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Sintering of strontium titanate in the presence of lithium salts in a reducing atmosphere

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The possibility of preparing Type III ceramics for multilayer applications has been investigated in the strontium–titanium–oxygen system, using La_2O_3, Nd_2O_3 and "$La_{2/3}TiO_{3-\varepsilon}$" as dopants and lithium salts as sintering agents. The introduction of bismuth was also explored. The sintering process is carried out by adding the lithium salts to mixtures of strontium titanate and dopants which are previously calcined in a reducing atmosphere. The dielectric properties and the microstructure of the ceramics have been studied. The best characteristics have been observed for the particular nominal composition $SrTiO_3$ + 0.75 mol % $La_{2/3}TiO_{3-\varepsilon}$ + 3 mol % Bi_2O_3 + 10 mol % $LiNO_3$ leading to $\varepsilon = 20\,000$, $\tan \delta < 2\%$, $R_i = 10^{11}\,\Omega$ cm. These results are interpreted in terms of the formation of anionic vacancies and defects in the A sites of the perovskite ABO_3 and of extended defects "SrO" and "$Bi_2O_2^{2+}$" which are coherent with the perovskite matrix.

1. Introduction

The sintering of strontium titanate has been extensively studied for Type III boundary layer capacitors [1–5] owing to its ability to display high apparent dielectric constants, that is $\varepsilon \sim 20\,000$ to 150 000. Such a process is usually carried out in two steps involving first a reducing atmosphere and then a partial reoxidation of n-doped (and eventually p-counterdoped) strontium titanate. Unfortunately, in spite of their high apparent dielectric constant, these materials do not allow disc or MELF capacitors with a volume capacitance as high as classical Type II multilayer capacitors to be made. Extension of the multilayer technology to Type III materials could lead to a very high volume capacitance. However, among the different obstacles to the realization of such capacitors, one must notice the great size of the grains and the use of bismuth-based oxides which have to diffuse at the grain boundaries in order to form an insulting barrier. The presence of inner electrodes in the elaboration of multilayer capacitors makes difficult the diffusion of the bismuth compound after the sintering step as classically made in the case of discs or MELF's. Thus it appears that the bismuth oxide could be added before sintering. Such a process can be carried out by lowering the sintering temperature in order to avoid reaction of the bismuth compound with the dielectric and the electrodes.

In this respect the study of the sintering of strontium titanate in air in the presence of lithium salts [6–8] has shown the possibility of lowering the sintering temperature to about 1000° C. This result has been recently extended to the sintering of strontium titanate in a reducing atmosphere, using niobium oxides as donors [9, 10]. This latter study has shown the possibility of obtaining the formation of barriers with a sintering temperature of 1100° C. It must be pointed out that the elaboration of such a ceramic differs from the classical method used for Type III grain boundary layer capacitors by the fact that the starting mixed powders, containing the dopant, are calcined at 1350° C under a reducing atmosphere before sintering, in order to introduce defects and especially defects in the anionic sub-lattice of the perovskite. Such a process may lead to a partial reduction of Nb(V) to Nb(IV) and may influence the properties of the final ceramic. Thus the present work deals with the sintering of strontium titanate in the presence of lithium salts using the previous experimental conditions, but with lanthanum and neodymium as donors instead of niobium.

2. Experimental methods

The strontium titanate is prepared by mixing TiO_2 and $SrCO_3$ by dry-milling for one hour and then wet-milling in ethanol (50 vol %) for 48 h using a Turbula shaker-mill. The dried mixed powder is then calcined at 1150° C for one hour. Considering our previous results three Ti/Sr ratios were investigated, i.e. 1, 0.985 and 0.975. The donar dopant lanthanum (or neodymium) is either introduced included in a perovskite-type compound "$La_{2/3}TiO_{3-\varepsilon}$" or as the oxides La_2O_3 and $Nd_2O_3 \cdot La_{2/3}TiO_{3-\varepsilon}$ is prepared by mixing the two oxides La_2O_3 and TiO_2 and by heating the mixture at 1350° C in a reducing atmosphere containing nitrogen and 10% of hydrogen, with a heating and cooling

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TABLE I Dielectric constants (ε), losses ($\tan\delta$), insulating resistances ($R_2(\Omega\,\mathrm{cm})$) and shrinkage (S) of lanthanum (La_2O_3) and neodymium doped $SrTiO_3$; results are given for different Ti/Sr ratios and different lithium salts added

Added salts	Ti/Sr = 1.0125		Ti/Sr = 1		Ti/Sr = 0.985		Ti/Sr = 0.975	
	Nd	La	Nd	La	Nd	La	Nd	La
LiF	$\varepsilon = 500$	$\varepsilon = 800$	$\varepsilon = 3500$	$\varepsilon = 3000$	$\varepsilon = 2500$	$\varepsilon = 2000$	$\varepsilon = 3700$	$\varepsilon = 3500$
			$\tan\delta \sim 36\%$	$\tan\delta \sim 24\%$	$\tan\delta < 2\%$	$\tan\delta = 1.5\%$	$\tan\delta = 2\%$	$\tan\delta < 2\%$
	$R_i = 10^7$	$R_i = 10^8$	$R_i = 10^9$	$R = 10^{11}$	$R_i = 10^{12}$	$R_i = 10^{12}$	$R_i = 10^{11}$	$R_i = 10^{11}$
	$S = 2\%$	$S = 5\%$	$S = 14\%$	$S = 15\%$	$S = 14.7\%$	$S = 15.6\%$	$S = 14.8\%$	$S = 14.5\%$
Li_2CO_3		$\varepsilon = 700$	$\varepsilon = 7500$	$\varepsilon = 14000$	$\varepsilon = 3000$		$\varepsilon = 3000$	$\varepsilon = 2000$
			$\tan\delta \sim 6\%$	$\tan\delta = 7\%$	$\tan\delta = 5\%$		$\tan\delta = 4\%$	$\tan\delta = 2\%$
		$R_i = 10^8$	$R_i = 10^7$	$R_i = 10^7$	$R_i = 10^{12}$		$R_i = 10^{11}$	$R_i = 10^{11}$
		$S = 5\%$	$S = 15.3\%$	$S = 16.4\%$	$S = 15\%$		$S = 12.7\%$	$S = 15\%$
$LiNO_3$			$\varepsilon = 9500$	$\varepsilon = 5500$			$\varepsilon = 2600$	$\varepsilon = 3000$
			$\tan\delta = 5\%$	$\tan\delta = 5\%$			$\tan\delta = 5\%$	$\tan\delta = 5\%$
			$R_i = 10^6$	$R_i = 10^7$			$R_i = 10^{10}$	$R_i = 10^{10}$
			$S = 14.4\%$	$S = 14.9\%$			$S = 13.5\%$	$S = 14.8\%$

rate of 150° C h^{-1}. 0.5 mol % La (or Nd) is added to the strontium titanate and wet-mixed in a bowl (Fritsch Pulvérisette) for half an hour. The dried powder is then calcined at 1350° C for two hours with a temperature/atmosphere cycle as described for the synthesis of $La_{2/3}TiO_{3-\varepsilon}$. The lithium salts (10 mol % Li from $LiNO_3$, LiF or Li_2CO_3) and eventually bismuth oxide are then added to the grey semi-conductive powder using the same process as above. The powder is then pressed at 1 tonne cm^{-2} into discs of 12.6 mm diameter and about 1.5 mm thickness.

The discs are sintered at 1100° C for two hours with a heating and cooling rate of 150° C h^{-1} according to the following atmosphere/temperature cycle: during heating and the first hour of dwelling-time, the atmosphere is a nitrogen gas containing 10% hydrogen, and during the second hour of dwelling time and cooling the atmosphere is oxygen. The flow of gas is 18 l h^{-1}. The sintered ceramics are painted with an In–Ga alloy to form the electrodes. The apparent dielectric constant is measured at 1 kHz between −60 and +150° C. The insulating resistance is measured under a d.c. bias of 45 V mm^{-1}.

The calcined materials as well as the sintered ceramics are analysed by X-ray powder diffraction using Cu$K\alpha$ radiation. The microstructure of the samples is examined on fractures with a scanning electron microscope.

3. Results and discussion

The main results dealing with the sintering of strontium titanate with La_2O_3 or Nd_2O_3 as dopants are summarized in Table I. The values of the shrinkage show that good densification is observed whatever the nature of the lithium salts and the stoichiometry Ti/Sr < 1 may be. It must be pointed out that for Ti/Sr > 1 densification of the ceramic cannot be achieved. The behaviour is similar to that observed for the sintering of niobium-doped strontium titanate [10]. However, sintering in the presence of Li_2CO_3 or $LiNO_3$ leads to better dielectric characteristics than with lithium fluoride. For LiF sintered ceramics, the dielectric constant does not depend on the stoichiometry Ti/Sr and remains close to 3000. On the other hand, it can be seen that the highest dielectric constants are usually correlated with a decrease of the insulating resistance down to 10^6 to $10^7\,\Omega$ cm compared to $10^{11}\,\Omega$ cm for the lowest constants. The highest ε values ($\varepsilon = 14000$) correspond to a large grain size (up to a diameter of ~50 μm) that is too large for use in multilayer capacitors, as shown by the micrograph corresponding to the sample doped with La_2O_3 and sintered with Li_2CO_3 (Fig. 1a). The ε values obtained for sintering in the presence of $LiNO_3$ are generally smaller than those with Li_2CO_3, but correlatively the grain size is much more compatible with a multilayer capacitor structure. Thus it appears that

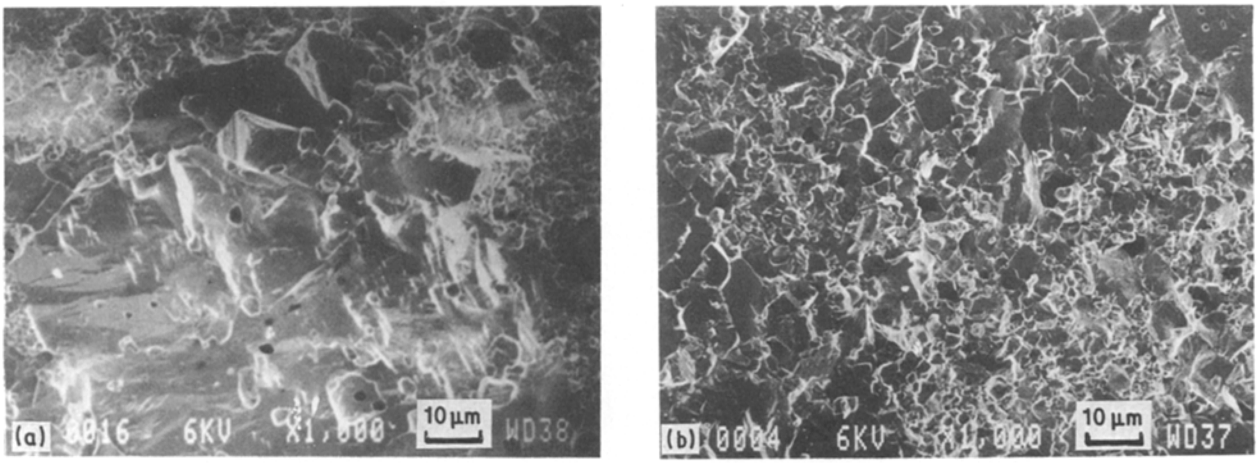

Figure 1 SEM micrographs of samples: (a) "$SrTiO_3$(Ti/Sr = 1) + 0.25 mol % La_2O_3 + $0.05Li_2CO_3$", (b) "$SrTiO_3$(Ti/Sr = 1) + 0.25 mol % La_2O_3 + $0.1LiNO_3$".

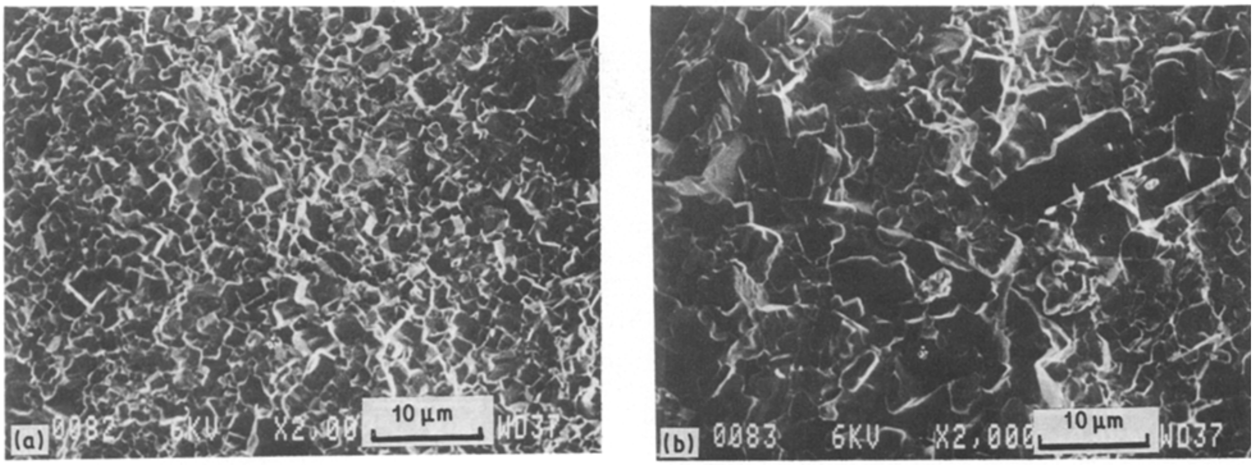

Figure 2 SEM micrographs of samples: (a) "$SrTiO_3$(Ti/Sr = 0.975) + 0.250 mol% La_2O_3 + $0.05Li_2CO_3$, (b) $SrTiO_3$(Ti/Sr = 0.975) + 0.250 mol% La_2O_3 + $0.10LiNO_3$".

the grain growth of the conductive strontium titanate grains is better controlled by using $LiNO_3$ as a sintering agent, as shown from the micrograph (Fig. 1b) which corresponds to the sample with 0.25 mol% La_2O_3 + 10 mol% $LiNO_3$ in which the grain size repartition is rather homogeneous in spite of the existence of some regions with grains larger than 10 µm. One can also notice the absence of intragranular porosity and with a slight porosity present only at the triple grain boundaries. Such a material, corresponding to a ε value of 6000 and to rather low dielectric losses (~ 4%), could be used for the preparation of multilayer capacitors. Nevertheless the insulating resistance, $R_i = 10^9\ \Omega$ cm, is too weak for capacitor applications The change of the microstructure with Ti/Sr ratio is interesting: increasing the strontium content leads to a rapid decrease of the grain size (see Fig. 2 for Ti/Sr = 0.975) and enhances the insulating character of the barriers, as shown by the high values of the insulating resistance and the low ε values.

The diffusion process during sintering will be governed principally by the presence of rather high contents of vacancies on the A sites and on the anionic sites. Considering the nominal stoichiometric composition $SrTiO_3$, anionic vacancies can be formed during the calcination in a reducing atmosphere and during the first step of the sintering, so that the existence of an oxygen deficient perovskite $SrTiO_{3-x}$ is most likely; the presence of $y/2$ moles of La_2O_3 (or Nd_2O_3) tends to decrease the number of oxygen vacancies, at least during the calcination step, according to the reaction

$$(y/2)\ La_2O_3 + SrTiO_{3-x}$$

$$\rightarrow Sr_{1-y}La_yTiO_{3-x+(3y/2)} + y\ SrO$$

Such a model would lead to the formation of intergrowths between the perovskite and the excess of SrO, which can be formulated $SrO(Sr_{1-y}La_yTiO_{3-x+(3y/2)})_n$. This hypothesis is supported by the fact that the X-ray diffraction spectra of the oxides calcined under a reducing atmosphere exhibit, besides the perovskite reflexions, lines characteristic of the oxides Sr_2TiO_4 and $Sr_3Ti_2O_7$ which correspond to the members $n = 2$ and $n = 3$ of the family $(SrTiO_3)_n \cdot SrO$ [11, 12]. The diffusion process is then drastically modified in the first step of sintering under the reducing atmosphere by the addition of lithium salts. From the previous studies [8, 9] it is now clear that whatever the nominal composition may be, the diffusion of the species is made easier by the introducion of lithium into the perovskite matrix. This leads to the formation of anionic defects, compatible with the ability of lithium to take both coordinations, octahedral and tetrahedral (Fig. 3). Thus the addition of $z/2$ moles of "Li_2O" in the form of $LiNO_3$ or Li_2CO_3 leads to the formation of vacancies in the A sites as well as additional anionic vacancies, and eliminates the intergrowth defects formed during the calcination according to the formula

$$Sr_{(1-y)/(1+z)}La_{y/(1+z)}Ti_{1/(1+z)}Li_{z/(1+z)}O_{[3+(z/2)-x+(3/y)]/(1+z)}$$

This excess of A and anionic vacancies, and above all the absence of intergrowths, favours the diffusion process and explains why the grain size will not be easily controlled. Moreover such a hypothesis suggests that the oxygen ions will tend to diffuse more rapidly towards the centre of the grains during the oxidization step due to the numerous oxygen vacancies, preventing fully oxidized barriers from forming near the surfaces of the grains. The rather low insulating resistances observed ($R_i \sim 10^7$ to $10^9\ \Omega$ cm) are in agreement with this latter point of view.

For Ti/Sr ratios smaller than unity, intergrowths

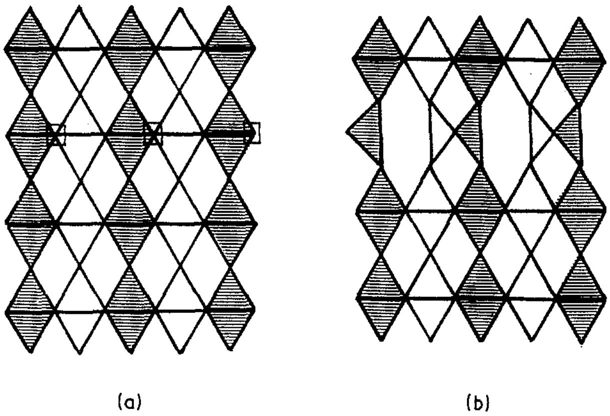

Figure 3 (a) Creation of rows of oxygen vacancies parallel to ⟨1 1 0⟩ in a perovskite matrix, leading to (b) the formation of layers of LiO_4 tetrahedra.

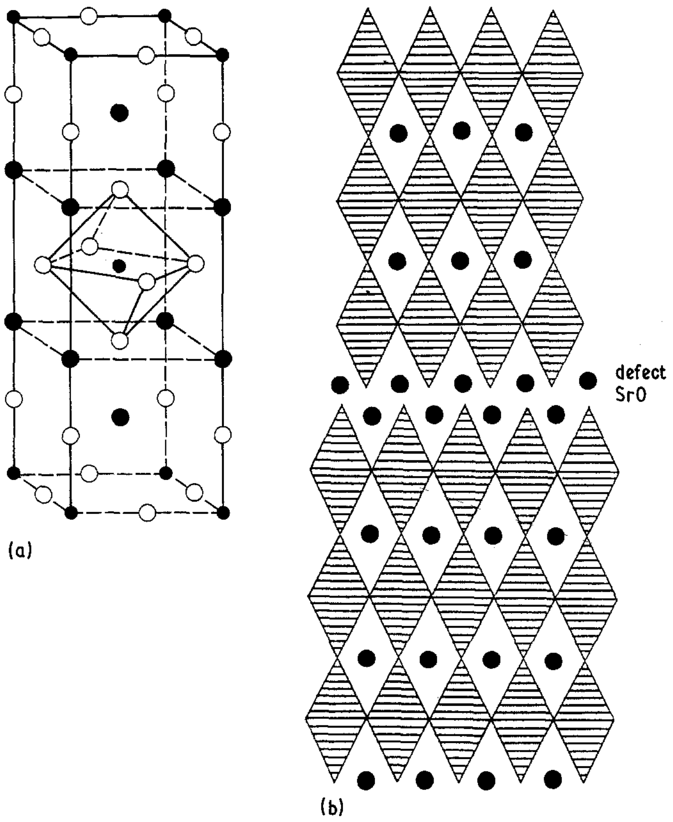

Figure 4 The $(SrTiO_3)_nSrO$ oxides, intergrowth of the perovskite structure and the SrO–NaCl-type structure: (a) Sr_2TiO_4 defect in an $SrTiO_3$ perovskite matrix, (b) the SrO sheet extended defect in a $SrTiO_3$ perovskite matrix. (○) Oxygen, (●) strontium, (•) titanium.

between the perovskite structure and SrO cannot be eliminated due to the excess of strontium. It follows that extended defects of SrO type can be developed in the perovskite matrix (Fig. 4) due to the bidimensional agreement between the perovskite and sodium chloride type SrO structures. Such defects, which correspond to close-packed layers of oxygen and strontium atoms, do not favour the diffusion of ionic species and may tend to slow down the grain growth, and also change the equilibrium conditions between the reduced perovskite and the atmosphere during the first step of sintering, especially if they are located near the grain boundary. This model can be applied equally for lanthanum or neodymium. The different results observed in the case of LiF can be explained by the possible introduction of fluorine on the anionic sites of the perovskite.

The second series of experiments was carried out with "$La_{2/3}TiO_{3-\varepsilon}$" as a dopant in order to introduce lanthanum and vacancies on the A sites without changing the perovskite framework (TiO_3). An equivalent amount of lanthanum (0.75% "$La_{2/3}TiO_{3-\varepsilon}$") to that of the first series of experiments (0.25% La_2O_3) was used in order that a comparison might be made between the two systems. Table II gives the main results obtained with "$La_{2/3}TiO_{3-\varepsilon}$". It must be stressed that no sintering could be achieved in the presence of lithium fluoride regardless of the stoichiometry (Ti/Sr = 1 or 0.975). Very high dielectric constants are observed only for Ti/Sr = 1, or smaller than 1 but very close to 1. The high ε values ($\varepsilon \sim 30000$) are correlated with the presence of very large grains (diameter greater than 50 μm), as shown from the micrograph of Fig. 5. Moreover it can be seen that the

TABLE II Dielectric constants (ε), losses ($\tan\delta$), insulating resistances (R_i(Ωcm)) and shrinkage (S) of "$La_{2/3}TiO_{3-\varepsilon}$" doped $SrTiO_3$; results are given for different Ti/Sr ratios and different additives

T/Sr ratio	Additive			
	LiF	Li_2CO_3	$LiNO_3$	$LiNO_3 + Bi_2O_3$
1.0125		$\varepsilon = 2000$ $R_i = 10^7$ $S = 6.8\%$		
1	$\varepsilon = 1500$ $\tan\delta = 1\%$ $R_i = 10^9$ $S = 11\%$	$\varepsilon = 30000$ $\tan\delta = 5\%$ $R_i = 10^3$ $S = 14\%$	$\varepsilon = 30000$ $\tan\delta \sim 7\%$ $R_i = 10^3$ $S = 13\%$	$\varepsilon = 20000$ $\tan\delta < 2\%$ $R_i = 10^{11}$ $S = 15.7\%$
0.995		$\varepsilon = 12000$ $\tan\delta = 2\%$ $R_i = 10^5$ $S = 17\%$		
0.975	$\varepsilon = 1000$ $\tan\delta \sim 2\%$ $R_i = 10^{12}$ $S = 9.5\%$	$\varepsilon = 1800$ $\tan\delta = 4\%$ $R_i = 10^{11}$ $S = 15.7\%$	$\varepsilon = 2000$ $\tan\delta = 3\%$ $R_i = 10^{11}$ $S = 12.7\%$	

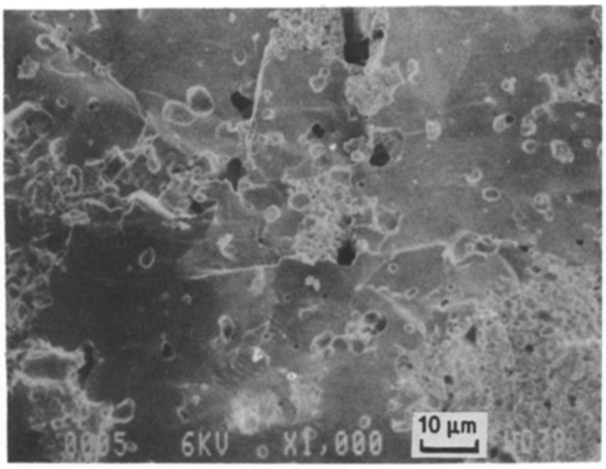

Figure 5 SEM micrograph of the sample "$SrTiO_3$(Ti/Sr = 1) + 0.75 mol % $La_{2/3}TiO_{3-\varepsilon}$ + $0.05Li_2CO_3$".

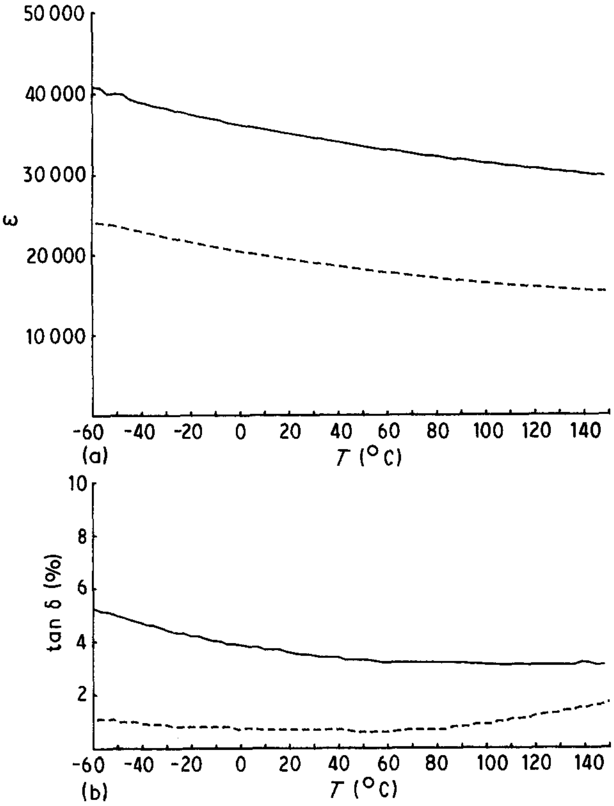

Figure 6 (a) Dielectric constants (ε) and (b) losses (tan δ) against the temperature T of "$La_{2/3}TiO_{3-\varepsilon}$" doped ceramics: (———) with $0.1LiNO_3$, (- - -) with $0.1LiNO_3$ + $0.03Bi_2O_3$.

distribution of the grain size spreads over a wide range. The very low insulating resistances, which make these ceramics unsuitable for applications, can be explained by the model described above. For the nominal stoichiometric composition Ti/Sr = 1, the reaction of "$La_{2/3}TiO_{3-\varepsilon}$" with the perovskite $SrTiO_3$ during the calcination step leads to a perovskite which exhibits both anionic and A defects and which can be formulated $Sr_{1-(3y/2)}La_yTiO_{3-x}$; the amount of these defects is then increased by the addition of lithium salts during the first step of sintering in a reducing atmosphere according to the formulation

$$Sr_{1-(3y/2)/(1+z)}La_{y/(1+z)}Ti_{1/(1+z)}Li_{z/(1+z)}O_{3-x+(z/2)]/(1+z)}$$

Thus the presence of those defects, and above all the absence of intergranular defects, favours the diffusion of oxygen in the perovskite matrix and prevents the formation of insulating barriers. The high insulating resistances observed for Ti/Sr < 1 confirm the role of the "SrO" intergrowth defects in the diffusion process.

The introduction of bismuth in the presence of "$La_{2/3}TiO_{3-\varepsilon}$" should improve the dielectric properties of the ceramic. However, in the case of multilayer capacitor applications, the bismuth oxide cannot be added after sintering, but must be added with the lithium salts before the sintering step under reducing atmosphere. It follows that Bi_2O_3 will be partially reduced and volatilized, contrary to the technology usually used in the classical Type III capacitors. Thus an excess of Bi_2O_3 is necessary. The following experiment was carried out: 3 mol % Bi_2O_3 and 10 mol % $LiNO_3$ were added to the calcined mixed powder corresponding to the nominal composition $SrTiO_3$ + 0.75 mol % $La_{2/3}TiO_{3-\varepsilon}$ and the sintering cycle was identical to that described above. The properties of the ceramic obtained are quite promising. The ceramic is well sintered, with an ε value of 20 000 and dielectric losses smaller than 2% (Fig. 6). The insulating resistance $R_i = 10^{11}\ \Omega$ cm confirms the efficiency of bismuth in creating insulating barriers for this particular composition. This result is very important from the application point of view since it shows that Bi_2O_3 can be added before sintering in spite of the use of a reducing atmosphere and a high temperature (1100° C). The microstructure (Fig. 7) is far from perfect: the grain size is not yet homogeneous, but wide regions characterized by a correct diameter of the grains (< 10 µm) are observed. The role played by Bi_2O_3 exhibits some similarity with that observed for an excess of SrO, in that it allows insulating barriers to be formed. The similarity can be explained by the ability of bismuth to form with titanium Aurivillius phases [13–17] $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{2+}$, whose structure is built up from multiple perovskite layers separated by simple $(Bi_2O_2)^{2+}$ layers formed of corner- and edge-sharing BiO_4 pyramids as shown for $Bi_4Ti_3O_{12}$ (Fig. 8a), which corresponds to the member $n = 3$ and is thus characterized by triple perovskite layers. Thus it must be likely that extended defects "$(Bi_2O_2)^{2+}$" are formed in the perovskite matrix (Fig. 8b) by adding an excess of Bi_2O_3. Such defects might also mainly be located near the surface of the grains, forming an insulating barrier and slowing

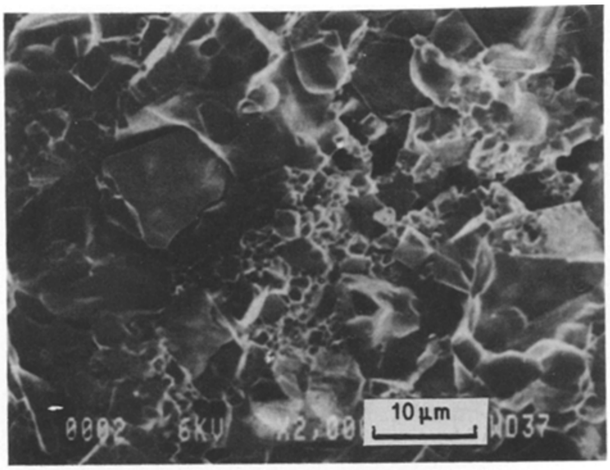

Figure 7 SEM micrograph of the sample "$SrTiO_3$(Ti/Sr = 1) + 0.75 mol % $La_{2/3}TiO_{3-\varepsilon}$ + $0.1LiNO_3$ + $0.03Bi_2O_3$".

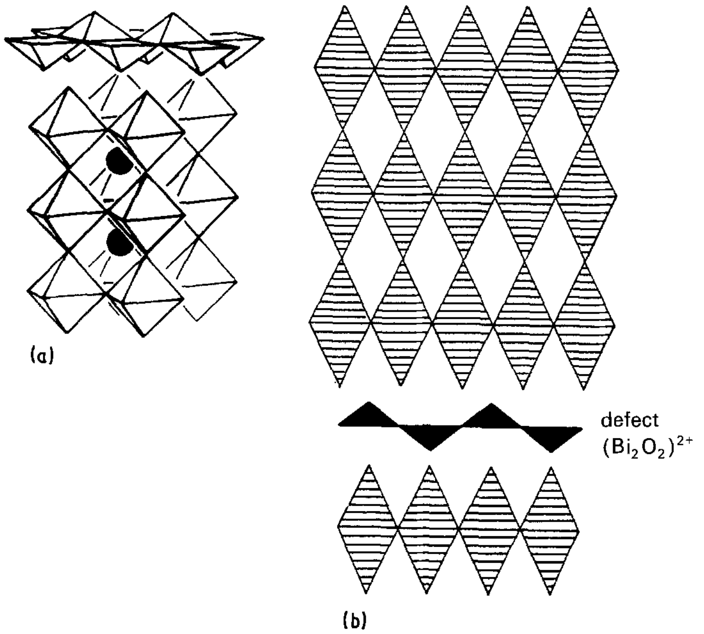

Figure 8 The Aurivillius $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ phases: (a) the third member $Bi_4Ti_3O_{12}$, (b) a $(Bi_2O_2)^{2+}$ sheet as a defect in a perovskite matrix.

down the diffusion of oxygen towards the centres of the grains. The Aurivillius phases $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2+}$ differ from the oxides $SrO(SrTiO_3)_n$ by their lamellar character. This latter property suggests that "$(Bi_2O_2)^{2+}$" defects will influence the grain growth in a different way from that observed for the "SrO" defects which are more closely linked to the perovskite framework and may induce strain effects.

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