

FORMATION AND PROPERTIES OF SOME Nb-DOPED SrTiO₃-BASED SOLID SOLUTIONS

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Abstract

It is well known that SrTiO₃ is one of the widely used materials in the electronic ceramic industry. Donor-type dopants are often added in order to improve the electrical properties of SrTiO₃-based ceramics.

In the present study, the formation and characteristics of undoped and Nb-doped SrTiO₃ were studied as a function of both the niobium dopant concentration and the Sr/Ti ratio (at the same Nb content). The formation mechanism of the mixed Sr(Ti,Nb)O₃ crystals was investigated by XRD and thermal analysis. The niobium solubility in the SrTiO₃ perovskite lattice was estimated by means of unit cell parameter data. The influence of Sr concentration on the microstructure of the ceramics obtained was investigated by SEM.

Ceramic properties pointed out the influence of the dopant concentration and stoichiometry on the sintering behavior of these materials.

Keywords: microstructure, Nb-doped SrTiO₃, solid solution, thermal analysis,

Introduction

Strontium titanate is one of the perovskite-structure materials widely used in electronic industry. Due to its high dielectric constant and excellent stability with temperature and applied voltage, strontium titanate ceramics has specific applications to electronic devices such as internal boundary layer (IBL) capacitors [1–3].

Donor-doping of SrTiO₃ essentially influences its electrical properties, both through changes in defect structure of the perovskite lattice as well as in microstructure of the obtained ceramics. Therefore, the electrical behaviour of a such material may be adjusted by the proper choice of the donor dopant and by its proper concentration into ceramics composition, taking into account the use of the ceramics.

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Besides the donor-doping, an important parameter acting in changing of the lattice defect structure and, as a consequence, of the electrical behaviour, is the cation stoichiometry of the material given by the cations ratio of the species taking part in the compound/solid solution formation [4].

The present study has been focused on the synthesis and the characteristics of some SrTiO₃-based ceramics with Nb as donor dopant and with deviation from stoichiometry for a constant proportion of Nb added.

Experimental

Samples with the compositions listed in Table 1 were prepared by classical ceramic method from high purity (>99.9 %) oxides and carbonates: TiO₂-rutil (Merck), Nb₂O₅ (Merck) and SrCO₃ (Fluka), by solid state reaction. The raw materials were weighted, homogenized by wet procedure in a planetary ball mill using ethanol as dispersing medium and then dried.

Table 1. Composition of the Sr(Ti,Nb)O₃-type investigated ceramics

Mixture	Composition
1	SrTiO ₃
2	SrTi _{0.998} Nb _{0.002} O ₃
a	SrTi _{0.995} Nb _{0.005} O ₃
3	Sr _{0.97} Ti _{0.995} Nb _{0.005} O ₃
b	Sr _{1.02} Ti _{0.995} Nb _{0.005} O ₃
c	
4	SrTi _{0.99} Nb _{0.01} O ₃
5	SrTi _{0.98} Nb _{0.02} O ₃
6	SrTi _{0.95} Nb _{0.05} O ₃
7	SrTi _{0.90} Nb _{0.10} O ₃

In order to study the changes which occur during thermal treatment, thermal analysis of raw materials as well of the mentioned mixtures was performed up to 1100°C using a STD 2960 simultaneous TG/DTA (TA Instruments) with a heating rate of 10°C/min. The mixtures were shaped by uniaxially pressing at 150 MPa into pellets of $\phi = 10$ mm and $h = 2-3$ mm and thermally treated in air, in temperature range 1000–1400°C with three-hour plateau.

The phase composition, as well as the phase formation of the compounds/solid solutions mentioned were studied by X-ray diffraction with a Bruker-AXS D8 Advance X-ray Diffractometer with Ni-filtered CuK_α radiation.

Microstructure and composition of the pellets was checked by scanning electron microscopy (SEM) using a JEOL JSM-6400 coupled with energy dispersion X-ray (EDX) microanalysis.

Results and discussions

Formation mechanism of SrTiO₃ and Sr(Ti,Nb)O₃-type solid solutions

- Thermal analysis of the raw materials points up specific effects only for SrCO₃, for which the DTA curve presents two endothermic peaks: the first one at 932°C, corresponding to orthorhombic hexagonal transformation and the second one at 1027°C, accompanied by a significant mass loss on the TG curve, due to the decomposition of SrCO₃.
- Thermal analysis performed for all the samples evidences:
 - for all the mixtures, DTA curves shows the thermal effects specific for SrCO₃, but weaker and shifted to lower temperatures. The shift of the decomposition temperature to lower values is characteristic for the carbonated systems in the presence of cations with acid character, such as Ti⁴⁺. The DTA/DTG results for SrCO₃ and two selected samples (1 and 5) are presented in Fig. 1.

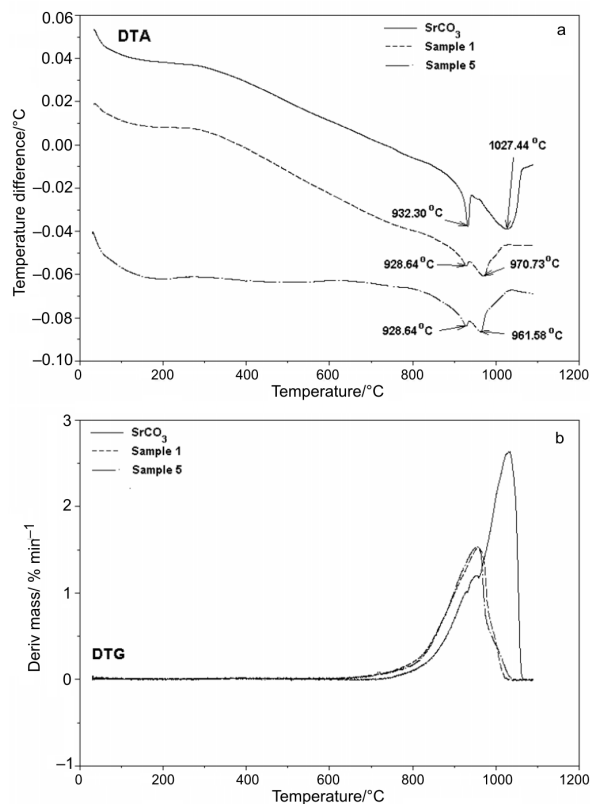
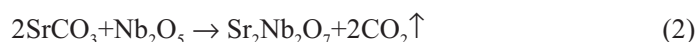


Fig 1. Thermal behaviour of SrCO₃ and samples 1 and 5.

– for the mixture 1, the second effect is, in fact, the result of two opposed effects (one can notice the presence of a shoulder both on the DTA and DTG curves) corresponding to two simultaneous processes: an endothermic decarbonation and an exothermic formation of Sr metatitanate, according to the reaction:



– in case of the mixtures containing Nb as a dopant, it seems that the two mentioned processes are accompanied by the formation of some Sr niobate-type second phase, too, according to the reaction:



The above mentioned facts are supported by X-ray diffraction data obtained for the mixtures thermally treated in dynamic conditions and lead to the conclusion that the SrTi_{1-x}Nb_xO₃-type solid solution formation does not take place by simple Nb⁵⁺ ions diffusion in the preformed SrTiO₃ lattice but by the solubilization of the Sr niobate (formed under 1000°C) into the perovskite lattice of SrTiO₃, according to the reaction:



The evolution of the phase composition at high temperatures observed by X-ray diffraction for the mixtures thermally treated in isothermal conditions is presented in Table 2.

Table 2. Phase composition of the analyzed mixtures

Mixtures	X	Sr/(Ti+Nb)	Phase composition			
			1000°C	1200°C	1400°C	
1	0	1	SrTiO ₃ ⁺⁺⁺	SrTiO ₃ ⁺⁺⁺⁺	SrTiO ₃ ⁺⁺⁺⁺	
2	0.002	1	SrTiO ₃ ss ⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺⁺	
a	0.005	1	SrTiO ₃ ss ⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺⁺	
3	b	0.005	0.97	SrTiO ₃ ss ⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺⁺
c	0.005	1.02	SrTiO ₃ ss ⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺⁺	
4	0.01	1	SrTiO ₃ ss ⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺⁺	
5	0.02	1	SrTiO ₃ ss ⁺⁺ , Sr ₂ Nb ₂ O ₇ t, Sr ₅ Nb ₄ O ₁₅ t	SrTiO ₃ ss ⁺⁺⁺ , Sr ₂ Nb ₂ O ₇ t	SrTiO ₃ ss ⁺⁺⁺⁺ , Sr ₂ Nb ₂ O ₇ t	
6	0.05	1	SrTiO ₃ ss ⁺⁺ , Sr ₂ Nb ₂ O ₇ ⁺ , Sr ₅ Nb ₄ O ₁₅ ⁺	SrTiO ₃ ss ⁺⁺⁺ , Sr ₂ Nb ₂ O ₇ t, Sr ₅ Nb ₄ O ₁₅ ⁺	SrTiO ₃ ss ⁺⁺⁺⁺ , Sr ₂ Nb ₂ O ₇ t	
7	0.1	1	SrTiO ₃ ss ⁺⁺ , Sr ₂ Nb ₂ O ₇ ⁺⁺ , Sr ₅ Nb ₄ O ₁₅ ⁺⁺⁺	SrTiO ₃ ss ⁺⁺⁺ , Sr ₂ Nb ₂ O ₇ ⁺ , Sr ₅ Nb ₄ O ₁₅ ⁺⁺	SrTiO ₃ ss ⁺⁺⁺⁺ , Sr ₂ Nb ₂ O ₇ ⁺ , Sr ₅ Nb ₄ O ₁₅ t	

t – traces; ⁺ - weak; ⁺⁺ - medium; ⁺⁺⁺ - strong; ⁺⁺⁺⁺ - very strong; ss - solid solution

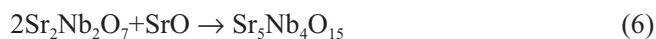
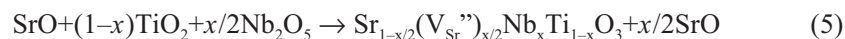
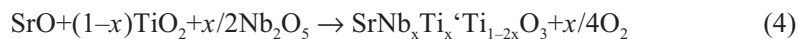
For the mixture 1, XRD data evidence, even at 1000°C, the presence of SrTiO₃ identified by all its main diffraction peaks. The increase of the temperature leads to more intense maxima because of the increase of the SrTiO₃ crystallinity degree.

For the compositions with reduced Nb concentration (< 2 at %) it is noticed that its solution into the perovskite lattice is total, so that no second phases are identified.

When Nb concentration exceeds 2 at%, two phenomena occur:

- the crystalline degree of the major phase consisting of SrTiO₃-type solid solution decreases, due to the increase of ionic defect concentration (cation vacancies in Ti sublattice) generated by the aliovalent substitution $5\text{Ti}^{4+} \rightarrow 4\text{Nb}^{5+}$, and
- Sr niobate-type second phases such as Sr₂Nb₂O₇ and Sr₅Nb₄O₁₅ appear.

The later compound may appear especially because of the structural accommodation of SrO excess generated as a consequence of the modification of the compensation mechanism. This mechanism changes to an ionic one, by cation vacancies (corresponding to compositions with higher amounts of donor element): from an electronic one (characteristic for lower amounts of donor dopant), according to the reaction:



Therefore, the higher the Nb concentration in the initial mixture, the higher the amount of the Sr₅Nb₄O₁₅ second phase exists in the obtained ceramics.

The increase of the thermal treatment temperature determines the enhancing of the crystallinity of the perovskite solid solutions, as well as the solubilization, in a large degree, of the niobate-type phase into the SrTiO₃ major phase structure. At 1400°C, Sr niobate-type phase is still clearly detected only in composition with maximum Nb concentration (10 at %). For the mixtures 3b and 3c, with deviation from stoichiometry (Sr excess or deficit) any changes in the phase composition have not been observed. Over a certain Nb concentration, SrO which results from the above mentioned process (Eq. 5); cannot be adjusted into SrTiO₃ lattice. In this case, SrO reacts with Sr₂Nb₂O₇ second phase generating a Sr-enriched niobate, Sr₅Nb₄O₁₅, as XRD data revealed.

The microstructure of the analyzed ceramics changes essentially, depending on both dopant concentration and deviation from Sr/(Ti+Nb)=1 stoichiometry deviation [5–7].

The SEM photographs for some selected compositions are presented in Fig. 2.

Undoped SrTiO₃ presents a relative homogeneous microstructure, made up from large grains of about 20–40 μm, lacks intergranular porosity but shows perfect triple grain junctions (Fig. 2a). The increase of the Nb concentration determines an important microstructural change consisting in a decrease of the grain dimensions, probably because of the inhibitor effect of the dopant. Thus, for the sample with x=0.01

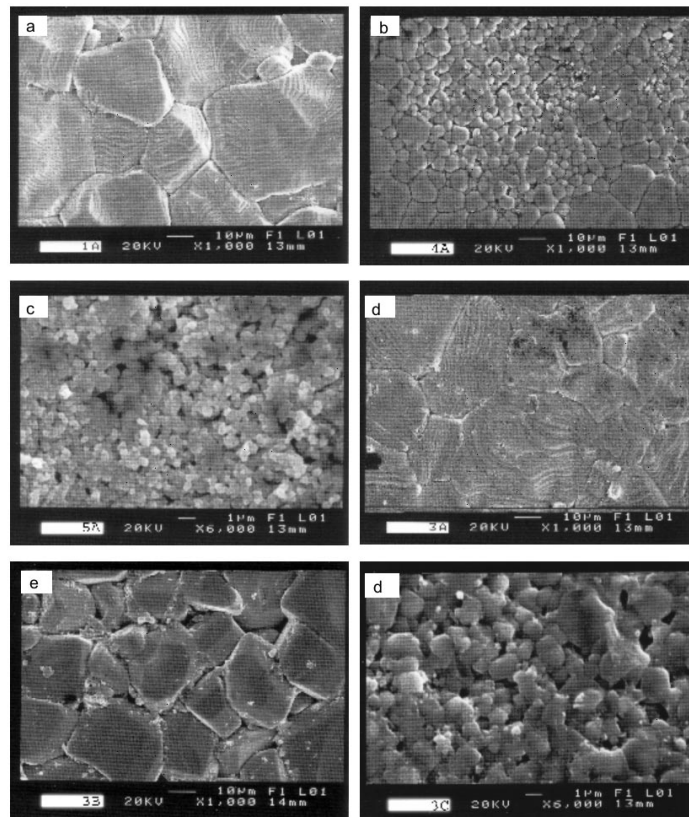


Fig 2. SEM photographs of some selected samples: a – sample 1; b – sample 4; c – sample 5; d – sample 3a; e – sample 3b and f – sample 3c.

(Fig. 2b), the microstructure is heterogeneous, large grains ($\sim 20 \mu\text{m}$) coexisting together with fine grains ($\sim 5 \mu\text{m}$).

The critical concentration at which the compensation mechanism of the Nb⁵⁺ donor charge modifies from electronic-type to ionic-type, is the composition with $x=0.02$ (Fig. 2c). That implies a microstructural change accompanied not only by the drastically grain size decrease ($<1 \mu\text{m}$), but also by the appearance of an important quantity of intergranular porosity. In comparison with the undoped sample and slightly Nb-doped samples, which exhibit a greyish-brown colour, the critical concentration sample is white and shows a low sinterability.

The influence of the stoichiometry deviation on the microstructure was studied for the mixtures with $x=0.005$. One can notice that, while Sr deficit does not essentially modify the grain dimension, generating only a disorder at intergranular boundaries, Sr excess modifies the microstructure in the same manner as the dopant concentration increase, that is the decrease of the grain dimension to $\sim 1 \mu\text{m}$ and the appearance of intergranular porosity (mixture 3c, Fig. 2f).

Table 3. Structural and sintering characteristics of the studied mixtures

Sample	X	Sr/(Ti+Nb)	$a/\text{\AA}$	$\rho_{\text{th}}/\text{g cm}^{-3}$	$\rho_r/\%$	
1	0	1	3.9106±0.0028	5.094	93	
2	0.002	1	3.9093±0.0017	5.101	98	
	a	0.005	1	3.9078±0.0007	5.111	89
3	b	0.005	0.97	3.9079±0.0002	5.037	91
	c	0.005	1.02	3.9078±0.0005	5.160	71
4	0.01	1	3.9085±0.0013	5.115	88	
5	0.02	1	3.9076±0.0015	5.131	71	
6	0.05	1	3.9083±0.0026	5.165	79	
7	0.1	1	3.9174±0.0024	5.192	83	

Structural data for the investigated mixtures are presented in Table 3.

One finds out that theoretical density increases with the Nb concentration increase because of the greater specific weight of Nb compared to that of the substituted Ti. The sinterability, expressed as relative density values, confirms the electron microscopy results.

The Nb concentration increase determines the decrease of the sinterability and ρ_r becomes minimal (71%) for the critical composition with $x=0.02$, at which the compensation mechanism of the donor charge changes due to the presence of the donor dopant amount. Over this value, the increase of the Nb content determines a slight increase of ρ_r .

Concerning the cation stoichiometry, one can notice that, while Sr deficit does not essentially modify the sinterability, on the contrary, Sr excess leads to a major decrease of ρ_r value (71%), because of the release of SrO, which in high quantity is difficult to be accommodate as a Ruddlesdon-Popper perovskite structure.

Conclusions

The formation mechanism of Nb-doped SrTiO₃-based solid solutions depends both on the Nb concentration and on the cation stoichiometry in the perovskite structure.

The mixtures with a Nb concentration lower than a critical value ($x<0.02$) exhibit an electronic-type compensation mechanism (by Ti⁴⁺ to Ti³ transitions), while the mixtures with a Nb concentration over the mentioned value, show a ionic-type compensation mechanism (by Sr vacancies) which contributes to the essential change of the microstructure, accompanied by a strong decrease of the sinterability. Sr excess determines the same effect.

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