

# Solubility of lanthanum in strontium titanate in oxygen-rich atmospheres

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Perovskite ( $ABO_3$ )-type lanthanum substituted strontium titanate ceramics (lanthanum content  $x$ ), which had been sintered in pure oxygen at  $1400^\circ\text{C}$ , were investigated from  $x = 0$  up to  $x = 0.6$  by light optical and scanning electron microscopic means in conjunction with X-ray analysis, X-ray diffraction, and pycnometry in order to determine the mechanism being responsible for the compensation of the electronic excess charge resulting from the "donor" lanthanum. A pure strontium vacancy compensation mechanism was observed for lanthanum contents up to  $x = 0.3$ . Above  $x = 0.4$  titanium vacancies occur additionally but their concentration remains negligible compared to the predominating strontium vacancies. No indication of a solubility limit of lanthanum at  $x = 0.4$ , as stated in former works was observed. At  $x = 0.5$  and  $0.6$  the lattice structure was found to be slightly distorted, tetragonally and orthorhombically, respectively. The lattice parameter obeys Vegard's law up to the end member  $\text{La}_{2/3}\square_{1/3}\text{TiO}_3$  ( $\square$ : vacant site). These results were completely confirmed by pycnometry data.

## 1. Introduction

Being used as powders for ceramic multilayer capacitors or multilayer actors,  $ABO_3$ -type titanates are the most important group of electronic ceramics. Technically employed titanates show a wide variety in the A-site and B-site composition, in doping content (acceptor-type and donor-type), and also in the A:B ratio. Due to its cubic structure strontium titanate ( $\text{SrTiO}_3$ ) is often regarded as a simple model substance [1]. The results of the investigations on this model substance can serve as a basis for the further development of ceramic electronic devices. Additionally, donor-doped  $\text{SrTiO}_3$  ceramics are used as resistive oxygen sensors for combustion control [2, 3], as well as for non-linear electronic devices (varistors) [4] or humidity sensors [5]. This paper deals with lanthanum (donor)-doped  $\text{SrTiO}_3$ . However, in contrast to most of the other studies [6–8] this report is concerned with lanthanum contents up to 60%.

$\text{La}^{3+}$  substitution of  $\text{Sr}^{2+}$  in  $\text{SrTiO}_3$  (SLT, lanthanum content  $x$ ) results in an excess charge, which has to be compensated. It is well known, that sintering in reducing atmospheres causes a change in the titanium valency from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  to ensure electroneutrality [8]. Since the  $\text{Ti}^{3+}$  concentration and the concentration of conduction electrons (charge carrier density)  $n$  are equal, this compensation mechanism is also called electronic compensation [9], which leads to semiconducting ceramic samples. Recently, the existence of this mechanism could even be proven for lanthanum-doped samples up to  $x = 0.5$  by means

of chemical  $\text{Ti}^{3+}$  titrations along with conductivity, thermopower, and Hall measurements [10, 11].

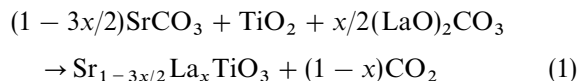
However, donor-doped  $\text{BaTiO}_3$  or  $\text{SrTiO}_3$  samples sintered in oxidizing atmospheres become electrically insulating. Therefore compensation by cation vacancies was proposed by several authors for small lanthanum doping levels. See Refs [9, 12–15] for  $\text{BaTiO}_3$  and Refs [6, 16] for  $\text{SrTiO}_3$ . For a long time it was unclear, whether A-site vacancies or B-site vacancies are the main compensating point defects. In the last few years it became apparent, that Ti vacancies predominate in donor-doped  $\text{BaTiO}_3$  [17, 18], whereas in  $\text{SrTiO}_3$  only strontium vacancies occur [6, 8]. Our own investigations at  $x = 0.1$  confirm this [19].

The behaviour of very high "doping" levels, which should better be considered as ternary systems of  $\text{BaO/SrO-La}_2\text{O}_3\text{-TiO}_2$  (B/SLT) is still under discussion. Recent detailed investigations of the BLT system [17] found a strong preference for titanium vacancies. Reports on the SLT system have existed for some time [20, 21], but the results are not consistent. The studies found strong indications for strontium vacancy compensation. However, Balachandran and Erer [21] reported on a solubility limitation level of  $x = 0.4$ , whereas the results of Tien and Hummel [20] clearly showed superstructure lines above  $x = 0.467$ . It is the aim of this study to examine the SLT system comprehensively, in order to clarify these points and in order to examine the compensation mechanisms as well as the solubility limits of the SLT system in oxygen at  $1400^\circ\text{C}$ .

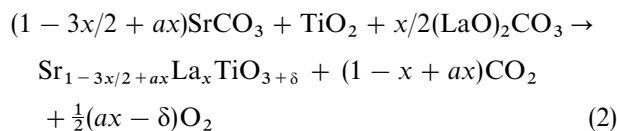
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## 2. Preparation and characterization

Ceramic powders were prepared by a conventional mixed oxide technique, starting with  $\text{SrCO}_3$ ,  $\text{TiO}_2$  (rutile), and  $(\text{LaO})_2\text{CO}_3$ . Since the previous studies, mentioned above, showed prevailing strontium vacancy compensation, a first series of SLT ceramics was prepared, according to Equation 1.



In the course of the investigations an additional amount  $a$  of strontium was added



$\delta$  denotes an oxygen excess and will be explained later. All powders were mixed, calcined in air at  $1250^\circ\text{C}$  for 15 h, reground, moulded, isostatically pressed, and sintered in oxygen at  $1400^\circ\text{C}$  for 10 h to very dense compacts of about  $5 \times 5 \times 15$  mm (see micrographs and Fig. 7). No additives to improve sintering had to be added. The density was measured in a helium pycnometer. Additional tests, using the buoyancy method in low-surface-tension water confirmed the results. After that the samples were sliced (thickness approximately  $750 \mu\text{m}$ ). One of the slices was polished for microscopy investigations (scanning electron microscope (SEM) and light optical microscope). Another slice was reground and its powder was analysed by X-ray diffraction (XRD; Siemens D500,  $\text{CuK}_\alpha$ ) at room temperature. For the determination of the lattice parameters  $\text{SiO}_2$  powder (JCPDS 33-1161) was added as an internal standard. A comprehensive description of both preparation and characterization can be found in Moos [19].

## 3. Results

In a first series samples with  $x = 0, 0.1, 0.2, 0.3$  and  $0.4$  were prepared according to Equation 1. Very dense ceramics, with a porosity below 1% could be achieved. Up to  $x = 0.3$  the polished sections do not show any second phases (Fig. 1,  $x = 0.3$ ). The colour of the compacts changed from light brown for undoped  $\text{SrTiO}_3$  to green ( $x = 0.1$ ), dark green ( $x = 0.3$ ), and black-green ( $x = 0.4$ ). All sliced specimens were translucent. Reaching a lanthanum level of 40%, second phases appear. The back scattered electron (BSE) micrograph in Fig. 2 shows distinct dark areas around and between the grains, which could be identified by energy dispersive X-ray analysis (EDX) to contain titanium only (oxygen could not be detected) and by XRD patterns of the pulverized sample to be  $\text{TiO}_2$  (rutile). The rounded shape of the grains in conjunction with the large grain size indicates a liquid phase sintering.

In order to obtain second phase-free samples with  $x = 0.4$ , a new strontium enriched powder series was prepared in accordance to Equation 2. The details are compiled in Table I and the results are shown in the corresponding Figs 3 and 4. Comparing Fig. 2 with Fig. 3 it becomes evident that it suffices to augment

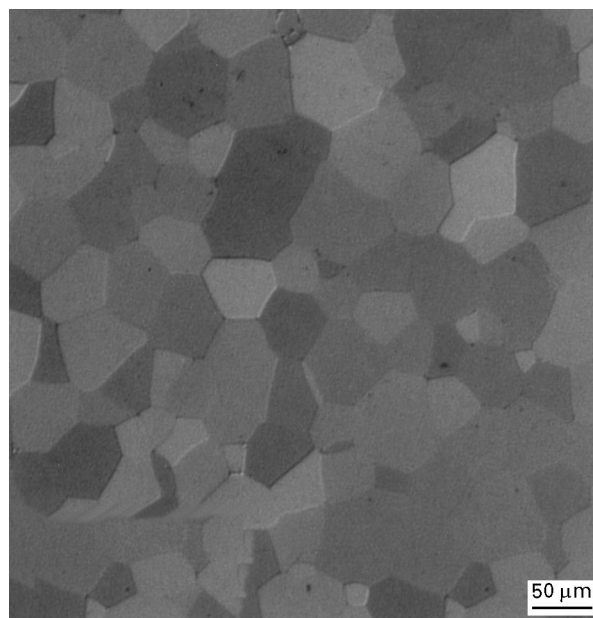


Figure 1 Polished section of a  $\text{Sr}_{0.55}\text{La}_{0.3}\text{TiO}_3$  sample. No second phases and only very few pores can be found.

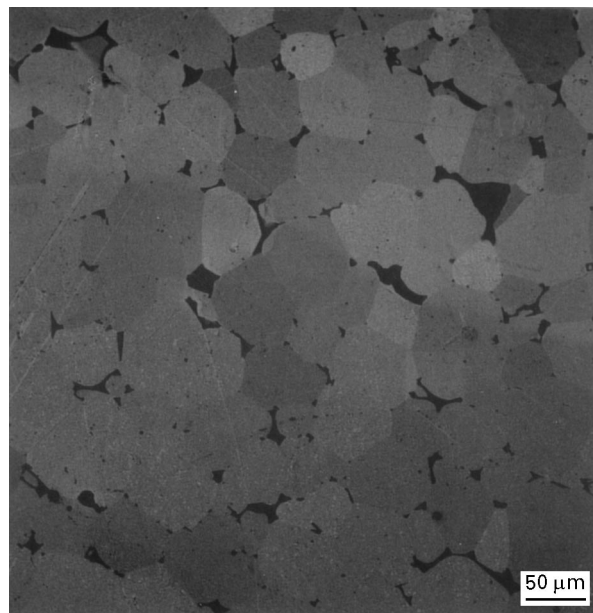


Figure 2 SEM-BSE picture of a  $\text{Sr}_{0.4}\text{La}_{0.4}\text{TiO}_3$  sample. The  $\text{TiO}_2$  second phases appear dark due to their lower atomic weight.

the strontium content by 1% only (from 0.4 to 0.404) to avoid second phases. A further increase in strontium diminishes the sintering activity enormously and leads to an increasing porosity. Fig. 4 illustrates this behaviour clearly.

Investigations for  $x = 0.5$  and  $0.6$  came to similar results. The single phase compositions are  $\text{Sr}_{0.255}\text{La}_{0.5}\text{TiO}_{3+\delta}$  and  $\text{Sr}_{0.126}\text{La}_{0.6}\text{TiO}_{3+\delta}$ , respectively. In contrast to the  $x = 0.4$  compositions, ceramics with 50 or 60% lanthanum containing not enough strontium to be second phase-free, show needle-shaped pyrochlore-type  $\text{La}_2\text{Ti}_2\text{O}_7$  second phases, instead of rutile liquid phases. Again, all samples were electrically insulating ( $\rho > 10^8 \Omega \text{cm}$ ). Even samples with  $x = 0.6$  show a small translucent behaviour.

In the XRD-patterns (Fig. 5) of the reground second phase-free specimens superstructure lines appear

TABLE I Strontium enrichment at constant lanthanum content  $x = 0.4$

Composition	$\text{Sr}_{0.400}\text{La}_{0.4}\text{TiO}_3$	$\text{Sr}_{0.404}\text{La}_{0.4}\text{TiO}_{3+\delta}$	$\text{Sr}_{0.410}\text{La}_{0.4}\text{TiO}_{3+\delta}$	$\text{Sr}_{0.440}\text{La}_{0.4}\text{TiO}_{3+\delta}$	$\text{Sr}_{0.600}\text{La}_{0.4}\text{TiO}_{3+\delta}$
Strontium enrichment $ax$	0	0.004	0.010	0.040	0.200
Relation $\text{Ti}/(\text{Sr} + \text{La})$	1.250	1.244	1.235	1.190	1.000
Sintering behaviour	Liquid phased	Porosity < 1%	No open porosity	Porous	Very porous
Observed second phases	Rutile	–	–	–	–

Sintering conditions: 1400 °C, 10h, O<sub>2</sub>.

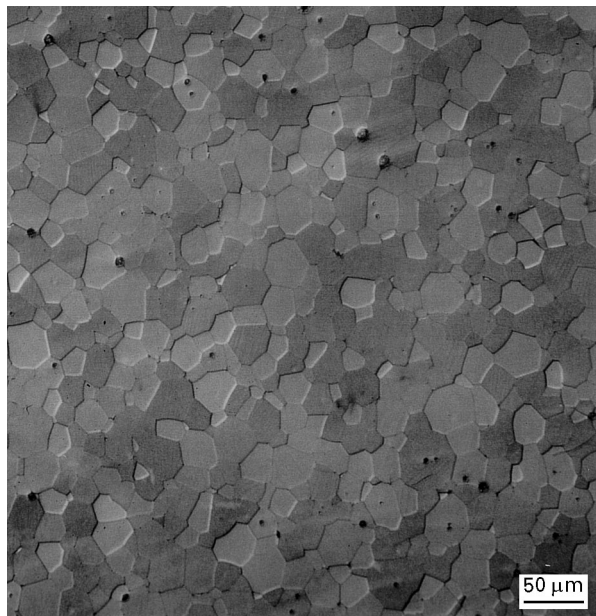


Figure 3 Polished section of a single phased sample with the strontium-enriched composition  $\text{Sr}_{0.404}\text{La}_{0.4}\text{TiO}_{3+\delta}$ .

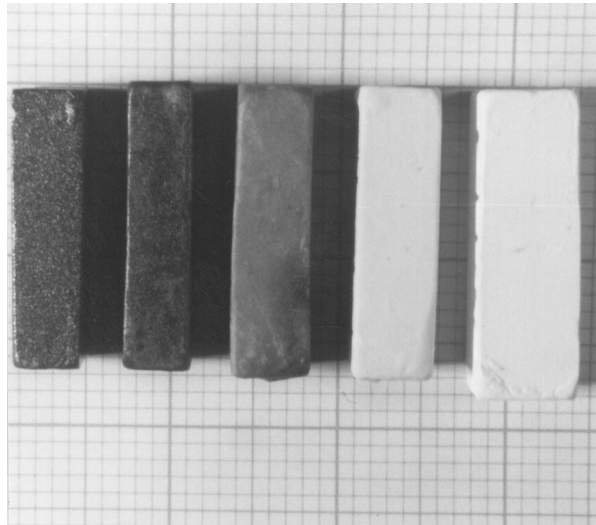


Figure 4 Photography of  $x = 0.4$  samples with different strontium contents sintered under the same conditions: 1400 °C, 10 h, O<sub>2</sub>. Left-hand side:  $\text{Sr}_{0.4}\text{La}_{0.4}\text{TiO}_3$ . Right-hand side:  $\text{Sr}_{0.6}\text{La}_{0.4}\text{TiO}_{3+\delta}$ . This figure coincides with Table I.

for  $x \geq 0.5$ . Their intensity rises with the lanthanum content. The most noticeable line at  $2\theta \approx 11.3^\circ$  fits well with the double cell edge of  $2 \times 0.39 \text{ nm} = 0.78 \text{ nm}$ . All superstructure lines are congruent with those of  $\text{La}_{2/3}\square_{1/3}\text{TiO}_3$  (“ $\square$ ” denotes a vacant site), synthesized and described firstly by Abe and Uchino [22]. A more detailed analysis of the peaks indicate of

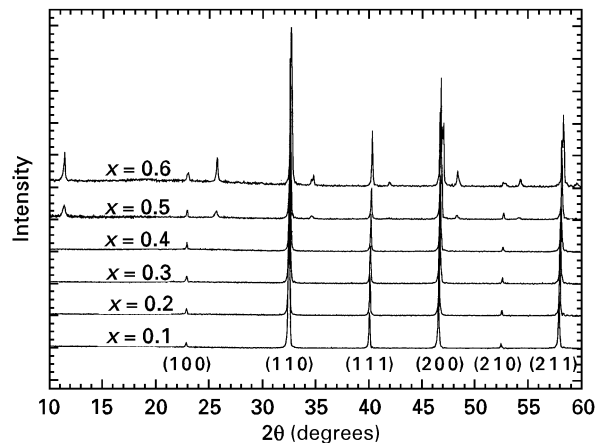


Figure 5 XRD pattern of single phased samples with different lanthanum contents. The  $(hkl)$  indices denote the lines of the cubic perovskite. Superstructure lines occur for  $x \geq 0.5$ .

a tetragonal distortion at  $x = 0.5$  and of a orthorhombic one at  $x = 0.6$ . Table II compiles the crystal data of the single phased compositions. The lattice constant  $d_{\text{lat}}$  in the cubic case or the effective lattice parameter,  $d_{\text{lat,eff}}$ , which is defined here as the cubic root of the simple perovskite cell volume ( $d_{\text{lat,eff}} = V_{\text{cell}}^{1/3}$ ), were calculated from the XRD patterns and plotted in Fig. 6. Error bars denote the measuring inaccuracy. The result can be described by the dotted regression line

$$d_{\text{lat,eff}} = 0.3905 \text{ nm} - 0.003825 \text{ nm} \times x \quad (3)$$

The meaning of the upper abscissa of Fig. 6 will be discussed later.

Fig. 7 shows the pycnometer density of the most dense sample of each lanthanum content. Again, error bars denote the measuring inaccuracy. The dotted line results from the calculation, respecting the molar weights in conjunction with the lattice parameter function (Equation 3). The bar on the lower right-hand corner illustrates the change of the density for a porosity of 1%.

## 4. Discussion

Density measurements as well as photomicrographs and XRD investigations confirm, that for lanthanum contents up to  $x = 0.3$  strontium vacancy compensation is the only existing compensation mechanism, if sintered in pure oxygen at 1400 °C. From  $x \geq 0.4$  on another additional charge compensation mechanism must occur, since this is the only possibility to explain the formation of titanium-rich second phases (see Fig. 2). The complete formula of the simple perovskite cell of the strontium enriched, second phase-free and

TABLE II Observed second phase-free compositions and their crystal structures at different lanthanum contents

Lanthanum content $x$	0 . . . 0.3	0.4	0.5	0.6
Single phased composition	$\text{Sr}_{1-3x/2}\text{La}_x\text{TiO}_{3+\delta}$	$\text{Sr}_{0.404}\text{La}_{0.4}\text{TiO}_{3+\delta}$	$\text{Sr}_{0.255}\text{La}_{0.5}\text{TiO}_{3+\delta}$	$\text{Sr}_{0.106}\text{La}_{0.6}\text{TiO}_{3+\delta}$
Crystal structure	Cubic	Cubic	Tetragonal	Orthorhombic
Superstructure lines	No	No	Yes	Yes
Lattice parameter (nm)	see Equation 3	0.38895	0.38855	0.38821

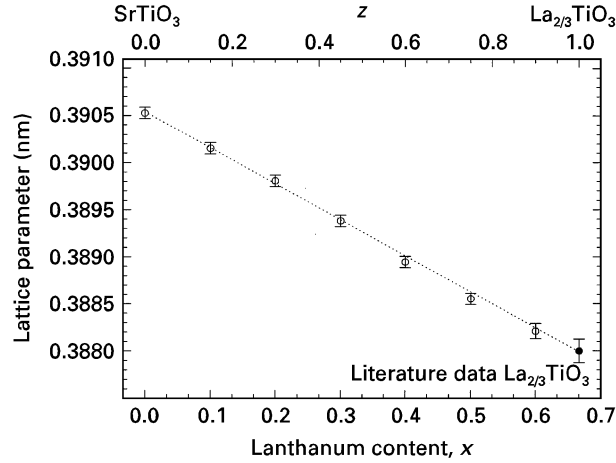


Figure 6 Effective lattice parameter versus lanthanum content of the single phased samples. On the lower right-hand side: data of  $\text{La}_{2/3}\text{TiO}_3$ , from Abe and Uchino [22]. For the upper abscissa see text.

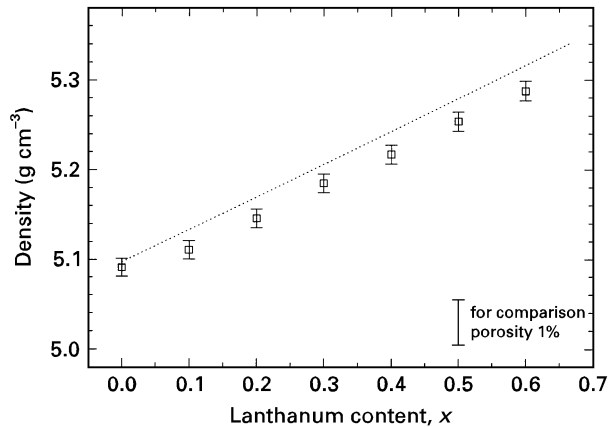
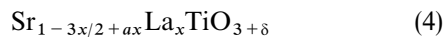


Figure 7 Calculated density and measured density of the most dense and single phased sample of each lanthanum content. The bar on the right hand side illustrates the change of the density for a porosity of 1%.

dense ceramics for  $x \geq 0.4$  can be written as

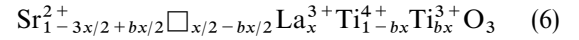
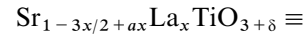


where  $ax$  denotes the additional strontium content compared to the pure strontium vacancy compensation.  $\delta$  stands for the oxygen excess, which depends on the compensation mechanism (pure cation vacancy compensation:  $\delta = ax$ ; pure electronic compensation:  $\delta = 0$ ). Table II shows, that for any lanthanum contents  $x \geq 0.4$ , a strontium enrichment of

$$a = 0.01 \quad (5)$$

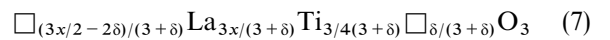
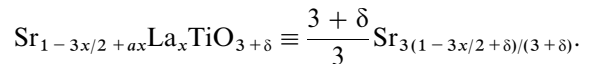
is enough to ensure the lack of second phases.

Assuming now, that a small fraction  $b$  of the lanthanum donors is compensated by electrons (i.e.  $bx$  titanium ions change their valence state from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ ). Then Equation 4 can be transformed to



with  $b = 2a$  and  $\delta = 0$ . If the lanthanum content is assumed to be  $x = 0.5$ ,  $bx = 1\%$  of all the titanium ions should be in the reduced state. In other words, a charge carrier density of approximately  $1.7 \times 10^{20} \text{ cm}^{-3}$  should be observed for samples with  $x = 0.5$ . Due to the electronic absorption, this would lead to black ceramics with a high conductivity. However, since the samples are translucent insulators, the idea of a partial electronic compensation seems to be not very plausible, in spite of in other donor-doped titanates, which have been sintered in air, e.g. in slightly donor-doped  $\text{BaTiO}_3$  (typical PTC ceramic) a partial electronic compensation has already been proven [23, 24].

Assuming now a small amount of titanium vacancies  $\delta/(3 + \delta)$  partly compensating the lanthanum donors. In this case the  $\text{Ti}^{4+}$  valence state remains stable and no electronic charge carriers occur. This coincides with the observed optical translucency and also with the electrical insulating behaviour. Then Equation 4 can be transformed into



with  $\delta = ax$ . Table III shows the calculated titanium vacancy content  $\delta/(3 + \delta)$ , as well as the fraction  $f$  of donors being compensated by titanium vacancies

$$f = 4 \times \frac{\delta}{3 + \delta} \times 1/\{3x/(3 + \delta)\} \times 100\% = \frac{4\delta}{3x} \times 100\% \quad (8)$$

With  $\delta = ax$ , the fraction  $f$  remains independent on the donor concentration  $f = 4a/3 \times 100\%$ . We are quite sure that this mechanism – compensation of the donor dope by a small fraction of titanium vacancies – is working in our materials.

It is astonishing how many strontium vacancies can be “incorporated” into the titanate lattice without a significant change of the compensation mechanism. According to Equation 7 for  $x = 0.5$  an A-site vacancy concentration of  $4.2 \times 10^{21} \text{ cm}^{-3}$  occurs. Then nearly one-fourth of all A-sites are unoccupied. Even at highest donor concentrations only a very low fraction

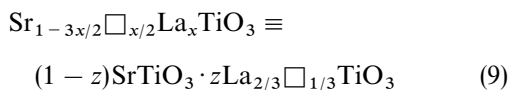
TABLE III Second phase-free compositions and calculated values with respect to the titanium vacancy compensation

Lanthanum content $x$	0 . . . 0.3	0.4	0.5	0.6
Single phased composition	$\text{Sr}_{1-3x/2}\text{La}_x\text{TiO}_3$	$\text{Sr}_{0.404}\text{La}_{0.4}\text{TiO}_{3.004}$	$\text{Sr}_{0.255}\text{La}_{0.5}\text{TiO}_{3.005}$	$\text{Sr}_{0.106}\text{La}_{0.6}\text{TiO}_{3.006}$
Additional strontium content $ax$	0	0.004	0.005	0.006
Titanium vacancy content $\delta/(3 + \delta)$	0	0.13%	0.17%	0.20%
Fraction $f$ of donors compensated by titanium vacancies	0%	1.33%	1.33%	1.33%

( $f = 1.33\%$ ) of the donors is compensated by acceptor-type titanium vacancies. Bearing in mind that each titanium vacancy compensates four donors, it becomes evident that the fraction of titanium vacancies has to be very small, although it increases with the lanthanum content to a maximum of 0.2% at  $x = 0.6$  (see Table III).

Reports on other titanates also show that A-site and B-site vacancy compensation may exist jointly. Hennings and co-workers [25–27] investigated the PLT and PLZT systems (P, lead; Z, zirconium) and defined a B-site elimination parameter,  $\alpha$ .  $\alpha$  can be derived from the strontium enrichment factor  $a$  of this paper by  $\alpha = 1.5 - a$ .  $\alpha = 1.5$  ( $a = 0$ ) denotes pure A-site vacancy compensation and  $\alpha = 0.75$  ( $a = 0.75$ ) stands for compensation by B-sites vacancies only. For high lanthanum contents ( $0.3 \leq x \leq 0.57$ ) these authors found pure A-site vacancy compensation. Below  $x = 0.3$ , either A-site vacancies only or A-site and B-site vacancies occurred in a variable relation ( $0.9 < \alpha < 1.5$ ), depending on the PbO partial pressure of the sintering atmosphere. Compared with the study of PLT, the value of  $a = 0.01$  ( $\alpha = 1.49$ ) found in this study for SLT corresponds to a nearly negligible titanium vacancy content.

In 1967 the region of A-site vacancy compensation had already been investigated on SLT by Tien and Hummel [20]. They considered SLT as a solid solution of  $z\text{La}_{2/3}\square_{1/3}\text{TiO}_3$  in  $\text{SrTiO}_3$



with  $z = 3x/2$ . In Fig. 6  $z$  is laid off as upper abscissa. They synthesized powders up to  $z = 0.94$  ( $x = 0.63$ ) and prepared dense samples up to  $z = 0.6$ . In the present study it was possible to prepare dense compacts of almost the complete system  $(1-z)\text{SrTiO}_3 \cdot z\text{La}_{2/3}\square_{1/3}\text{TiO}_3$  by means of a small strontium enrichment. Balachandran and Eror [21] reinvestigated the SLT system in 1982, using powders prepared by a liquid mix technique. They found a solubility limit of  $x = 0.4$ . Above  $x = 0.4$  they reported  $\text{La}_2\text{Ti}_2\text{O}_7$  second phases. Hence their XRD patterns did not show any superstructure lines. Between  $x = 0$  and  $x = 0.4$  the lattice parameters determined therein are in accordance with Tien and Hummel and agree with Fig. 6 and Equation 3. However, in strong contrast to Fig. 6, the limited solubility results in a lanthanum-independent lattice parameter. The lattice parameters determined in the present paper for  $x > 0.4$  agree with the results of Tien and Hummel, who could evaluate lattice parameters up to

$z = 0.8$  ( $x = 0.53$ ). Furthermore, the results of the present study extend as far as  $z = 0.9$  ( $x = 0.6$ ); Equation 3 can be explained by a straight line denoting Vegard's law up to the end member  $\text{La}_{2/3}\square_{1/3}\text{TiO}_3$ .

The question arises for what reasons the strongly strontium-enriched samples (see Fig. 4 and Table I) do not exhibit strontium-rich second phases. In the phase diagram solid solutions of  $\text{SrO} \cdot n\text{SrTiO}_3$ , the so-called Ruddlesden–Popper phases [28], exist. The existence of such phases in SLT has also been reported [6]. The lattice structure is characterized by a consecutive sequence of  $n$  cubic perovskite cells followed by one SrO layer. Next neighbouring  $n$  cubic cells are displaced by half a lattice constant. Such structures can be detected neither by SEM nor by light optical microscopy. XRD patterns are available for  $n \leq 3$  (JCPDS 22-1444). Patterns from samples with  $n \geq 4$  cannot be distinguished from pure  $\text{SrTiO}_3$  patterns. Therefore the XRD pattern of the even most strontium enriched sample  $\text{Sr}_{0.6}\text{La}_{0.4}\text{TiO}_{3.2}$  (rewritten as  $0.2\text{SrO} \cdot \text{Sr}_{0.4}\text{La}_{0.4}\text{TiO}_3$ , i.e.  $n = 5$ ) exhibits perovskite lines only.

## 5. Conclusion

The assumption that lanthanum donors in  $\text{SrTiO}_3$  are compensated by the formation of strontium vacancies (solely up to  $x = 0.3$  and mainly above  $x = 0.4$ ) is justified. Moreover a complete solution of the “donor” lanthanum in  $\text{SrTiO}_3$  was found. Due to the simple cubic lattice structure up to  $x = 0.4$  along with very small dependence of the lattice parameters on the lanthanum content and in conjunction with the stable valence state of the lanthanum ion the system lanthanum doped strontium titanate can be regarded as a true simple model system for the titanate ceramics.

As an outlook it would be interesting to study whether doping with non-ideal but technically employed donors (like  $\text{Nb}^{5+}$  occupying  $\text{Ti}^{4+}$ -sites) also leads to a compensation by strontium vacancies.

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