Effect of dopants on the microstructure and lattice parameters of lead zirconate–titanate ceramics*

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The effect of dopants on the microstructure and lattice parameters of $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics was studied. Small amounts (0 to 0.3 wt%) of Cr_2O_3, MnO_2, Co_2O_3 and U_3O_8 were used as dopants. In a few compositions two oxides were used, namely U_3O_8 with Cr_2O_3 as well as MnO_2 with Cr_2O_3. X-ray diffraction investigation of powdered samples showed that all the compositions (both modified and unmodified) were of perovskite type with tetragonal symmetry. The Curie temperature was decreased with the decrease of tetragonal distortion indicated by the axial ratio, c_0/a_0, in all cases. The average grain sizes for the doped and undoped compositions were determined from SEM photomicrographs of polished and acid-etched surfaces using the linear intercept technique. The average grain size for the undoped composition was found to be 10.7 μm. The addition of a small amount of dopants controlled the grain growth to give rise to the average grain size of 6.4 to 9.5 μm, which appeared to have some effect on the improvement of the piezoelectric properties of the ceramics.

1. Introduction

The effect of dopants on the dielectric and piezoelectric properties of $Pb(Zr–Ti)O_3$ ceramics near the morphotropic phase boundary was studied by us earlier [1]. It was observed that the modified compositions, especially those made by doping with small amounts of Cr_2O_3 and U_3O_8, as well as some modified compositions made by doping with both U_3O_8 and Cr_2O_3, showed some promise for use in ceramic electric wave filters with wide frequency spacing. The work has been extended to study the crystallographic parameters of the same compositions with a view to ascertaining whether any relation exists between the lattice parameters and the nature and concentration of doping materials, as a result of which the properties of the ceramics have been modified to a considerable extent. Further, it is a common practice nowadays that additives are used for the aid of densification [2, 3] or control of grain growth [4–7] so as to improve the useful properties of the ceramics. In view of this we have examined the effect of dopants on the microstructure of the same lead zirconate–titanate ceramics. The results for the said investigations are reported in this paper.

If it is assumed that Cr^{3+}, Mn^{4+}, Co^{3+} and U^{4+} enter the B sites (zirconium and titanium) of the perovskite structure, they will mostly behave as acceptor-type dopants and the charge deficit of the trivalent ions at the B sites should be compensated mostly by oxygen vacancies which pin the walls of ferroelectric domains by local strain of the lattice. In the cases of Mn^{4+} and U^{4+} these vacancies would be filled. The existence of quadrivalent and bivalent manganese has been reported at the site of titanium for certain perovskite-type ceramics, namely $SrTiO_3$ [8] and $PbTiO_3$ [9]. Hennings and Pomplun [9] observed by thermogravimetric and ESR measurements that at low partial pressures of O_2 and PbO vapour, Mn^{2+} is favoured at the A sites and Mn^{3+} enters both A and B sites. At higher partial pressures of PbO, Mn^{4+} is mostly formed at the B sites. In this investigation our experiments have been carried out on maintaining proper PbO atmospheres; hence it is expected that manganese has entered into the B sites in a quadrivalent state. Further, it may be possible that uranium in higher valence states (pentavalent or hexavalent) may enter the B sites, making the ceramic a donor type. However, neither the site distribution nor the valence states of chromium, manganese, cobalt and uranium ions incorporated with $Pb(Zr, Ti)O_3$ have been determined experimentally in this work.

It may be pointed out that during preparation, the addition of chromium, manganese, cobalt and uranium may be balanced with additional lead. For example if Cr_2O_3 is added, a quantity of PbO may be added sufficient to give the stoichiometric proportions for lead chromate ($PbCrO_4$). When a heavier element like uranium is used, the quantity in weight percentage (as used in this investigation) would be proportionally higher in order to provide the same number of uranium atoms as there are chromium atoms in the added Cr_2O_3. Similarly, in the case of MnO_2-doped compositions the quantity of dopant (in weight percentage) should be lower in order to have the same number of manganese atoms as there are chromium atoms, since the molecular weight of MnO_2 is approximately

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half that of Cr_2O_3. However, no excess PbO was added to the composition during the preparation of the materials.

2. Experimental details

The lead zirconate–titanate ceramics (modified and unmodified) used in this study were the same as those used in previous work [1]. The details of the preparation have been described elsewhere [1]. The compositions were prepared according to the general formula given below:

$$Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3 + x\,\text{wt}\,\%\text{ of metal oxides}$$

The metal oxides used were Cr_2O_3, MnO_2, Co_2O_3 and U_3O_8. In cases of two oxides doped compositions, x wt % of one oxide and y wt % of another were used. The concentration of doping materials was varied in steps of 0.05 wt % and the study was made up to the addition of 0.3 wt % of doping material. Altogether 33 compositions including the undoped one were studied.

X-ray diffraction examination of the compositions was made using crushed ceramic disks. Lattice constants were determined using a Philips X-ray diffractometer, Model PW 1730 with nickel-filtered Cu$K\alpha$ radiation at a 2θ scanning rate $1°\,\text{min}^{-1}$. The angular range of 2θ covered was 20 to 80°. The peak angles were carefully indexed. The (0 0 2) and (2 0 0) peaks of the tetragonal phase appearing at $2\theta = 43$ to 45° were chosen to determine the lattice constants.

The scanning electron photomicrographs of the test samples were taken using a scanning electron microscope (Cambridge Stereoscan 150, Cambridge, England). The test specimens were polished with 600 mesh emery powder slurry with water and the polished surfaces were etched for 30 min with a dilute (5%) solution of HCl and distilled water containing 7 drops of 35% HF per decilitre of solution [10]. The polished and acid-etched surfaces, as well as the as-fired surfaces, were sputtered with gold employing a sputter coater, Model E5000 (Polaron Equipment Ltd, Watford, UK) so as to eliminate or reduce the electronic charge which builds up rapidly in a non-conducting specimen when scanned by a beam of high-energy electrons.

3. Results and discussion

3.1. X-ray measurements

The X-ray powder patterns for the modified and unmodified lead zirconate–titanate ceramics were identical and no additional phase was observed. The results of measurements for the lattice parameters for $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with the oxides of chromium, manganese, cobalt and uranium are summarized in Table I. The results for compositions doped with two oxides are given in Table II. The plots of lattice parameters against the concentration of dopant are shown in Fig. 1. It is observed that in the case of Cr_2O_3, Co_2O_3 and U_3O_8 modified

TABLE I Lattice parameters for $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with the oxides of chromium, manganese, cobalt and uranium at room temperature; symmetry in all cases was tetragonal

Concentration of doping material (wt %)	a_0 (nm)	c_0 (nm)	c_0/a_0	Unit cell volume (nm^3)	Curie temperature* (°C)
Cr_2O_3-doped compositions					
0.00	0.4036	0.4128	1.023	0.067242	355
0.05	0.4036	0.4129	1.023	0.067258	350
0.10	0.4043	0.4134	1.022_5	0.067574	350
0.15	0.4045	0.4139	1.023	0.067722	355
0.20	0.4045	0.4134	1.022	0.067641	355
0.25	0.4047	0.4135	1.022	0.067724	350
0.30	0.4045	0.4130	1.021	0.067575	350
MnO_2-doped compositions					
0.05	0.4032	0.4125	1.023	0.067060	350
0.10	0.4020	0.4115	1.023_6	0.066500	353
0.15	0.4028	0.4109	1.020	0.066668	350
0.20	0.4020	0.4109	1.022	0.066403	345
0.25	0.4023	0.4106	1.020_6	0.066454	345
0.30	0.4028	0.4098	1.017_4	0.066489	345
Co_2O_3-doped compositions					
0.05	0.4038	0.4133	1.023_5	0.067390	350
0.10	0.4041	0.4130	1.022	0.067441	350
0.15	0.4047	0.4133	1.021	0.067691	345
0.20	0.4047	0.4133	1.021	0.067691	345
0.25	0.4050	0.4133	1.020_5	0.067791	345
0.30	0.4045	0.4118	1.018	0.067379	345
U_3O_8-doped compositions					
0.05	0.4038	0.4128	1.022	0.067309	352
0.10	0.4040	0.4129	1.020	0.067392	355
0.15	0.4048	0.4130	1.020	0.067675	345
0.20	0.4045	0.4135	1.022	0.067657	342
0.25	0.4047	0.4130	1.020_5	0.067642	342
0.30	0.4034	0.4125	1.022_5	0.067126	340

*Data taken from an earlier paper [1].

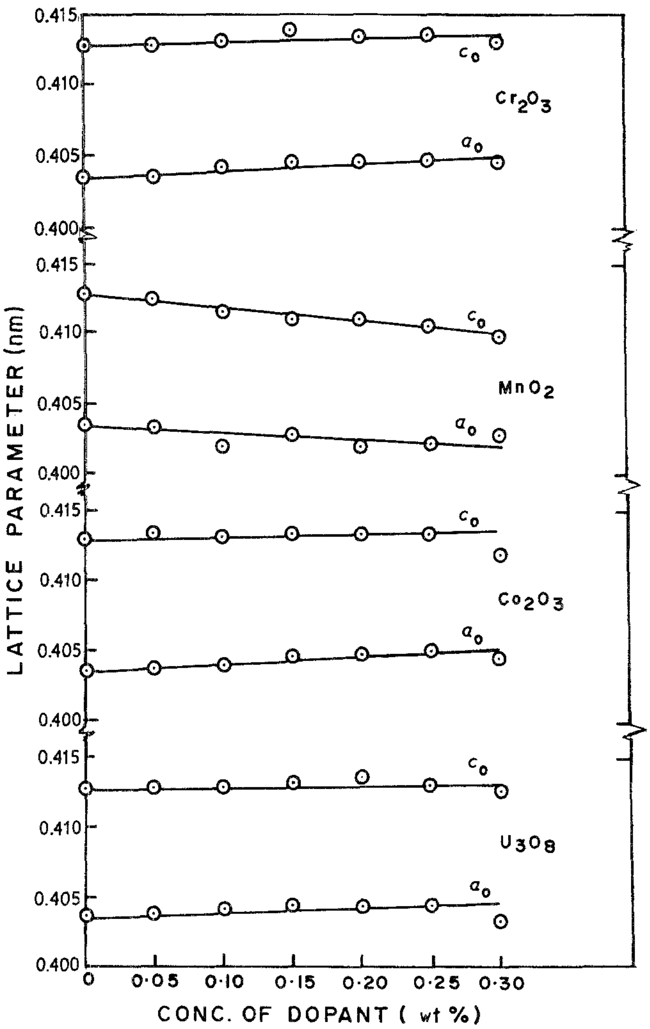

Figure 1 Plots of lattice parameters as a function of doping material concentration for $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with Cr_2O_3, MnO_2, Co_2O_3 and U_3O_8.

compositions, the unit cells are relatively elongated along the a_0 axis which is perpendicular to the polar axis for the tetragonal system. In contrast to this, in the case of MnO_2 doped compositions, as also of the compositions doped with two oxides, the unit cells were relatively contracted along the c_0 axis which is parallel to the polar axis in the tetragonal system. The plots of unit cell volume as a function of doping material concentration are shown in Fig. 2. The unit cell volumes also show an increase in the case of compositions made by doping with Cr_2O_3, Co_2O_3 and U_3O_8, and a decrease in the case of compositions made by doping with MnO_2 and with two oxides.

Preliminary experiments showed that there was an increase in weight of the doped specimens over that of the control specimens of unmodified ones when sintered in a PbO atmosphere. The gain in weight of the specimens indicates that the additives have been incorporated at B sites because the sample picks up PbO from the vapour phase, thus increasing the weight of the specimen. On the other hand when additives are incorporated at the A sites, PbO vapour would be eliminated from the specimen and a loss in weight would be registered which was not evident in our case.

In the perovskite structure ABO_3, the A cation is

TABLE II Lattice parameters for $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with two oxides at room temperature; symmetry in all cases was tetragonal.

Concentration of doping oxides (wt %)		a_0 (nm)	c_0 (nm)	c_0/a_0	Unit cell volume (nm^3)	Curie temperature* (°C)
(x)	(y)					
U_3O_8 (x) + Cr_2O_3 (y) doped compositions						
0.025	0.05	0.4032	0.4120	1.022	0.066978	346
0.05	0.10	0.4032	0.4113	1.020_6	0.066799	346
0.075	0.15	0.4024	0.4103	1.019_6	0.066438	346
0.10	0.20	0.4020	0.4098	1.019	0.066225	340
MnO_2(x) + Cr_2O_3 (y) doped compositions						
0.025	0.05	0.4034	0.4124	1.022	0.067110	340
0.05	0.05	0.4028	0.4119	1.022_6	0.066830	335
0.075	0.075	0.4028	0.4115	1.021_6	0.066764	338
0.10	0.10	0.4028	0.4121	1.023	0.066862	338

*Data taken from an earlier paper [1].

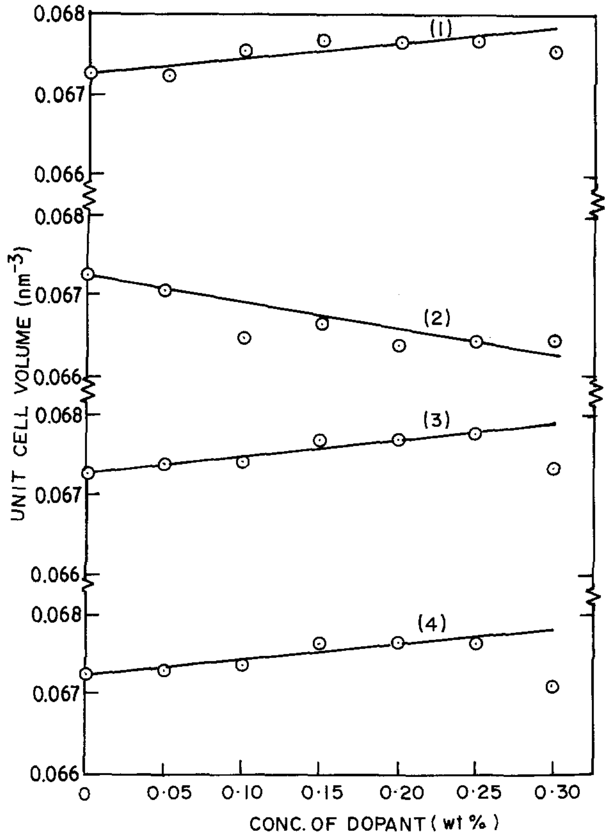

Figure 2 Plots of unit cell volume as a function of doping material concentration for $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with metal oxides: (1) Cr_2O_3 (2) MnO_2 (3) Co_2O_3 (4) U_3O_8.

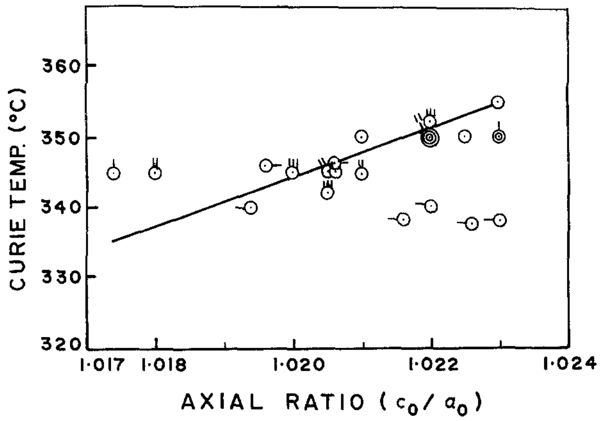

Figure 3 Plots of Curie temperature as a function of axial ratio measured at room temperature for $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with single and double metal oxides: (⊙) Cr_2O_3 (ȯ) MnO_2, (ö) Co_2O_3, (ö) U_3O_8, (⊙–) U_3O_8 + Cr_2O_3, (–⊙) MnO_2 + Cr_2O_3.

coordinated with 12 oxygen ions and the B cation with 6, thus the B cation is normally found to be smaller than the A cation. In $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramic both the Pb^{2+} ion ($r = 0.120$ nm) and the Sr^{2+} ion ($r = 0.112$ nm) are much larger than any out of the Cr^{3+} ($r = 0.063$ nm), Mn^{2+} ($r = 0.080$ nm), Co^{3+} ($r = 0.063$ nm) and U^{4+} ($r = 0.097$ nm) ions, and possibly these would be too small to enter the A sites of the perovskite lattice (all r values are Ahrens values). On the other hand the average ionic radius of Ti^{4+} ($r = 0.068$ nm) and Zr^{4+} ($r = 0.079$ nm) is 0.074 nm. Here also a considerable size misfit exists between Cr^{3+}, Co^{3+}, Mn^{4+} ($r = 0.060$ nm) and U^{4+} ions, and the average of Ti^{4+} and Zr^{4+} ions if the dopants are incorporated at the B sites. The increase of unit cell volumes with U_3O_8 and decrease with MnO_2 are reasonable because the ionic radius of U^{4+} is larger and Mn^{4+} is smaller than the average ionic radius of Ti^{4+} and Zr^{4+}. However, it is not understood why the unit cell volumes in the case of Cr_2O_3- and Co_2O_3-doped compositions showed an increase even though the ionic radii of Cr^{3+} and Co^{3+} are smaller than the average ionic radius of Ti^{4+} and Zr^{4+}. The probable reason may be that the foreign ions that are introduced into the crystal structure are interstitial instead of substitutional in this case.

All compositions were further examined to determine whether any relation existed between the crystallographic parameters and the Curie temperatures listed in Tables I and II. The Curie temperatures for the compositions have been taken from our earlier paper [1]. The relation between Curie temperature and axial ratio, c_0/a_0, is shown in Fig. 3. The compositions on the curve are all tetragonal with (0 0 1) polar axis and show a positive slope. The effect of a small proportion of additives appears to be to decrease the tetragonal distortion with a decrease of Curie temperature. Since the double-oxide doped compositions have the same tetragonal symmetry, the data for these have been used to draw a single curve. However, the data for combined MnO_2 and Cr_2O_3-doped compositions are comparatively far off the curve. The scatters in the data are due to the very small shifts of Curie temperature with the addition of dopants, and the limitations of the method used for the determination of Curie temperature with precision. For example, the shifts of Curie temperature of 0.3 wt % addition of Cr_2O_3, MnO_2, Co_2O_3 and U_3O_8 are 6, 10, 9 and 13°, respectively, which implies that for each step addition of 0.05 wt % of dopant, a shift of 1 to 2° C (approx.) of Curie temperature has taken place. However, the Curie temperature in this work has been determined from the peaks of dielectric constant against temperature curves [1] which are not very sensitive to such small changes.

It is noteworthy that as many as four modifying cations are included in the base composition, and yet the resulting ferroelectric compositions which have the same structure exhibit a common relation. It may be pointed out that similar to the present observation, in our earlier study [11] on the compositional changes between "soft material", $Pb(Ti_{0.455}Zr_{0.245}Sn_{0.300})O_3$ + 0.5 wt % Nd_2O_3 (or 1.5 wt % La_2O_3), and "hard material", $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ + 0.05 wt % NiO, the curve relating axial ratio and Curie temperature showed a positive slope for tetragonal symmetry. Further, Gless *et al.* [12] have observed that in the compositional changes in the $A^+A_2^{2+}Nb_5O_{15}$ series (where A^+ and A_2^{2+} refer to potassium, and to strontium, barium and lead, respectively) the curves relating the axial ratio and the Curie temperature showed a positive slope for tetragonal symmetry and a negative slope for orthorhombic symmetry.

3.2. Microstructure of the ceramic bodies

The microstructures of surfaces of the $Pb_{0.94}Sr_{0.06}$

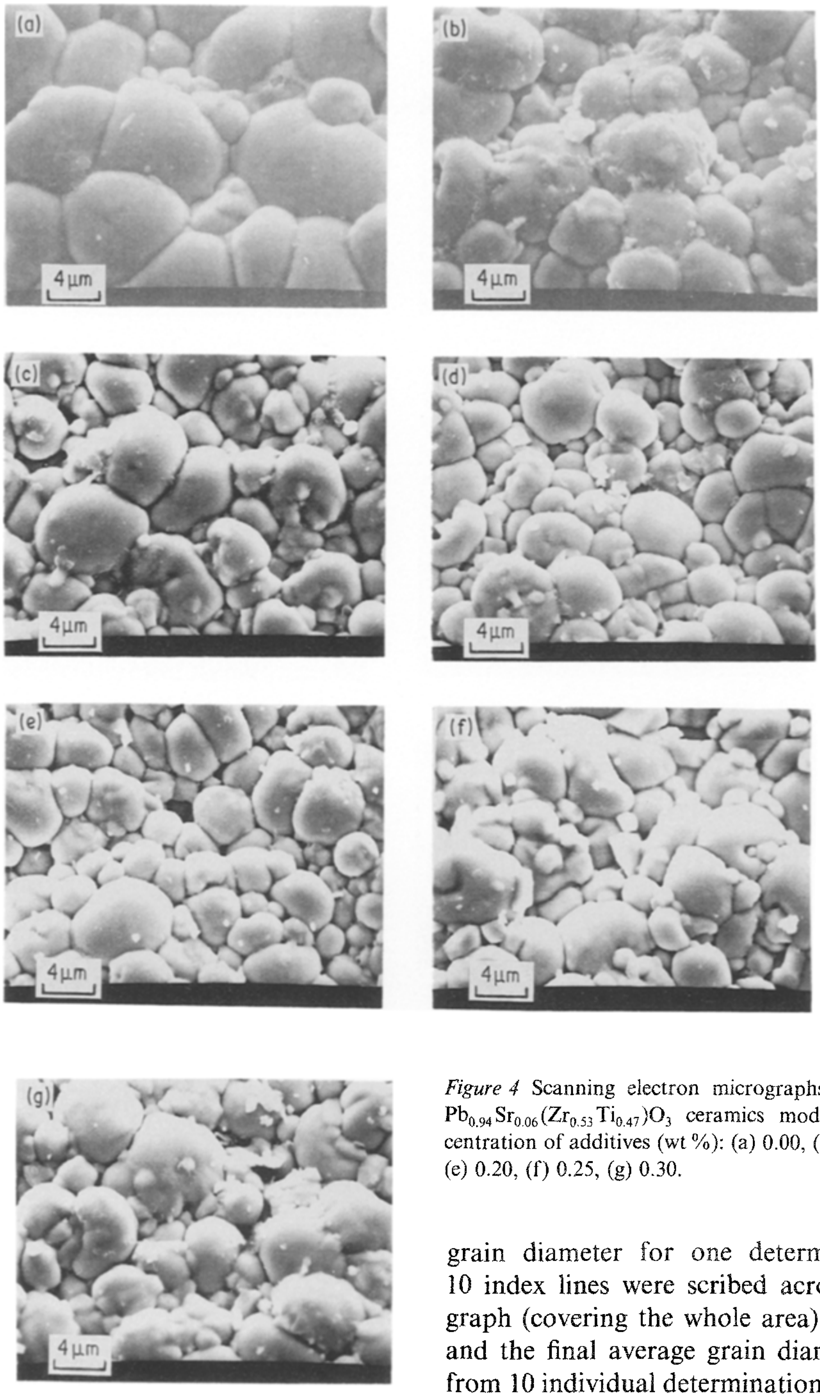

Figure 4 Scanning electron micrographs of as-fired surfaces of $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with Cr_2O_3. Concentration of additives (wt %): (a) 0.00, (b) 0.05, (c) 0.10, (d) 0.15, (e) 0.20, (f) 0.25, (g) 0.30.

$(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with the oxides of chromium, manganese, cobalt and uranium were examined using a scanning electron microscope. In case of Cr_2O_3-doped compositions, both as-fired surfaces as well as polished and acid-etched surfaces for the same specimens were examined, whereas for other compositions (prepared by doping with MnO_2, Co_2O_3 and U_3O_8) only polished and acid-etched surfaces were examined. Typical photomicrographs of the as-fired as well as the polished and acid-etched surfaces of Cr_2O_3-doped compositions are shown in Figs 4 and 5 respectively. It is evident from Figs 4 and 5 that the size of the grains decreases with increase of doping material concentration.

The average grain diameter, D, was calculated by the linear intercept method [13], i.e. the number of grain boundaries intercepting a given index line was counted. This number divided into the length of the index line (calibrated in micrometres) gave the average grain diameter for one determination. Altogether 10 index lines were scribed across the photomicrograph (covering the whole area) of each test sample and the final average grain diameter, D, was taken from 10 individual determinations. From this average value, the true grain size, $\bar{D}$, was obtained from the relation $\bar{D} = 1.56\,D$. The proportionality constant 1.56 is essentially a correction factor which was derived by Mendelson [14] for random slices through a model system consisting of space-filling tetrakaidecahedrally shaped grains with a log-normal size distribution.

The data for average grain sizes of Cr_2O_3-doped compositions determined from the surfaces of the as-fired specimens are given in Table III, while the data determined from the polished and acid-etched surfaces for the same specimens are given in Table IV. The other results for the grain-size measurements on the polished and acid-etched surfaces for different compositions made by doping with the oxides of manganese, cobalt and uranium are given in the same Table IV. The average diameters as determined from the as-fired surfaces (range: 5.0 to 8.1 μm) are slightly lower than of the values determined from the polished and acid-etched surfaces for the same specimens

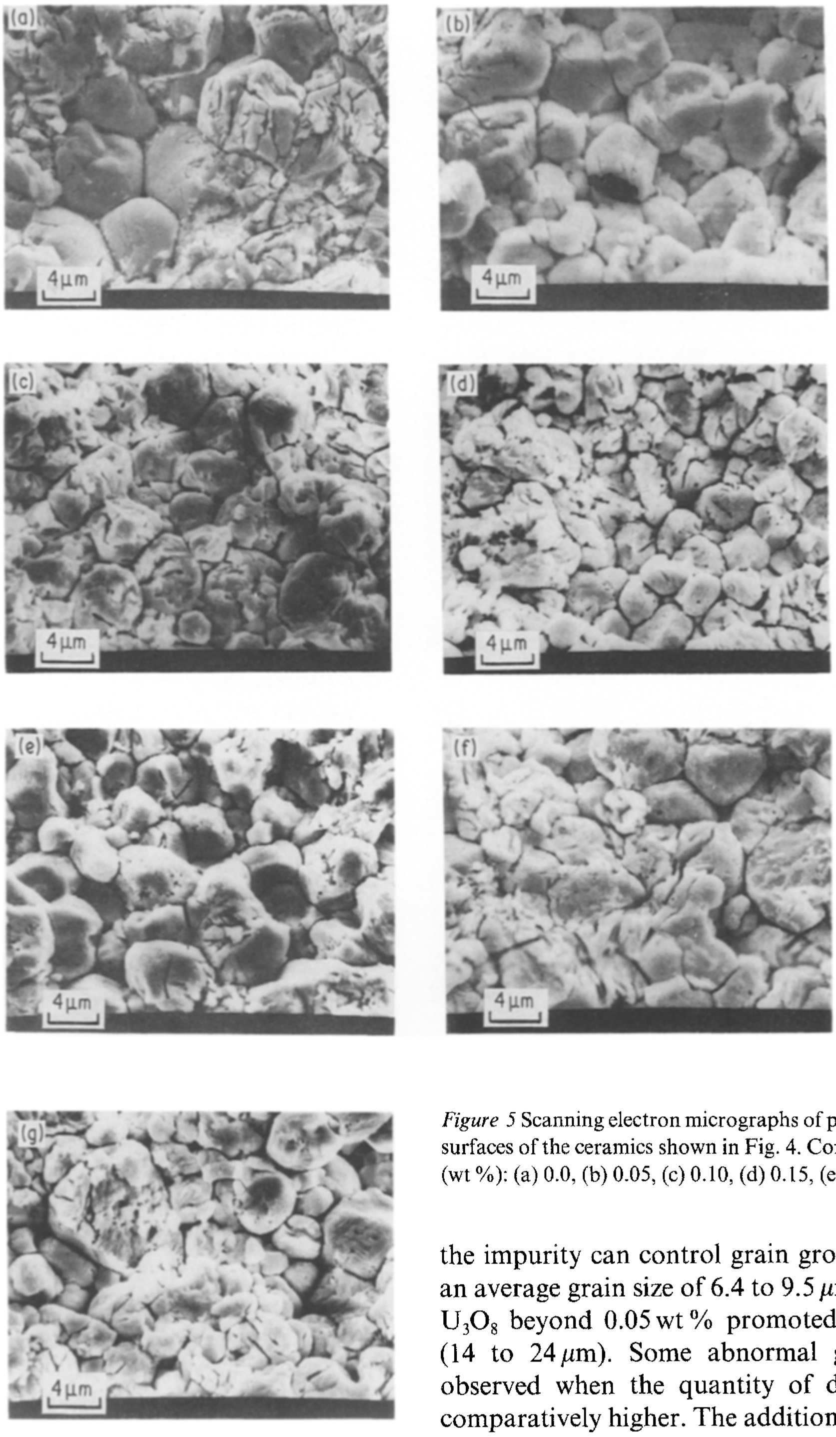

Figure 5 Scanning electron micrographs of polished and acid-etched surfaces of the ceramics shown in Fig. 4. Concentration of additives (wt %): (a) 0.0, (b) 0.05, (c) 0.10, (d) 0.15, (e) 0.20, (f) 0.25, (g) 0.30.

(range: 7.1 to 10.7 μm). This difference may be due to surface inhomogeneities of the as-fired surfaces. From Table IV it is observed that the average grain diameter for the unmodified sample is 10.7 μm, which has been reduced considerably (up to 6.4 μm) by the addition of small amounts of the metal oxides. The same decrease of average grain size was observed when the base composition was modified with two oxides, especially with the combined oxides of uranium and chromium. The results of average grain-size measurements for compositions prepared with the addition of two oxides, namely U_3O_8 with Cr_2O_3 and MnO_2 with Cr_2O_3, are summarized in Table V.

The effect of additives on 53/47 lead zirconate–titanate ceramics may be described in terms of an inhibition of grain growth by the inclusion. This implies that the addition of a small amount of impurity may be useful for enhancing the piezoelectric effect if the impurity can control grain growth to give rise to an average grain size of 6.4 to 9.5 μm. The addition of U_3O_8 beyond 0.05 wt % promoted the grain growth (14 to 24 μm). Some abnormal grain growth was observed when the quantity of dopant added was comparatively higher. The addition of two oxides also inhibited the grain growth, especially in the case of U_3O_8 with Cr_2O_3. Relatively coarse grains were produced by the addition of both MnO_2 and Cr_2O_3. In this connection it may be pointed out that a similar type of inhibition of grain growth was observed when Dy_2O_3 [4] or TiO_2, BaO or any other element [6] was

TABLE III Average grain size of $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with the oxide of chromium (determined from the photomicrograph of as-fired specimens)

Concentration of doping material (wt %)	Density, ϱ (10^{-3} kg m^{-3})	Average grain size (μm)
0.00	7.32	8.1
0.05	7.39	6.6
0.10	7.46	5.7
0.15	7.25	4.9
0.20	7.30	4.8
0.25	7.23	4.7
0.30	7.23	5.0

TABLE IV Average grain size of $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with the oxides of chromium, manganese, cobalt and uranium (determined from the photomicrographs of polished and chemically etched surfaces of specimens)

Concentration of doping material (wt %)	Density, ϱ (10^{-3} kg m^{-3})	Average grain size (μm)
Cr_2O_3-doped compositions		
0.00	7.32	10.7
0.05	7.46	8.1
0.10	7.47	9.5
0.15	7.30	8.8
0.20	7.35	7.1
0.25	7.30	8.8
0.30	7.45	7.5
MnO_2-doped compositions		
0.05	7.48	7.3
0.10	7.33	7.7
0.15	7.40	7.7
0.20	7.16	7.9
0.25	7.33	8.3
0.30	7.19	9.2
Co_2O_3-doped compositions		
0.05	7.28	8.5
0.10	7.39	8.5
0.15	7.36	6.5
0.20	7.28	6.4
0.25	7.28	8.2
0.30	7.39	6.6
U_3O_8-doped compositions		
0.025	7.39	6.9
0.05	7.33	9.4
0.075	7.37	15.0
0.20	7.19	16.2
0.25	7.13	13.9
0.40	6.40	24.5

added to $BaTiO_3$ ceramics in a small quantity. Yamaji *et al.* [4] have observed that the average grain size of $BaTiO_3$ ceramics decreases with increasing dysprosium content and is controlled at $\approx 1.5\,\mu$m by 0.8 at % Dy. Kuwabara [6] observed that the addition of a small amount of TiO_2 or BaO enhances the positive temperature coefficient of resistivity (PTCR) effect if the impurities can control the grain growth to give rise a grain size in the range of 2 to 5 μm.

4. Conclusions

The lattice parameters of the tetragonal ferroelectric phase showed that the axial ratio, c/a_0, decreased with the increase of concentration of doping material. Similar behaviour was also observed in the case of compositions doped with two oxides. The Curie temperature decreased with the decrease of tetragonal distortion (axial ratio) and the plots of axial ratio as a function of Curie temperature showed a positive slope for the tetragonal symmetry. Axial ratios are essentially determined by the modifying cations, which in turn regulate the transition temperature of the compositions. The unit cell volumes had shown an increase for U_3O_8-doped compositions and a decrease for MnO_2-doped compositions, since the ionic radii of U^{4+} and Mn^{4+} are respectively larger and smaller than the average ionic radius of Ti^{4+} and Zr^{4+}. The discrepancy that the unit cell volumes for compositions made by doping with Cr_2O_3 and Co_2O_3 showed an increase, even though the ionic radii of Cr^{3+} and Co^{3+} are smaller than the average ionic radius of Ti^{4+} and Zr^{4+}, is probably due to interstitial addition of foreign atoms instead of substititutional addition to the crystal structure.

TABLE V Average grain size of $Pb_{0.94}Sr_{0.06}(Zr_{0.53}Ti_{0.47})O_3$ ceramics modified with two oxides (determined from the photomicrographs of polished and acid-etched surfaces of specimens)

Concentration of doping oxides (wt %)		Density, ϱ (10^{-3} kg m^{-3})	Average grain size (μm)
x	y		
$U_3O_8(x)$ + $Cr_2O_3(y)$ doped compositions			
0.025	0.05	7.41	7.4
0.05	0.10	7.43	8.0
0.075	0.15	7.30	8.9
0.10	0.20	7.34	8.6
MnO_2 (x) + Cr_2O_3 (y) doped compositions			
0.025	0.05	7.46	12.3
0.05	0.05	7.37	8.9
0.075	0.075	7.33	10.3
0.10	0.10	7.35	9.1

Addition of small amounts of Cr_2O_3, MnO_2, Co_2O_3 and U_3O_8 controlled the grain growth of the lead zirconate–titanate ceramics. However, addition of U_3O_8 beyond 0.05 wt % promoted the grain growth. Addition of the combined oxides U_3O_8 with Cr_2O_3 also inhibited the grain growth. Relatively coarse grains were produced by the addition of MnO_2 with Cr_2O_3. The additions of impurities in small amounts appears to be useful to enhance the piezoelectric properties if the impurity can control the grain growth to give rise a grain size of 6.4 to 9.5 μm.

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