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Pitfalls in the synthesis of nanoscaled perovskite type compounds. Part II: Influence of different sol-gel preparation methods and characterization of nanoscaled mixed crystals of the type $Ba_{1-x}Sr_xTiO_3$ ($0 \leqslant x \leqslant 1$)

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Abstract

The preparation of mixed crystals $Ba_{1-x}Sr_xTiO_3$ ($0 \leqslant x \leqslant 1$) by an acetate based sol-gel method was monitored by TG/DTA, TG–MS and XRD with respect to the reaction paths and the quality of the products. Depending on x, there is a more or less pronounced segregation of the alkaline earth compound leading at first to by-products richer in Ba than the perovskite phase itself. Chemical homogeneity will only be restored after prolonged heating at high temperatures where the primary crystallites of the ABX_3 compound will have left the nanoregime and new ones will be formed during the decomposition of the by-products giving a more bimodal size distribution. Due to such pitfalls the desired properties of the products and especially their physical characteristics important for use in electrical devices will not always be ensured. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In Part I of this paper series,[1] the synthesis of nanoscaled $BaTiO_3$ by different sol-gel methods has been described and a short survey of the applications was given. Solid solutions of $BaTiO_3$ with $SrTiO_3$ are also considered for applications such as delay lines, slow wave structures, optical modulators, etc.[2] They are therefore also topic of actual investigations. $SrTiO_3$ itself is also a good candidate for insulating buffer layers and for photocatalysts.[3]

A disadvantage for the dielectric use of $BaTO_3$ is the curie point at 120°C. To use the specific dielectric properties which exist at the curie-point for ferroelectric applications it would be necessary to keep such devices at this temperature. A substitution of Ba by Sr ions moves the Curie point to lower temperatures allowing an adjustment of the Curie point for individual applications.

The conventional synthesis of solid solutions of $BaTiO_3$ and $SrTiO_3$ is shaping and firing ceramic pellets from mixtures of powders of appropriate educts.[4] This method is circuitous and tends to give inhomogeneous samples. Sol-gel methods allow quite fast synthesis at low temperatures and more exact and homogenous mixing of the educts. The synthesis of nanoscaled powders with defined properties is feasible.[5–7]

In Part I of this series, we have evaluated several sol-gel procedures for the synthesis of nanoscaled $BaTiO_3$ and we have described the influence of the different routes on the properties of the nano-products. Of these the so-called acetate method has turned out to be least favorable because of the strong tendency for $BaCO_3$ formation during the process of thermal decomposition which inevitably also leads to the formation of Ti-rich ternary phases. The question arising is wether this will also be a drawback for the synthesis of the mixed crystal systems aimed at here. A second observation of importance for this work is the poor solubility of $Sr(OH)_2$ in

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solvent mixtures of isopropanol and acetic acid. For the synthesis of perovskites containing up to 30 at.% Sr it may still be used in the so-called hydroxide-methode, but for higher contents this educt is less suitable. The other methods explored are more costly and need preparation in absolutely inert atmospheres. They seem therefore less suitable for an industrial application. In view of these findings we have chosen a pure acetate-method only for the synthesis of $Ba_{1-x}Sr_xTiO_3$ mixed crystals in the whole range of $0 \leqslant x \leqslant 1$. In this paper we report on the reaction pathways during thermal decomposition of acetate-based gels as investigated by DTA/TG and TG–MS. X-ray measurements show the development of crystalline phases and provide data for the determination of cell parameters, crystallite distortions and mean sizes and their distribution. ICP-OES analysis was used for the control of the chemical composition.

2. Experimental

2.1. Sol-gel acetate method

About 17 g of an appropriate mixture of dry $Ba(OAc)_2$ and $Sr(OAc)_2$ was dissolved in 70 ml glacial acetic acid which was warmed up on a heating plate for complete dissolution. After cooling to room temperature this mixture was given into a prepared solution of stoichiometric amounts of titanium-isopropoxide in 70 ml isopropanol in a flask with inert gas atmosphere. After stirring for 1 h, the homogenous solution was activated by slow addition of 5 ml water followed by refluxing for 2 h. A slight increase of the temperature initiates the gelation. The clear gel was dried at 40°C and subsequently calcined for 2 h at different temperatures in a laboratory tube furnace to obtain $BaTiO_3$ powders.

2.2. Characterization methods

The DTA/TG and TG–MS measurements of the as prepared powders were performed on a STA 409 analyser (Netzsch, Germany). The precursors were put in quartz crucibles and heated in air at a rate of 5°C/min in the temperature range 20–1200°C. An empty quartz crucible was used as reference.

Powder X-ray diffraction measurements were performed at room temperature on a D 5000 diffractometer (Siemens, Germany) operating with CuK_{α_1} radiation. The lattice parameter, the average particle size, the size distribution and the lattice distortion were determined from the X-ray data using the program FormFit.[8]

The elemental analysis of the composition of the produced powders was performed by ICP-OES (Plasma 2000, Perkin-Elmer, Germany). About 0.3 g of powdered sample were weighed exactly into a PFA-beaker and treated with 10 ml conc HCl. After warming up in a sand bath for about 10 min a few drops of H_2O_2 (30%) were added. After a few minutes the dissolution was completed giving a light orange coloured and clear solution which was transferred to a 100 ml PFA volumetric flask and diluted with deionised water (Millipore GmbH, Eschborn, Germany).

3. Results and discussion

All precursor systems prepared according to the recipe given are white coloured and agglomerated powders smelling slightly of acetic acid. Fig. 1 traces the thermal decomposition of differently composed precursors via TG plots. All compositions show quite similar steps of decomposition. After the initial removal of solvent residues we see the burning of the organic contents up to about 400°C. Apart from the different temperature regimes there is also a difference in the chemistry along the decomposition route. TG–MS measurements show quite different relations of the various gaseous products at different temperatures depending on the Sr or Ba content. Fig. 2(a) and (b) gives such results for the pure $BaTiO_3$ and $SrTiO_3$ precursor in comparison.

The decomposition of carbonate phases starts at 600°C and goes on up to 1000°C depending on the Ba content. In some cases, there is a further weight loss step at about 1000°C due to the decomposition of residual carbonate.

The X-ray diagrams taken after different thermal treatments help understanding the process in more detail. Fig. 3 shows diagrams of mixtures containing only Sr and no Ba heated to different temperatures. At 400°C, $SrCO_3$ is the only crystalline phase; $SrTiO_3$ begins to form from 600°C on. The carbonate disappears only beyond 1000°C. Besides these two compounds, no other phases are observed.

Fig. 4(a) and (b) shows the development of the different phases from mixtures with different Sr/Ba ratios at different temperatures. Especially interesting parts of the diagram are depicted. Apart from the shift of the

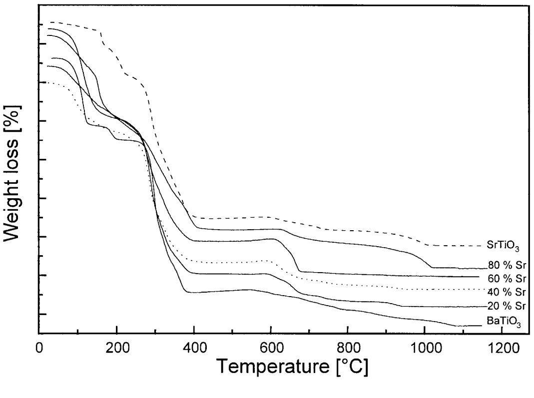

Fig. 1. TG plots of precursors with different Ba/Sr contents synthesized by the sol-gel acetate method.

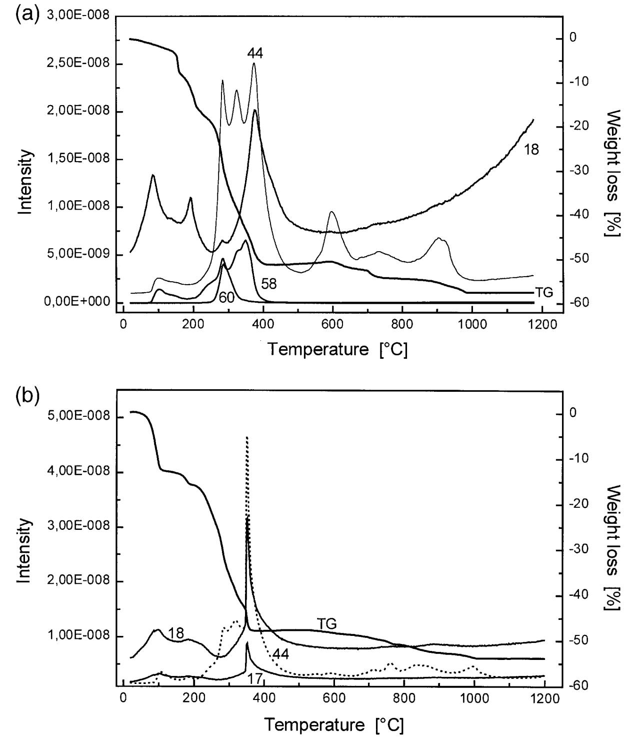

Fig. 2. TG–MS plots of precursors synthesized by the sol-gel acetate method (Mass numbers are placed next to the curves): (a) $BaTiO_3$ precursor; (b) $SrTiO_3$ precursor.

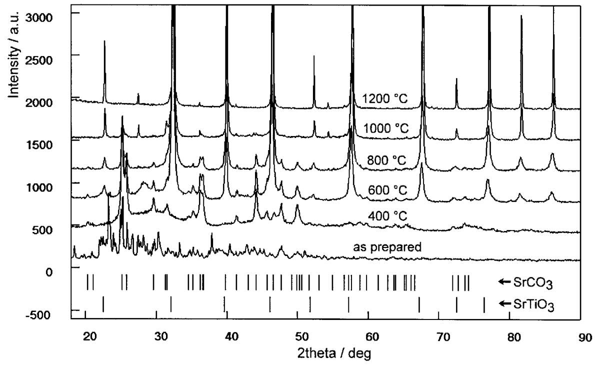

Fig. 3. X-ray diffraction diagrams for $SrTiO_3$ and its precursors calcined for 2 h at different temperatures (theoretical diagrams of possible impurity phases are given).

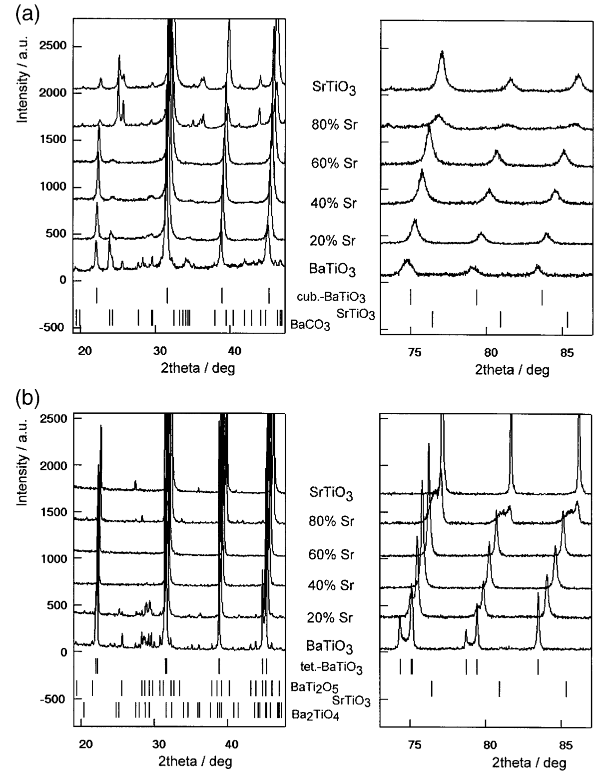

Fig. 4. X-ray diffraction diagrams of samples with different Ba/Sr contents calcined at (a) 800°C; (b) 1200°C (theoretical diagrams of possible impurity phases are given).

perovskite reflections due to the incorporation of alkaline earth cations with a different size we see the formation of several by-products. At lower temperatures, these are carbonates especially in the composition regions near the two boundary phases. At higher temperatures, these phases disappear and new unwanted ones develop in those specimens with higher Ba content. The diagrams can be assigned to Ba_2TiO_4 which is evidently formed near carbonate grains in a local action of the newly formed BaO on the perovskite phase produced before. As stated above, a comparable ternary phase does not exist in the system $SrO–TiO_2$, such orthotitanates are therefore not formed, neither do we find other Sr-rich compounds which are known in literature. (It is surprising that Ti-rich ternary Sr compounds have never been encountered, whereas faint shoulders in the reflection profiles of some $BaTiO_3$ reflection indicate that compounds like $BaTi_2O_5$ are formed in traces in Ba-rich mixtures due to the $BaCO_3$ formation.)

The results in the case of the mixture containing 80 at.% Sr point to a specific problem in this type of synthesis. The reflections of the product treated at 800°C indicate the existence of one cubic perovskite phase only. They are quite broad as expected for very small crystallites. When annealing at higher temperatures, the reflections split up in a way which cannot be attributed to a tetragonal distortion. The evaluation of lattice parameters shows that in this experiment a heterogeneous mixture of two different mixed crystals with 70 and 90 at.% Sr has formed which has just this Sr-content only on the average. This can be proven by equilibrating the mixture at very high temperatures for long times. Fig. 5 shows how the reflection pattern changes by such a treatment giving a single phase cubic perovskite compound.

It must be emphasised that these findings are not the result of an "accident". We have repeated the synthesis procedure for mixed crystals containing Sr in the range of 80% and found this segregation effect again. The micro-heterogeneity seen here evidently results from the fact that the distribution of Sr and Ba is disturbed during the history of the total reaction. We have refined the lattice parameters of the mixed Sr/Ba-carbonate phases found at lower temperatures. By comparing with Végard lines for the different compositions[9] their values indicate that the Sr/Ba-ratio is considerably smaller than would be expected from the contents of the starting gel, i.e. Ba is preferably trapped in the intermediate carbonate phase. In other words: The carbonate phase — which is in an "equilibrium" with the perovskite phase formed during the reaction — has a higher Ba content than the perovskite phase. A perovskite containing 80% Sr will be accompanied by a witherite phase containing about 60% Sr. Furthermore, the decomposition mechanisms and temperature differ considerably for different Sr/Ba ratios in the precursor systems as shown in Fig. 1. It is just in the region between 60 and 80 mol% Sr that the decomposition characteristics change drastically, the carbonate decomposes at much higher temperatures only. So Ba and Sr trapped in the carbonate will be released later during the reaction when there is already a certain amount of perovskite phase present which has formed from the precursor directly. Looking at Fig. 4(a) and (b), one will see that at 80 mol% Sr the patterns are different compared with the others. At 800°C the diffraction angles are larger, i.e. the lattice constant is smaller than expected within the series, and the reflections are broader, i.e. the crystallites are smaller than in the other cases. This part is richer in Sr since more Ba has gone into the witherite phase at the beginning of the process and it is more nanoscaled since it resulted directly from the decomposition of the precursor. It is only after firing at higher temperatures that the reflection splitting appears. That part which is due to the phase formed earlier now has sharper reflections since these crystallites have had the opportunity to grow. The newly formed crystallites "fed" by the decomposing Ba-rich carbonate are smaller, the shoulders at smaller diffraction angles are broader. It is only after a prolonged heat treatment at very high temperatures that the homogeneity of the material is attained by diffusion processes. The genesis of the products may be given schematically as in Fig. 6.

The X-ray data were evaluated by the program FormFit[8] and lattice parameters, crystallite size and microstrains were determined. The latter two parameters will not be discussed here since they reflect the same situation that has been discussed in part I of this series.[1] Fig. 7 illustrates the variations of c/a parameters and the transition from the tetragonal to the cubic structure at room-temperature which takes place at about 40–50% Sr depending on the crystallite size as it develops at different calcination temperatures. The smaller the crystallites are the earlier does this phase transition take place. Below a critical size (approx. 30 nm) only the cubic structure exists even for pure $BaTiO_3$. The effect of crystallite size on this transition is well known in literature (see, e.g. Ref. 10) and a core shell model has been discussed to explain the simultaneous existence of both phases in a certain size regime, the cores are believed to be tetragonal covered by a shell of cubic material. We find that the critical size for this transition is much lower and we shall present experimental evidence for another model of different symmetry in domains within the crystallites in a forthcoming paper.[11]

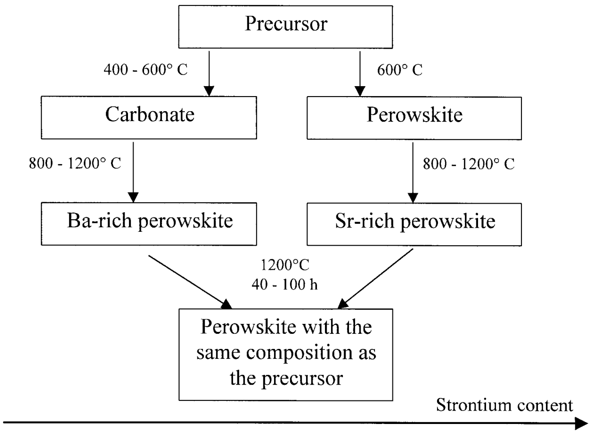

Fig. 6. Schematic diagram of intermediate steps in the formation of $Ba_{1-x}Sr_xTiO_3$ compounds.

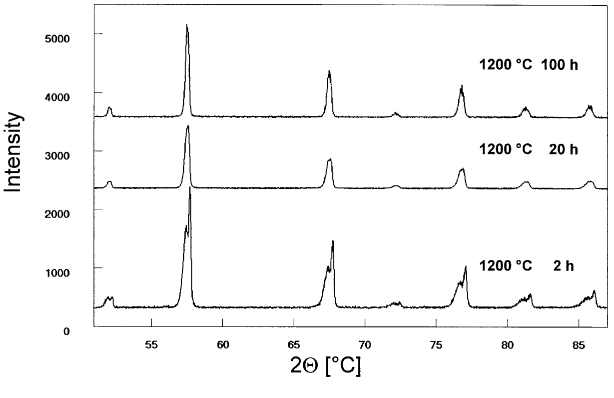

Fig. 5. X-ray diffraction diagrams of samples with 80 at.% Sr calcined for different times at 1200°C.

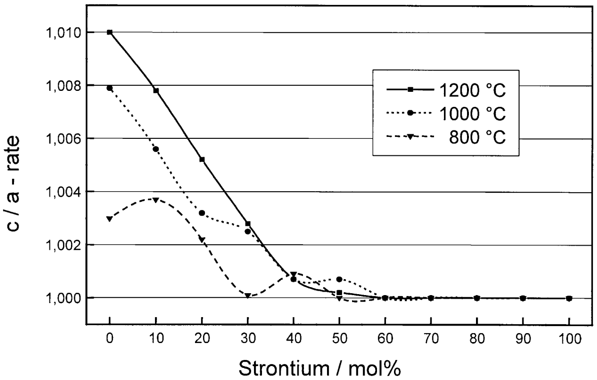

Fig. 7. Development of c/a ratios with composition and temperature.

4. Conclusion

In Part I of this series, we have shown how inhomogeneities in crystallite sizes for $BaTiO_3$ may occur due to a complex history of the decomposition reaction. In the work presented here, we see that the sol–gel process is also prone to compositional inhomogeneity because of the formation of intermediate phases which do not necessarily "transport the stoichiometric information of the educt system to the products". During the synthesis of mixed crystals $Ba_{1-x}Sr_xTiO_3$ this may lead to inhomogeneous powders containing crystals with different Ba/Sr ratios and also different crystallite sizes because they have developed at different stages of the process and have grown for different times. Such size distributions tend to be bimodal. Chemical homogeneity and a more uniform size distribution will only be achieved after prolonged treatment at higher temperatures. However, under such conditions the system will have left the nanoscale regime. This and the inhomogeneities described will eventually have a great influence on the physical properties of the ceramic devices made via such procedures.

Acknowledgements

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