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Sintering of $SrTiO_3$ in a reducing atmosphere in the presence of the perovskite "$SrLi_{1/4}Nb_{3/4}O_3$"

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The sintering of $SrTiO_3$ in a reducing atmosphere in the presence of perovskite $Sr(Li_{1/4}Nb_{3/4})O_3$ as a dopant and lithium salts ($LiNO_3$, Li_2CO_3 and LiF) as sintering agents has been studied. Three compositions, Ti/Sr = 1.0125, 1 or 0.975, were investigated. The latter two were shown to exhibit inhomogeneous microstructures, especially when sintering in the presence of $LiNO_3$ or Li_2CO_3. The dielectric properties of those materials were interpreted in terms of anionic defects and intergrowths. Different processing parameters were investigated such as the mixing grinding method and the grinding time; the influence of the heating rate and temperature sintering was also studied. The changes induced by each parameter on the dielectric properties and the microstructure were discussed. From these results it appears that the inhomogeneous character of the microstructure could be due to the formation of a liquid phase involving lithium. This study shows the possibility of synthesizing $SrTiO_3$-based type III ceramic capacitors following a suitable process with multilayer technology.

1. Introduction

The classical synthesis of $SrTiO_3$-based Type III dielectrics consists of a sintering at 1400° C in a reducing atmosphere followed by a partial reoxidation taking place at the grain boundaries in order to realize a microstructure built of semiconductive grains separated by an insulating layer. This process which leads to high dielectric constants, is in fact more complex: in order to obtain low dielectric losses and also a good insulating resistance–voltage behaviour a double "n–p type dopage" is necessary requiring a double step sintering. This complex sintering method does not allow the type III materials to be used in the multilayer technology. The presence of internal electrodes indeed prevents the diffusion of the secondary phase and the high sintering temperature leads to a potential reaction between the electrodes and the dielectric.

Recent papers [1, 2] have shown the possibility of lowering the sintering temperature of $SrTiO_3$ in air from 1400 to 1100° C, by using lithium salts. These latter results, and the possibility of sintering $SrTiO_3$ at low temperature in a reducing atmosphere [3, 4] suggests the possible compatibility of this type III dielectric with multilayer technology. The present paper thus deals with the study of the sintering of $SrTiO_3$-based type III material doped with perovskite $Sr(Li_{1/4}Nb_{3/4})O_3$.

2. Method

2.1. Choice of the dopant

Nb_2O_5 oxide is currently used as a dopant for the realization of type III dielectrics in order to introduce niobium as a donor on the octahedral sites of the perovskite [5]. The low reactivity of this oxide is not favourable for a sintering at low temperature. In this respect the perovskite $Sr(Li_{1/4}Nb_{3/4})O_3$ which is susceptible to form a solid solution with $SrTiO_3$ should favour the introduction of niobium on the titanium sites and therefore be an appropriate dopant. Moreover, the presence of lithium can effectively lower the sintering temperature as previously shown [1–4].

2.2. Synthesis and stability of $Sr(Li_{1/4}Nb_{3/4})O_3$

The perovskite $Sr(Li_{1/4}Nb_{3/4})O_3$ which was isolated for the first time by Hikichi *et al.* [6] was synthesized in the following way: the carbonates Li_2CO_3 and $SrCO_3$ and the oxide Nb_2O_5 were mixed in alcohol using an agate bowl. The mixture was then heated to 1000° C for 16 h, ground, and heated again up to 1000° C for 16 h. It is noticeable that an excess of lithium was necessary to obtain a pure perovskite from the X-ray powder pattern. This excess of lithium remains in the material even after the reaction; atomic absorption spectroscopy shows that 31 mol % Li remains instead of 25% corresponding to the theoretical formula. This additional lithium oxide which cannot be observed by X-ray diffraction, was considered to complete the role of sintering agent of the lithium salt.

$Sr(Li_{1/4}Nb_{3/4})O_3$ is stable up to 1400° C in air, temperature above which Li_2O evaporates leaving the oxide $Sr_5Nb_4O_{15}$. In a reducing atmosphere (N_2 + 10% H_2) a regular weight loss plotted from room temperature up to 730° C, does not coincide with the lithium excess; the X-ray diffraction patterns remain unchanged up to this temperature, i.e. characteristic of the perovskite phase. Beyond 730° C, no weight loss can be recorded but the phase turns grey and at 1350° C, a light purple colour is observed which indicates a slight departure of oxygen. The phase $Sr_5Nb_4O_{15}$ appears in the X-ray diffraction pattern beside the perovskite. At 1430° C, the perovskite has

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nearly disappeared, and is replaced by the oxide $Sr_5Nb_4O_{15}$.

In order to understand the reactivity between $Sr(Li_{1/4}Nb_{3/4})O_3$ and $SrTiO_3$, an equimolar mixture of those compounds was heated to 1350° C per 2 h under a hydrogen–nitrogen mixture (10% H_2). In these conditions, no complete solid solution was obtained, and no $Sr_5Nb_4O_{15}$ was formed. The X-ray powder patterns showed the beginning of a disorganization of the $Sr(Li_{1/4}Nb_{3/4})O_3$ network. For the further calcination conditions and for smaller amounts of dopant (0.67 mol %), $Sr(Li_{1/4}Nb_{3/4})O_3$ may enter into $SrTiO_3$ lattice in a solid solution form without any decomposition.

2.3. Calcination of strontium titanate in the presence of 0.67 mol% $Sr(Li_{1/4}Nb_{3/4})O_3$

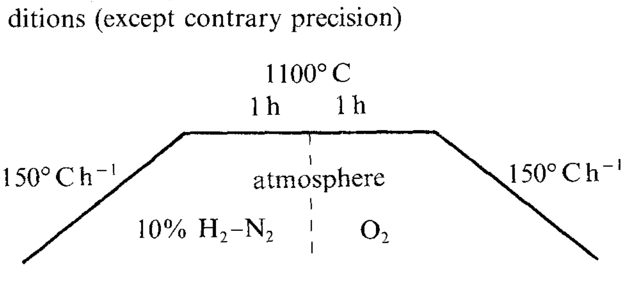
In order to understand the influence of stoichiometry on the nature of the calcinated products, three different strontium titanates were calcinated under a reducing atmosphere (N_2, H_2 10%) at 1350° C for 2 h, with 0.67 mol % $Sr(Li_{1/4}Nb_{3/4})O_3$ corresponding to a molar ratio of titanium to strontium of 1.0125, 1, and 0.975 respectively.

For Ti/Sr = 1 and 0.975, the grey colour of the calcinated powders suggests rather high anionic vacancies contents. The similar conductivities of both samples agree with the fact that an excess of SrO does not introduce additional electronic defects. This is confirmed by the X-ray diffraction patterns of the samples Sr/Ti = 0.975, which exhibit peaks characteristic of the intergrowth $SrO(SrTiO_3)_n$, showing that the SrO excess has been intercalated between the $SrTiO_3$ perovskite layers.

For Ti/Sr = 1.0125 a slight shrinkage of the sample and a darker grey colour of the powder are observed, which suggest a higher reactivity. The temperature must be lowered down to 1250° C in order to avoid the shrinkage. In this latter case, the light grey powder reveals a much lower density of anionic defects, and a poor conductivity compared to the sample Ti/Sr = 1 and 0.975. Thus it appears that a TiO_2 excess lowers the sintering temperature: the solubility limit of TiO_2 in $SrTiO_3$ is indeed overpassed for this molar ratio [7, 8] and shear structure Ti_nO_{2n-1} [9] are likely to form in agreement with the results obtained for the $SrTiO_3$-based materials doped with Nb_2O_5 for Ti/Sr = 1.004 and sintered in a reducing atmosphere [10, 11].

2.4. Sintering of the strontium titanate doped with $Sr(Li_{1/4}Nb_{3/4})O_3$

The three preceding calcinated samples were sintered at 1100° C using three sorts of sintering agents (10 mol % of lithium from $LiNO_3$, Li_2CO_3 and LiF) and according to the following experimental conditions (except contrary precision)



3. Results

For Ti/Sr = 0.975, we observe the following characteristics:

(i) the shrinkage reaches a mean value of 15%,

(ii) the microstructure (Fig. 1) are rather inhomogeneous for Li_2CO_3 with grain sizes ranging from 1 to 5 μm whereas an homogeneous distribution is observed for LiF,

(iii) the lithium content after sintering measured by atomic absorption is weak (smaller than 0.5%),

(iv) the dielectric constants are as low as 2000 at room temperature (Fig. 2), whereas the insulating resistances are close to $10^{12}\,\Omega$ cm under 50 V mm^{-1}, whatever the lithium salt may be.

For Ti/Sr = 1, shrinkage is very similar in the three cases, close to 16% and the lithium content after sintering is higher than for Ti/Sr = 0.975 (1.5%). The inhomogeneous character of the microstructures in the case of Li_2CO_3 and $LiNO_3$ and the homogeneous distribution of the grain size (about 10 μm) in the case of LiF are confirmed. The dielectric constants at 20° C are much higher than the previous ones: they are greater than 7500 (Fig. 3) at room temperature. High insulating resistance ($10^{11}\,\Omega$ cm under a d.c. bias field of 45 V mm^{-1}) are measured when sintering with LiF. On the other hand the values decrease to $10^9\,\Omega$ cm when sintering with Li_2CO_3 or $LiNO_3$.

For Ti/Sr = 1.0125, sintering of samples calcinated at 1350° C is inhibited by the shrinkage state resulting from calcination; less than 10% shrinkage is observed for instance with LiF. On the other hand the samples calcinated at 1250° C exhibit a good shrinkage (15.5% with LiF for instance). Nevertheless, even in these latter conditions the dielectric constants are low (smaller than 2000) due to the low conductivity of the grains which does not allow an actual type III-dielectric to be realized. The microstructures are very different from those observed for Ti/Sr = 1 or 0.975. The grain size cannot be determined from the fractures which seem to be intragranular.

4. Discussion

For Ti/Sr > 1, the Li^+ cations will tend to occupy the octahedral sites of the perovskite, forming additional anionic vacancies, according to the equation

$$Li^+ \rightarrow Li'''_{Ti} + 2V_O^{\cdot\cdot} \qquad (1)$$

The anionic vacancies will then be partially occupied by oxygen coming from Li_2O (for an addition of $LiNO_3$ or Li_2CO_3) or by fluorine (for an addition of LiF). Nevertheless the number of anionic vacancies increases by addition of "Li_2O" or "LiF" and favours the diffusion, i.e. the grain growth. This latter phenomenon is partly limited for the LiF sintering agent, due to the smaller number of anionic vacancies resulting from their occupancy by fluorine. The higher dielectric constants observed for the stoichiometric composition with $LiNO_3$ and Li_2CO_3, result mainly from the higher mean size of the conductive grains.

For Ti/Sr < 1, the SrO excess accommodated in the form of intergrowth defects $SrO\,(SrTiO_3)_n$ in the absence of lithium, will be in fact partially destroyed

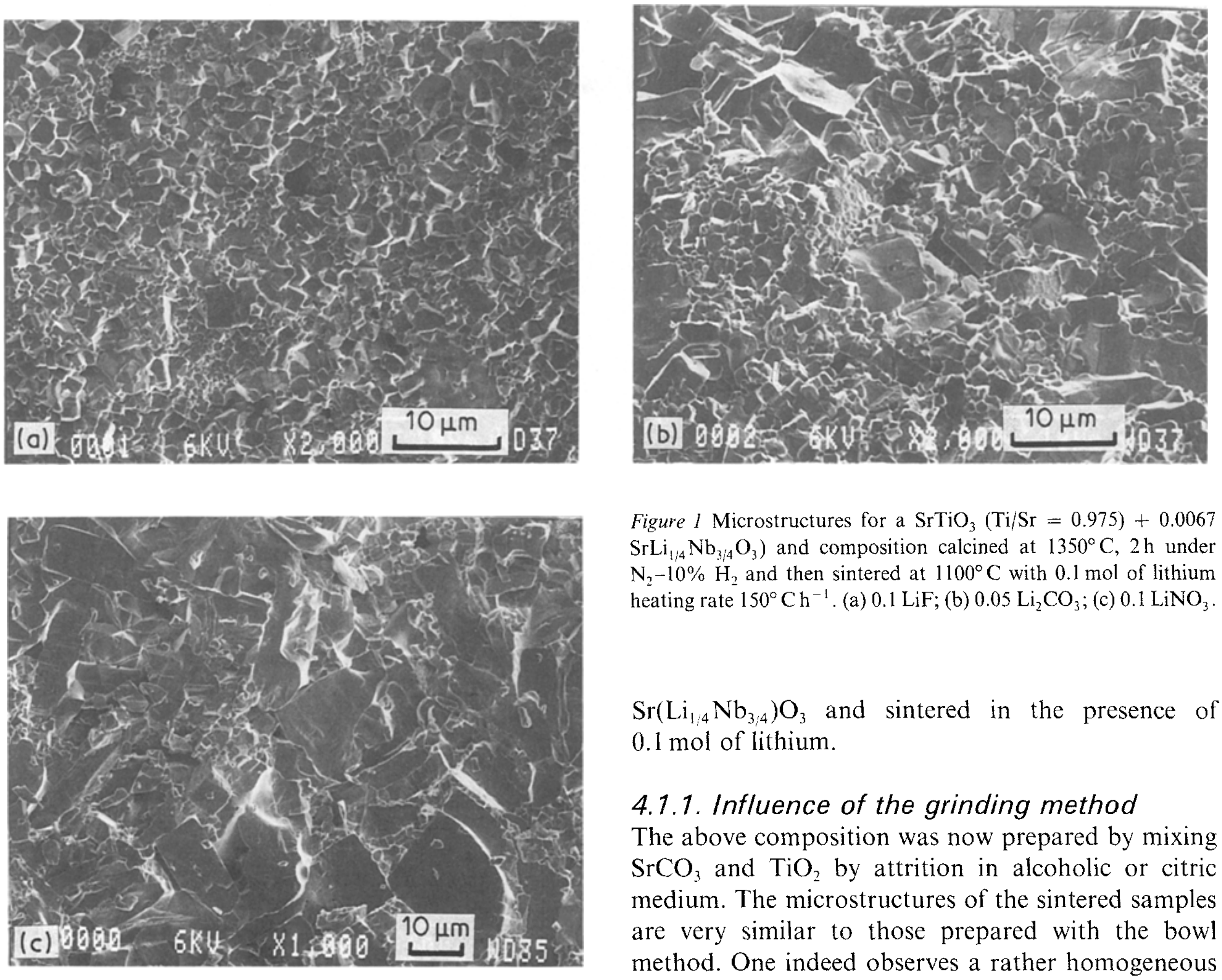


Figure 1 Microstructures for a $SrTiO_3$ (Ti/Sr = 0.975) + 0.0067 $SrLi_{1/4}Nb_{3/4}O_3$) and composition calcined at 1350° C, 2 h under N_2–10% H_2 and then sintered at 1100° C with 0.1 mol of lithium heating rate 150° C h^{-1}. (a) 0.1 LiF; (b) 0.05 Li_2CO_3; (c) 0.1 $LiNO_3$.

by addition of lithium salts according to the equations

$$LiF + \text{``SrO''} \rightarrow Sr_{Sr}^{X} + O_{O}^{X} + Li_{Ti}^{'''} + F_{O}^{\cdot} + 1V_{O}^{\cdot\cdot} \quad (2)$$

$$Li_2O + \text{``2SrO''} \rightarrow 2Sr_{Sr}^{X} + 3O_{O}^{X} + 2Li_{Ti}^{'''} + 3V_{O}^{\cdot\cdot} \quad (3)$$

Nevertheless, the presence of those intergrowths SrO-$(SrTiO_3)_n$ would slow down the grain growth and stabilize the role of lithium as shown by the microstructures observed for Ti/Sr = 0.975, which exhibit much smaller grain sizes.

The resistivity is also closely related to the stoichiometry. The highest resistivities are indeed obtained for Ti/Sr = 0.975 for all lithium salts ($R_i = 10^{12}\,\Omega$ cm) or for Ti/Sr = 1 in the presence of LiF ($R_i = 10^{11}\,\Omega$ cm). This property which corresponds to grain boundary phenomena, is easily explained by the tightly grain size distribution of those samples: a greater and more regular reoxidation of the surface of the grains is indeed more easily obtained for smaller grains.

4.1. Origin of the inhomogeneity

The preceding considerations do not explain completely the inhomogeneous character of the microstructures obtained with Li_2CO_3 and $LiNO_3$. In order to understand this phenomenon the influence of different parameters involved in the method of preparation was tested on the inhomogeneous composition $SrTiO_3$ Ti/Sr = 1 doped with 0.0067 mole of $Sr(Li_{1/4}Nb_{3/4})O_3$ and sintered in the presence of 0.1 mol of lithium.

4.1.1. Influence of the grinding method

The above composition was now prepared by mixing $SrCO_3$ and TiO_2 by attrition in alcoholic or citric medium. The microstructures of the sintered samples are very similar to those prepared with the bowl method. One indeed observes a rather homogeneous microstructure with LiF, whereas the grain size ranges from 1 to 50 μm with Li_2CO_3 or $LiNO_3$.

The dielectric characteristics are also similar. However, a better compromise microstructure–dielectric constant–insulating resistance can be obtained. An ε value of 11 000 can be reached for a grain size smaller than 15 μm with LiF, the mixture $SrCO_3$–TiO_2 being done in a citric medium before calcination. Moreover the insulating resistance of this ceramic remains greater than $10^{10}\,\Omega$ cm up to 80 V mm^{-1} (Fig. 4). This good behaviour under a d.c. bias field, without any secondary phase added at the grain boundary and without any post heating, after sintering is very promising: this characteristic is indeed close to the commercial limit (10 Ω cm under 100 V mm^{-1}).

4.1.2. Influence of the mixing–grinding time

In the previous samples prepared by using a bowl no inhomogeneity was detected by EDX analysis (in particular concerning the niobium distribution in the grains) but this cannot rule out a bad distribution of the different species.

The influence of the mixing–grinding time was thus tested by changing it from 30 min to 1 h, as the lithium salt was added in a bowl. An homogeneous distribution of the sintering agent and a decrease in the size of the agglomerates and aggregates sizes are then expected.

The dielectric constants for 1 h mixing are rather close to those observed for 30 min mixing but are generally smaller (Fig. 5).

The microstructures are more dependent on the

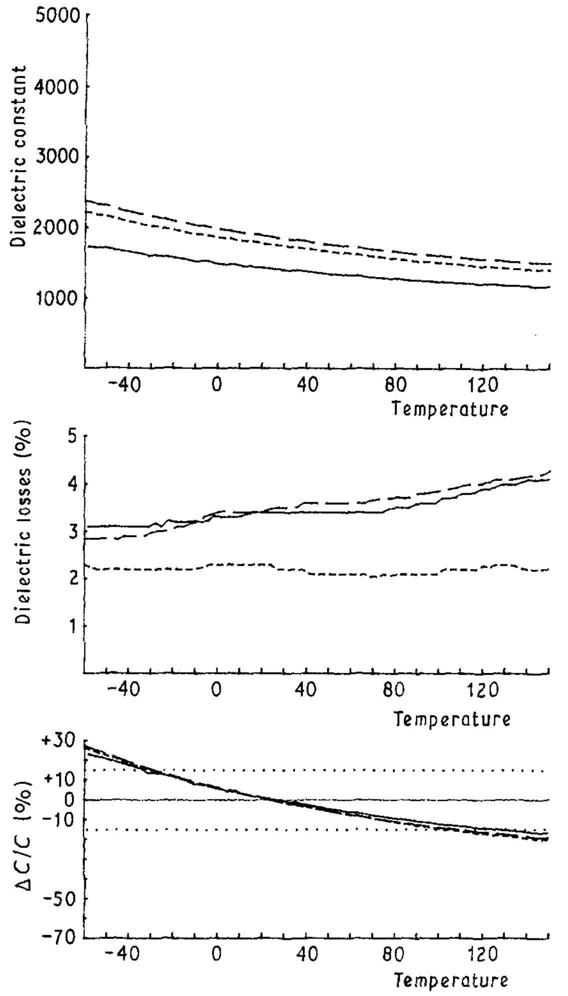


Figure 2 Dielectric characteristics for materials corresponding to Fig. 1. (Sintering agent: —— LiF, - - - Li_2CO_3, — — $LiNO_3$.)

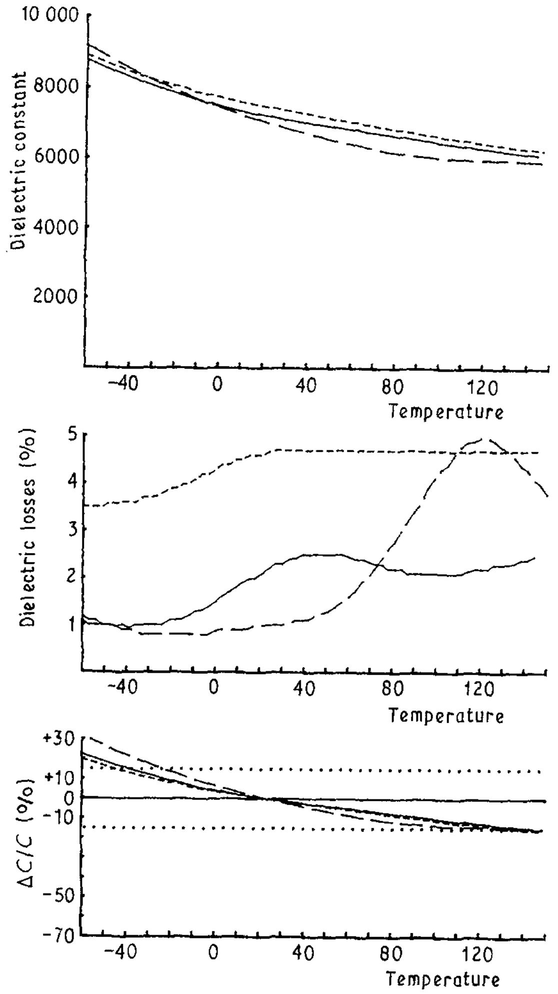


Figure 3 Dielectric characteristics for $SrTiO_3$ (Ti/Sr = 1) + 0.0067 $SrLi_{1/4}Nb_{3/4}O_3$ calcined at 1350° C, 2 h, under N_2–10% H_2 and then sintered at 1100° C with 0.1 mol of lithium heating rate $150°C\,h^{-1}$. (Sintering agent: —— LiF, - - - Li_2CO_3, — — $LiNO_3$.)

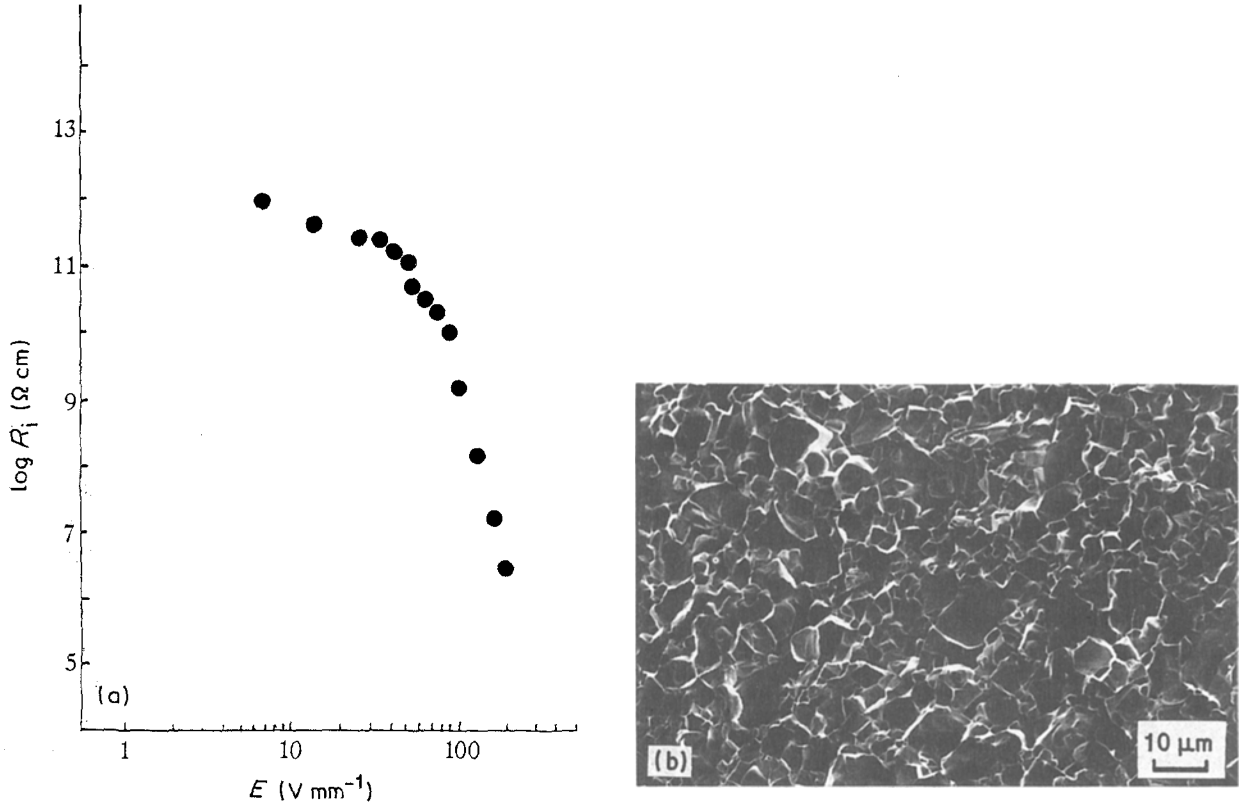


Figure 4 (a) Resistivity plotted against bias field for a $SrTiO_3$ (Ti/Sr = 1) + 0.0067 $SrLi_{1/4}Nb_{3/4}O_3$ calcined at 1350° C, 2 h, under N_2–10% H_2 and then sintered at 1100° C with 0.1 mol of LiF. (Attritor milling in citric acid medium.) (b) Microstructure of the material corresponding to Fig. 4a.

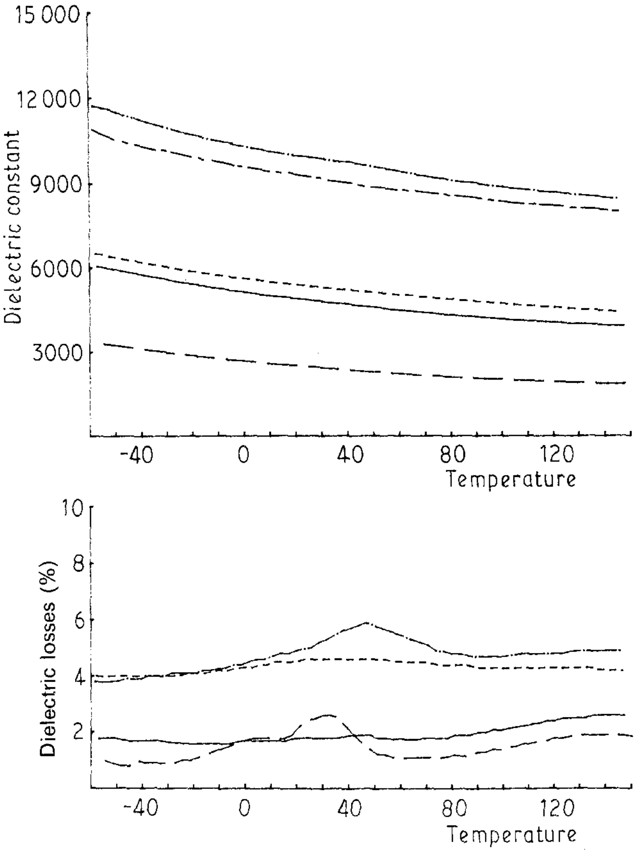


Figure 5 Dielectric characteristics for $SrTiO_3$ (Ti/Sr = 1) + 0.0067 $SrLi_{1/4}Nb_{3/4}O_3$ calcined at 1350° C, 2 h, under N_2–10% H_2 and then sintered at 1100° C with 0.1 mol of lithium. Heating rate 150° C h^{-1} (contrary to Fig. 4 the mixing-grinding time is 1 h when the lithium salt is added). (—— LiF (a), --- Li_2CO_3 (b), —·— $LiNO_3$ (b′), —— $LiNO_3$ (c), --- $LiNO_3$ (c′).)

mixing time. The LiF sample still exhibits an homogeneous microstructure but with larger grains (10 to 15 μm) and a more important residual porosity (Fig. 6a). The $LiNO_3$ and Li_2CO_3 samples still have inhomogeneous microstructure (Figs 6b and 6c) but with greater amounts of large grains. In the latter case the shrinkage values do not depend on the mixing time and remain close to 16% (Table I).

TABLE I ($SrTiO_3$ Ti/Sr = 1 + 0.0067 $SrLi_{1/4}Nb_{3/4}O_3$) calcined at 1350° C under N_2–10% H_2 and sintered at 1100° C with 0.1 mol of lithium influence of the mixing grinding time when adding the lithium salt

Sintering agent		Mixing grinding time	
		1 h	30 min
	ε_{20}	3500	7000
0.1	tan δ	< 3%	< 4%
LiF	R_i	10^{10}	5×10^{11}
	R	16.2%	16.5%
	ε_{20}	5750	8000
0.05	tan δ	< 8%	< 5%
Li_2CO_3	R_i	7×10^{11}	10^8
	R	16.3%	16.4%
	ε_{20}	5000	7500
0.1	tan δ	5%	< 5%
$LiNO_3$	R_i	7×10^{11}	10^9
	R	16%	15.5%

R_i = insulating resistance (Ω cm) measured under a d.c. bias field of 40 to 50 V mm^{-1}.
R = shrinkage.

Thus the variation of the mixing time does not change really the microstructure development; this suggests that the lithium distribution and the powder granulometry were already correct after 30 min mixing.

4.1.3. *Influence of the sintering parameters*

4.1.3.1. The sintering temperature. The sintering temperature was lowered from 1100 to 1000° C, the other parameters being unchanged in comparison with the preceding experiments. At this temperature a normal shrinkage is observed (greater than 15%) whatever the lithium salt may be. The microstructures are only

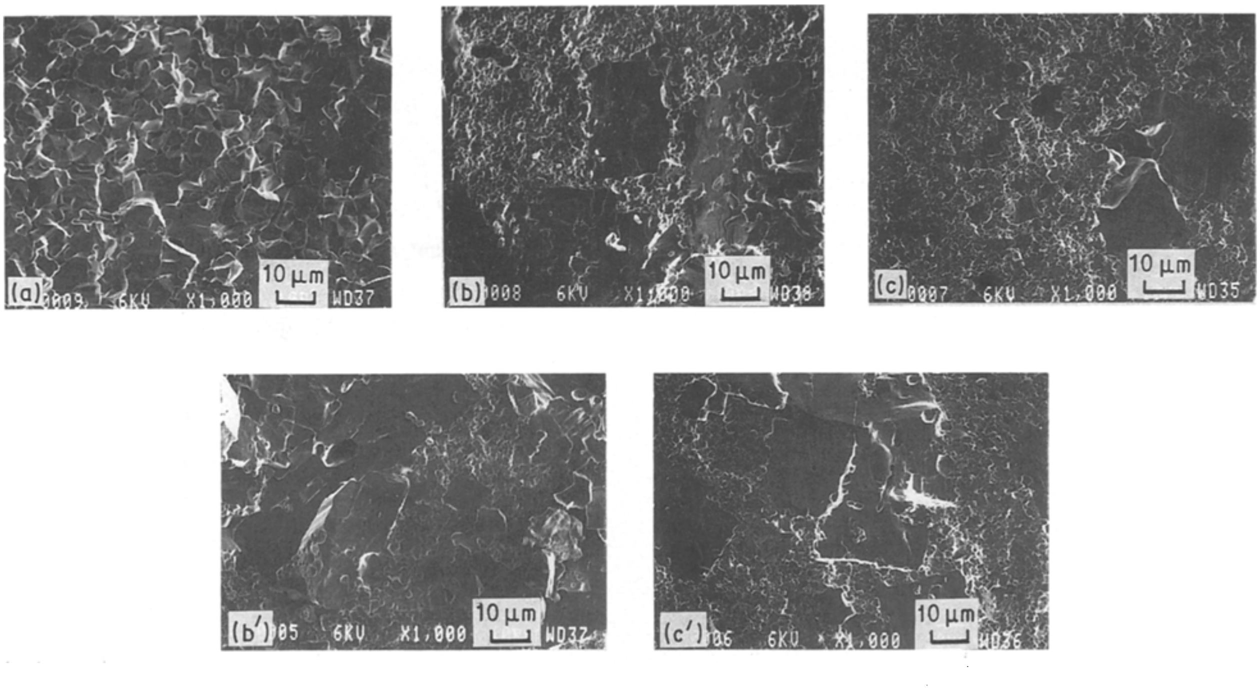


Figure 6 Microstructures corresponding to the materials characterized in Fig. 5. (a) 0.1 LiF; (b) (b′) 0.05 Li_2CO_3; (c) (c′) 0.1 $LiNO_3$.

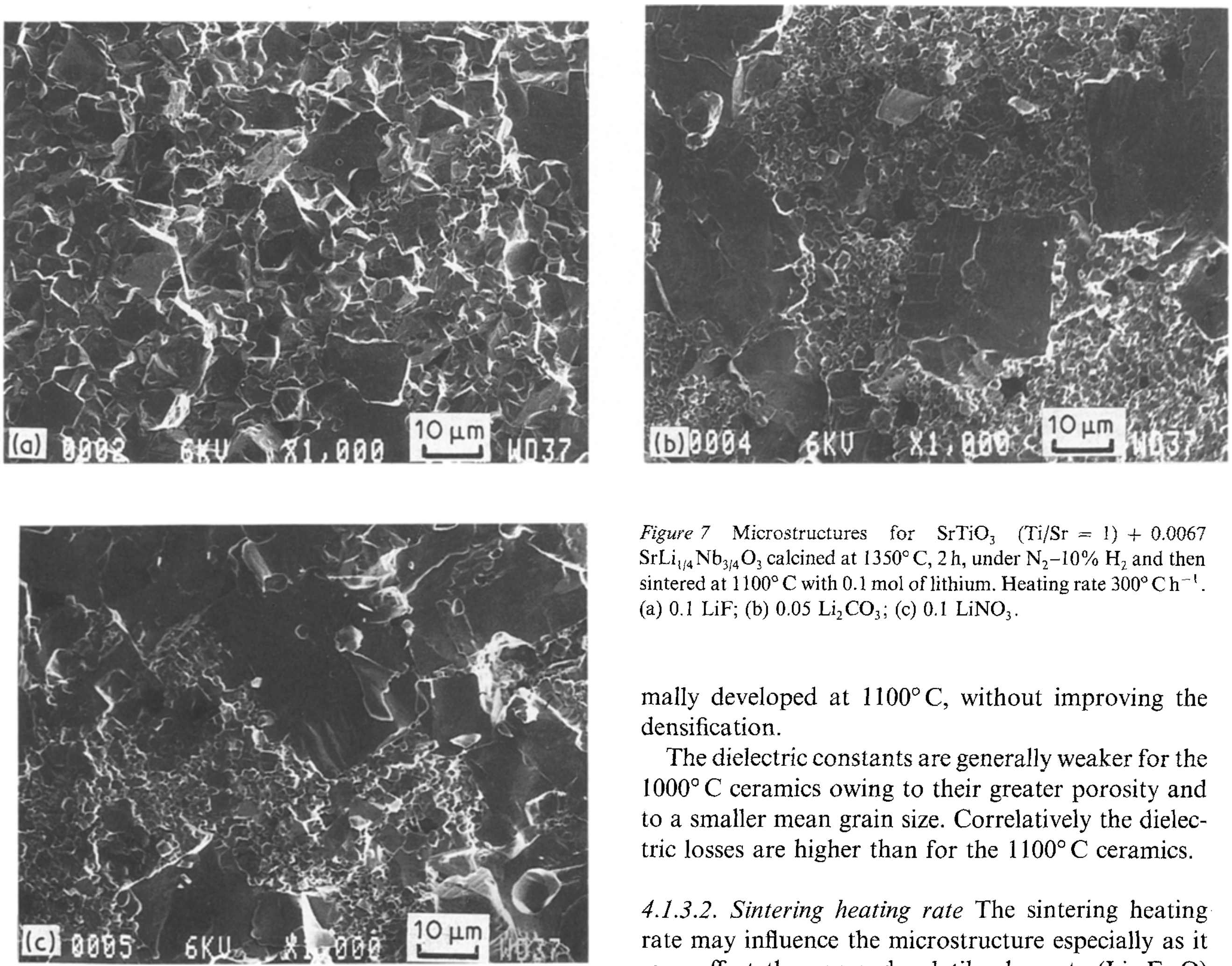


Figure 7 Microstructures for $SrTiO_3$ (Ti/Sr = 1) + 0.0067 $SrLi_{1/4}Nb_{3/4}O_3$ calcined at 1350° C, 2 h, under N_2–10% H_2 and then sintered at 1100° C with 0.1 mol of lithium. Heating rate 300° C h^{-1}. (a) 0.1 LiF; (b) 0.05 Li_2CO_3; (c) 0.1 $LiNO_3$.

slightly different. The LiF ceramic is very porous after sintering at 1000° C and the grains are smaller. The Li_2CO_3 and $LiNO_3$ samples have a microstructure similar to that obtained at 1100° C; numerous nuclei showing a discontinuous grain growth are already observed at 1000° C, which are then abnormally developed at 1100° C, without improving the densification.

The dielectric constants are generally weaker for the 1000° C ceramics owing to their greater porosity and to a smaller mean grain size. Correlatively the dielectric losses are higher than for the 1100° C ceramics.

4.1.3.2. Sintering heating rate The sintering heating rate may influence the microstructure especially as it may affect the gas and volatile elements (Li, F, O) departure.

We compare here the results obtained with a heating rate of 300° C h^{-1} instead of the classical one being 150° C h^{-1}, for a sintering temperature of 1100° C.

The microstructures of samples Li_2CO_3 and $LiNO_3$ do not change. The LiF ceramic has its microstructure more homogeneous for a 300° C h^{-1} rate than for a 150° C h^{-1} one, even if from time to time larger grains

TABLE II $SrTiO_3$ Ti/Sr = 1 (different mixing-grinding method) + 0.0067 $SrLi_{1/4}Nb_{3/4}O_3$ calcined at 1350° C under 10% H_2–N_2 and sintered at 1100° C with a lithium salt. Influence of the mixing grinding method of ($SrCO_3$ + TiO_2) and of the heating rate sintering (150° C h^{-1} or 300° C h^{-1})

Lithium salt		($SrCO_3$ + TiO_2) Mixing–grinding method				
		Shaker mill		Attritor C_2H_5OH medium		Attritor citric medium
		150° C h^{-1}	300° C h^{-1}	150° C h^{-1}	300° C h^{-1}	150° C h^{-1}
0.1 LiF	ε_{20}	7000	3000	9000	7250	8500
	tan δ	< 4%	< 2%	< 4%	⩽ 4%	< 3%
	R_i	5×10^{11}	5×10^{12}	5×10^{11}	5×10^{11}	4×10^{11}
	R	16.2%	17%	18.8%	18%	16.7%
0.1 $LiNO_3$	ε_{20}	7000		14250	5600	
	tan δ	< 5%		< 5%	< 8%	
	R_i	10^8		5×10^{10}	10^{11}	
	R	15.5%		18.4%	15.4%	
0.05 Li_2CO_3	ε_{20}	7000		10600	4350	
	tan δ	< 5%		< 4%	< 7%	
	R_i	10^9		10^{12}	3×10^{11}	
	R	15.5%		15.4%	17.2%	

R_i: insulating resistance (Ω cm) measured under a d.c. bias field of 40 to 50 V mm^{-1}.
R: shrinkage.

(20 to 25 μm) surrounded by 10 μm diameter grains are observed (Fig. 7). However, the dielectric constants are significantly weaker than for a 150° C h^{-1} heating rate (Table II).

4.1.3.3. Sintering agent: nature and content. The discontinuous grain growth observed could also result from a sintering in the presence of a liquid phase. Indeed, if the volume of this liquid phase is not large enough for a uniform distribution on the surface of all the grains, a segregation can then result and the concentration gradient of this phase may lead to an abnormal grain growth. Such a development is often observed for $BaTiO_3$ dielectric materials [12] especially in the presence of a TiO_2 excess.

In the present work, the lithium salts may introduce such a liquid phase. For this reason the influence of the lithium content (0.05 here instead of 0.1 mol per $SrTiO_3$ previously) added at LiF and as Li_2CO_3 separately, is studied. Finally three mixtures of LiF and Li_2CO_3 corresponding to a total lithium content of 0.1 mol per formula "$SrTiO_3$ Ti/Sr = 1 + 0.0067 $Sr(Li_{1/4}Nb_{3/4})O_3$ were also investigated.

All the other experimental conditions are identical to those described in Sections 2.3 and 2.4.

The microstructure of the 0.05 LiF ceramic is less homogeneous than that of 0.10 LiF ceramic: larger grains (15 μm) are actually distributed in a rather dense matrix, containing mainly very small grains (1 μm). For the 0.025 Li_2CO_3 ceramic, the microstructure inhomogeneity is more obvious than for LiF: large blocks (35 μm) are regularly distributed in the small grains matrix. The decrease of the lithium content is here accompanied by a decrease of the size (35 μm instead of 50 μm and more) and of the number of the large grains. LiF and Li_2CO_3 lead both to a mean grain size smaller for 5% Li than for 10% Li, corresponding to smaller dielectric constants.

These observations for Li_2CO_3 are in agreement with a sintering mechanism involving a liquid phase containing lithium: the number of potential nuclei and their development decrease as the volume of this liquid phase decreases.

The shrinkage measured for these low sintering agent contents (5% Li from Li_2CO_3 or LiF) is close to 18% and much greater than previously observed. A discontinuous grain growth, less important, and less developed may be at the origin of a better densification. Consequently, 5% mol of lithium are sufficient to ensure a complete densification of the ceramic but do not allow a good homogeneity to be achieved.

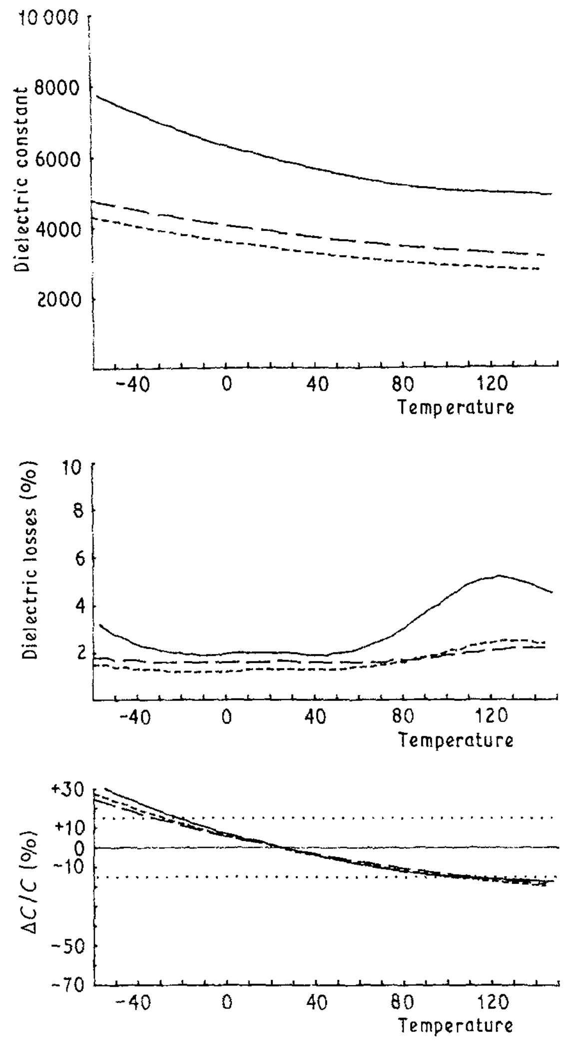


Figure 8 Dielectric characteristics for $SrTiO_3$ (Ti/Sr = 1) + 0.0067 $SrLi_{1/4}Nb_{3/4}O_3$ calcined at 1350° C, 2 h, under N_2–10% H_2 and then sintered at 1100° C (heating rate 150° C h^{-1}) with x LiF + y Li_2CO_3 as sintering agent: (—— $x = 0.075$, $y = 0.0125$; - - - $x = 0.050$, $y = 0.0250$; — — $x = 0.025$, $y = 0.0375$).

Among the three following LiF–Li_2CO_3 mixtures, (a) 0.075 LiF + 0.0125 Li_2CO_3; (b) 0.05 LiF + 0.025 Li_2CO_3; (c) 0.025 LiF + 0.0375 Li_2CO_3, the compositions (a) and (b) lead to similar microstructures characterized by small grains, with rare regions of abnormal grain growth, which number decreases with the Li_2CO_3 content. These blocks are absolutely isolated one from the other and characterize a long distance inhomogeneity. On the other hand the (c) composition leads to a short distance inhomogeneity with much shorter distances between by large grains (30 μm) and small grains (5 μm). These results are still in agreement with the hypothesis of liquid phase sintering. Unfortunately the dielectric constants (Table III, Fig. 8) are always smaller than for LiF or Li_2CO_3 alone.

TABLE III ($SrTiO_3$ Ti/Sr = 1 + 0.0067 $SrLi_{1/4}Nb_{3/4}O_3$) calcined at 1350° C under N_2–10% H_2 and sintered in the presence of various lithium compounds

Lithium salt	LiF	0.075 LiF + 0.0125 Li_2CO_3	0.05 LiF + 0.025 Li_2CO_3	0.025 LiF + 0.0375 Li_2CO_3	Li_2CO_3
ε_{20}	7000	5800	3800	4000	8000
tan δ	< 4%	< 6%	< 3%	< 3%	< 5%
R_i	5×10^{11}	8×10^{11}	5×10^{12}	6×10^{12}	10^8
R	16.5%	17.7%	18%	16.8%	15.5%

R_i: insulating resistance (Ω cm) measured under a d.c. bias field of 40 to 50 V mm^{-1}.
R: shrinkage.

5. Conclusion

This original doping of $SrTiO_3$ by $Sr(Li_{1/4}Nb_{3/4})O_3$ allows type III ceramics to be synthesized with interesting dielectric constants ($\varepsilon \sim 10\,000$), considering the small grain size especially in the presence of LiF as sintering agent ($10\,\mu m$ instead of $50\,\mu m$). Another quality of this material is its good behaviour under an electrical field, without any diffusion of an additional phase at the grain boundaries.

An application of such a material to multilayer technology may now be considered. The main problem deals with the inhomogeneity of the microstructure which is interpreted by the formation of a liquid phase during sintering.

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