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Oxide Slurries Stability and Powders Dispersion: Optimization with Zeta Potential and Rheological Measurements

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Abstract

Slurries stability and powder dispersion are highly dependent on both the pH and their density. The analysis of these parameters allows us to keep the slurries defloculated, leading to an optimum mix of powders before calcination and reaction. The present work is devoted to the mixing of the different oxide and carbonate components in slurries to be synthesized by solid state reaction of the (Zr,Sn)TiO_4 (ZST) microwave dielectric and the Pb($Mg_{1/3}$ $Nb_{2/3}$)O_3 (PMN) compositions. Their rheological properties and zeta potential measurements characterized slurries. These techniques allowed us to optimize the dispersion parameters of the oxide slurries. We have therefore been able to synthesize as well pure PMN and ZST microwave resonators with very high performances. © *1999 Elsevier Science Limited. All rights reserved*

Keywords: rheology and zeta potential, mixing, powders-solid state reaction, milling.

1 Introduction

Mixing and grinding of oxide slurries is often the first step of the ceramic processing. It is of first importance to be able to control the state of dispersion of the powders into the slurry in order to obtain, after drying, mixed powders composed of homogeneously dispersed particles leading to easy diffusion processes and well controlled solid state reactions when calcining them. In contrast, inhomogeneous mixtures of powders allow the formation of phases with a stoichiometry different from the one of the ceramic composition. The presented results act as illustrations of this with either the synthesis of pure or impure Pb($Mg_{1/3}Nb_{2/3}$)O_3 (PMN) for relaxor capacitors, or of (Zr,Sn)TiO_4 (ZST) with reproductible and high microwave dielectric characteristics, synthesized by solid state reaction.

2 Dispersion of Powders, Rheological Behavior of Slurries and Zeta Potential

The state of dispersion of powders in slurry is highly related to its rheological behavior characterized by rheogramms, representing for example the viscosity versus the shear rate[1]. Non-dispersed, flocculated powder slurries are known to present a shear-thinning (pseudoplastic) behavior generally associated with higher viscosities that decrease with increasing shear rate. This can be explained if considering the break of links between flocs with shear rate, allowing an easier flow of the liquid. On the contrary, well-dispersed stable, defloculated slurries have a shear-thickening (dilatant) behavior.

This is directly dependent on the zeta potential (ζ) of the powders, that represents the potential difference between the surface of the grains and the external plane of Helmholtz (see the model for the electric double layer after Bockris[2] in Fig. 1. The higher this potential with the same polarity is, the more important the electrostatic repulsion between particles. On the other side, when close to the isoelectric point ($\zeta = 0$), the particles tend to flocculate, as illustrated in Fig. 2.

For a given slurry, zeta potential is directly dependent on the pH. When dispersing oxide powders in water, there is a surface reaction leading to the formation of M-OH type hydroxides groups that can dissociate as leak acids or bases:

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$M\text{-}OH_{surface} \Longleftrightarrow M\text{-}O^{-}_{surface} + H^{+}$ in a basic slurry;
$M\text{-}OH_{surface} + H^{+} \Longleftrightarrow M\text{-}OH^{+}_{2\,surface}$ in an acid slurry.

pH of slurries is determinant on the electrostatic charges on the surface of oxide particles and therefore on the potential zeta value, hence on their dispersion state. Previous works[3] devoted to the mixing of titanium oxide and barium carbonate showed the evidence of the importance of pH and density in slurries.

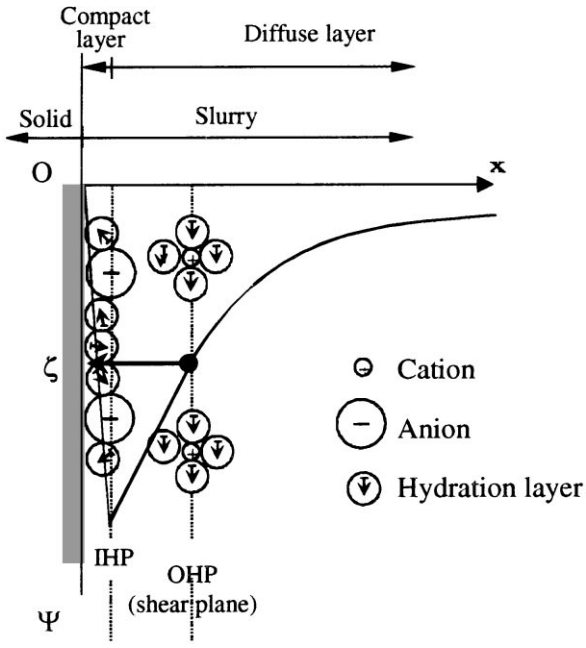

Fig. 1. Model for the electric double layer at the solid-solution interface. The surface going through the centers of ions which are specifically adsorbed on the solid surface is so-called 'Inner Helmholtz Plane' (IHP). The 'Outer Helmholtz Plane' (OHP) indicates the closest distance of approach of hydrated ions in solution (after[2]).

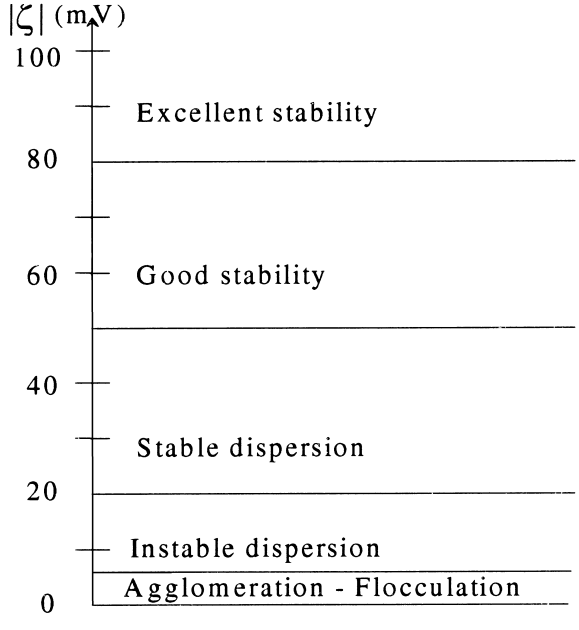

Fig. 2. Slurry stability versus zeta potential.

3 Experimental

Slurries have been dispersed by attrition milling, using a homemade laboratory device. pH adjustments have been made using HCl or NH_4OH. Rheogramms have been established using PHYSICA Rheolab MC10 equipped with cylinders for shear rates ranging from 0 to 1000 s^{-1}. Zeta potential measurements versus pH have been made using MALVERN Zetasizer.

4 Mixing of Powders for ZST Synthesis

The target is to mix together before calcination TiO_2, SnO_2 and ZrO_2 powders, with some NiO and La_2O_3 addition, in weight concentration of 40–50% water slurries. Characteristics of oxides are given in Table 1. It is notable that two zirconium oxides, characterized by different specific surface, are used together.

Figure 3 shows zeta potential value versus pH for each individual powder in water and Fig. 4 shows Zeta potential versus pH of the mixed oxides slurry.

It is clear that, considering the zeta potential behavior, it is necessary to mix the slurry with a basic pH, above 10, to be sure of getting well-dispersed powders. With acid slurries, there is the danger to get some of the constituents not well dispersed. Furthermore, La_2O_3 dissolves in acid slurries when pH is lower than 5.

Figure 5 gathers, for a 40 wt% slurry, the rheogramms recorded for pH values equal, respectively, to 9·9 and 10·5.

Figure 6 shows the viscosity of both 40 and 50 wt% mixed slurries versus pH. It is noteworthy that, for pH above 10, 40 wt% slurries are highly fluid, and characterized by a shear-thickening behavior. On the contrary, with pH lower than 10, slurries are very viscous and present a shear-thinning behavior. The critical pH value is 10·5 for 50 wt% slurries.

So we have determined here conditions to obtain stable dispersions of oxides in water slurries. They

Table 1. Characteristics of oxides

	Purity (%)	*Specific surface BET (m^2/g^{-1})*	*Mean diameter (μm)*
TiO_2 (anatase)	99	9·5	0·5
ZrO_2 (1)	99·5	6·8	11·3
ZrO_2 (2)	99·5	22	1·1
SnO_2	99·9	3·2	0·3
NiO	76% Ni	0·8	9·3
La_2O_3	98	0·5	86·6
PbO	99·7	0·37	6·5
$MgCO_3$	40–43% MgO	17·7	28·4
Nb_2O_5	99·9%	6·98	0·7

depend both on pH and solid particles concentration.

The mixed powders, after calcination and sintering, lead to microwave resonators with very high and reproducible characteristics when mixed in basic conditions (Q*F quality factor higher to 50 000 at 4 GHz).[4,5] On the contrary, when mixing the powders in pure water leading to pH of slurries lower to 10, the too high viscosity of the slurry made it impossible to carry on the process with densities higher to 25 wt%. With lower densities, the measured microwave characteristics of the sintered resonators were much lower and not reproducible.

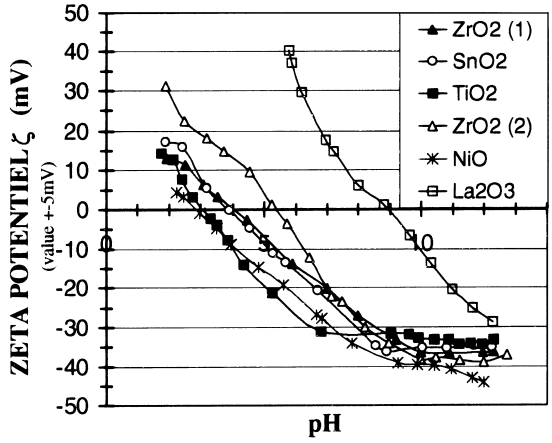

Fig. 3. Zeta potential value for each individual powder to be mixed versus the pH of the slurry for ZST.

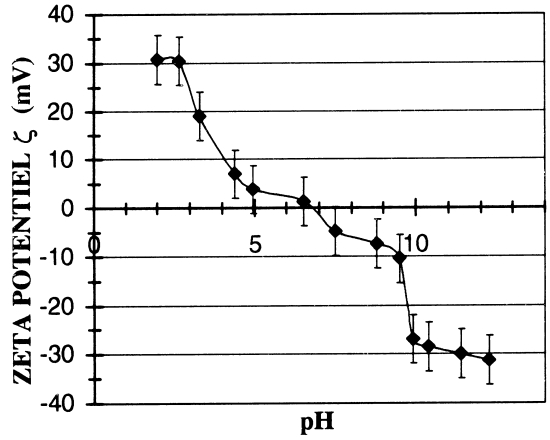

Fig. 4. Zeta potential of the mixed slurry versus pH.

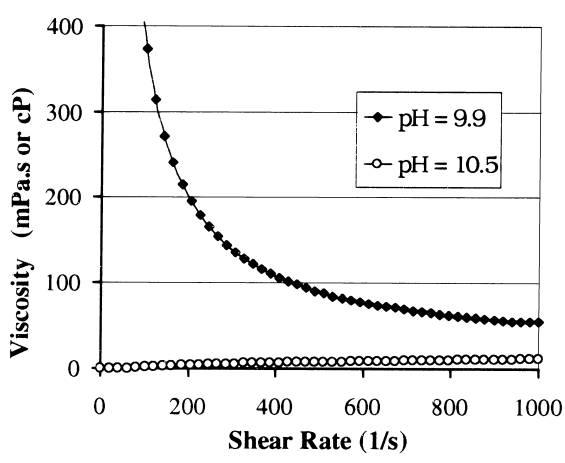

Fig. 5. Rheogramms for ZST raw material slurries (40 wt% density) for two different pH.

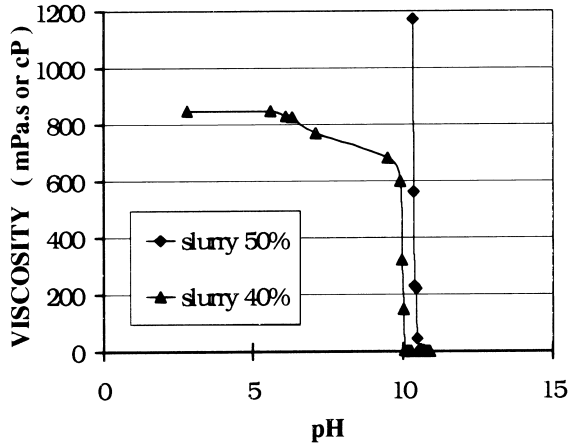

Fig. 6. Viscosity of slurries with solid load of 40 and 50 wt%, for a shear rate of 60 s^{-1}, versus pH.

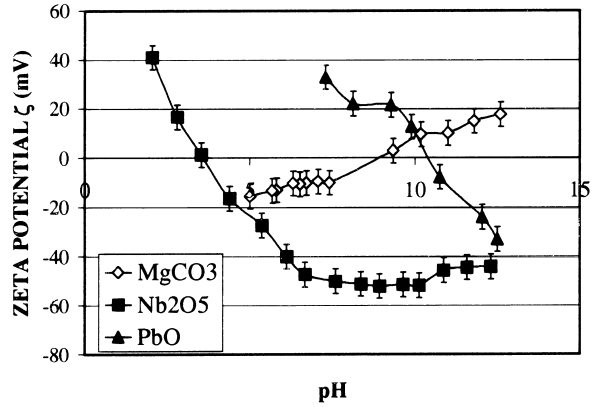

Fig. 7. Zeta potential value for each individual powder to be mixed versus the pH of the slurry for PMN.

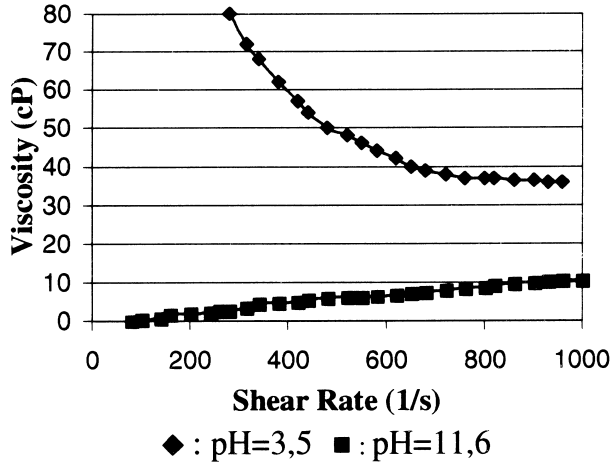

Fig. 8. Rheogramms for Nb_2O_5 slurries at two different pH, for a density of 50 wt%.

Table 2. Behavior of different constituent slurries

	PbO	Nb_2O_5 (cf.Fig. 8)		$MgCO_3$
Density of slurry	50–75 wt%	40–50 wt%	50–75 wt%	25 wt%
Rheological behavior	pseudoplastic	pseudoplastic	dilatant	pseudoplastic
pH of slurry	$11 < pH > 12$ whatever the pH of water is neutral or basic	$3 < pH < 5$ when water is acid or neutral	$pH = 11{\cdot}6$ when water is basic	$8 < pH < 10$ when water is acid or neutral $11 < pH < 13$ when water is basic

5 Mixing of Powders for PMN Synthesis

The target is to mix together before calcination PbO, $MgCO_3$ and Nb_2O_5 powders (characteristics of raw materials are given in Table 1) with stoichiometric amounts in order to obtain, after calcination, a pure relaxor PMN phase. This is a real challenge, as most authors, to be able to get this target, either use a complicated route of synthesizing columbite $MgNb_2O_6$ as an intermediate phase,[6] or cheat a bit and use a slight excess of either lead or magnesium.[7] A previous study showed the possibility to prepare PMN from those three powders but without trying to understand and find the best conditions to have optimal state of dispersion of the slurry.

Figure 7 shows, for each individual powder to be mixed, the zeta potential value versus the pH of the slurry. We can see that values of zeta potential measured for $MgCO_3$ are lower than 20 mV whatever the pH is. So, even if we could find a common pH for the two other powders, the addition of $MgCO_3$ powder explains the difficulty of getting well-dispersed slurries.

Figure 8 shows the rheogramms (viscosity versus shear rate) for both acid and basic Nb_2O_5 slurries. Table 2 summarizes the behaviors of the slurries of the different raw materials. There is a strong correlation between zeta potential values and the corresponding slurry behaviors. It is, *a priori*, impossible to define a pH of the mixed slurry leading to a defloculated state. Whatever the density of the slurry and the pH of the water (the dispersing medium) are, the rheogramm shows a shear-thinning behavior characteristic of a flocculated slurry while the pH of the slurry is measured between 11·6 and 12·3, and the zeta potential is lower than 10 mV.

So it is very difficult to ameliorate slurry dispersion during the attrition milling by adjusting the pH of the slurry. This behavior can explain the difficulty in synthesizing pure PMN by calcination of mixed powders when using stoichiometric proportions even if the apparition of a pyrochlore phase during calcination can be attributed, of course, as well to other parameters. In fact, if an homogeneous slurry is obtained, pure relaxor phase can be obtained thanks to short diffusion paths. Although, if a pyrochlore phase appears, no process of homogenization is able to make it disappear during further high temperature treatments owing to thermodynamic stability. It is only when slurries with low densities have been mixed (using a high energy grinding process as attrition milling) and calcination with a confined atmosphere has been processed, that we have been able to obtain directly stoichiometric pure PMN.[9]

6 Conclusion

The control of the pH of mixed oxides in aqueous slurry can allow defloculation, as in the case of ZST precursor powders. Then, further calcination can lead to the synthesis of reproducible materials.

Rheology measurements and zetametry are two complementary analysis techniques that help to predict the slurry behaviors and, therefore, to easily define optimum mixing experimental parameters.

Acknowledgement

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