Optimization of the mixing/grinding of $MgO+TiO_2$ powders for $MgTiO_3$ solid state synthesis

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Abstract:

Through the dielectric materials used for the making of type I multilayer ceramic capacitors, the ilmenite magnesium titanate $MgTiO_3$ *is of particular importance. Yet, it seems difficult to get pure* $MgTiO_3$ *with a controlled stoechiometry. In order to be able to synthesize it by solid state reaction, we therefore studied the mixing/grinding behavior of the precursors* $MgO + TiO_2$*.*

The evolution versus pH of the zeta potential values of both MgO and TiO_2 *(anatase) powders shows that it is impossible to get correct pH values allowing a good dispersion state and thus an easy control of the mixing of these two species when considering only electrostatic repulsion. So, we considered to add dispersants in order to get a steric dispersion behavior. Rheological characterization of the slurries showed that we were able to get a good dispersion state allowing after calcination the obtaining of pure magnesium titanate with a controlled stoechiometry.*

1. Introduction

It is often reported in the literature that it is highly difficult to get by solid state reaction pure ilmenite magnesium titanate $MgTiO_3$ without any $MgTi_2O_5$ additional phase. That is high detrimental to the industrial use of this material in spite of its high importance for type I multilayer ceramic capacitors. We previously studied[1] the mixing/grinding behavior of ($ZrO_2+TiO_2+SnO_2$+some oxide additives) in order to make microwave resonators after synthesis of the material by solid state reaction. We showed that 1/ good dispersion conditions could be obtained when the zeta potentials of the different powders were all higher to 20 mV with the same sign, the zeta potential values being governed with the pH of the slurry, and 2/ that a good characterization of the dispersed (deflocculated) or not dispersed (flocculated) state of the slurry was the measurement of rheograms (i.e. τ (shear stress) = f($\dot{\gamma}$) (shear rate) or η (viscosity) = f($\dot{\gamma}$).

Newtonian liquids, such as water or most solvents and oils, are characterized by a viscosity independent on the shear rate value. A viscosity that increases with shear rate characterizes shear-thickening fluids. This seems to be characteristic of high-solid concentration suspensions[2,3,4]: they are characterized by a shear thinning behavior at low shear rates and own often a dilatant rheological comportment at high shear rates, typically higher than 50 s^{-1}. This behavior has been extensively studied. Although this is not yet completely understood, two different mechanisms have been proposed: the order to disorder transition and the hydrodynamic clustering[5,6]. On the other side, viscosity that decreases with shear rate characterizes shear-thinning liquids. For flocculated slurries, this behavior can be related to the breaking of the links between particles gathered in the flocculates[2,7]. Thus, rheological measurements performed on slurries can reflect their flocculated or deflocculated state.

The goal is to make the powders react and form new phases by solid-state reactions induced by contact between the grains and processed by diffusion during the thermal cycle. Thus, the mixture of precursor powders must be extremely intimate and homogeneous so that paths for further diffusion are as short as possible. An intimate mixture promotes easy reaction at lower temperatures and deters the formation of secondary phases. As it will be shown further, the problem here is that it is difficult to get shear-thickening slurries and thus to disperse and mix together MgO and TiO_2 powders in an aqueous slurry. We have therefore made an attempt to get this deflocculated state by steric dispersion.

2. Experiment

The powders to be mixed were 98% “light” grade Rhone Poulenc periclase MgO and Cerac 99.9% anatase TiO_2. As MgO reacts easily with CO_2 and H_2O always present in air, we calcine it at 600°C for 2 hours just before weighing, so we can assume we get the correct amount of magnesium into the mix and thus the good stoechiometry Mg/Ti = 1.

Measurements of ζ versus the pH of the dispersion medium were performed using a ZetaSizer 3000 (Malvern Instruments, Malvern, U.K.) coupled with an automatic titrator. Powders were first dispersed using an impeller mixer in 0.22 µm filtered desonized water. After ultrasonic dispersion and 15 minutes of sedimentation, a drop of the upper part of this mixture was taken and diluted into the ZetaSizer in such a concentration that the analyzed signal is correct. The pH of the dispersion was adjusted from these initial conditions by 0.22 µm filtered hydrochloric acid or ammonia additions and measurements performed. Not any inert electrolyte was used to fix the ionic strength in order to be as close as possible to the dispersion conditions of the ground slurries.

Rheograms were performed with a rheometer (Model No. Rheolab MC10, Physica Messtechnik, Stuttgart, Germany) using the Couette geometry (cell dimensions: $\phi = 48$ mm; height = 116 mm. cylinder dimensions: $\phi = 45$ mm; height = 68 mm. gap = 1.5 mm). Before any experimental evaluation of the rheological behavior, the time needed for the shear stress to stabilize under each shear must be determined. The time necessary for stabilization, independent of the shear rate, is for this particular rheometer ~ 2 s. Thus, when the rheograms of the different slurries were performed, the shear rate was varied between 0 and 1000 s^{-1}, either increasing or decreasing with 50 measurements in each direction, and was applied 4 s before every measurement. Rheograms were either performed on samples after 1 hour dispersion using an impeller mixer or just taken from the batches being ground. When adding liquid steric dispersants, some powder ($MgO+TiO_2$) is added to the batch in order to keep the same density of the slurry (i.e. the same solid/liquid ratio).

Grinding and dispersion/mixing of the powders to be calcined were performed by attrition milling. Under such a process, powders or agglomerates are sheared between small, hard-material balls that are forced to stir in a limited volume. The present dispersion medium was deionized water. Prior to grinding, the powders were pre-mixed in this dispersion medium using an impeller mixer. Balls (0.8 mm in diameter) of zirconia were used in a horizontal attrition mill (Dyno-Mill®, CB Mills, Gurnee, IL), which allowed high-energy grinding in a continuous process and recycling of the slurry. Batches of 0.5 to 1 kg were ground in this manner. The normalized grinding time, t_N, which represents the real grinding time, is defined as

$$t_N = \frac{t_A . V_S}{V_T} \qquad (3)$$

where t_A is the total attrition time, V_S the volume of slurry ground in the attrition chamber, and V_T the total volume of the batch. The batches have been mixed with 1 hour normalized grinding time before calcination. We focused our attention on 25 and 50 wt% slurries (25 or 50 weight % of oxide powders in water).

Calcining was performed in air in a chamber furnace at 1000°C with 1 hour soak time using alumina vessels. The obtained calcined powders where characterized by X-ray diffraction using a D5005 Siemens with a $\theta/2\theta$ configuration and a copper tube. The k_β spectrum line is eliminated using a Ni filter, and the $k_{\alpha 2}$ one by calculation.

3. Attempts to disperse MgO/TiO_2 slurries by electrostatic repulsion

Most solid surfaces are electrically charged. All of the links of a crystal are unsaturated, resulting in chemisorption, which entails the capture of foreign atoms, ions, or molecules on the surface. The surface electrical charge of particles dispersed in water or an electrolyte solution can be much more significant than that of particles in air. The electrical charges result from either dissolution of the solid into the liquid, ionization of surface groups (particularly OH^-) or substitution of ions belonging to the lattice of the solid. They are compensated by opposite-sign charges from the ions of the liquid, resulting in the formation of the so-called Helmholtz's double layer[7]. The potential at the Outer Helmholtz's Plane (OHP), which indicates the closest distance of approach of the hydrated ions in the solution, is assimilated into the zeta potential, ζ [8].

The Deryagin, Landau, Verwey and Overbeek (DLVO) theory assumes that the stabilization of slurries by electrostatic repulsion is possible only when repulsion forces are higher than attraction forces. The stabilization of electrostatic repulsion depends on both the radius of the particles and their surface potential, ψ_0. This latter parameter depends directly on the surface charges and is independent of the grain size of the powders. Consequently, the pH of the slurry, the concentration of the adsorbed ions and their nature are the main parameters to be taken into account. The value of the ζ potential depends directly on the concentration in the slurry of the ions determining the potential, that is on the pH of the slurry and on their nature. The ζ potential 0 is the IsoElectric Point (IEP) (that is the same as the Zero Point of Charge, ZPC as we assume that there is not any specific adsorption here) at which repulsion forces disappear and flocculation occurs. On the other hand, a higher ζ potential value results in higher repulsion forces and a more stable suspension. It is generally admitted that $|\zeta|$ values > 20 mV allow good dispersion states. When mixing different powders together, ζ values all of the same sign have to be achieved for deflocculation to occur.

Zeta potential characterization of both powders have been performed in water, that is to say the same dispersing medium that the one of the slurries. It is noteworthy that periclase MgO reacts with water to form brucite $Mg(OH)_2$ while TiO_2 seems not to react. Effectively, a 50wt% slurry mixed in water and characterized by X-ray diffraction is formed exclusively of anatase TiO_2 and brucite $Mg(OH)_2$.

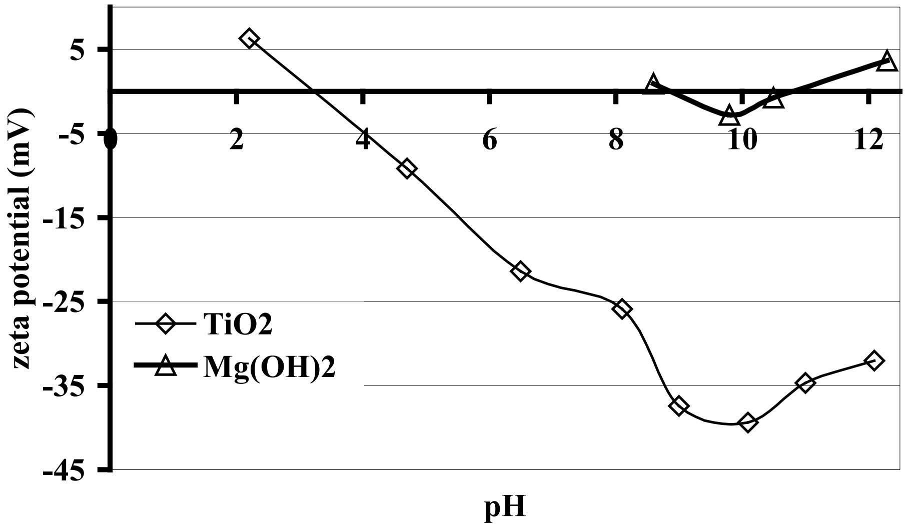

Figure 1: zeta potentials of TiO_2 anatase and $Mg(OH)_2$ brucite versus pH

Figure 1 shows the zeta potentials values for TiO_2 anatase and $Mg(OH)_2$ brucite versus pH. The measured values of the TiO_2 ζ potentials, positive for low pH, decrease when pH goes up and are negative for a basic pH. That result is in agreement with the model for hydroxide groups adsorbed onto the surfaces of grains. The IEP value is close to pH 3. The $|\zeta|$ value is higher to 20 mV for ph>6, allowing good dispersion conditions for basic slurries.

$Mg(OH)_2$ behavior is quite different: for pH<8, brucite seems to dissolve, making thus any ζ measurement impossible. For pH ranging from 8.5 to 12, ζ keeps close to 0. It seems thus difficult, working only with electrostatic repulsion, to disperse MgO in aqueous slurries and mix it with TiO_2.

It is noteworthy that MgO dispersed in water owns a highly basic character: even for low densities slurries (25wt%), it has been impossible to make the pH of MgO ($Mg(OH)_2$) + TiO_2 stoechiometric slurries) to evolve from the initial 11.3 value. The rheogram Figure 2 confirms the highly shear thinning behavior characteristic of a flocculated non dispersed slurry.

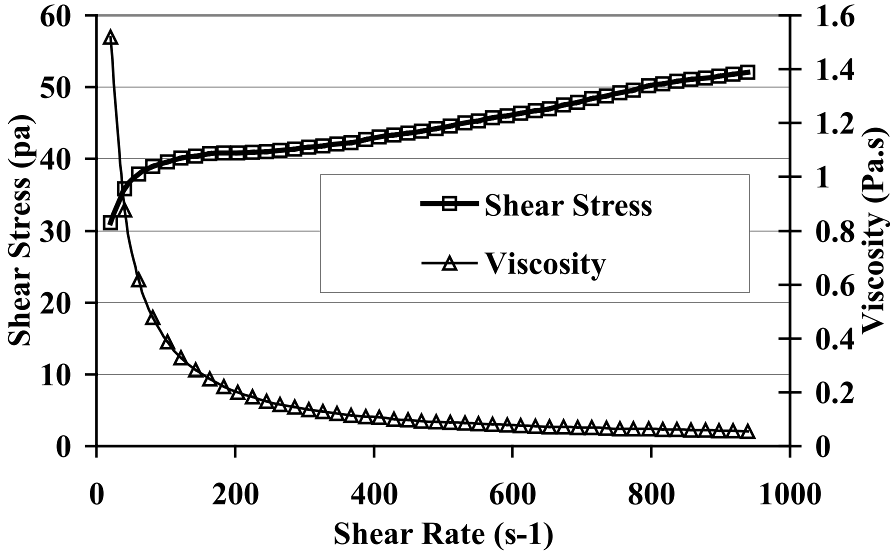

Figure 2: Rheogram of an aqueous MgO/TiO$_2$ 25wt% slurry

These observations demonstrate the impossibility to disperse by electrostatic repulsion and mix together powders including MgO in aqueous slurries. Another solution will consist on the steric dispersion of the oxide powders.

4. Attempts to stabilize the slurries and disperse the powders by steric repulsion

The DLVO theory only takes into account the surface adsorption of ionic species and not at all the one of a polymer. Yet, some polymer addition to a colloidal suspension can either enhance its stabilization or, on the contrary, make it flocculate. Steric dispersion theory helps to understand these behaviors. Polymer molecules adsorption on particles can create links between these particles or, on the other hand, induce the dispersion of particles by steric repulsion. Materials inducing such behaviors are so-called dispersants.

The addition of dispersants helps the obtaining of deflocculated slurries because they have an influence on the distance occurring between particles. There exist different kinds of dispersants: the non ionic polymers, the polyelectrolites and the co-polymers. The choice of the dispersant to be used has to be made with considerations on its affinity with the solvant (the liquid medium of the slurry) in order to get a large steric repulsion[9]. In the particular application presented here, the dispersant we used was Dolapix CA® that is a polyelectrolite basic anionic dispersant.

Figure 3 shows the evolution of the rheological behavior of a 25w% slurry versus the amount of Dolapix CA added into 80 cm^3. The addition of only 1 cm^3 (that is to say 1.25 volume %) leads the viscosity at low shear rates to dramatically decrease compared to the one observed on a dispersant free slurry (as noticed Figure 2): the viscosity value is 30 times lower for a 100 s^{-1} shear rate. It is noteworthy that the amount of solid in the slurry is adjusted after every liquid dispersant addition in order to assume that the observed decrease of the viscosity is only due to a steric effect and not on a dilution effect. For this particular 25w% slurry, the transition from the shear thinning behavior to the dilatant one seems to occur when adding 2 cm^3 of Dolapix CA to 80 cm^3. An unambiguous slight dilatant behavior is obtained with a 2.5 cm^3 addition.

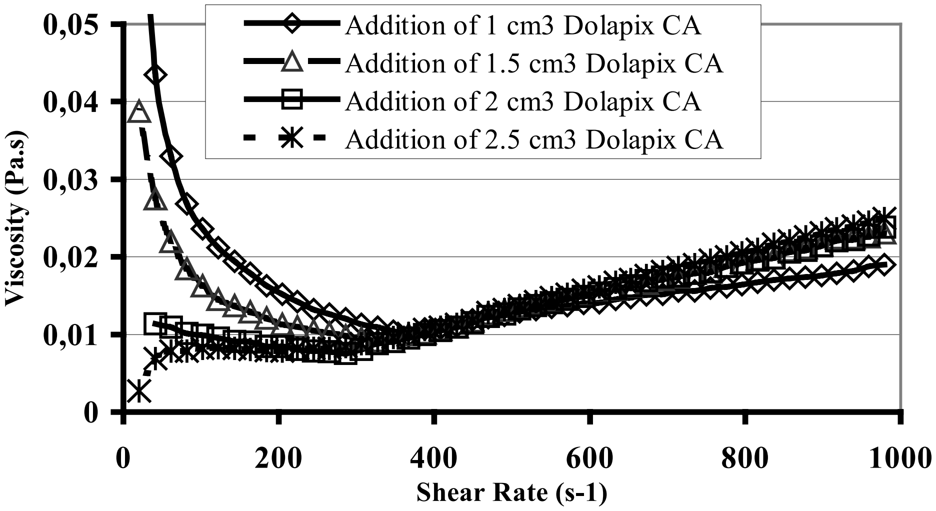

Figure 3: Rheological behavior of a 25w% MgO/TiO$_2$ slurry versus the dispersant amount

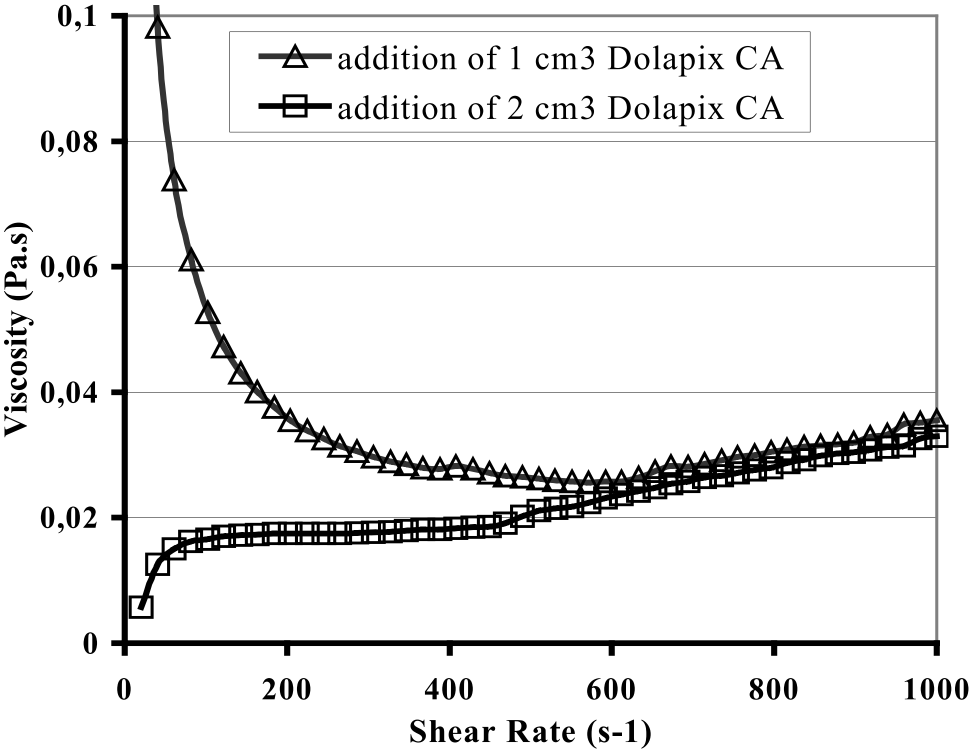

Figure 4: Rheological behavior of a 50w% MgO/TiO$_2$ slurry versus the dispersant amount

The shear thickening behavior can be observed as well with more dense slurries as illustrated Figure 4 for 50w% slurries. Although the density of the slurry is higher, that is to say the volume ratio solid/liquid more important, it is noteworthy that the dispersant amount allowing the obtaining of 50w% deflocculated slurries is lower to the one observed when mixing 25w% one. We have not imagined any fully satisfying explanation for this surprising observation. One hypothesis could be that the grafting rate of the solid particles is not the same in both cases. In a diluted medium, the particles to particles or the particles to dispersant species distances are important compared to the one occurring in a more concentrated medium. In diluted slurries, it is thus more difficult for the particles to be in contact with the dispersant species, that is to say that the grafting rate of the polymeric chains on the solid particles is low compared to the one occurring in 50w% slurries. In consequence, for low density slurries, some dispersant polymeric chains are kept free with a higher ratio free chains/linked chains. In respect with this hypothesis, one has to consider the optimum experimental conditions gathering the density of the slurry as high as possible together with a minimum amount of steric dispersant for a slightly shear thickening behavior to occur. Yet, some unsuccessfully attempts for dispersing 66.66w% slurries have been made. The flocculated character of the slurry remained whatever the amount of Dolapix CA was. In the case of 50w% slurries it is noteworthy that, when the deflocculated behavior is obtained, viscosity value is twice the one of 25w% shear thickening one.

We succeeded thus on the obtaining of deflocculated MgO/TiO_2 slurries. The problem is now to keep these powders dispersed in order to grind and mix them intimately before calcining.

5. Rheological behavior of slurries and solid state synthesis of $MgTiO_3$

Some different experiments were made with 50w% slurries in which MgO and TiO_2 were mixed in order to get stoechiometric (Mg/Ti = 1) $MgTiO_3$. Attrition milling time was 1 hour. Amounts of Dolapix CA were determined by the rheological measurements previously described. The rheological behavior of the slurry is continuously controlled all the grinding process long and small amounts of Dolapix CA are added when necessary for the slight dilatant behavior to be preserved. After milling, the slurries were spray-dried in order to prevent the flocculation during the drying process and to freeze the dispersion state of the different powders. Calcination occured then at 1000°C in alumina vessels and the calcined powders purity was controlled by X-ray diffraction.

As an example, two different X-ray diffraction patterns are gathered in Figure 5. Figure 5 b/ is a typical X-ray diffraction pattern of a slurry the rheological behavior of which was badly controlled during the grinding process with a shear thinning comportment that existed at some moment. One can observe together with the (012) diffraction peak of $MgTiO_3$ (06-0494 JCPDS file) a little peak that is attributed to the (101) diffraction peak of $MgTi_2O_5$ (35-0792 JCPDS file). In opposition, Figure 5 a/ shows a typical X-ray diffraction pattern of powders calcined after mixing magnesium and titanium oxides in a slurry showing continuously a slight shear thickening comportment. Only pure $MgTiO_3$ can be detected now.

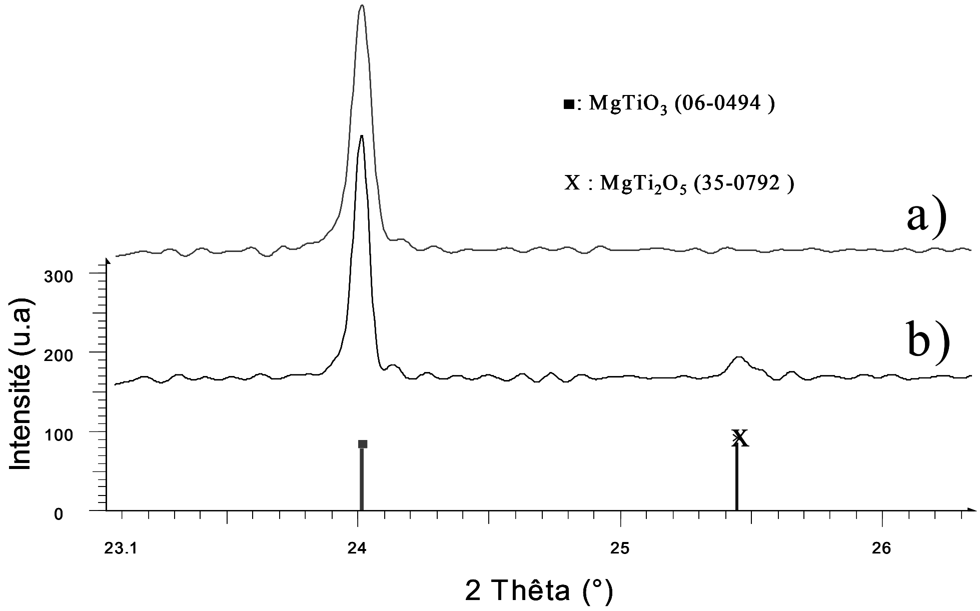

Figure 5: X ray diffraction analysis of two calcined powders
a/ dispersed in a slightly shear thickening deflocculated slurry
b/ dispersed in a shear thinning flocculated slurry.

6. Conclusions

Zeta potential characterizations of magnesium and titanium oxides show that it is impossible to stabilize by electrostatic dispersion deflocculated slurries of a mixing of these two powders. The zeta potential of magnesium oxide is close to 0 for pH ranging from 8,5 and 12 and the powders dissolve in water when pH is lower than 8.5. Rheological characterizations of aqueous slurries of these two oxides mixed together confirm that they are, whatever the pH is, characterized by a shear thinning behavior characteristic of flocculation. Stabilization of such slurries by electrostatic repulsion seems therefore impossible to process. Yet, the addition of steric dispersants in correct amounts related to the density of the slurry allows the obtaining of a slight shear thickening behavior characteristic of well dispersed powders. It has been shown that it was possible to maintain this slight dilatant characteristic of the slurry during the whole grinding process by a continuous control permitting a careful adjustment of the defloculant amount. In such conditions, after spray drying, the mixed powders can react by solid state diffusion at 1000°C and form a pure stoechiometric $MgTiO_3$.

Acknowledgments

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