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# Surface modification of $Dy_2O_3$–$Nb_2O_5$ dope mix for dielectric materials in aqueous dispersion

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## Abstract

The electrokinetic mismatch between the basic dielectric compound (Ba,Ca)(Ti,Zr)$O_3$ (BCTZ) and $Dy_2O_3$–$Nb_2O_5$ dope mix in aqueous suspensions has been improved by a pre-firing and milling treatment of the dope mix. Pre-fired dope mix showed a much higher zeta potential which resulted in a drastic improvement of the particle dispersion in aqueous slurries. By use of surface-modified dope mix the homogeneity of the micro structure of multilayer ceramic capacitors is improved and the break-down voltage of thin (7 μm) dielectric layers increased. The results observed indicate the critical influence of the micro structural homogeneity on the breakdown voltage of MLCCs. © 2000 Published by Elsevier Science Ltd. All rights reserved.

*Keywords:* $BaTiO_3$ and titanates; Dielectric properties; Multilayer ceramic capacitors; Perovskites; Suspensions

## 1. Introduction

Recently, multilayer ceramic capacitors (MLCC) have been developed showing very high capacitance per volume. The specific capacitance of these capacitors was increased mainly by a reduction of the dielectric thickness. The dielectric layers are normally produced from ceramic foils which are tape casted from aqueous slurries of ceramic powder, organic polymeric binder and a plasticizer. With decreasing thickness the homogeneity of the ceramic layers becomes a critical problem. The quality of the foils is determined by the chemical and physical properties of the powder suspension and its constituents. The homogeneity of the suspension can be improved by careful control of the suspension chemistry, so that flocculation of the ceramic particles cannot occur in the slurry.[1]

The stability of aqueous suspensions, consisting of two or more ceramic powders is controlled by differences in the electrokinetic properties of the individual constituents. These differences commonly lead to flocculation of the particles which in turn negatively influences the homogeneity and hence the electrical reliability of the dielectric ceramic layer. Therefore, in order to obtain MLCCs of superior performance, considerable efforts have been made to improve the stability of multi-constituent suspensions by modifying the surface of the ceramic particles.[2,3] The normal way to modify the surface of ceramic particles is coating with a steric stabiliser, containing acidic or basic functional groups.[4]

This study deals with the improvement of the surface characteristics of $Dy_2O_3$ dope. Rare earth dopes like $Dy_2O_3$ are employed to suppress the electronic conduction of $BaTiO_3$-based dielectrics which are co-fired with (Ni) base metal electrodes in reducing atmosphere.[5] The distribution of Dy in the green foil is critical with respect to the break-down voltage and life stability of MLCCs with thin dielectric layers. Instead of varying the dispersant, the surface of the $Dy_2O_3$ dope was modified by co-firing with $Nb_2O_5$, having a much better dispersion behaviour in aqueous suspension.

## 2. Experiments

### 2.1. Preparation of materials and MLCCs

To commercial (Ba,Ca)(Ti,Zr)$O_3$ (BCTZ) powder (Nippon-Chemical, Tokyo) 1–2 mol% of the dope mix of $Dy_2O_3$ (Merck, Darmstadt, Germany) and $Nb_2O_5$

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(H.C. Starck, Goslar, Germany) were added. The powder characteristics are listed in Table 1. $Dy_2O_3$ and $Nb_2O_5$ were mixed in a pre-determined molar ratio of 8:3 and thereafter calcined at various temperatures in the range 700–1100°C. Ceramic powders were then mixed with an aqueous solution of polyvinyl alcohol (PVA) binder to prepare a slurry. Mixing and milling were carried out in water, using a ball mill with 2 mm∅-stabilized zirconia balls. Ceramic green foils were tape-casted to a thickness of ≈12 μm. After sieve printing of Ni electrodes the foils were stacked, laminated and cut to form MLCCs of the size 1206 with 150 active dielectric layers. The MLCCs were fired at 1300°C for 2 h in a reducing atmosphere of moist nitrogen and hydrogen, having an oxygen partial pressure of $P_{o_2} = 1.2\times10^{-14}$ bar. The fired chips were terminated with Cu electrodes and then electroplated with nickel and tin to provide surface mountable MLCCs.

### 2.2. Methods

The dispersion behaviour of BCTZ and doping oxides was studied in aqueous suspension as function of pH and the amount of ammonium poly-acrylate (Dispex A, molecular weight ≈4000, Allied Colloids, Hamburg, Germany). Disintegration of particle aggregates was achieved by use of ultrasonic energy. The colloidal stability of the aqueous suspensions was determined by measuring the electrophoretic mobility (zeta potential analyser Model 1202, Micromertics, Norcross, USA). 0.01 g powder was suspended in 100 ml water, containing 5 vol% 0.01 molar KCl solution. The pH of the powder dispersion was adjusted by adding a few drops of either 0.01 molar HCL or 0.01 molar NaOH solution. For sedimentation experiments powder dispersions showing a solid content of 60 wt% were filled in tubes of 50 cm length.

Photo-electron spectra of Dy and Nb were measured, using a XPS spectrometer (ESCA, LAB SIMS Vacuum Generator, USA). Mg-$K_\alpha$ radiation (1253.6 eV) was used as X-ray source. The measured binding energies were 161.8 eV for Dy(4d5) and 213.2 eV for Nb(3d5) without considering charge compensation. Carbon contaminations which were most probably due to carbonates were assumed to have no influence on the measured Dy/Nb ratios.

Table 1
BCTZ, $Dy_2O_3$ and $Nb_2O_5$ powder characteristics

| Power | BET | Particle size (μm) | | |
|---|---|---|---|---|
| | (m²/g) | d90 | d50 | d10 |
| BCTZ | 3.6 | 1.72 | 0.92 | 0.45 |
| $Dy_2O_3$ | 6.3 | 1.56 | 0.78 | 0.25 |
| $Nb_2O_5$ | 10.5 | 0.83 | 0.30 | <0.10 |

X-ray diffraction (XRD) measurements on calcined mixtures of $Dy_2O_3$ and $Nb_2O_5$ were carried out with Cu-$K_\alpha$ radiation, using a vertical goniometer (PHILIPS PW 1050/81, Almeloo, The Netherlands).

The composition of sedimentation layers was studied using electron microbeam analyses (EDAX Inc., Mahwah NJ, USA) in SEM (XL 30 FEG, FEI & PHILIPS, Eindhoven, The Netherlands). Powder layers were carefully pipetted and dried and thereafter semiquantitatively analysed for Nb and Dy. Deviations from the original $Dy_2O_3/Nb_2O_5$-ratio 8:3 into Nb- or Dy-rich fractions could be thus easily detected.

Microstructures have been studied with SEM on MLCCs which have been broken perpendicular to the dielectric layers and covered with 30 nm carbon layers. The insulation resistance (IR) of MLCCs was measured with a digital electrometer (Advantest TR8652). The breakdown voltage was determined at a rate of 100 V/min (detector current: 1 mA).

## 3. Results and discussion

### 3.1. Zeta potential of BCTZ, $Dy_2O_3$ and $Nb_2O_5$

It is well known that in aqueous media the electric charge, controlling the agglomeration of particles, depends on the pH, the nature and concentration of electrolytes. Fig. 1 shows the electrophoretic mobility as function of pH for the three compounds BCTZ, $Dy_2O_3$ and $Nb_2O_5$. The isoelectric point (IEP) of BCTZ was found at pH≈5 and that of $Dy_2O_3$ at about pH≈9. There was no IEP detected for suspensions of $Nb_2O_5$ which were negatively charged over the whole range pH≈2–11. Because of the chemical instability of $BaTiO_3$ in contact with water the values reported for Zeta potential and IEP vary considerably in aqueous suspension. BaO is washed out from the particle surface so that the IEP values of BCTZ are often similar to those reported for $TiO_2$.[6] The surface of $Dy_2O_3$ is assumed to

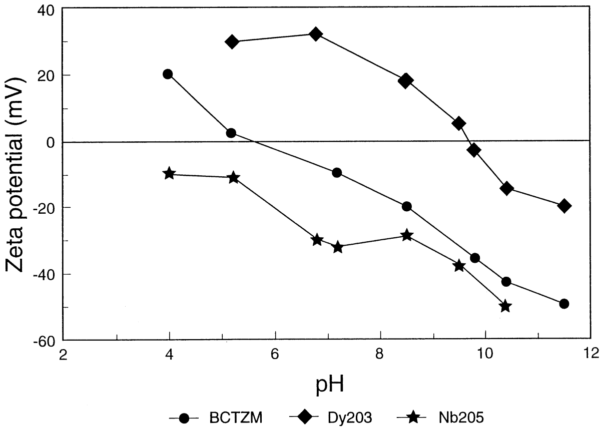

Fig. 1. Zeta potential of BCTZ, $Dy_2O_3$ and $Nb_2O_5$ as a function of pH.

be initially covered with a layer of $OH^{\xi}$ groups which are able to gain or loose a proton, resulting in an electrically charged surface.[7]

Interpreting the results of electrophoretic measurements, mutual flocculation of BCTZ, $Dy_2O_3$ and $Nb_2O_5$ is expected to occur in aqueous suspensions between pH 4 and 9, where the oxides are oppositely charged.[8] Stable suspensions of BCTZ, $Dy_2O_3$ and $Nb_2O_5$ can be expected for pH > 9.

### *3.2. Firing effects of $Dy_2O_3$ and $Nb_2O_5$ on zeta potential*

Mixtures of $Dy_2O_3$–$Nb_2O_5$ (Dy:Nb≈8:3) were fired for 30 min at five temperatures, 700, 800, 900, 1000 and 1100°C. XRD pattern did not reveal the existence of new phases formed during firing. At temperatures above 700°C the IEP of $Dy_2O_3$–$Nb_2O_5$ mixtures was significantly affected by the pre-firing procedure and shifted between those of pure $Dy_2O_3$ and pure $Nb_2O_5$ (Fig. 2). A minimum pH≈6.3 was obtained for the IEP after pre-firing at 900°C (Fig. 3). In contrast to pre-firing in the range 700–900°C, the IEP was shifted to higher pH values after pre-firing in the range 900–1100°C.

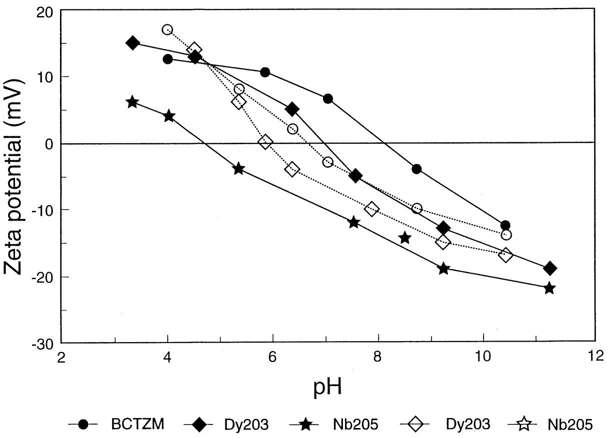

Fig. 2. Effect of (30 min) pre-firing temperature on Zeta potential of $Dy_2O_3$–$Nb_2O_5$ mixtures as a function of pH.

From the observed changes of IEP has been deduced, that the atomic ratio of Dy and Nb on the surface, determining the zeta potential, has been changed by firing. It may be assumed, when more Nb is present on the surface, the isoelectric point is shifted to a lower pH. On the contrary, when more Dy is present on the surfaces, the IEP is shifted to a higher pH. As a plausible explanation of the pre-firing effect, surface diffusion of $Dy_2O_3$ or $Nb_2O_5$ or a chemical interaction between both oxides have possibly given rise to the shift of the IEP from pH≈9 to 6.3 in the temperature range 700–900°C. At temperatures > 900°C presumably a reduction of the Nb content on the surface has taken place. For confirmation of this assumption, the surface of the mixture was analysed using XPS (Section 3.4).

The effect of firing time on the IEP was found to be only moderate in contrast to that of the firing temperature. After 4 h soaking at 900°C the IEP increased from pH≈6.5 to 8. This result suggests again a reduction of the Nb content on the surface of the mixture.

### *3.3. Effect of milling on the electrophoretic mobility of pre-fired $Dy_2O_3$–$Nb_2O_5$ mixtures*

In the previous sections it has been stressed that for higher firing temperatures (> 900°C) or longer soaking times (> 1 h) depletion of Nb on the surface of powder particles may occur. For elucidation of this effect $Dy_2O_3$–$Nb_2O_5$ mixtures were pre-fired at two different temperatures and then ball milled for several hours in water.

Samples fired for 30 min at 900°C, showed an IEP at pH≈6.6 and those fired for 4 h at 1100°C had an IEP at pH≈9.1. Surprisingly, the isoelectric points of the two mixtures shifted into opposite directions with increasing milling time. As shown in Fig. 4, after 8 h milling the IEP of $Dy_2O_3$–$Nb_2O_5$ pre-fired for 30 min at 900°C

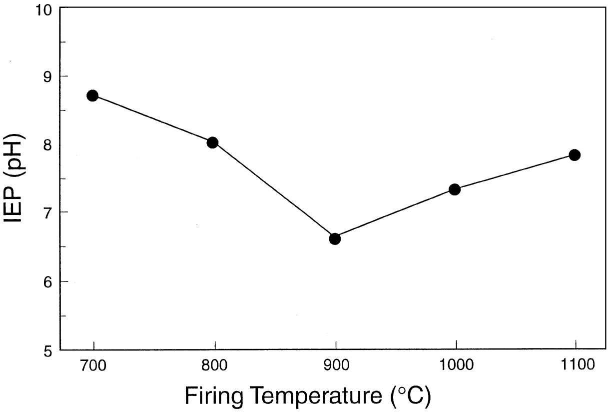

Fig. 3. IEP of $Dy_2O_3$–$Nb_2O_5$ mixtures as a function of pre-firing (30 min) temperature.

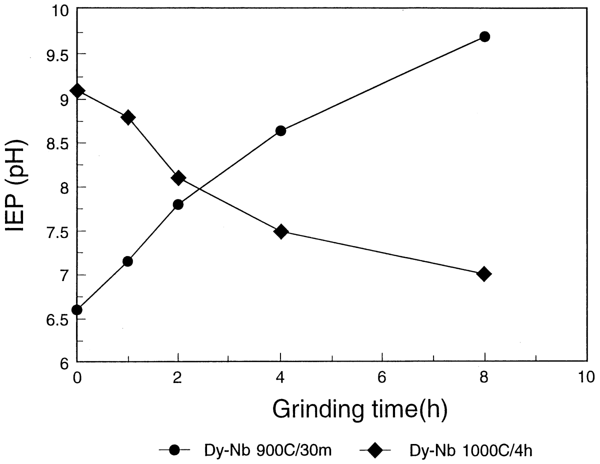

Fig. 4. IEP of $Dy_2O_3$–$Nb_2O_5$ mixtures, pre-fired for 30 min at 900°C and for 4 h at 1100°C as function of grinding time.

increased from pH≈6.6 to ≈9.75, while that of the sample fired for 4 h at 1100°C decreased from pH≈9.1 to ≈7.

These results are probably associated with the surface concentrations of Nb and Dy in $Dy_2O_3$–$Nb_2O_5$. According to our previous assumption, more Nb is present on the surface of mixtures fired at lower temperature and shorter soaking time, while more Dy is present on the surface of mixtures fired at higher temperature or for longer time.

In mixtures fired for 30 min at 900°C, the surface concentration of Nb was probably decreased with increasing milling time. The lower Nb concentration contributed thus to the increase of the IEP. The reduction of the IEP with increasing milling time observed for mixtures fired for 4 h at 1100°C is explained by the assumption that the Dy concentration on the surface is gradually decreased during ball milling. In the next section the composition of the surface of differently pretreated $Dy_2O_3$–$Nb_2O_5$ mixtures is analyzed, using XPS to confirm the above presumption.

### 3.4. XPS analyses

X-ray photo-electron spectroscopy technique (XPS) was found to be a powerful tool to determine the surface composition of differently pre-treated $Dy_2O_3$–$Nb_2O_5$ mixtures. The different surface compositions of 4 pre-treated mixtures could be confirmed by intensity changes of the XPS peaks of Dy and Nb. The XPS results are shown in Table 2.

- $Dy_2O_3$–$Nb_2O_5$ mixtures fired for 30 min at 900°C clearly showed the highest Nb content on the surface. With increasing milling time the outer layers of the particles were removed and the composition of the core of the particles was uncovered which had a lower Nb content.
- With increasing pre-firing temperature and time the Nb content on the surface is greatly decreased which may be due to diffusion of Nb into the interior or of Dy to the surface of the particles. With increasing milling time the outer layers of the particles were removed again so that the core of the $Dy_2O_3$–$Nb_2O_5$ particles appeared, showing a higher Nb content.

Table 2
ESCA data of Dy–Nb mixtures for different pre-treatment conditions

| Pre-treatment condition | | | Element concentration (mol%) | | | | |
|---|---|---|---|---|---|---|---|
| Temperature | Time | Milling time | O | C | Nb | Dy | Nb/Dy ratio |
| 900°C | 30 min | Without | 45.7 | 34.5 | 15.4 | 4.4 | 3.5 |
| 900°C | 30 min | 4 h | 41.2 | 47.2 | 7.1 | 4.5 | 1.58 |
| 1100°C | 4 h | Without | 37.5 | 50.8 | 5.2 | 6.5 | 0.80 |
| 1100°C | 4 h | 8 h | 45.9 | 43.5 | 7.8 | 2.8 | 2.79 |

The results of XPS analyses of the surface composition of the $Dy_2O_3$–$Nb_2O_5$ dope mix demonstrate the different surface chemical properties after thermal treatment and milling. The measured surface concentrations of Nb correlate well with the isoelectric points. The IEP can thus be in fact considered as a useful indicator of the Nb content on the particle surface.

### 3.5. Dispersion and sedimentation

For foil casting of dielectric layers water-based slurries of ceramic powder and binder were used. The ceramic powder must be stabilized by means of a polyelectrolyte dispersant in the slurry. For investigation of the dispersion behaviour various treated and untreated $Dy_2O_3$–$Nb_2O_5$ mixtures were dispersed in water, using 0.8 wt% ammonium polyacrylate as dispersant. Since aqueous suspensions of differently treated powders exhibited different pH values, ranging from pH≈8 to 10, the pH was adjusted to a value of 9.5 in all suspensions.

As the dispersant is adsorbed onto the powder surface, the negative surface charge density will be increased, thus enhancing the electrophoretic mobility.[9] As can be seen in Fig. 5, the zeta potential increases strongly for low ammonium polyacrylate concentrations (<0.8 wt%), regardless of the pre-treatment condition for the $Dy_2O_3$–$Nb_2O_5$ mixtures. Above 0.8 wt% dispersant, the zeta potential levels off to a constant. It can be seen again that pre-treatment of the dope mix is of great importance for the dispersion behaviour. The Zeta potential of $Dy_2O_3$–$Nb_2O_5$ mixtures, pre-treated for 30 min at 900°C without grinding, is quite similar to that of BCTZ. However, it changes considerably after 30 min milling.

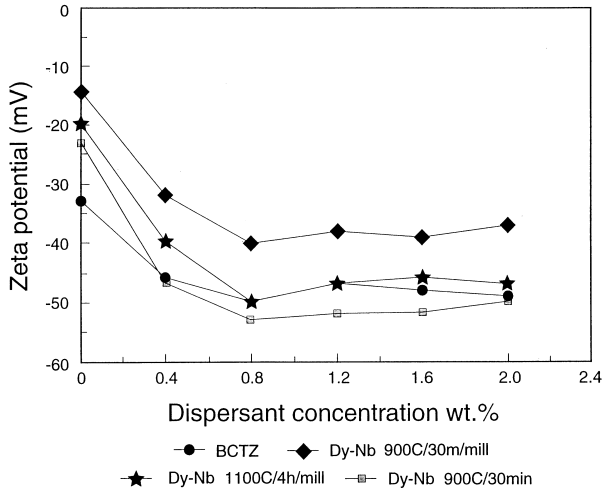

Fig. 5. Zeta potential of BCTZ, $Dy_2O_3$ and $Nb_2O_5$ mixtures with different pre-treatment as a function of dispersant (Dispex A) concentration at pH = 9.5.

The colloidal stability of dielectric powder dispersions was determined by sedimentation experiments. Fig. 6 schematically depicts sedimentation heights of various $Dy_2O_3$–$Nb_2O_5$ slurries containing 0.8 wt% dispersant. The most stable dispersion had the highest particle packing density and thus the smallest sedimentation volume. The pH of the suspensions was the same as for the zeta potential measurements. For untreated $Dy_2O_3$ and $Nb_2O_5$ the slurries separated into a bottom layer consisting of densely packed $Nb_2O_5$ and loosely packed $Dy_2O_3$ rich sediments just above. The composition of the sedimentation layers was semiquatitatively determined by EDAX in SEM as described in Chapter 2. No clear boundary could be identified between sediments and the quite turbid upper liquid. Grinded $Dy_2O_3$–$Nb_2O_5$ which had been treated either for 30 min at 900°C or 4 h at 1100°C, showed two layers, consisting of densely packed $Dy_2O_3$–$Nb_2O_5$ mixture on the bottom and above a small $Nb_2O_5$ or $Dy_2O_3$ rich layer respectively. According to the previous discussion, a $Nb_2O_5$-rich upper layer was in the mixture pre-fired for 30 min at 900°C and a $Dy_2O_3$-rich upper layer on the mixture pre-fired at 1100°C for 4 h. On the contrary, only one sedimentation layer was observed for the $Dy_2O_3$–$Nb_2O_5$ mixture pre-treated at 900°C for 30 min without further grinding. The liquid above the sediment was clear and the boundary between the compact $Dy_2O_3$–$Nb_2O_5$ sediment was very sharp. This mixture showed the lowest sedimentation volume.

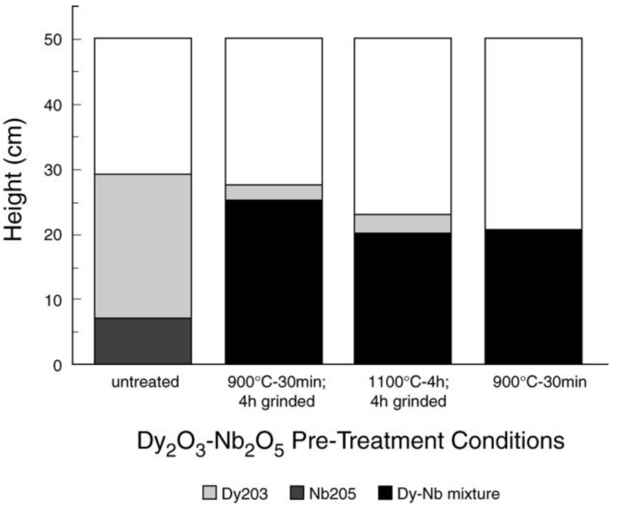

Fig. 6. Sedimentation height of various pre-treated $Dy_2O_3$–$Nb_2O_5$ dope mixes in aqueous suspension, containing 0.8 wt% dispersant.

### 3.6. Microstructure and break-down voltage of MLCCs

MLCCs with 150 dielectric layers of 7 μm thickness were prepared, using BCTZ and various pre-treated mixtures of $Dy_2O_3$–$Nb_2O_5$. MLCCs produced from unmilled, 30 min at 900°C pre-treated dope mix exhibited rather homogeneous microstructures, showing grains of 3–5 μm average diameter. MLCCs produced from untreated dope mix exhibited a broader grain size distribution, ranging from 2–7 μm. As a consequence, the homogeneity of the microstructure of MLCCs can be significantly improved by thermal pre-treatment of the dope mix. Increasing the degree of dispersion by reducing the mismatch of IEP between BCTZ and the doping oxide mixture is thus an important step to produce homogeneous green products and to improve the microstructure.[10]

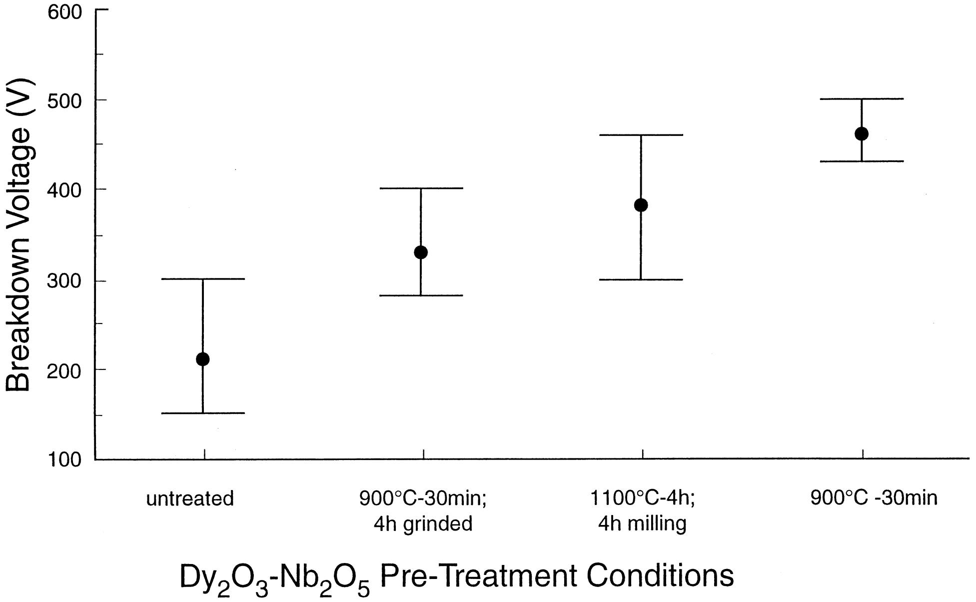

Fig. 7. Dependence of DC break-down voltage of MLCCs prepared, using various pre-fired and grinded $Dy_2O_3$–$Nb_2O_5$ dope mixes. Error bars refer to the standard deviation of Vbd.

Fig. 7 shows the breakdown voltage (Vbd) of MLCCs with 150 layers of 7 μm which have been prepared from BCTZ and differently pre-treated $Dy_2O_3$–$Nb_2O_5$ dope mixtures. It is worthy to note, that not only the mean value of Vbd but also the standard deviation of Vbd are both improved after use of pre-treated dope mix. MLCCs prepared using $Dy_2O_3$–$Nb_2O_5$ dope mix, pre-treated at 900°C for 30 min without milling, showed the highest performance. It is already known that there is a direct relationship between breakdown voltages and the microstructure of MLCCs.[11] High values of Vbd are observed in MLCCs showing the most homogeneous grain the size distribution. The observed correlation between the dispersion behaviour of Dy-Nb dope mix and breakdown voltage agrees well with previous investigations of Y. Yoneda[12] who stated that the distribution of Dy in green foil has a strong influence on the electrical break-down behaviour.

## 4. Conclusions

The following conclusions were drawn from the experimental results.

Mismatch of the electrokinetic behaviour of $Dy_2O_3$, $Nb_2O_5$ and the basic dielectric composition (Ba,Ca)(Ti,Zr)$O_3$ in aqueous suspension can be largely reduced by a surface modification of the $Dy_2O_3$ which is attained by cofiring the $Dy_2O_3$ with $Nb_2O_5$.

It has been demonstrated that the electrokinetic behaviour of the $Dy_2O_3$–$Nb_2O_5$ doping oxide mixture is mutually affected by the firing temperature, firing time and milling time. Isoelectric points correlate well with the Nb content on the particle surface, reflecting a surface behaviour ranging from almost pure $Dy_2O_3$ as one extreme, to predominant $Nb_2O_5$ as the other extreme.

Heat treatment of the dope mix of $Dy_2O_3$ and $Nb_2O_5$ leads to a strong improvement of the dispersion degree of BCTZ and the doping oxides which is closely correlated with a large improvement of the microstructure homogeneity and the electrical properties.

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