

# Highly Donor-doped $\text{La}_x\text{Ba}_{1-x}\text{TiO}_3$ Ceramics

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Sol-gel processing of  $\text{BaTiO}_3$  ceramics doped with La(0.01~1.00 at.%) were prepared from metal barium, titanium n-butoxide and lanthanum iso-propoxide. Characterization of the sol-gel-derived powder using XRD, SEM is also reported. The obtained results showed that insulator to semiconductor transition for highly donor-doped barium titanate was closely related to the incorporation of donor into the grains and to the resultant grain size, which were significantly affected by the sinterability of  $\text{BaTiO}_3$  powders and sintering conditions used.

*Keywords* : Sol-gel processing,  $\text{BaTiO}_3$  ceramics, Donor-doped, Barium titanate, Grain

## 1. INTRODUCTION

It is well known that  $\text{BaTiO}_3$  can be converted to an n-type semiconductor when it is doped with a small proportion (0.1~0.3 at.%) of trivalent or pentavalent cations, such as  $\text{La}^{3+}$ ,  $\text{Y}^{3+}$ , or  $\text{Nb}^{5+}$ , and that semiconducting barium titanate ceramics exhibit an anomalous increase in resistivity above the Curie point ( $T_c \sim 120^\circ\text{C}$ ) [1]. A number of workers have studied  $\text{BaTiO}_3$  in which small (up to 5 at.%) amounts of lanthanum have been added [2]. However in none of these cases has the study been made throughout the complete range of lanthanum substitution (x varies from 0 to 1). In addition no studies of the crystallography of these materials have been reported. Among the many methods of the preparation of fine-grained barium titanate or lanthanum titanate, the alkoxide method is known to give a stoichiometric precursor of the oxide [3,4]. Sol-gel processing of oxide powders has gained much interest because of its (1) simplicity, (2) low processing temperature, (3) chemical homogeneity. This is especially important for applications of the oxides as electronic devices (e.g. oxide capacitors or conducting oxides with positive temperature coefficients) [5-7]. Nevertheless, subtle variations of the preparation proved to give quite different properties of the final product. We chose a reaction between Ti, Ba and La alkoxides to

obtain  $\text{La}_x\text{Ba}_{1-x}\text{TiO}_3$  system, expecting better stoichiometric control by replacing the ion by La and/or Ba ions. The primary objective of this work is to determine the relation between crystallite size and phase at a given temperature as a function of the composition in the lanthanum-barium titanate system for a well-characterized  $\text{La}_x\text{Ba}_{1-x}\text{TiO}_3$  powder.

## 2. EXPERIMENTAL

### 2.1 Sample preparation

As a first step a fine particles sol was prepared by dissolving barium metal (Furuuchi Chemical Tokyo, Japan) in absolute butanol alcohol in a mixed solution with 2-methoxyethanol (2-MOE, Aldrich Chemical Co) and stoichiometric amount of titanium (IV) butoxide  $\text{Ti}(\text{n-OBu})_4$  (Tri-chemical, Yamanashi, Japan) refluxed at  $125^\circ\text{C}$  for 4 h under a dry argon atmosphere until the barium metal was completely dissolved. Then the solution was cooled to  $80^\circ\text{C}$ . The Ba-Ti complex alkoxide used as a starting material for the  $(100-x)\text{BaO}_x\text{TiO}_2$  compositions with  $\text{La}_2\text{O}_3$ . Lanthanum iso-propoxide was diluted with iso-propyl alcohol and added slowly to barium-titanium complex alkoxide. The mixture was stirred and refluxed at  $125^\circ\text{C}$  for 1 h. The handling of chemicals and procedures was conducted in a dry argon chamber. The resultant complex alkoxide

Table 1. BET Values (Surface Area) for La<sub>x</sub>Ba<sub>1-x</sub>TiO<sub>3</sub> powder.

Composition La <sub>x</sub> Ba <sub>1-x</sub> TiO <sub>3</sub>	Surface area (m <sup>2</sup> /g) of dried gel			Surface area of calcined powder
	Air dry	Vacuum dry	Freeze dry	
La <sub>0.1</sub> Ba <sub>0.9</sub> TiO <sub>3</sub>	136.4	151.9	154.6	59.9
La <sub>0.5</sub> Ba <sub>0.5</sub> TiO <sub>3</sub>	142.1	163.2	174.3	48.1
La <sub>0.9</sub> Ba <sub>0.1</sub> TiO <sub>3</sub>	129.6	131.7	144.2	46.4

with a designed composition was subjected to a hydrolysis-condensation reaction. The complex alkoxide was diluted in a closed vessel with anhydrous iso-propanol in a molar ratio to the alkoxide of 13. Subsequently, water diluted with anhydrous iso-propanol was slowly added dropwise with stirring in order to avoid the local formation of precipitates. The total amount of iso-propanol in the final solution was in a molar ratio to the alkoxide of 20. The molar ratio of added water to Ti in the alkoxide was 1.5. No base or acid catalyst was used. The homogeneous, transparent, and yellowish solution prepared above was transferred to a polypropylene beaker. The solution increased in viscosity as the hydrolysis-condensation reaction preceded, and set to gel after 5 h to 7 h depending on the alkoxide composition. Then gel dried at 100°C and heated from 200°C to 600°C at a rate of 10°C/min compared drying methods, such as air, vacuum, freeze drying to show the surface reactivity of synthesized powders (Table 1).

## 2.2 Phase transition measurement

Employing BET surface area measurement made the surface area determination, SEM, TEM and XRD line broadening effect. Single-phase formation of the powder was confirmed by XRD measurement. SEM was used to observe the morphology of the powders and the particle size. A few samples were observed by TEM and STEM to confirm that each primary particle was essentially a crystallite so that we could regard the calculated particle size from the BET measurement as the crystallite size.

## 3. RESULTS AND DISCUSSION

Table 1 shows that the specific surface area is dependent on drying method for the powders. Generally, the smaller the particle size, the greater is the specific area. You can see, that various drying procedures made no so much difference in the surface area. The X-ray data obtained from this study is found in Table 2. All data are recorded for single-phase samples. It has been found that La<sub>x</sub>Ba<sub>1-x</sub>TiO<sub>3</sub> is a simple cubic perovskite throughout most of its composition range. At both ends, x=0 and x=0.9~1.0 the system becomes non-cubic. At the end where x=0 there is the well-known compound

BaTiO<sub>3</sub> which is tetragonal at room temperature and cubic above 120°C. Apparently 5% or less La substitution is sufficient to decrease the transformation point to below room temperature [8]. It was found that "cubic" lattice parameter extrapolated to room temperature the thermal expansion data available for temperatures above 120°C.

Table 2. Compositions and their lattice parameters.

Nominal composition	Lattice parameter	wt.% Ti <sub>3+</sub> Calc.	wt.% Ti <sup>3+</sup> Found
BaTiO <sub>3</sub>		0	0.27
La <sub>0.02</sub> Ba <sub>0.98</sub> TiO <sub>3</sub>		0.41	0.90 ± 0.06
La <sub>0.05</sub> Ba <sub>0.95</sub> TiO <sub>3</sub>	3.997	1.03	1.31 ± 0.03
La <sub>0.1</sub> Ba <sub>0.9</sub> TiO <sub>3</sub>	3.990	2.05	2.06 ± 0.02
	3.989		2.08 ± 0.02
	3.978		2.18 ± 0.02
La <sub>0.25</sub> Ba <sub>0.75</sub> TiO <sub>3</sub>	3.968	5.13	4.78 ± 0.06
La <sub>0.5</sub> Ba <sub>0.5</sub> TiO <sub>3</sub>	3.968	10.2	8.9 ± 0.2
	3.958		8.0 ± 0.1
La <sub>0.75</sub> Ba <sub>0.25</sub> TiO <sub>3</sub>	3.960	15.3	13.9 ± 0.06
	3.957		13.6 ± 0.05
La <sub>0.85</sub> Ba <sub>0.15</sub> TiO <sub>3</sub>	3.957		
La <sub>0.9</sub> Ba <sub>0.1</sub> TiO <sub>3</sub>	3.958	17.4	12.6 ± 0.11
La <sub>0.75</sub> TiO <sub>3</sub>	3.923		
LaTiO <sub>3</sub>	3.895		14.6 ± 0.05

The symmetry of LaTiO<sub>3</sub> (where x=1) is no longer that of a simple cubic perovskite as evidenced by a number of additional lines on the X-ray pattern. These lines persist on samples that have been annealed and slowly cooled from 600°C, indicating that these lines are not characteristic of a high temperature phase [8]. The X-ray data for LaTiO<sub>3</sub> is quite easily indexed on the basis of a cubic perovskite cell, which is doubled along all axes. A preparation of La<sub>0.9</sub>Ba<sub>0.1</sub>TiO<sub>3</sub> has similar symmetry and almost an identical parameter indicating that the symmetry change occurs between x=0.85 and x=0.90. The resolution of lines in LaTiO<sub>3</sub> is not felt sufficient to discriminate between the orthorhombic a and b axes. It might be pointed out that orthorhombic

symmetry for  $\text{LaTiO}_3$  has been suggested by Roth [9] on the basis of ionic radii.

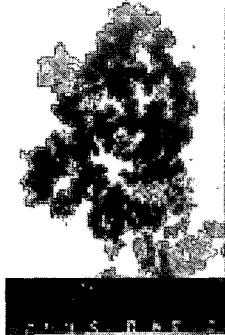


Fig. 1. TEM photograph of  $\text{BaTiO}_3$  dried at  $100^\circ\text{C}$ .

As shown in Fig.1, the  $\text{BaTiO}_3$  particle size was approximately  $0.08\text{--}0.10\ \mu\text{m}$  with a narrow size distribution. XRD analysis of this raw material indicated a cubic structure at room temperature. Chemical analysis of this alkoxy derived  $\text{BaTiO}_3$  indicated only very minor amounts of impurity.

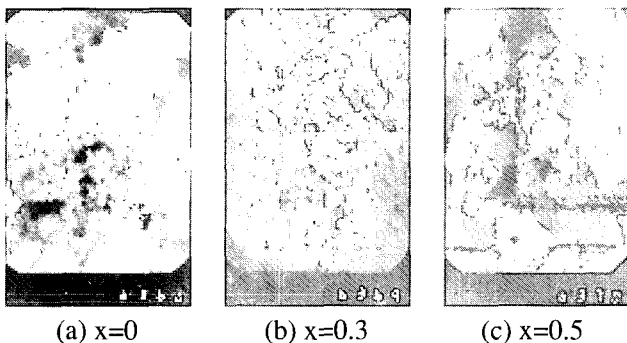


Fig. 2. SEM microstructure of  $\text{La}_x\text{Ba}_{1-x}\text{TiO}_3$ : calcined at  $600^\circ\text{C}$  for 2h after freeze drying.

Figure 2 shows the as-sintered microstructures of specimens having different La-doping contents. It was found, that powders prepared by air-drying had the strongest agglomerate and freeze-dried powders had the weakest agglomerates. A change of grain size with increasing doping content can be clearly observed. Of particular significance is the observation by Ward and Cotton [10] that  $\text{LaTiO}_3$  is the only instance in which perovskite has been made having La defects such that the value  $z$  is 0.25 and 0.2 in the formula  $\text{La}_{1-z}\text{Ti}_{1-3z}\text{Ti}_{3z}^{3+}\text{Ti}_{3z}^{4+}\text{O}_3$ . These samples gave very broad simple cubic perovskite X-ray lines and showed weak impurity lines. The perovskite lattice parameter increased linearly with the lanthanum content and reported a single phase region existing from  $\text{La}_{0.75}\text{TiO}_3$  to  $\text{LaTiO}_3$ . The increase in lattice parameter with  $\text{La}^{3+}$  is what would be expected

since  $\text{La}^{3+}$  is filling vacancies and small  $\text{Ti}^{4+}$  ions are being converted to larger  $\text{Ti}^{3+}$  ions. The composition  $\text{La}_{0.75}\text{TiO}_3$  had approximately the same lattice constant as for  $\text{LaTiO}_3$ , which might suggest the possibility that the products were to a certain extent La deficient. The X-ray patterns of these products are sharp single phase, essentially cubic (the 321 and 330, 411 lines are slightly split), and the lattice parameter is approximately equal to that of  $\text{La}_{0.75}\text{TiO}_3$  prepared by arc melting [9].

One of the most useful tools for examining the electrical properties of this system is the thermoelectric power measurement. The measurement is not highly sensitive to inevitable variations in sample density and the possibility of small amounts of surface oxidation. The thermoelectric power,  $\alpha$ , might be naively expected to be related to  $k/e \ln\{x/(x+1)\}$  resulting in high negative values of  $\alpha$  at low values of  $x$ ,  $\alpha=0$  at  $x=0.5$ , and high positive values of  $\alpha$  at high values of  $x$ . The experimental results are shown in Fig. 3.

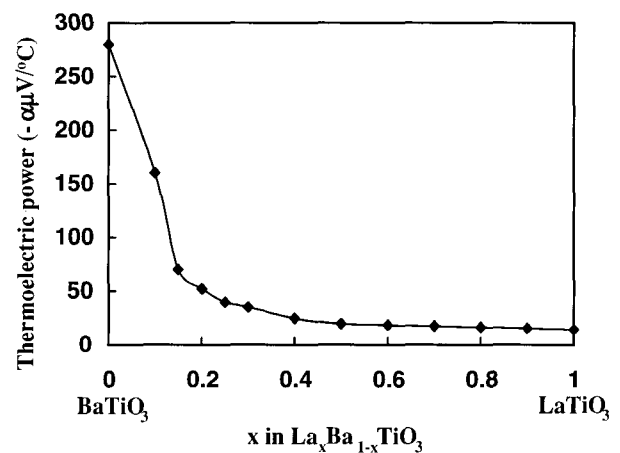


Fig. 3. Thermoelectric power vs. composition.

At small lanthanum contents the thermoelectric power is negative as a result of the formation of  $\text{Ti}^{3+}$ , which acts as an electronic conductor. The thermoelectric power also decreases with  $x$  as would be expected. Beyond the vicinity  $x=0.5$  the thermoelectric power does not change sign and does not increase to large positive values with  $x$ . Such experimental results are contrary to what would be expected if the material were to behave as a hole conductor on the basis of the presence of a relatively small amount of  $\text{Ti}^{4+}$  in a lattice made up of predominantly  $\text{Ti}^{3+}$ . Instead, the thermoelectric power remains as a low negative value suggesting that  $\text{LaTiO}_3$  and compositions nearby are metallic in their electrical behavior. This may be interpreted in terms of unpublished data of Mazelsky who studied a number of mixed valence perovskites. Mazelsky found almost without exception that when the transition metal of the

perovskite existed primarily in a very stable valence state (e.g.,  $\text{BaTi}^{4+}\text{O}_3$ ,  $\text{LaFe}^{3+}\text{O}_3$ ,  $\text{LaCr}^{3+}\text{O}_3$ ,  $\text{KNb}^{5+}\text{O}_3$ ) the material was an insulator and when doped became a normal semiconductor. However, when the transition metal existed in an unstable valence state (which are incidentally frequently hard to prepare) (e.g.,  $\text{LaTi}^{3+}\text{O}_3$ ,  $\text{LaMn}^{3+}\text{O}_3$ ,  $\text{SrNb}^{4+}\text{O}_3$ ) the materials exhibited either metallic behavior or rapidly went intrinsic. This is no doubt due to the ease of the thermally excited reaction of the unstable transition metal ion to the more stable valence state. (e.g.,  $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+} + e$ ). According to the formula  $\text{La}_x^{3+}\text{Ba}_{1-x}^{2+}\text{Ti}_{1-x}^{4+}\text{O}_3^{2-}$  these materials contain reduced titanium in proportion to the amount of lanthanum added. The instability of  $\text{Ti}^{3+}$  ion is the reason for prior investigations being limited to very low lanthanum additions and is what necessitates the precautions cited in the preparation procedure.

For example, when the graphite getter is omitted, samples become badly oxidized with the result that the  $\text{Ti}^{3+}$  content decreases. In the case of  $\text{La}_{0.1}\text{Ba}_{0.9}\text{TiO}_3$ , samples fired in the graphite protection tube have values of the thermoelectric power of  $-165 \mu\text{V}/^\circ\text{C}$  as can be seen on Fig. 3. If the graphite is omitted, the thermoelectric power rises to  $-470 \mu\text{V}/^\circ\text{C}$  since the number of charge carriers (which may be equated with  $\text{Ti}^{3+}$ ) are decreased. Even at room temperature oxidation is a problem. Finely powdered samples were observed to turn from pure black to gray color in a matter of days. Analytical chemical results support the oxidation in these cases. For sample the  $\text{Ti}^{3+}$  content of  $\text{La}_{0.1}\text{Ba}_{0.9}\text{Ti}_{0.1}^{3+}\text{Ti}_{0.9}^{4+}\text{O}_3$  changed from 2.24 to 1.54 percent on storage as a powder. Despite all precautions it will be noted from the tables that practically all samples appear to be somewhat oxidized according to the  $\text{Ti}^{3+}$  analysis. Further, the amount of spurious oxidation is more severe in the samples having the highest reduced titanium content. Oxidation of the sample as it is ground to a powder immediately prior to analysis, oxidation during storage and handling, and oxidation during the preparation probably all contribute to these results. In general, only  $\text{Ti}^{3+}$  was determined. By assuming a formula of the type  $\text{La}_{1-y}^{3+}\text{Ti}_{1-3y}^{3+}\text{Ti}_{3y}^{4+}\text{O}_3^{2-}$ , it is possible to calculate the value  $x$  on the basis of either  $\text{La}$  or  $\text{Ti}^{3+}$  content.

#### 4. CONCLUSION

In the present study, the incorporation of  $\text{La}$  in  $\text{BaTiO}_3$  has been studied with higher concentrations. The present method has shown the possibility of preparing submicrometer barium-lanthanum titanate system by simple sol-gel technique. The following conclusions can be drawn from this study:

(1) stoichiometric  $\text{LaTiO}_3$  is very probably orthorhombic; (2)  $\text{LaTiO}_3$  with lanthanum defects is very close to simple cubic perovskite with the lattice parameter increasing with the lanthanum content, the presence of additional phases possibly depending on the conditions of preparation, and (3) lanthanum may be lost in the course of  $\text{LaTiO}_3$  preparations in some unknown manner; (4) firing time is not a critical determination of particle size; through particles have a slight tendency to grow over longer holding periods.

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