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High dielectric constant ceramics in the $PbSc_{0.5}Ta_{0.5}O_3$–$PbZrO_3$ and $PbSc_{0.5}Ta_{0.5}O_3$–$PbTiO_3$ systems

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The properties of $(1\text{-}x)PbSc_{0.5}Ta_{0.5}O_3$–$(x)PbZrO_3$ ceramics $(0.075 < x < 0.2)$, have been investigated using three different mixed oxide preparation routes. These were (i) a single-stage calcination (at 900 °C) between lead, scandium, tantalum and zirconium oxides, (ii) the reaction between single phase $PbSc_{0.5}Ta_{0.5}O_3$ and $PbZrO_3$ powders (also at 900 °C), and (iii) the formation of zirconium-modified scandium tantalate (via a high-temperature prereaction stage) prior to calcination with lead oxide. It was found that this third preparation route results in transparent, 100% dense, single-phase perovskite ceramics which exhibit particularly sharp first-order ferroelectric to paraelectric phase transitions. Material with a maximum relative permittivity of 36×10^3 at 64 °C, and a dielectric loss of 7.5×10^{-4}, was obtained for an x value of 0.125. Results are compared with those for ceramics in a similar range of compositions in the $(1\text{-}x)$ $PbSc_{0.5}Ta_{0.5}O_3$–$(x)PbTiO_3$ system; these were prepared using only one of the above routes, and involved calcining $PbSc_{0.5}Ta_{0.5}O_3$ with $PbTiO_3$ powder.

1. Introduction

A large number of dielectrics with the general formula $Pb(B_1B_2)O_3$, where B_1 is a low valence cation and B_2 is a high valence cation, have been investigated [1] for their unusual dielectric and pyroelectric properties. In particular, the relaxor material $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) has been studied because of its anomalously large dielectric constant, and ceramics in the $(1\text{-}x)PMN$–$(x)PbTiO_3$ system have been reported [2] to have maximum dielectric constants in excess of 36×10^3 (for $x = 0.3$). Lead scandium tantalate (PST) ceramic has also been shown [3, 4] to be a ferroelectric material with the perovskite $Pb(B_1B_2)O_3$ structure, and having a first-order phase transition at 25–30 °C. The material has a reversible pyroelectric effect under bias, and it has been fully assessed for thermal detector applications [5]. More recently, the properties of a solid solution of $(1\text{-}x)PST$–$(x)PbTiO_3$ have been reported [6, 7]; for an x value of 0.4, the Curie temperature was increased to 182 °C and the maximum dielectric constant was $> 30 \times 10^3$. This paper presents results of a study into the solid solution $(1\text{-}x)PST$–$(x)PbZrO_3$, $(0.075 < x < 0.20)$, and in particular discusses the optimum ceramic processing route for obtaining a dielectric exhibiting a sharp phase transition, a high maximum dielectric constant and a low dielectric loss; the results for lead zirconate (PZ)-modified PST are also compared with our own results for lead titanate (PT)-modified PST.

2. Experimental procedure

2.1. Ceramic preparation

Three processing routes were investigated for the preparation of $(1\text{-}x)PST$–$(x)PZ$ ceramics using metal oxide powder precursors. The starting materials were PbO, Sc_2O_3, Ta_2O_5 and ZrO_2, all with purities greater than 99.9%. The first method (Method A) involved the ball milling and single calcination at 900 °C of the above oxides. This was then followed by hot pressing the powder at 40 MPa and 1200 °C for 6 h. The second method (Method B) involved the initial formation of single-phase $ScTaO_4$ via the high-temperature wolframite prereaction stage [8], and then the separate preparation of PST and PZ powders using standard ball milling and calcination conditions. The PST and PZ powders were milled together and calcined at 900 °C. The powder was hot pressed as above, and the ceramic was annealed at temperatures between 1200 and 1400 °C for 4 h in an alumina crucible. The cooling rate after annealing was $100\,°C\,h^{-1}$. A PZ spacer powder was used in the crucible in order to maintain a partial pressure of PbO. The third method (Method C) involved the prereaction of Sc_2O_3, Ta_2O_5 and ZrO_2 to form a ZrO_2-"modified" $ScTaO_4$ phase. This was then calcined with PbO at 900 °C and hot pressed at temperatures between 1100 and 1200 °C. Ceramics prepared via this route were left unannealed. PST/PT ceramics were prepared using Method B only, with the exception that TiO_2 was used in place of ZrO_2.

PST–PZ and PST–PT powders prepared from all the above routes contained an initial 5 wt % excess PbO in order to compensate for the loss of this phase during the hot-pressing and annealing stages.

2.2. Characterization

Dielectric measurements were made on wafers or blocks using an indium gallium electrode paste and a Wayne Kerr B6425 automatic bridge operating at 400, 1500 and 20 kHz. The recording of data over the temperature range 0–120 °C, was achieved using a computer with IEEE interface to the bridge, and also to a voltmeter with microvolt resolution (for accurate temperature measurements). Phase analysis was achieved using an automated Philips PW 1820 diffractometer system using CuK_α radiation, and grain size was determined from scanning electron micrographs of fractured ceramic surfaces. Optical transmission measurements were made using a Perkin–Elmer 1600 series spectrophotometer.

3. Results and discussion

3.1. (1-x)PST–(x)PZ compositions

3.1.1. Samples prepared via Method A

The X-ray data for the ceramic produced via Method A (Sample AL131) indicated about 20 wt % of the undesirable pyrochlore phase together with 80 wt % of the perovskite phase. The diffraction lines corresponding to ordering were weak and almost below the limits of detection (1–2 wt %). Fig. 1 shows the dielectric response of this material; the phase transition is seen to be very diffuse with a maximum dielectric constant, (ε_r), of below 9000 occurring at about 70 °C. This poor value was attributed to the relatively large concentration of the low permittivity pyrochlore phase. It was found that subsequent annealing of this sample at 1300 and 1400 °C resulted in only a minor reduction in the percentage of pyrochlore phase being present, and the dielectric properties remained virtually unchanged.

3.1.2. Samples prepared via Method B

Hot-pressed ceramics (for $0.075 < x < 0.2$) prepared using Method B, exhibited two peaks in dielectric constant and loss (D) over the temperature range 0–120 °C. For all samples, the lower transition temperature, T_1, occurred at approximately 35 °C, whereas the higher transition temperature, T_h, was dependent on the ratio of PZ to PST. It was also found that the relative heights of the two peaks were dependent on the PST–PZ ratio; this can be observed by comparing the dielectric data given in Figs 2 and 3, for $x = 0.075$ and $x = 0.125$. Table I gives details of the properties for all the compositions prepared using this route.

After annealing at 1400 °C, the above ceramics were found to have single, sharper peaks in dielectric constant and loss, and the T_h value was reduced. This can be seen by comparing Fig. 4 with Fig. 3, and from the results given in Table II.

X-ray diffraction patterns for the calcined powder, hot-pressed ceramic and annealed ceramic ($x = 0.125$), can be compared with undoped PST ceramic (prepared using Method C, $x = 0$) in Fig. 5a. Similar X-ray data, to those shown in Fig. 5, were obtained from powders and ceramics with the other compositions given in Table II. Whereas at least two distinct phases are observed from the PST–PZ powder and the hot-pressed ceramic (Fig. 5b and c, respectively), the annealed ceramic (Fig. 5d) has a

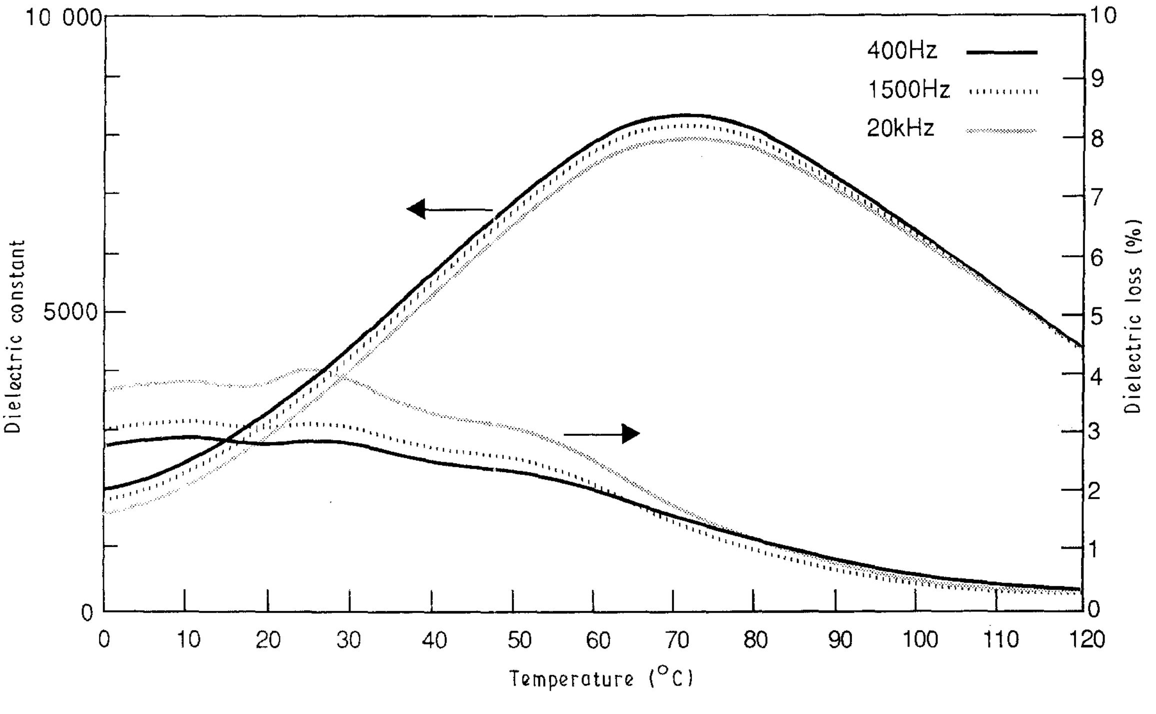

Figure 1 Dielectric properties of 0.875PST–0.125PZ (Sample AL131) prepared using Method A.

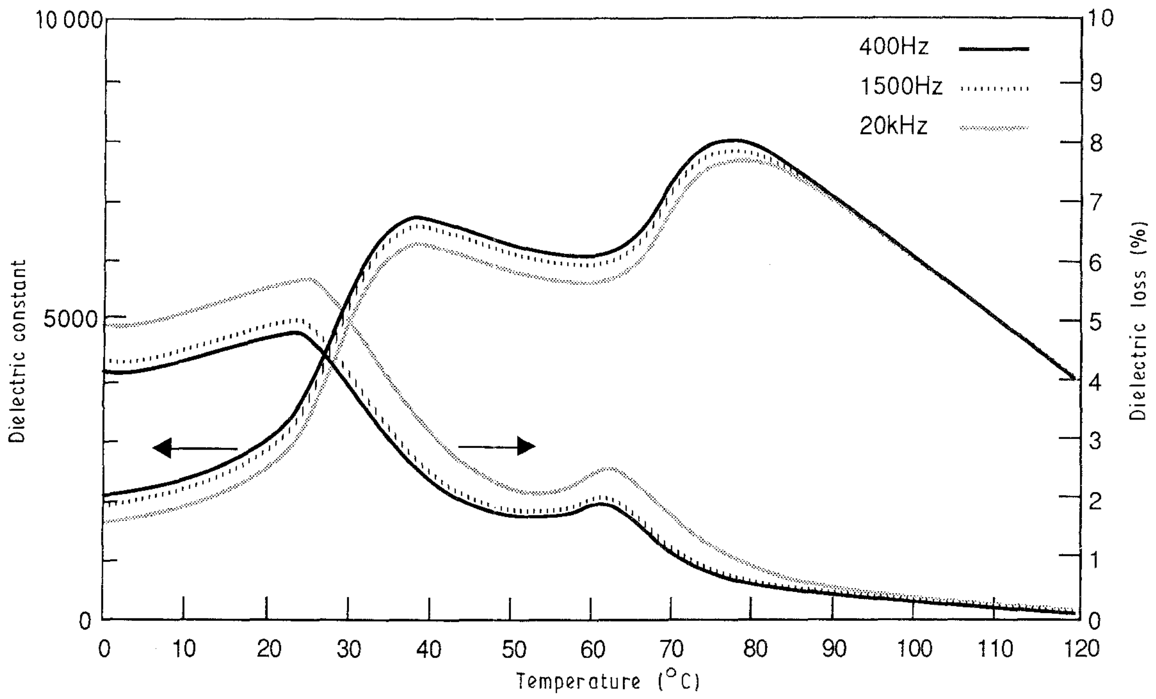

Figure 2 Dielectric properties of 0.925PST–0.075PZ (Sample AL124) prepared using Method B (no anneal).

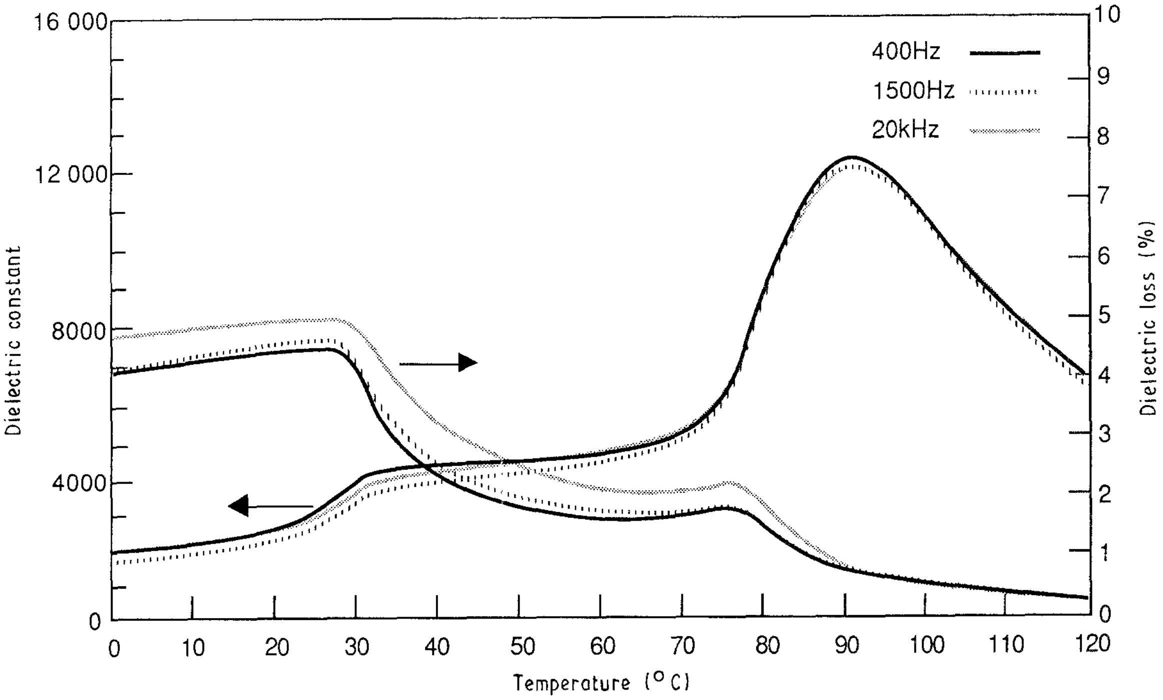

Figure 3 Dielectric properties of 0.875PST–0.125PZ (Sample AL125) prepared using Method B (no anneal).

single-phase perovskite crystal structure. It is interesting to note that the only samples prepared via Method B which did not exhibit strong second-order diffraction lines, were the ceramics annealed at 1300–1400 °C. These results, together with the dielectric data, therefore indicate that the calcination of PST + PZ at 900 °C, does not form a complete PST–PZ solid solution. Likewise, a mixture of the two phases still exists after hot-pressing. It is only after high-temperature annealing that the single-phase (1-x)PST–(x)PZ solid solution is formed.

Grain-size measurements of the above ceramics showed that the hot-pressed samples had a fine grain size of 1–2 μm, whereas the annealed materials had average grain sizes of 10–20 μm. However, it was not clear from these results whether a coarse grain structure was necessary in order to produce the sharp peak and high dielectric constant as seen in Fig. 4. A number of samples (with $x = 0.125$) were therefore hot-pressed at 1200 °C and annealed at various temperatures between 1200 and 1400 °C. The dielectric and microstructural properties of these samples are given in Table III.

It can be seen from Table III, that for PST–PZ ceramics processed using Method B, the maximum dielectric constant at T_h is strongly dependent on

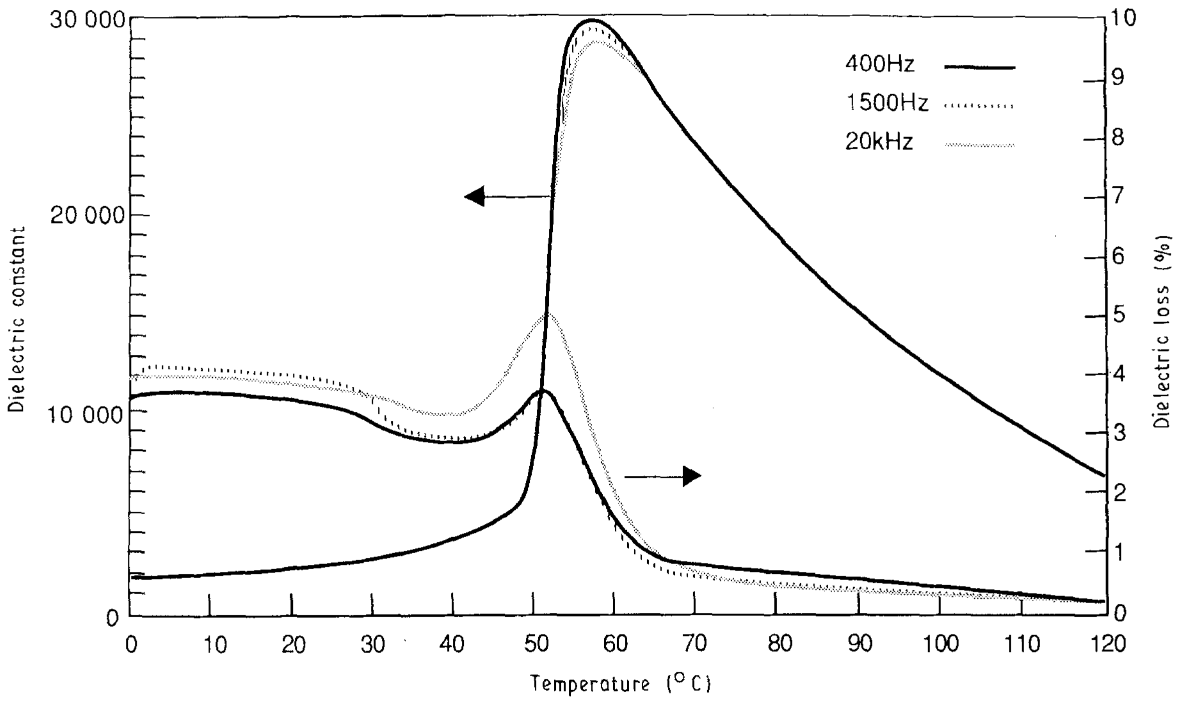

Figure 4 Dielectric properties of 0.875PST–0.125PZ (Sample AL125) after annealing at 1400 °C.

TABLE I Properties of PST–PZ ceramics after hot pressing, prepared using Method B

x	Sample	T_h (°C)	ε_r(at T_h) (1500 Hz)	D(at 120 °C) (1500 Hz)	Density (g cm^{-3})
0.075	AL124	74	8000	0.00085	8.944
0.100	AL118	78	10200	0.00150	8.926
0.125	AL125	82	14200	0.00090	8.842
0.150	AL132	88	13000	0.00220	8.847
0.200	AL133	98	16000	0.00375	8.815

TABLE II Properties of PST–PZ ceramics after annealing at 1400 °C, prepared using Method B

x	Sample	T_h (°C)	ε_r (at T_h) (1500 Hz)	D (at 120 °C) (1500 Hz)	Density (g cm^{-3})
0.075	AL124	48	26400	0.00030	8.939
0.100	AL118	58	24200	0.00410	8.794
0.125	AL125	60	30000	0.00080	8.887
0.150	AL132	68	25000	0.00240	8.847
0.200	AL133	87	26000	0.00310	8.803

TABLE III Properties of PST–PZ samples (for $x = 0.125$) annealed at different temperatures

Annealing temperature (°C)	T_h (°C)	ε_r(at T_h) (1500 Hz)	Grain size
Unannealed	82	12000	Mostly fine grain (1–2 μm). A small percentage of grains 2–8 μm
1200	83	14000	A mixture of fine grains (1–2 μm) and larger grains (2–8 μm)
1250	82	15000	A small percentage of fine grains, but most grains in the range 2–10 μm
1300	78	17000	Most grains > 12 μm
1350	69	24500	Moderately uniform grain size of 15–20 μm. Few grains 1–2 μm
1400	60	30000	Uniform grain size of 15–20 μm. Very few grains 1–2 μm

annealing temperature, and this suggests that grain size plays an important role in determining the dielectric properties. It was also found that there was a gradual change in the phase transition at T_l (the transition became less prominent), and the sharpness of the dielectric peak at T_h increased with an increase in annealing temperature, from that shown in Fig. 3, to that given in Fig. 4. Fig. 6 shows a scanning electron micrograph of AL125 after annealing at 1400 °C. Despite the relatively uniform grain size, porosity within grains is clearly visible. This suggests that during annealing, the rate of grain-boundary migration is greater than that of the pores; hence, pores are left trapped inside, or on the surface of grains.

3.1.3. Samples prepared via Method C

Fig. 7 shows the dielectric properties for PST–PZ ceramic, for $x = 0.125$, after hot pressing at 1200 °C. It is noticeable from this data that a very high dielectric constant and sharp dielectric peak have been obtained without high-temperature annealing. Fig. 8 shows the coarse-grain microstructure for this material, and it can be seen that there is an absence of porosity within

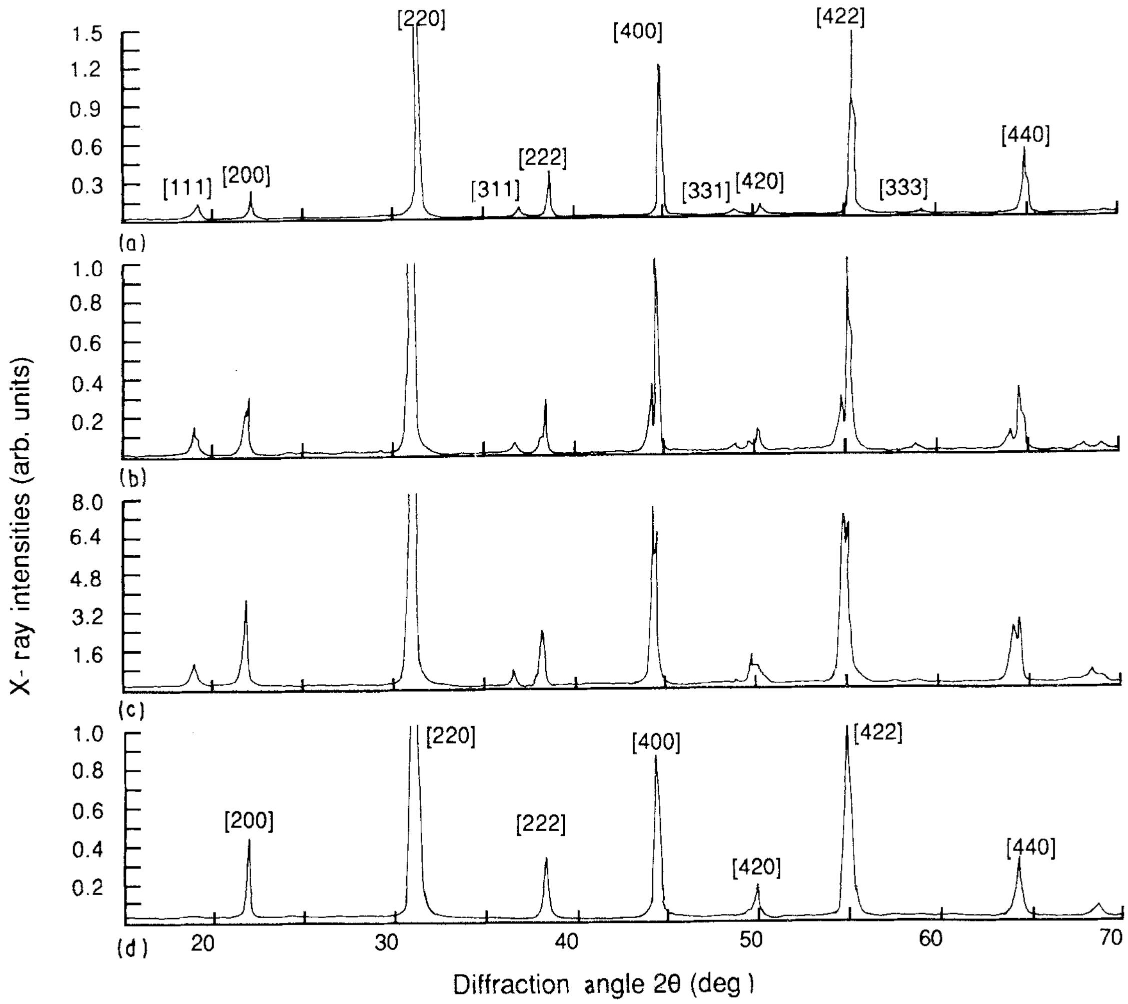

Figure 5 X-ray diffraction patterns for (1-x)PST–x(PZ) : (a) $x = 0$, hot-pressed ceramic, (b) $x = 0.125$, calcined powder, (c) $x = 0.125$, hot-pressed ceramic, (d) $x = 0.125$, ceramic annealed at 1400 °C.

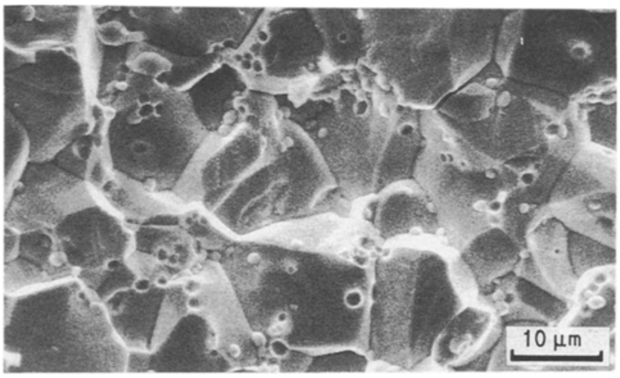

Figure 6 Microstructure of Sample AL125 after annealing at 1400 °C.

individual grains. X-ray data from the calcined powder and the ceramic showed that there was little or no ordering in the lattice. Because these results indicated that a solid solution had probably been formed during the calcination stage at 900 °C, this material was also hot pressed at 1100 and 1150°C. The results are summarized in Table IV. A number of interesting correlations can be seen; firstly, unlike the samples produced via Method B, samples with a fine grain size exhibit very high permittivities. Secondly, the phase transition temperature, T_h, decreases with increasing hot-pressing temperature. Also, it is interesting to note that the density values are all approximately 100% of the single-crystal value calculated from X-ray data (8.900 g cm^{-3}); this would explain the transparency that these samples exhibit over the visible spectrum, and out to a wavelength of almost 6 μm (1670 cm^{-1}). The transmission characteristics for sample AL 135 (0.7 mm thick and measured without anti-reflection coatings) are shown in Fig. 9.

3.2. (1-x)PST–(x)PT compositions

Tables V and VI give summaries of properties for hot-pressed and annealed ceramics, respectively, in the (1-x)PST–(x)PT system. Fig. 10 shows the dielectric constant and loss for hot-pressed 0.9PST–0.1PT and Fig. 11 gives these parameters for this sample after annealing at 1400 °C. Clearly it can be seen that there are a number of properties exhibited by ceramics in this system which are similar to those for PST–PZ prepared via Method B. These include (i) a substantial change in the dielectric properties of the annealed materials compared with those for the hot-pressed samples (indicating the presence of two phases prior to annealing), (ii) an increase in T_h with increase in the x value, (iii) a large decrease in T_h (for a given x value)

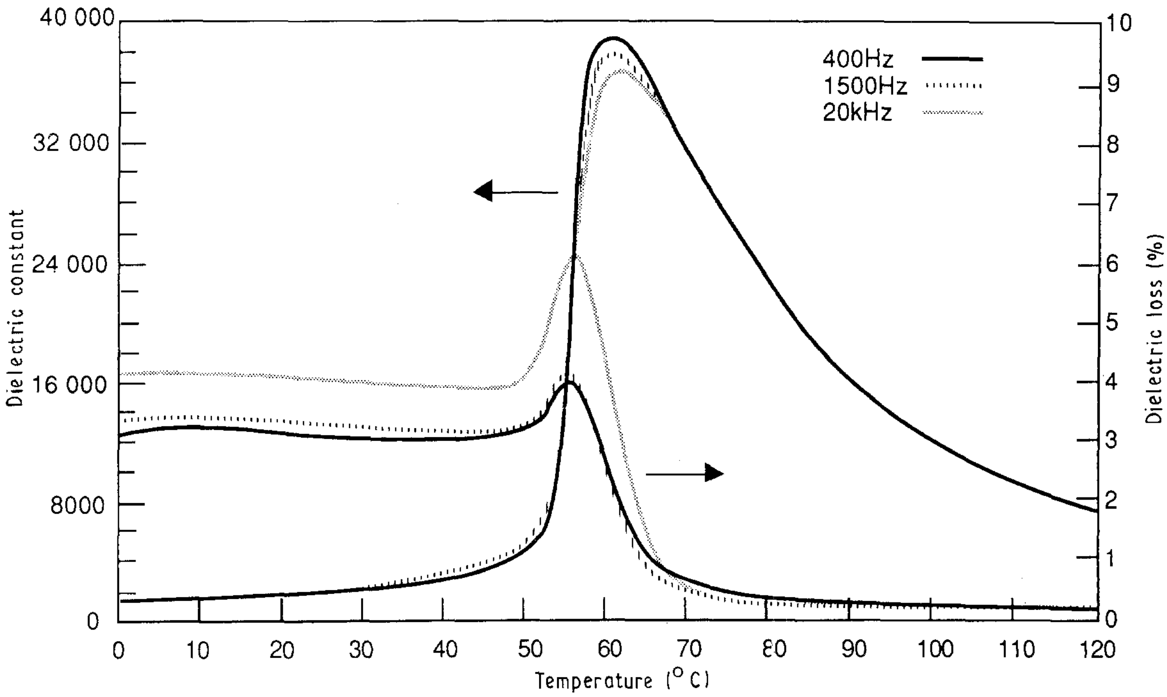

Figure 7 Dielectric properties of 0.875PST–0.125PZ (Sample AL135) prepared via Method C (no anneal).

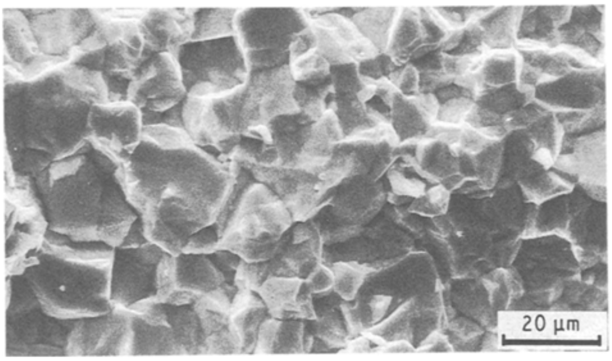

Figure 8 Microstructure of Sample AL135 after hot pressing at 1200 °C.

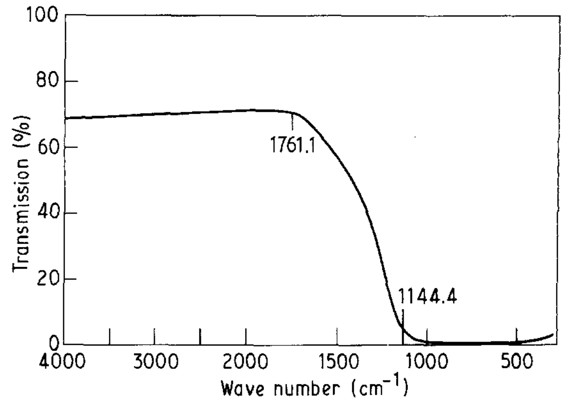

Figure 9 Transmission characteristics of Sample AL135 hot pressed at 1200 °C.

TABLE IV Properties of PST–PZ ceramics (for $x = 0.125$) prepared via Method C

Hot-pressing temperature (°C)	Sample	T_h (°C)	ε_r (at T_h) (1500 Hz)	D (at 120 °C) (1500 Hz)	Density (g cm^{-3})	Average grain size (µm)
1200	AL135	64	36000	0.00075	8.891	15
1150	AL143	70	27500	0.000 85	8.898	4
1100	AL145	75	24000	0.001 00	8.901	2

TABLE V Properties of (1-x)PST–(x)PT ceramics after hot pressing at 1200 °C

x	Sample	T_h	ε_r (at T_h) (1500 Hz)	D (at 120 °C) (1500 Hz)	Density (g cm^{-3})
0.050	MB363	76	9200	0.002 80	9.012
0.0625	AL114	86	9100	0.006 75	8.997
0.0875	AL113	90	8500	0.008 55	8.963
0.100	AL103	94	9500	0.009 85	8.944
0.125	AL115	109	8300	0.007 20	8.920

after annealing at 1400 °C, and (iv) a decrease in density after annealing.

The dielectric constants given in Table VI broadly agree with those given by Giniewicz *et al.* [6], who calcined PbO and TiO_2 with $ScTaO_4$ powder pre-reacted using the wolframite method. However, the T_h values measured here are significantly higher than those previously reported (e.g. for $x = 0.10$, $T_h = 30$ °C [6]). This difference is thought to be due to the high sintering temperatures (1560 °C) used in this

TABLE VI Properties of (1-x)PST-(x)PT ceramics after annealing at 1400 °C

x	Sample	T_h (°C)	ε_r (at T_h) (1500 Hz)	D (at 120 °C) (1500 Hz)	Density (g cm^{-3})
0.05	MB363	49	12000	0.00215	8.880
0.0625	AL114	57	12000	0.00215	8.875
0.0875	AL113	66	16900	0.00230	8.877
0.10	AL103	67	23400	0.00150	8.767
0.125	AL115	77	15300	0.00405	8.810

earlier work, and which were probably required due to the absence of a hot-pressing stage.

4. Conclusions

From the above results, it can be seen that the PST–PZ composition which exhibits the highest dielectric constant has an x value of 0.125. The optimum preparation route for this composition was found to be Method C; this gave hot-pressed material with a

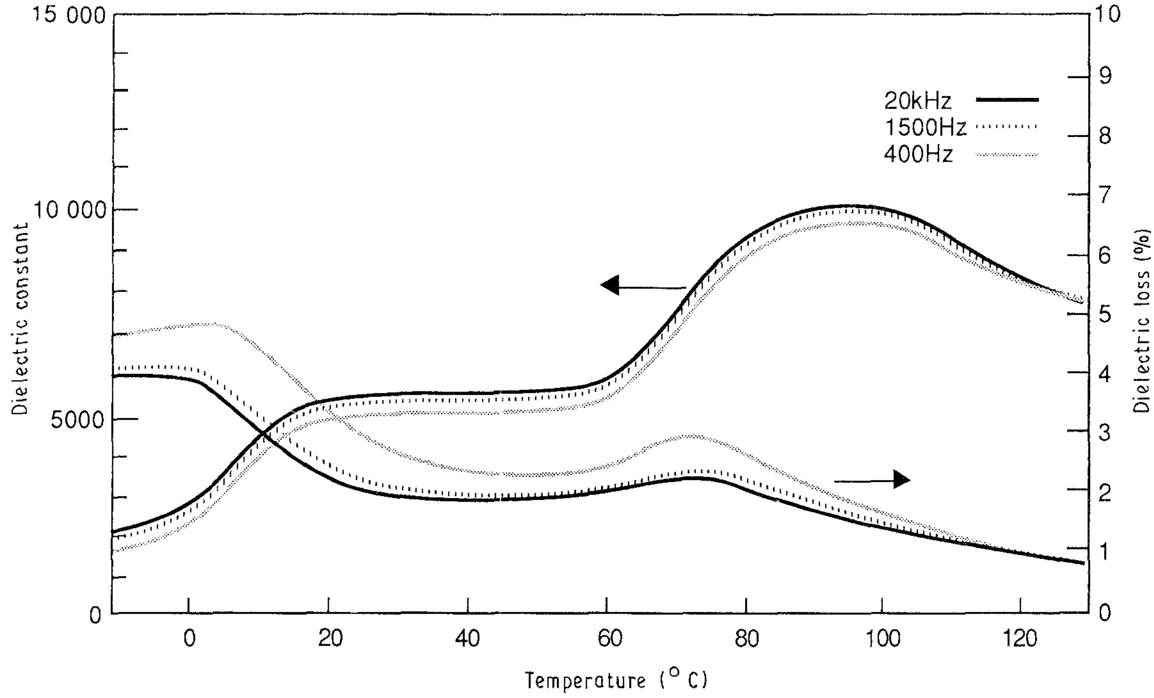

Figure 10 Dielectric properties of 0.9PST–0.1PT (Sample AL103) prepared using Method B (no anneal).

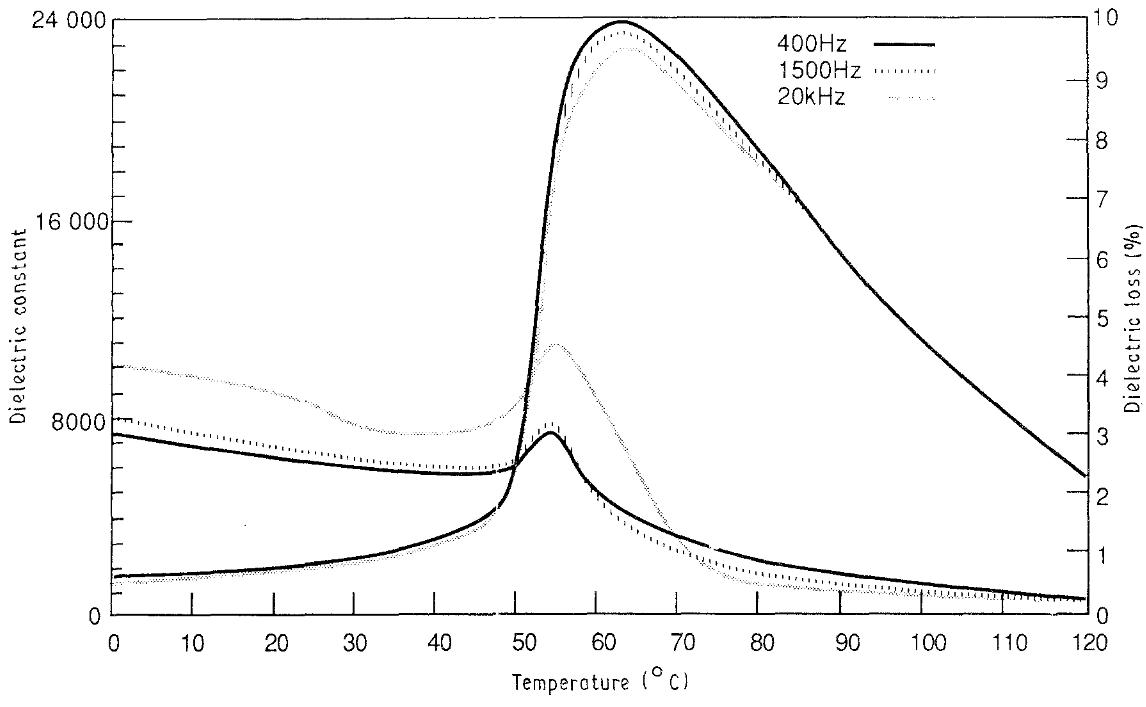

Figure 11 Dielectric properties of 0.9PST–0.1PT (Sample AL103) after annealing at 1400 °C.

dielectric constant and loss of 24 000 and 0.1%, respectively, when the average grain size was 2 μm, and values of 36 000 and 0.075%, respectively, for a grain size of 15 μm. These samples had theoretical density and exhibited an optical transmission of almost 70% out to a wavelength of 1760 cm^{-1} (5.7μm). The microstructure and dielectric properties of PST–PZ samples prepared using Method B were found to be highly dependent on the annealing temperature. X-ray and dielectric measurements for these samples indicated that the PST–PZ solution was only achieved when the annealing temperature was > 1300 °C. PST–PT ceramics (prepared using Method B) were found to have many similar properties to the PST–PZ materials fabricated from this route. Further work is required to study the properties of PST–PT ceramics produced from a titanium-modified scandium tantalate precursor. This would allow direct comparison with PST–PZ prepared via Method C.

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References

1. G. A. SMOLENSKII and A. I. AGRANOVSKAYA, *Sov. Phys. Tech. Phys.* **3** (1958) 1380.
2. S. W. CHOI, T. R. SHROUT, S. J. JANG and A. S. BHALLA, *Ferroelectrics* **100** (1989) 29.
3. C. G. F. STENGER and A. J. BURGGRAAF, *Phys. Status. Solidi.* (*a*) **61** (1980) 275.
4. C. ZHILI, Y. XI and L. E. CROSS, *Ferroelectrics* **49** (1983) 213.
5. N. M. SHORROCKS, R. W. WHATMORE and P. C. OSBOND, *ibid.* **106** (1990) 1223.
6. J. R. GINIEWICZ, A. S. BHALLA, and L. E. CROSS, *Ferroelectrics Lett.* **12** (1990) 355.
7. *Idem*, *Ferroelectrics* **118** (1991) 157.
8. T. R. SHROUT and A. HALLIYAL, *Amer. Ceram. Soc. Bull.* **66** (1987) 704.

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