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Detection Of Barium Ion Leaching From Barium Titanate Powder In Water By EDTA Titration

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ABSTRACT

An obstacle for using a water-based processing of barium titanate ($BaTiO_3$) powders in the electro-ceramics industry is the leaching of Ba^{2+} in water due to the thermodynamic instability of $BaTiO_3$. It is demonstrated here that the amount of Ba^{2+} leaching from $BaTiO_3$ in water can be determined by the EDTA titration method. In order to confirm the reliability of this method, a blank test is performed with the known amount of Ba^{2+} by dissolving Ba-acetate in water. The effect of some organic processing additives on EDTA titration is also examined. The results show that the EDTA titration method is quite reliable in measuring the amount of Ba^{2+} from $BaTiO_3$ in water unless a precipitate is formed by the reaction between Ba^{2+} and organic materials added. © 2005 Trade Science Inc. - INDIA

KEYWORDS

Barium titanate;
Ceramic;
Leaching;
EDTA titration;
MLCC.

INTRODUCTION

Barium titanate ($BaTiO_3$) is one of the most widely used ceramic raw materials in the electro-ceramics industry such as multi-layer ceramic capacitors (MLCCs), communication filters, PTC thermistors and sensors[1-4]. For many of these applications, dispersion of $BaTiO_3$ in liquid medium is required. Non-aqueous media have traditionally been used for this purpose[5]. For economic and environmental reasons, however, water-based formulation has been receiving increasing attention nowadays[6].

One of the obstacles for using a water-based $BaTiO_3$ processing in the electro-ceramic industry is the leaching of Ba^{2+} in water, resulting in an inconsistent Ba/Ti stoichiometry in the system[7,8]. An inconsistent Ba/Ti ratio in the system changes the properties of the final products[9,10]. In addition,

leached Ba^{2+} from the $BaTiO_3$ surface can interact in an adverse manner with various polymeric additives such as binder, dispersant and plasticizer which are added to facilitate the ceramic processing[11,12]. Therefore, in order to use the water-based system in the electro-ceramics industry with greater reliability, understanding and controlling the Ba^{2+} leaching are essential. These will help preserving the chemical homogeneity in the final product and preventing adverse interactions with such organic additives as dispersants and binders.

Better known methods for quantitative analysis of Ba^{2+} in a solution are inductively coupled plasma (ICP) spectroscopy[13] and atomic absorption spectroscopy (AAS)[7,14]. Although ICP and AAS have been used widely, spectral interference may present a problem[15]. Due to the high temperature of the plasma, the spectra are complex with many atom and ion lines[15]. Therefore, spectral line interference can be severe and may necessitate the use of a less sensitive line to solve a particular analytical problem[15]. In addition, both of the equipment are quite expensive. A third way to determine the amount of leached Ba^{2+} in relatively faster, easier and cheaper way is titration with ethylenediaminetetraacetic acid (EDTA)[16]. Methyl thymol blue is used as a color indicator for the Ba^{2+} ion to detect the titration end point. Adding a small amount of this color agent into the Ba^{2+} solution forms a blue complex with Ba^{2+}. When all the free Ba^{2+} ions are chelated by EDTA titrant, the indicator is displaced from the barium, causing the color to change from blue to gray. In this titration, 1 mol of EDTA corresponds to 1 mol of Ba^{2+} ion[16]. Although this method has been used for the quantitative determination of Ba^{2+} for a long time[17], no one applied this method for the detection of Ba^{2+} leaching from $BaTiO_3$ powder in water. Therefore, this study reports on the detection of Ba^{2+} leaching from $BaTiO_3$ powder by EDTA titration and the effect of several organic additives on the titration.

EXPERIMENTAL

Materials

A hydrothermally synthesized $BaTiO_3$ powder (BT-8, Cabot Performance Materials, Boyertown, PA) with a mean particle size of 0.24 μm and a specific surface area of 8.50 m^2/g was used in this study. A reagent grade 0.05M EDTA solution, Ba-acetate, citric acid, and oxalic acid were purchased from Aldrich (Milwaukee, WI). Dispersant used were a modified polymethylmethacrylate (PMMA/PEG) (Hypermer KD-6, Uniqema, New Castle, DE), an ammonium salt of polyacrylic acid (APA) (Geosperse 644A, Geo Chemicals, Horsham, PA), and a sodium salt of polyaspartic acid (PApA-Na) (Amisorb, Donlar Corp., Bedford Park, IL).

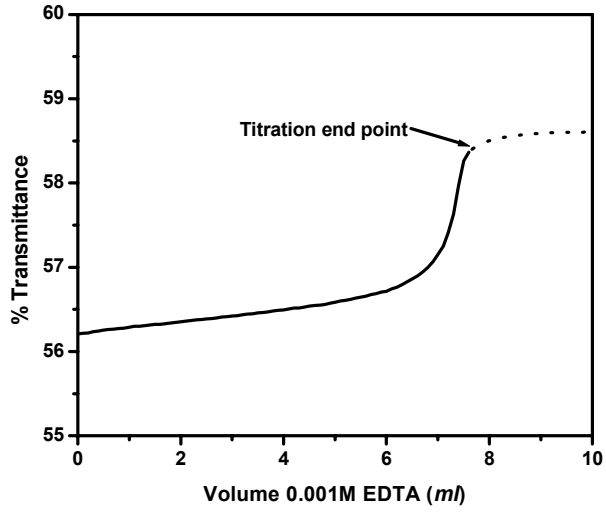

Figure 1: A typical EDTA titration curve for Ba^{2+} measurement

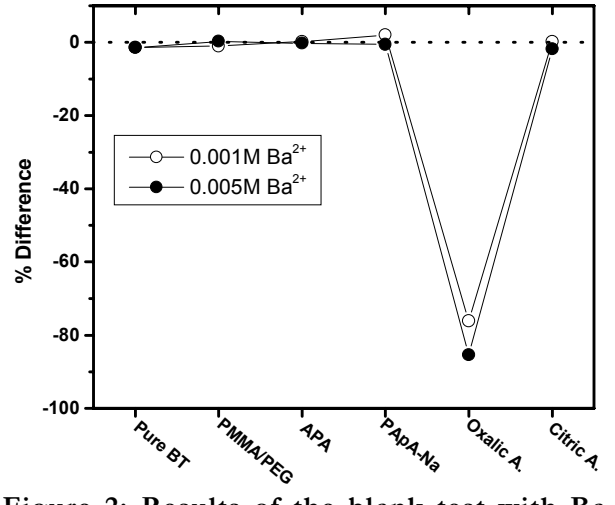

Figure 2: Results of the blank test with Ba-acetate solution and with a different organic material in water.

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Methods

As a first test, 0.001M or 0.005M of Ba-acetate was dissolved in water to check the reliability of the EDTA method in measuring the amount of Ba^{2+}. After adding 30 mg of methyl thymol blue into 50 ml of solution, the pH was adjusted to 12 by a 10 M KOH solution. The solution was titrated with a 0.001 M EDTA solution after dilution in water using a Mettler Titration Meter (DL50 Titrator, Mettler Toledo, Switzerland). The effect of the addition of organic materials such as dispersants, oxalic acid and citric acid was also checked in this blank test.

As a second test, to determine the amount of Ba^{2+} ion leaching from the $BaTiO_3$ particles, 6 g of BT powder were dispersed into 24 ml of deionized water. This mixture was then stirred mildly by hand with a spatula for 1 minute to disperse the particles. The Ba^{2+} ion leaching behavior was checked at various pHs after 1 and 2-days leaching. NH_4OH and CH_3COOH were used to adjust the solution pH by using an Accumet 925 pH/ion Meter (Fisher Scientific, Pittsburgh, PA). The solution pH was readjusted after an equilibration period of 5 hours, if drift from the initial pH was observed. After being aged for the desired length of time in air, the slurry of $BaTiO_3$ was centrifuged at room temperature at 13,000 rpm for 30 min. After diluting the 12 ml aliquote of supernatant to 50 ml with deionized water, the pH was adjusted to 12 by a 10 M KOH solution followed by titration.

RESULTS AND DISCUSSION

Figure 1 shows a typical EDTA titration curve for the determination of the Ba^{2+} concentration in solution. The graph shows a sharp titration end point corresponding to a stoichiometric complex between Ba^{2+} and EDTA, which makes it easy to determine the amount of Ba^{2+} in solution. Figure 2 shows the blank test results of Ba-acetate at two different concentrations with various kinds of organic additives. The y-axis represents the percent difference between the actual amount of Ba^{2+} and the titrated value. As the data show, the titrated values of the samples agree with the actual amount of Ba^{2+} with the difference within ±3%; only oxalic acid shows a difference. To determine the exact amount of Ba^{2+} in a real system, any interference by organic additives such as dispersants and binders should be avoided. With oxalic acid, however, precipitates were observed during the titration process whose Ba^{2+} included was not accounted for in the titration. It is well-known that alkaline earth oxalates are easily formed, quite insoluble and hamper any volumetric determination with EDTA[16,17].

Figure 3 shows the amount of Ba^{2+} leaching determined by EDTA titration and the resultant Ba/

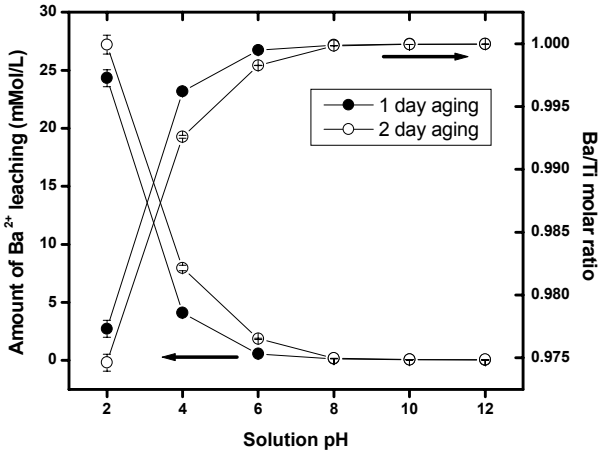

Figure 3: The amount of Ba^{2+} leaching and the resultant Ba/Ti molar ratio of the powder as a function of the solution pH without organic material.

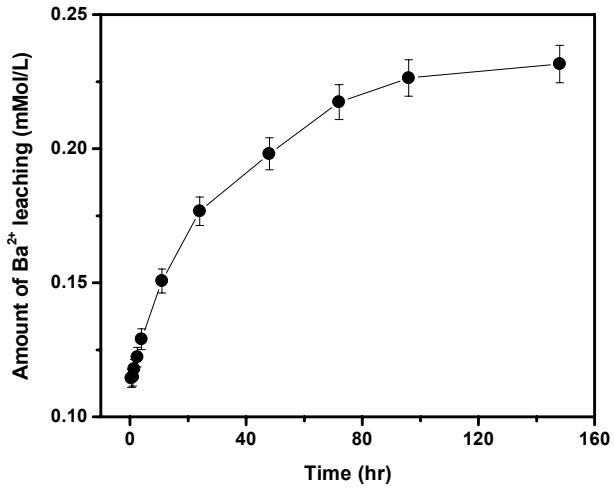

Figure 4: The amount of Ba^{2+} leaching vs. time at pH=8 and at room temperature.

Ti molar ratios of the pure $BaTiO_3$ powder calculated after being aged for 1 and 2 days in various pH solutions. The amount of Ba^{2+} leaching shows a significant dependency on the solution pH, i.e., the higher leaching amount and the faster leaching rate at the lower pH. Even though the system is not in equilibrium condition, this pH-dependent Ba^{2+} leaching behavior shows the similar trend of the equilibrium condition which was reported by Lencka and Riman[18]. As explained by theoretical model[18], it was found that there was a linear log relationship of $[Ba^{2+}]$ with pH approximately.

Figure 4 shows the Ba^{2+} leaching behavior at pH=8 and at room temperature as a function of aging time since the usual industrial practice is in pH of 8 to 10. The amount of Ba^{2+} leaching for the first 30 minutes could not be measured due to the time needed for the sample preparation. As shown in Figure 4, the amount of Ba^{2+} leaching is quite high for the first measurement at 30 minutes of aging. After 30 minutes, the leaching rate gradually decreases reaching a plateau at a time greater than 100 hours. When compared to the other reported values using ICP and AAS[5,19,20], our results of EDTA titration agree well with them. Based on the results of blank test and the comparison between Ba^{2+} leaching behavior using EDTA titration in this study and other reported values[5,18-20], we can conclude that the EDTA titration method can be used to detect the amount of dissolved Ba^{2+} ions accurately unless a precipitate is formed.

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