquid-phase sintering aids may either enter the PZT lattice structure or remain at the grain boundaries as a second phase. Each alternative can have a substantial damaging effect on the final electrical and physical properties of the end ceramic. In an attempt to determine the location of the sintering aid after the firing process, several sintered ceramics using this aid were investigated using EDS. Elemental detection of copper was used to locate the aid. Initial attempts at scanning within and between individual grains were found ineffective, as Cu levels are so small. It is worth noting that although 5 wt.% aid is utilised, only 20 mol% of this aid consists of Cu_2O,

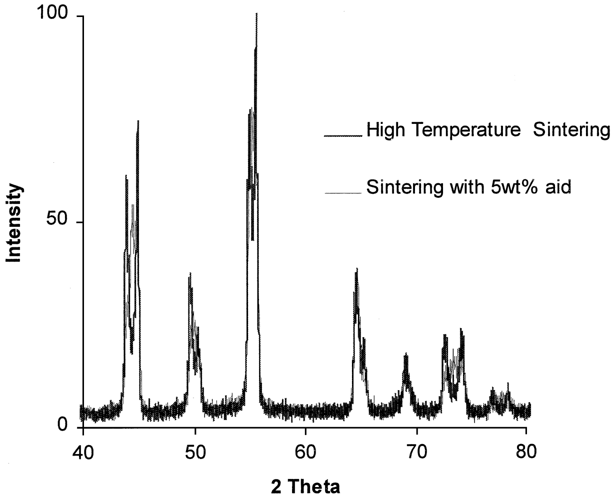

Fig. 2. Showing X-ray diffraction profiles of Pz26 ceramics produced using solid-state and liquid-phase sintering.

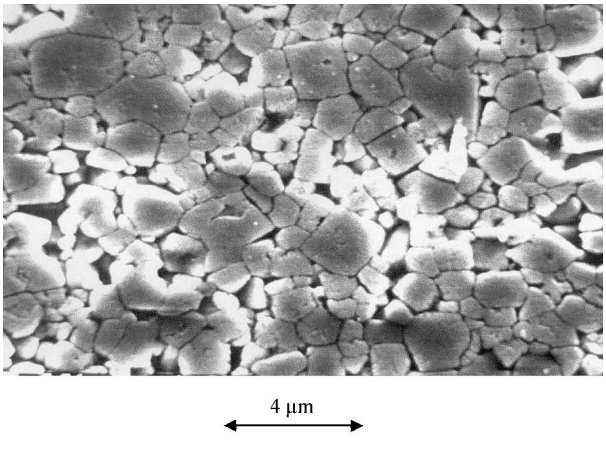

Fig. 3. Depicting Pz26 ceramic microstructure fired at 850°C using 5 wt.% sintering aid.

hence reducing the final Cu content to almost undetectable levels. However, some indication of the positioning could be established by comparing etched and unetched samples over a scan range incorporating both grains and grain boundaries. The etching process was carried out using dilute (10%) HF for 10–20 s. When etched samples are investigated, no trace of Cu can be observed whether a scan is made over one grain or over a large area incorporating several grain boundaries. When an unetched pellet is examined, Cu becomes clearly observable. The process of etching should only remove material from the grain boundaries. This implies that in this case the sintering aid remains at the grain boundaries after firing. Further evidence is apparent from later TEM analysis and will be reported shortly.

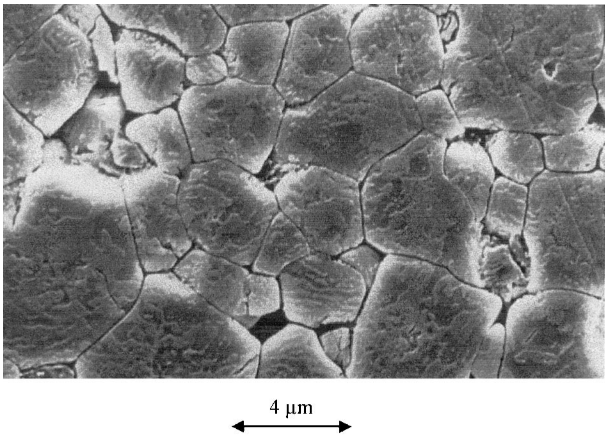

Fig. 4. Depicting Pz26 ceramic microstructure after 1260°C sintering without sintering aid.

This conclusion is supported using X-ray diffraction scans taken on samples prepared with sintering aid at 850°C and without sintering aid at 1260°C. High-resolution XRD profiles were collected on a D5005 Siemens diffractometer using 0.01° step size, 7 s/step over the 2θ range 15–100°. A comparison of the observed profiles is depicted in Fig. 2 over a section of this range. Although peak broadening is observed in the profile associated with the sintering aid, the peak positions that translate into the lattice cell parameters indicate no deviation. This again indicates that the aid is not incorporated into main crystal lattice as only a small penetration of Cu into the lattice would be expected to cause significant modification of the lattice cell parameters.

The greater breadth of individual X-ray peak profiles depicted in the liquid-phase sintering profile is worth considering at this point. It must be remembered that the conventional sintering process enhances the electrical response of the ferroelectric ceramic via promotion of

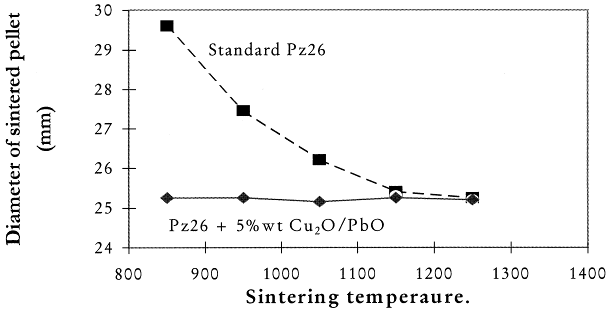

Fig. 5. Depicting relative linear shrinkage during sintering process.

Table 1
Selected properties for Ex26CP with 3, 5 or 7 wt.% sintering aid, as obtained with a median powder grain size of 1.7 µm and five different sintering temperatures: density, relative permittivity, dielectric loss, coupling factors and transverse strain coefficient[a]

Code	$d_{0.5}$ (µm)	T_s (°C)	ρ (g/cm^3)	$\epsilon_{33,r}$	tan δ (%)	k_p (%)	k_t (%)	k_{31} (%)	-d_{31} (pC/N)	-g_{31} (mV·m/N)
Pz26	1.6	1260	7.70	1300	0.30	57.0	47.0	33.0	130	11
3 wt.%	1.7	750	6.25	544	0.72	17.9	27.2	10.7	33.1	6.94
		800	6.90	720	0.76	34.2	41.0	20.1	61.9	9.81
		850	7.54	889	1.05	45.6	43.5	26.8	83.0	10.7
		900	7.70	1010	1.91	46.9	41.8	27.5	91.0	10.3
		950	7.63	1075	0.84	36.7	35.5	21.4	76.7	8.13
5 wt.%	1.7	750	7.34	785	1.35	33.6	36.4	19.6	58.1	8.45
		800	7.65	873	1.13	43.1	42.4	25.2	75.3	9.83
		850	7.73	890	1.66	45.7	42.3	26.8	80.8	10.4
		900	7.66	983	2.09	29.9	37.0	17.5	58.2	6.76
		950	7.58	830	1.91	33.8	37.0	19.9	61.8	8.30
7 wt.%	1.7	700	5.95	465	1.06	14.5	24.9	8.68	34.7	6.81
		750	7.66	823	1.38	32.4	31.3	18.9	54.7	7.58
		800	7.73	868	1.54	40.1	37.7	23.4	69.8	9.06
		850	7.71	760	1.80	35.8	38.6	20.9	59.3	8.90
		900	7.61	814	2.97	29.6	31.7	17.3	52.2	7.31

[a] Catalogue values for standard Pz26 are given for comparison. All properties measured on thin discs (k_{31}, d_{31} and g_{31} calculated from impedance measurements).

the ferroelectric phase and increasing crystallinity. It is an oversimplification to consider sintering as just densification. The high temperatures associated with conventional sintering complete the formation of the PZT phase and increase long-range order of the perovskite structure. With this in mind it must be considered that even if full densification could be achieved at low temperatures and without resulting in an additional inactive second phase, it would still be expected that the final electrical properties of the sintered ceramic would be reduced as the atomic crystal structure would be less developed.

3.1.2. Microstructure

A further discussion point is derived from the fact that the use of the sintering aid will affect the ceramic's electrical response due to its influence on the final grain formation. When densification is obtained predominantly through the liquid-phase rather than solid-state sintering, final grain size and morphology is affected. In order to quantify the significance of this effect, SEM cross sections were examined of Pz26 ceramics fired both with and without the sintering aid.

Comparison of Figs. 3 and 4 emphasises the different sintering processes involved. While "capillary forces"

Table 2
Selected properties for Ex26CP with 3, 5 or 7 wt.% sintering aid, as obtained with a median powder grain size of 1.1 μm and five different sintering temperatures: density, relative permittivity, dielectric loss, coupling factors and transverse strain coefficient[a]

Code	$d_{0.5}$ (μm)	T_s (°C)	ρ (g/cm^3)	$\epsilon_{33,r}$	tanδ (%)	k_p (%)	k_t (%)	k_{31} (%)	-d_{31} (pC/N)	-g_{31} (mV·m/N)
Pz26	1.6	1260	7.70	1300	0.30	57.0	47.0	33.0	130	11
3 wt.%	1.1	750	6.43	575	0.76	19.3	28.8	11.4	34.4	6.82
		800	7.26	784	0.85	33.1	33.2	19.4	57.8	8.41
		850	7.83	960	1.04	51.7	44.1	30.4	94.8	11.3
		900	7.76	1033	1.31	49.2	42.4	28.6	95.6	10.6
		950	7.67	1103	0.90	38.4	37.4	22.4	80.9	8.36
5 wt.%	1.1	750	7.68	864	1.02	40.5	38.4	23.8	70.2	9.27
		800	7.80	912	1.13	46.4	42.4	27.3	81.7	10.2
		850	7.81	924	1.38	48.4	42.3	28.4	87.2	10.8
		900	7.66	896	2.29	37.6	36.6	22.0	69.6	8.86
		950	7.57	959	2.10	33.0	32.4	19.5	65.2	7.76
7 wt.%	1.1	700	6.06	495	1.03	14.5	27.6	8.85	27.0	6.23
		750	7.84	865	1.39	36.3	34.1	21.1	61.4	8.09
		800	7.77	885	1.49	42.0	36.6	24.7	73.2	9.43
		850	7.76	831	1.08	40.3	40.7	23.5	69.2	9.49
		900	7.61	808	3.35	31.9	34.8	18.9	71.5	8.07

[a] Catalogue values for standard Pz26 are given for comparison. All properties measured on thin discs (k_{31}, d_{31} and g_{31} calculated from impedance measurements).

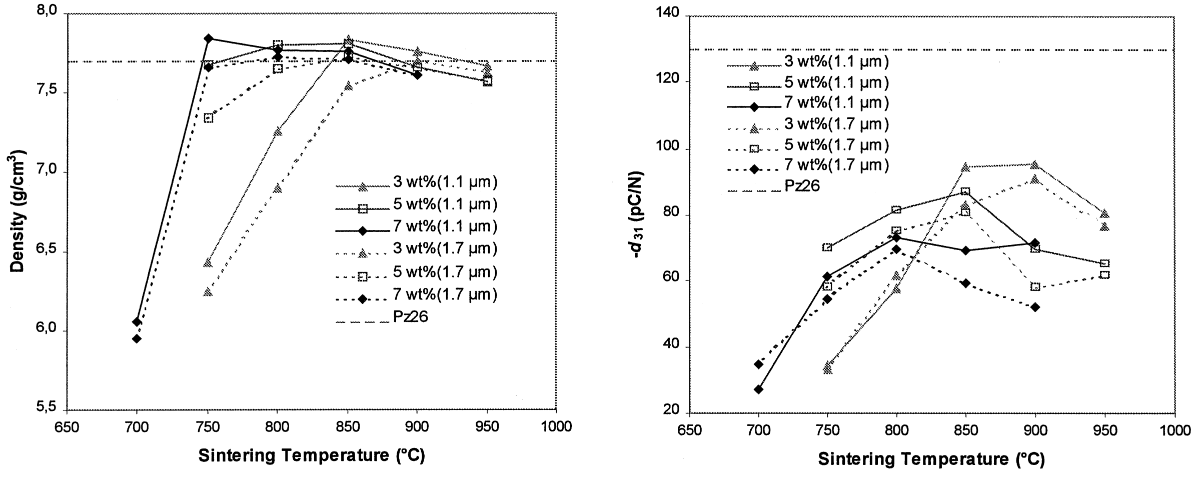

Fig. 6. Density (left) and transverse strain coefficient (right) of modified Pz26 with 3, 5 and 7 wt.% sintering aid as a function of sintering temperature (holding time 2 h). Grain sizes of powders are given in parentheses, and the level of standard Pz26 (sintered at 1260°C) is indicated by a horizontal line. d_{31} Has been calculated from impedance measurements on thin discs.

and "wetting" are dominant in the 850°C ceramic pellet sintered with liquid-phase aid, as the temperature increases solid-state sintering becomes the over-riding process. Physically, this translates into a large difference in the exhibited grain sizes. Many sub-micrometer grains are observed in the ceramic prepared using liquid-phase sintering, Fig. 3, whilst a typical grain size of around 5 μm is observed with a conventionally prepared ceramic using only solid-state sintering, Fig. 4. This variation will no doubt translate into both poling and electrical property differences as grain surface area, domain complexity and potential drop between grains are all significantly altered. It is worth noting that not all property changes associated with the smaller grain size would be for the worse. Although greater losses may be observed, ceramics with a reduced grain size would feasibly be stronger and the resultant ceramic more adaptable to MST devices, e.g. lapping to 15 μm would be more practical when processing a 1 μm, rather than 5 μm grained ceramic.

3.2. Physical and electrical characterisation

The results obtained from the preliminary densification experiment with unmodified Pz26 and 5 wt.% addition are depicted in Fig. 5. The success of this sintering aid in accelerating the densification process is clear from this simple experiment. High density is achieved at temperatures as low as 850°C.

For the more comprehensive study, density and corresponding electrical properties are reported in Table 1 for all samples with standard grain size ($d_{0.5}$ in the range 1.6–1.7 μm), and in Table 2 for ceramics prepared from the fine-grained powder ($d_{0.5} = 1.1$ μm). Although the performance of modified compositions is lower than standard Pz26, electrical properties quite acceptable for many applications are obtained at temperatures below 900°C. One property, the transverse voltage coefficient g_{31}, is actually higher for some modified samples than for Pz26, but this is of course directly related to the reduced permittivity. Generally a positive effect of the reduced grain size is seen, especially for the 3 wt.% samples. The overall best properties at low temperature are obtained for the fine-grained 3 wt.% batch sintered at 850°C. With 5 wt.% the sintering temperature can be lowered to 800°C without a serious loss of performance. The results for the 7 wt.% batches show that although increasing the sintering aid results in further densification, the increase in second phase results in an overall deterioration of electrical response.

These tendencies are seen clearly from Fig. 6, showing the density and the transverse strain coefficient for both grain sizes as a function of sintering temperature. It is apparent that an increased amount of sintering aid results in a decrease in the onset temperature of densification, and a reduced grain size has a similar though less pronounced effect. Although the eutectic in use lies at approximately 680°C, complete densification requires temperatures in the range 750–850°C, depending on the addition. For each composition, the variation in piezoelectric properties as exemplified by d_{31} agrees well with that of the density (at least close to the optimum temperature), and the gradual tendency of deterioration with increased addition is also clear.

4. Conclusions

Low-temperature sintering of Pz26 ceramics has been shown possible using a new liquid-phase sintering aid comprising of Cu_2O and PbO. Both physical and electrical characteristics have been reported which demonstrate high densification at temperatures as low as 800°C. Compared to conventional firing at 1260°C, substantial financial rewards should be achievable with utilisation of this aid. Particular cases of benefit will be observed where the end device requires co-firing with electrodes, as cost-effective metallic materials may be used. From the results presented, optimum properties using low temperatures may be achieved using 3 wt.% at 850°C for 2 h, and almost equally good properties using 5 wt.% at only 800°C for 2 h. Some electrical deterioration is exhibited and it is expected that this be due to three factors:

1. The formation of a second non-piezoelectric phase in the final sintered ceramics.
2. Reduced comparative grain size as liquid-phase sintering replaces solid-state sintering.
3. Reduced crystallinity and hence electric dipole moment of the PZT phase itself.

This final point was demonstrated in the broad peak shapes observed in the X-ray diffraction profiles reported. Reduced crystallinity is not dependent on sintering aid but is an unfortunate consequence of all low-temperature sintering processes. It is, therefore, considered that further improvements of this aid will rely on the first factor, i.e. an improved electrical performance will be achieved by reduction of the second phase whilst still maintaining equivalent densification. It is expected that this may be achieved by optimisation of mixing procedures and hence deployment of sintering aids prior to firing. This optimisation, however, will be specific to the manufacturing process in question.

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