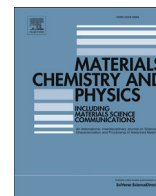




Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Materials science communication

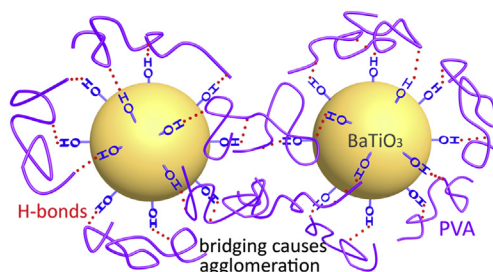
Effect of surface hydroxyl groups on the dispersion of ceramic powders

Tse-Hsing Ho^a, Shinn-Jen Chang^b, Chia-Chen Li^{a,*}^a Institute of Materials Science and Engineering, and Department of Materials & Mineral Resources Engineering, National Taipei University of Technology, Taipei 10608, Taiwan^b Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 30011, Taiwan

HIGHLIGHTS

- Effect of surface hydroxyl group on the dispersity of oxides was explored.
- Larger amount of dispersant was required for dispersing hydroxylated oxides.
- Organic additives became more competitive to adsorb on the hydroxylated oxides.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 4 September 2015

Received in revised form

15 January 2016

Accepted 23 January 2016

Available online xxx

Keywords:

Ceramics

Oxides

Adsorption

Surface properties

ABSTRACT

The effect of surface hydroxyl groups (–OH) on the dispersity of ceramic powders was explored using the common ceramic powder barium titanate (BaTiO₃) as the study model. To simulate the presence of –OH on the powder, which is generally formed because of atmospheric storage, oxidative hydroxylation with hydrogen peroxide was used to produce and adjust the concentration of surface –OH. Owing to the presence of a lot of surface –OH, BaTiO₃ particles aggregated because of hydrogen bonding and required a large amount of dispersant such as the ammonium salt of poly(acrylic acid) (PAA-NH₄) for its dispersion stabilization. In addition, the commonly used binder poly(vinyl alcohol) (PVA) became more competitive with PAA-NH₄ for adsorption onto the hydroxylated BaTiO₃, thereby reducing the efficiency of the dispersant and impeding the dispersion of the powder.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Most ceramic powders have characteristics of both ionic and covalent bonding; therefore, they are usually polar, particularly when the ionic character is more significant, as in the case of barium titanate (BaTiO₃), alumina (Al₂O₃), zirconia (ZrO₂), and titania (TiO₂) [1,2]. Because of their significant polarity and large

surface area, ceramic powders easily absorb water vapor from the atmosphere during storage. In general, water vapor does not simply adsorb physically but tends to be transformed by hydration upon chemical adsorption, thereby producing hydroxyl groups (–OH) on the surface of the powder [3–6]. Because hydration is a chemical reaction, it is irreversible; regular drying in an oven does not easily remove the produced –OH. Hydrogen bonds (H–bonds) between surface –OH groups of powders (caused by hydration) tend to initiate powder aggregation and make subsequent dispersion processes more difficult. The resultant poor dispersity and low compatibility of the powder with other materials will restrict its

* Corresponding author.

E-mail address: ccli@ntut.edu.tw (C.-C. Li).

applications.

BaTiO₃ is a popular dielectric material in the industry of passive electronic components [7–10]. It is the most essential dielectric ceramic for commercial products consisting of multilayered ceramic capacitors (MLCCs). In the fabrication of MLCCs, BaTiO₃ powder is blended with other additives in a solvent to form homogeneous slurry in the initial steps. Several studies [11–15] report the importance of using water as a solvent for the preparation of ceramic slurries for economic and environmental reasons. Because BaTiO₃ is generally stored under ambient conditions prior to processing, it tends to undergo hydration due to water vapor in the air. Furthermore, it may be hydrated by water from the aqueous process during fabrication. Both the above hydration routes irreversibly produce surface –OH. This phenomenon is more severe with nanosized powders; yet, such powders are in high demand for the development of small electronic devices.

In preliminary research [15–17], we found that mild oxidative conditions could produce –OH on the surface of BaTiO₃ particles. As the corresponding technique and mechanism of BaTiO₃ hydroxylation have been established and well studied, hydroxylated BaTiO₃ is suitable for use as a study model to explore the effect of surface –OH on the dispersibility of ceramic powders. The interaction between the surface –OH of BaTiO₃ and organic additives, such as the dispersant and binder, was also investigated. Results of this investigation closely correlated to the dispersion of ceramic powders.

2. Materials and methods

High-purity BaTiO₃ powder (99.8%; Fuji Titanium, trace-metal basis, Japan) having ~0.63 μm median size, 3.7 m²/g surface area, and 0.997 barium/titanate ratio was used. An aqueous solution of hydrogen peroxide (H₂O₂; 50.38%, Echo Chemical Co., Taiwan) was used for the hydroxylation of BaTiO₃. The dispersant used was ammonium poly(acrylic acid) (PAA-NH₄; Darvan-821A, R. T. Vanderbilt, Norwalk, CT) with molecular weight of 6000 g/mol. The binder used was poly(vinyl alcohol) (PVA; 88.0% hydrolysis, Chang Chun Petrochemical, Taiwan) with molecular weight of 27,000–32,000 g/mol. Deionized water was used as the dispersion medium.

For hydroxylation, 1 g of BaTiO₃ powder was refluxed in a specific volume of H₂O_{2(aq)} at 106 °C for 4 h [15–17]. After reflux, the hydroxylated BaTiO₃ was filtered and washed with deionized water until the filtrate reached a pH higher than 6.5. It was then rinsed with acetone to extract most of the moisture. The powder was dried and stored in a vacuum desiccator for at least one day. In the dispersion experiments on adsorption and in rheology measurements, aqueous suspensions with 5 wt% and 10 vol% BaTiO₃ powder (based on the weight of solvent) were respectively prepared by mixing powder with PAA-NH₄ and PVA at various concentrations (based on the weight of BaTiO₃). The suspensions were then mixed and de-agglomerated by ball-milling with 10 mm Y₂O₃-stabilized ZrO₂ media for 72 h. The adsorptions of PAA-NH₄ and PVA on BaTiO₃ were respectively measured by potentiometric titration [11,13] and thermogravimetric analysis (Q50, TA Instruments Ltd., UK). The apparent viscosities of the powder suspensions were measured at various shear rates by using a concentric cylinder rheometer (AR1000, TA Instruments Ltd., UK). Cone-plate geometry fixtures with a diameter of 20 mm and cone angle of 1° were chosen for the steady-shear rotation tests. Also, the respective viscosities of two aqueous solutions of 1 wt% PAA-NH₄ and 10 wt% PVA were measured at various shear rates for the further calculations of relative viscosities of powder suspensions. The interaction between PAA-NH₄ and PVA was characterized by Fourier transform infrared (FT-IR) spectroscopy (DA 8.3, Bomen, Canada) using a sample of the mixture at a 1:1 weight ratio.

3. Results and discussion

To simulate the presence of –OH on BaTiO₃ caused by hydration under ambient conditions, BaTiO₃ was mildly hydroxylated by surface treatment with H₂O₂ [15–17]. Fig. 1 compares the FT-IR spectra of BaTiO₃ powders hydroxylated with H₂O₂ at various concentrations. As-received BaTiO₃ (labeled as PBT) was dried at 80 °C for 24 h before FT-IR characterization; however, it exhibited slight IR absorption corresponding to –OH stretching at 3000–3600 cm⁻¹ [18]. This result shows that –OH, which is mostly due to hydration of the powder, was chemically bonded and could not be easily removed. For the hydroxylated BaTiO₃ powders that were surface-treated with H₂O₂ at concentrations of 10, 25, 40, 60, 90, and 120 mL/g BaTiO₃ (mL/g BT) (labeled as HBT-10, HBT-25, HBT-40, HBT-60, HBT-90, and HBT-120, respectively), the IR absorption of –OH (3000–3600 cm⁻¹) significantly increased with increasing the H₂O₂ treatment concentration. This increase demonstrated that oxidative hydroxylation by H₂O₂ could simulating the varied –OH concentration on the BaTiO₃ surface.

Fig. 2(a) shows the adsorbed amount of the dispersant PAA-NH₄ on various BaTiO₃ powders as a function of the equilibrium concentration of PAA-NH₄ in the suspension. In all cases of adsorption on the various BaTiO₃ powders, the adsorbed amount of PAA-NH₄ initially increased and then reached a saturation limit, showing the characteristic behavior of monolayer adsorption [11,13,19,20]. This result indicates that the mechanism of PAA-NH₄ adsorption on the powders was not affected by the increased concentration of surface –OH. Nevertheless, more hydroxylated BaTiO₃ exhibited a higher saturation limit for PAA-NH₄. As the increase in polarity, resulting from the greater degree of hydroxylation of BaTiO₃, enhanced the polar–polar and ion–polar interactions, more hydroxylated BaTiO₃ may have increased the adsorption of PAA-NH₄. Fig. 2(b) shows the

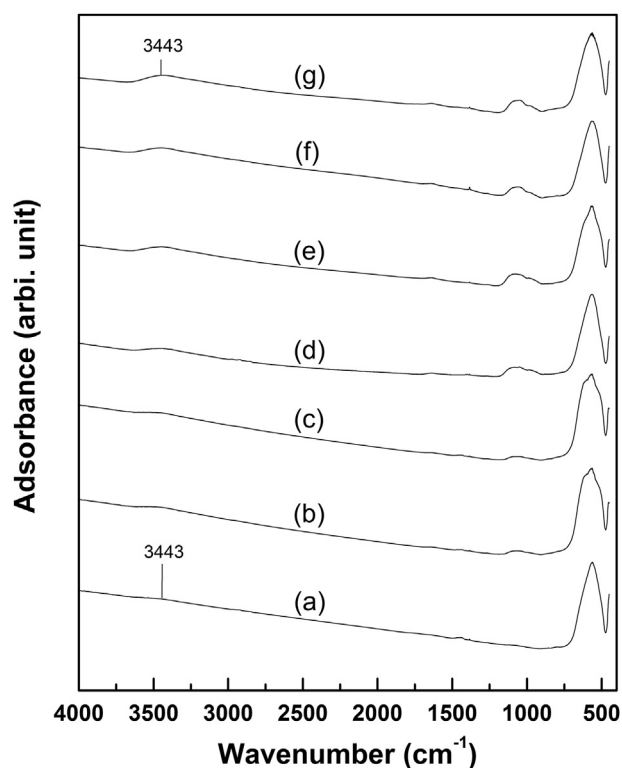


Fig. 1. FT-IR spectra of (a) as-received BaTiO₃ and of hydroxylated BaTiO₃ surface-treated with H₂O₂ with concentrations of (b) 10, (c) 25, (d) 40, (e) 60, (f) 90, and (g) 120 mL/g BT.

Download English Version:

<https://daneshyari.com/en/article/1520799>

Download Persian Version:

<https://daneshyari.com/article/1520799>

[Daneshyari.com](https://daneshyari.com)