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GRAIN SIZE AND CONDUCTIVITIES ANOMALY IN DONOR - DOPED BARIUM TITANATE*

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Abstract

A thermodynamic model was used to consider the grain size and conductivity anomalies in donor-doped barium titanate. It was found that all crucial experimental results support the thermodynamic approach for the explanation of the grain size anomaly.

Introduction

Barium titatante is one of the most important ceramic materials in electronics. As an intrinsic ferroelectric material it can be used in various applications, for example: as a capacitor, a multilayer capacitor, a grain boundary capacitor and thermistor.

In order to modify the properties of this outstanding electronic material with a perovskite structure, some acceptors or donors are usually incorporated in to the crystal lattice. However, when three valent oxides are incorporated and enter the barium and/or titania lattice sites the extrinsic and intrinsic properties change abruptly. A discontinuity in the intrinsic and extrinsic properties is observed at a donor critical concentration of about 0.3 at%, for all the dopants used. The electrical grain conductivity decreases dramatically and the microstructure development is prevented. Both these phenomena are linked and in the literature are known as the anomalious grain growth and anomaly in the electrical conductivity. As the consequence of the importance of barium titanate

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*"Dedicated to the memory of Prof. Dr. Jože Šiftar"

these phenomena have been the subject of intense investigation for more than three decades.

This phenomenon has been a challenge for many scientists, in particular those who were involved in material development, applications and the industrial production of thermistors.

Many papers have been published in which the study of this phenomenon was reported. Most authors were convinced that the explanation of this phenomenon i.e. the prevention of grain size development is kinetic in origin, while the anomaly in the electrical conductivity was mostly ascribed to a dramatic change in the defect chemistry during the increase in the amount of donor in the samples.

However, in spite of the great activity in terms at experimental work and the evaluation of results no completely satisfactory answer to this intriguing phenomenon has been offered with the kinetic approach. In order to solve this problem we have used the thermodynamic model.

Thermodynamic model

Many reactions with a positive energy change associated with grain growth may accompany sintering and hinder grain growth. These include the incorporation of large ions which induce mechanical stresses [1]. Due to the size misfit and chemical reactions which accompany the grain growth can retard [2] or even stop the grain growth as in the case of sintered donor-doped barium titanate [3]. In the classical concept of sintering where the driving force for grain growth is expressed by one term only, such a thermodynamic inhibition of the grain growth can not be explained. However, it can be explained when a new concept is used in which the driving force for sintering, the excess of free surface energy G, is expressed by two terms [4,5].

$$G = \Sigma A_{ij}\gamma_s + \Sigma H_{ij}\gamma_e \qquad (1)$$

Here A_{ij} is the surface area of *i*th face on the *j*th cube and H_{ij} is the *i*th edge on the *j*th cube and γ_s and γ_e are the specific surface energy and energy per unit length. This is actually the stored energy in the case of an assembly of cubic isotropic grains and is equal to the work done when bonds were broken during the division of the original solid. Since for sintering the "local curvature" is important, that is the atoms exhibit a different bonding environment when compared to atoms located on faces. The atoms on edges and corners are more exposed and will change the bonding environment in order to decrease the energy and to ensure the most uniform possible bonding environment. In the case of isotropic specific surface energy, the cubes will change to spheres of the same volume. During that change the difference in the bounding environment disappeared and particles with the lowest surface to volume ratio are obtained, which exhibit a stored free surface energy.

The stored free energy

From an academic point of view, one should consider energy of a plane surface and define this as the initial free surface energy. However, from a realistic point of view, when we consider sintering, we are usually considering an assembly of grains, which exhibit the starting excess free surface energy, rather than with plane faces. As such, we can proceed from an assembly of identical grains with the smallest surface to volume ratio and isotropic surface energy. In this case, no change in the microstructure will occur during sintering, since there is no difference in the bonding environment between atoms due to the existence of a local curvature. Such an assembly of identical grains exhibits the stored free surface energy, which can be released only when there is an induced difference in the bonding environment between atoms, for instance by implantation of a seed grain in the matrix of a small grains, or due to other reasons. In that case the small grain will be "swallowed" by the large seed grain during anomalous grain growth. In this hypothetical case the process would terminate when one solid body reforms. However, in reality a coarse microstructure with large grains usually forms, since during the course of the sintering the nucleation of seed grains will occur more frequently, depending on temperature and time.

The local curvature

The local geometry necessary to trigger the grain growth is determined exclusively by the second term $\Sigma\ H_{ij}\gamma_e$ which can be shown to be proportional to the curvature [6] and represents the fluctuation of the initial free surface energy due to the existence of variation in local curvature.

In ionic crystals an almost complete transfer of one or more electrons occurs from one element to another, producing a set of positive and negative ions approaching a noble gas configuration. Such bonding is therefore predominately electrostatic possessing a negligible directed chemical bonding and is characteristic of ceramic oxides. During the building of an ionic lattice the distribution of oppositely charged ions on regular lattice sites enables a crystal structure with the lowest possible lattice energy to result while maintaining the electroneutrality of the ionic lattice.

However, in practice a complete “electroneutrality” can never be achieved since edges and corners exhibit an uncompensated Valence Bond Strength (VBS). This occurs because the ionic lattice continuum is being interrupted and ions on the exposed positions posses an excess of charge as a consequence of the uncompensated VBS. This excess electrostatic charge is distributed over the entire solid angle and/or surface associated with it. In the hypothetical case of a pure ionic solid the electrostatic forces govern the ionic solids and the excess electrostatic charge due to the uncompensated VBS induces the pressure on the surface of a sphere in accordance with elementary electrostatic theory and is oriented outwards. In the case of a sphere with a surface S the excess charge Q is equally distributed over a solid angle of 4π. In that case a pressure of $P = Q^2/2\varepsilon_o S^2$ is induced, which can for a regular sphere be expressed as $P \propto Q^2/2\varepsilon_o V r_o$, here V is the grain volume and r_o is the principal grain radius. Thus, in the hypothetical case of a sphere when the lattice is pure ionic and the bonds are not oriented, the uncompensated VBS is associated with a pressure.

Results and discussion

During our work on the sintering of donor-doped $BaTiO_3$ in air, we found that the anomalous grain growth and the formation of semiconducting grains is accompanied by oxygen release, being proportional to the amount of donor present in the samples. In the case where the donor concentration is close to the critical concentration which is about 0.3 at%, the anomalous grain growth, oxygen release and the formation of semiconducting $BaTiO_3$ are prevented, Fig. 1.

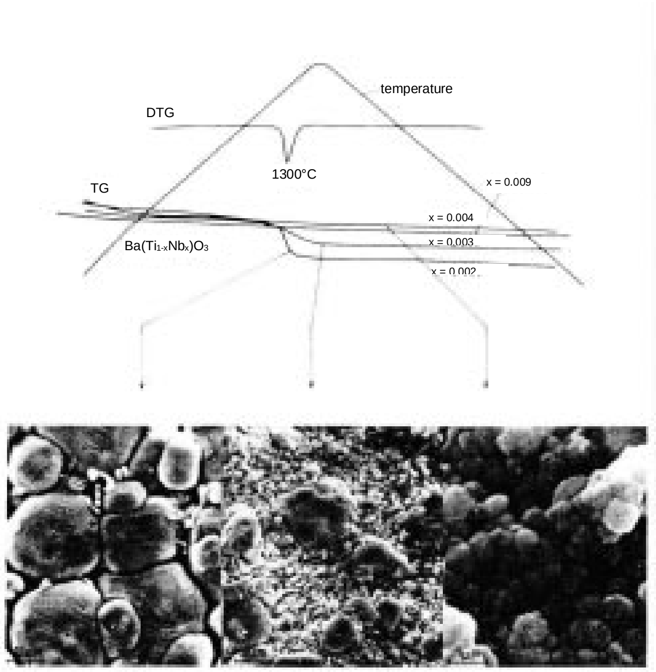


Figure 1 Weight loss for donor doped samples during anomalous grain growth, with corresponding microstructures [7].

In addition, it was found that the oxygen is also released at high oxygen pressures of 5 atm and above. That the barium titanate loses oxygen at higher temperatures in order to establish a thermodynamic equilibrium with the surrounding atmosphere is well documented. However, the doped $BaTiO_3$ loses during anomalous grain growth a stoichiometric amount of oxygen, proportional to the amount of dopant incorporated during grain growth.

The discovery that barium titanate releases oxygen during grain growth and the formation of semiconducting anomalous grains, was one of the key points in a new thermodynamic approach during the elucidation of this phenomenon of the grain size anomaly.

Further more, we found that in samples which contain two types of dopants, for instance K^+ and Sb^{3+}, the oxygen release during anomalous grain growth and dopant incorporation is absent. In that case the grain growth was not blocked even when the critical donor concentration was transgressed [7]. Also, this observation strongly supports the thesis, that the grain growth anomaly is associated exclusively with oxygen release and needs to be abbreviated in the frame of the thermodynamic model.

When constructing the thermodynamic model we assume that the energy for oxygen release is balanced by the free surface energy stored in the matrix of fine grains prior the start of anomalous grain growth. The total free energy change in this process can be expressed as

$$\Delta G = \Delta G_{ox} + \Delta G_s \qquad (2)$$

where ΔG_s is the excess free surface energy and ΔG_{ox} is the energy associated with oxygen release. During the consideration of this relationship the energy associated with oxygen release ΔG_{ox} was compared to the oxygen electron affinity diminished by the dissociation energy and entropy.

On the other hand, the free surface energy stored in the matrix of fine grains prior to the start of the anomalous grain growth was compared to the surface energy of the assembly of identical grains with the lowest surface to volume ratio $\Delta G_s = 3V\gamma_s/r_o$, where V is the molar volume, r_o is the grain radius and γ_s is the isotropic surface energy. When we take into account both estimates for the energy of oxygen release and free surface energy release we obtain for the energy change during gain growth associated with dopant incorporation and oxygen release the relation [3];

$$\Delta G = c^o \Delta G_{ox} + c^o RT\ln P - 3V\gamma_s/r_o \qquad (3)$$

In the case where $\Delta G = 0$ we obtain the relation $P = P(c^o_D)$ which represent the phase boundary of the system considered and divides the system into two parts, a reduced part where the anomalous grain growth with oxygen release occurs and a oxidized part, where no anomalous grain growth occurs. When typical values are inserted in the relation $P = P(c^o)$, we obtain the final relation;

$$\ln P = A/c^o - B \qquad (4)$$

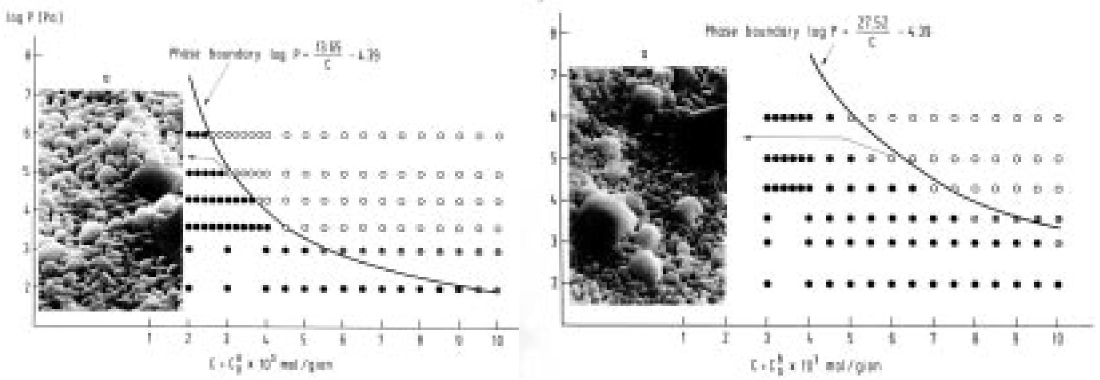
where A and B are constants and are related to the starting free surface energy of the assembly of spherical grains A = $\gamma_s S^o$ prior to the start of grain growth and to the energy of oxygen expulsion during donor dopant incorporation B = 4,39.

The experimental results obtained when we sinter variously donor doped $BaTiO_3$ samples at different oxygen pressures, fit very well to the estimated curve, which determines the phase boundary (3), Fig. 2.

This relation exhibits an interesting detail, namely at P = 1 atm the eq. (4) reduces to $c^oG_{ox} = \gamma_s S^o$, where S^o is the critical surface energy balanced with the critical donor concentration at the phase boundary.

At the phase boundary the stored free surface energy is directly balanced by the energy associated with oxygen release during grain growth. This means that a higher stored free surface energy (smaller initial average grain size) would shift the critical donor concentration to a proportionally higher critical donor concentration.

The experimental results are in the agreement with the prediction made by the model, Fig 2.



Figures 2 (a,b) Estimated and experimentally determined phase boundaries between the reduced and the “oxidized” phase at 1300 °C within the concentration range from 0.2 to 1.0 at %. Dark circles represent the reduced semiconducting samples and empty circles are isolators, where no grain growth was observed; a) Samples were prepared from powders with an average grain size of 1μ, b) Samples were prepared from the powder with average grain size of ½ μ.

The crucial parameter of the model is the constant $K = c^o/S^o = G_{ox}/S^o$ which is actually the ratio between the energy associated with oxygen release during dopant incorporation and the free surface energy release during anomalous grain growth. This constant can not be directly not evaluated, however it can be, when the following statement is made; the surface area annihilated during grain growth and oxygen release can be related via the number of bonds broken and the bonds simultaneously reformed.

By applying the bond valence approach and estimating the valence bond strength for nominator and denominator in the relation for K, one can obtain the values $K_{111} = 1{,}7$ and $K_{100} = 1$ respectively. The experimental values c^o/A^o are close to the estimated values K_{111} [6].

This is in agreement with the fact that the surface faces (111) are thermodynamically more stable and determine the characteristics of the surface structure character.

The most surprising observation was that not only the initial grain size but also the morphology of the powder influences the critical concentration. The critical concentration is strongly influenced by the stored free surface energy, which is to a first approximation related to the spherical grains with the smallest surface to volume ratio. Powder, on the other hand with a very high specific surface area and exhibiting a high surface to volume ratio (nonspherical grains) and which possess mostly the surface characterized by a different bonding environment possess a relatively low stored free surface energy in comparison to the powder composed of spherical grains.

In the case when powders composed of nonspherical grains with a very high specific surface areas and a high surface to volume ratio were used, the ability of these powders to incorporate donor-dopant in comparison to the original powder, with spherical grains and similar specific surface area, was much lower [9], Fig.3.

This demonstrates again, that the first term in Eq. (1) representing the local curvature and the specific surface associated with it, triggers the grain growth and/or grain rounding, while the second term determines the global stored energy which is responsible for the accompanying endothermic processes associated with anomalous grain growth.

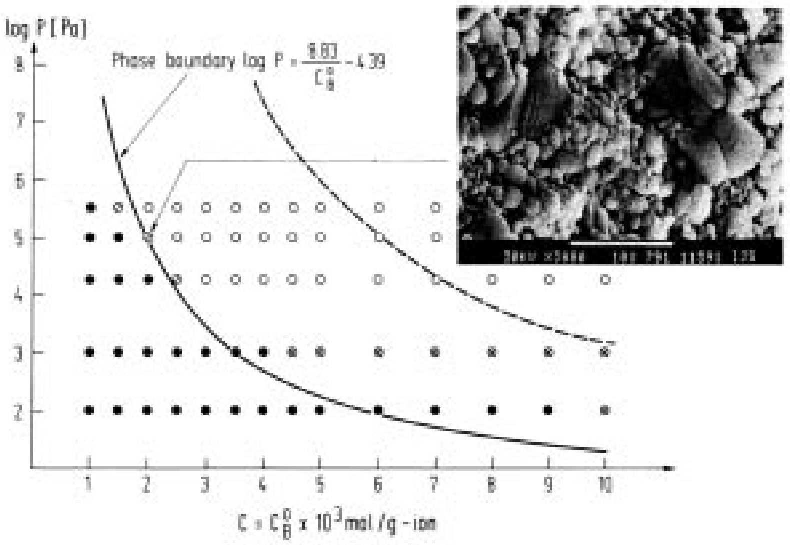


Figure 3 Critical donor - dopant concentration vs the oxygen partial pressure with estimated and experimentally determined phase boundary, separating the reduced and oxidized phase, during the sintering of donor doped barium titanate compacts. The dashed curve represents the untreated powder, while the solid curve represents the treated powder, exhibiting before thermal treatment, a similar initial specific surface to the starting $BaTiO_3$ powders.

Conclusion

The thermodynamic model applied for the grain size anomaly and conductivity anomaly was found to satisfy all the aspects of the considered phenomena. Up to now no discrepancy between the phenomena considered and the model described above was noted. This model was also confirmed when semiconducting $BaTiO_3$ was prepared at relatively low temperatures, well below 1200°C [10] the thermodynamic stability of these reduced phases in air. When a liquid phase was used with a low melting point, we could prepare a semiconducting ceramic with a PTCR effect via anomalous grain growth, even at 1100°C [11], demonstrating that the anomalous grain growth and the formation of the semiconducting donor-doped grains is a non equilibrium process driven by the release of stored free surface energy during anomalous grain growth.

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Povzetek

Uporabili smo termodinamski model in obravnavali anomalijo v rasti zrn v donorsko dopirani keramiki na osnovi barijevega titanata. Rezultati preiskav so potrdili, da model opiše in predvideva vse bistvene procese, povezane s tem pojavom, ki je v strokovni literaturi opisan kot ‘anomalija v rasti zrn in električni prevodnosti v donorsko dopiranem barijevem titanatu’.