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Humidity sensitivity characteristics of $BaTiO_3$ ceramics with PMMA additive at various working temperatures

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Barium titanate samples were prepared by a traditional powder metallurgy method. High-purity powders were mixed by ball-milling in order to produce powder mixtures. The resultant mixtures were dried, sieved and were uniaxially pressed into green samples. Green samples were then sintered at 1200-1500°C for 6 h in air to form a barium titanate phase. The average grain size and microstructural features were determined for each composition. The effects of porosity and working temperatures on the barium titanate ceramics were investigated by microstructural analysis and electrical conductivity measurements and the results were evaluated in terms of porosity.

Key words: Barium titanate, sintering, PMMA, microstructure, conductivity, humidity sensitivity.

Introduction

A number of porous metal oxides are often used as humidity-sensing materials. Ceramic humidity sensors are more chemically and thermally stable than polymeric humidity sensors. The sensing mechanism is by the adsorption of water vapour. The adsorption of water vapour improves the electrical conductivity of the as-sintered surface. High sensitivity, small hysteresis, good linearity, high durability and fast response are some of the requirements expected from a practical humidity sensor. For a given humidity sensor, low humidity sensitivity characteristic leads to the need for a larger signal amplification and increases the production cost [1-6]. The humidity sensitivity is generally determined by the type of ceramic material and process parameters. Since porosity is the result of sintering conditions and the type of the material, humidity sensitivity is strongly dependent on the porosity content of the sensing element [7-8]. There is another parameter which affects the humidity sensitivity characteristic i.e the working temperature at which the electrical conductivity measurements under a humid environment are carried out.

In the present study, three different porous compositions were prepared with a polymeric addition, PMMA (Polymethyl metacrylate). The three compositions were sintered at several sintering temperatures and times. The porosity content of the as-sintered specimens were determined and electrical conductivity tests were carried out under a humid environment and then transformed into humidity sensitivity values versus porosity percentages. In addition, the effect of the working temperature on the humidity sensitivity characteristic was also examined.

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Experimental Procedure

Barium titanate samples were prepared using the raw materials $BaCO_3$ and TiO_2 (> 99%, Merck KGaA, Germany) with a molar ratio of 1.00. The powders were doped with La_2O_3 0.18 wt.%. The mixture of ceramic powders and PMMA (1, 1.75 and 2.5 wt.% coded as P-1, P-2 and P-3, respectively) were ball-milled in acetone for 24 h in a plastic jar using ZrO_2 as the grinding media. The ball-milled slurries were dried at 100 °C in an oven for 30 minutes. The powders were then pressed into bars with dimensions of 15 × 12 × 7 mm. The green compacts were sintered at 1200-1500 °C for 2-6 h in air and then furnace cooled. The microstructure of the as-sintered ceramics was investigated using a scanning electron microscope (SEM) (JEOL 5600). The porosity of the ceramics was measured using the Archimedes method. Grain sizes were determined by the linear interception method. Electrical resistance was measured using a humidity chamber at room temperature in a range of 20-98% of relative humidity by DC 2-probe method.

Results and Discussion

SEM images obtained from the surface of the as-sintered samples are shown in Fig. 1. Rather large grains were observed after sintering at 1500 °C for 6 h. Porosity percentages as low as 15.2% and 17.9% were determined for P-1 and P-1 compositions with the maximum sintering conditions. Spaces were observed between the grains and the porosity type of the sintered ceramics were observed

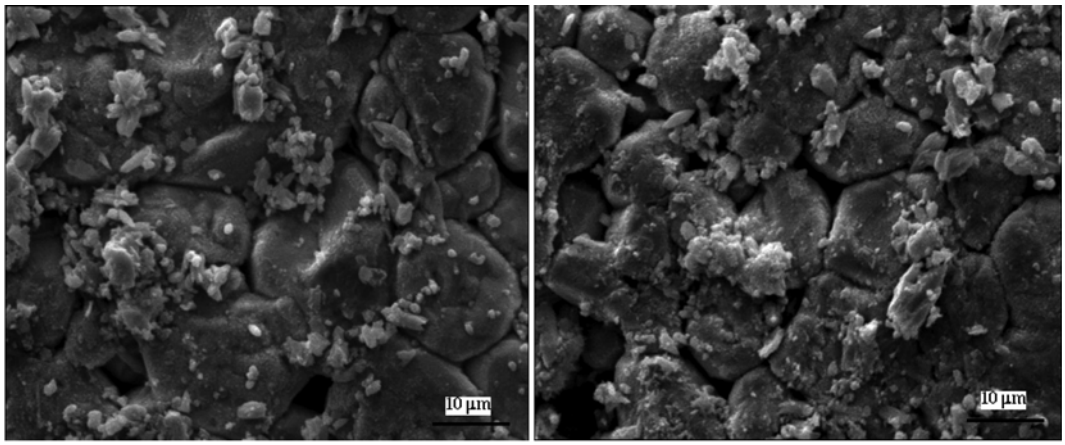

Fig. 1. SEM images for (a) P-1 and (b) P-3 compositions sintered at 1500 ºC for 6 h.

and determined to be intergranular. The apparent porosity present in the microstructures and their percentages were measured by the Archimedes method. Except for enhanced grain growth upon high-temperature sintering, all the sintering temperatures resulted in porous ceramics. On the other hand, a hydration tendency occurred upon exposure to a high relative humidity percentage i.e. 80%, for the samples sintered at lower temperatures. Three of the compositions (P-1/3) studied indicated typical porous structures up to 1500 ºC. SEM images showed uniformly distributed pores in the matrix at lower sintering temperatures. By sintering at 1500 ºC, the porosity was eliminated and the grain size increased significantly.

The grain size as a function of PMMA content after sintering at 1200-1500 ºC for several hours are given in Fig. 2. As can be seen from the curves, PMMA additions resulted in grain refinement for all the sintering temperatures. Besides grain growth, PMMA affected the grain morphology and other microstructural features. The grain morphology became more homogeneous, regular and globular due to the addition of PMMA. However, after sintering at 1500 ºC, globular grains disappeared and larger grains were formed. For the samples shown in Fig. 1, the grain size were measured to be 14.9 µm and 13.8 µm. The grain size value of the sample which contained 1.75 wt.% of PMMA was 14.3 µm. As the sintering time decreased to 2 h for this temperature, grain sizes became 12.3 µm and 11.4 µm for P-1 and P-3 compositions, respectively and that of the P-2 composition was 11.8 µm. In a range of 2-6 h, the grain size changed approxiamately by one order of magnitude for the P-1 composition. The maximum grain size obtained after sintering at 1200 ºC was determined to be 5.4 µm and the minimum value was 4.1 µm. The effect of sintering time on the grain sizes was quite limited for this temperature. In the 1-2.5 wt.% range of PMMA content, the grain size decreased by one order of magnitude. The maximum grain size after sintering at 1300 ºC was 7.6 µm for the P-1 composition. As the PMMA content increased to 2.5 wt.%, the grain size became 7 µm. The minimum grain size obtained at this temperature was measured to be 5.8 µm for the P-3 composition. The maximum and minimum grain sizes for samples sintered at 1400 ºC were 10.6 µm and 8.1 µm. In the range of 1200-1500 ºC, grain sizes changed by 3 orders of magnitude with the sintering temperature. The sintering temperature had a dominant effect on the grain growth behaviour of the fabricated ceramics.

The maximum porosity obtained for the porous barium titanate ceramics was 53.5%. This value was obtained after sintering at 1200 ºC for 2 h. It was clear that sintered density of fabricated ceramics decreased with a very low, i.e. 1 wt.% PMMA content. This result led to an easy production of porous ceramics with a low density using an organic addition. After sintering at 1200 ºC for 6 h, a porosity of 42.5% was obtained for the P-1 composition and the porosity requirements were satisfied with a homogeneous distribution of high porosity throughout the microstructures. As the PMMA content was raised to 2.5 wt.%, the porosity became 47.7% at 1200 ºC. The maximum and minimum porosity after sintering at 1300 ºC were measured to be 29.6% and 37.3%, respectively. One and a half order of magnitude change in porosity occurred with a 100 ºC increase of the sintering temperature and the maximum porosity value obtained after sintering at 1400 ºC was 26%. For all the sintering temperatures, the least porous samples were obtained after sintering at 1500 ºC and the maximum porosity was measured to be 19.95%. At this particular temperature stable microstructures related to high temperature processes were obtained by the addition of PMMA.

The electrical conductivity as a function of porosity graphs are given in Fig. 3. At room temperature the conductivity versus porosity relationship was linear for nearly all percentages of humidity. However, at 20% relative humidity, the conductivity changed exponentially with porosity with a maximum conductivity of $10^{-5.25}$ S.m^{-1}. When the relative humidity increased to 40%, the conductivity reached $10^{-4.125}$ S.m^{-1} and the conductivity versus porosity relationship was still somewhat exponential. At 60% and 80% relative humidity, the maximum conductivities were meas-

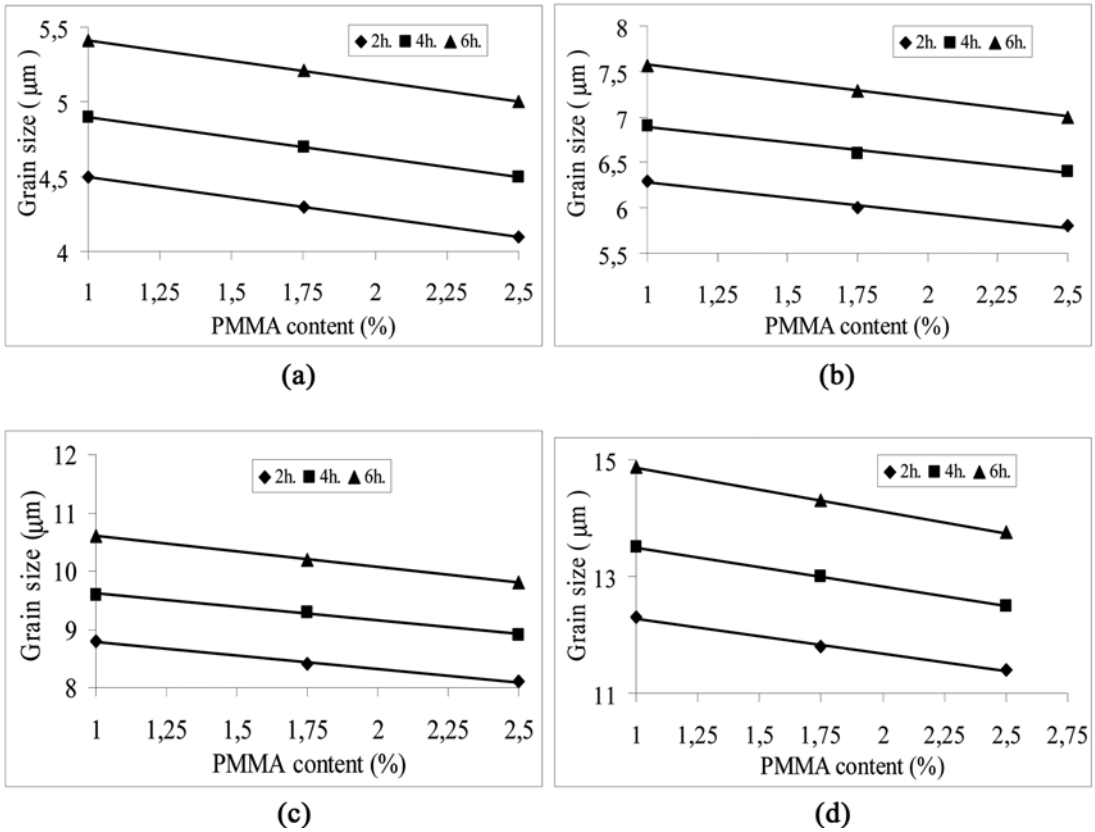

Fig. 2. Grain size versus PMMA content after sintering at (a) 1200 ºC, (b) 1300 ºC, (c) 1400 ºC and (d) 1500 ºC for 2-6 h.

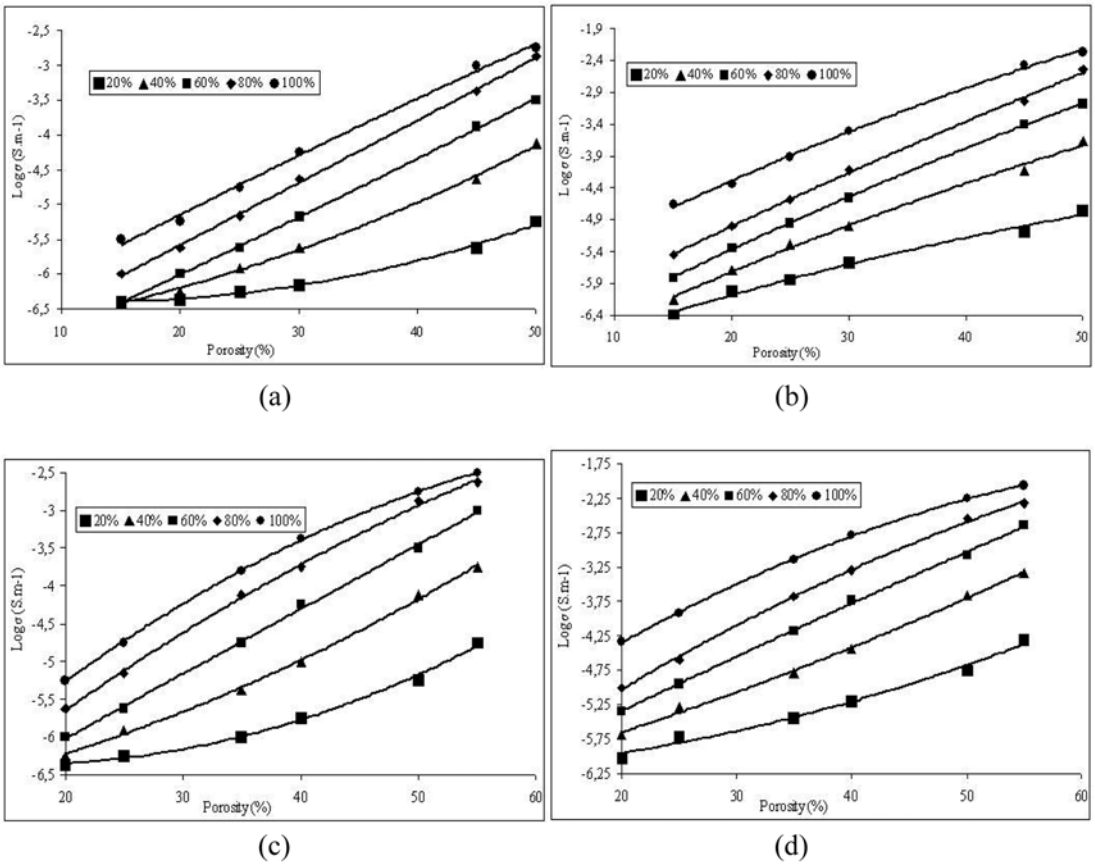

Fig. 3. Electrical conductivity versus porosity for P-1 at (a) 20 ºC, (b) 80 ºC and P-3 (c) 20 ºC, (d) 80 ºC.

ured to be $10^{-3.5}$ and $10^{-2.875}$ $S.m^{-1}$, respectively and the conductivity versus porosity relationship was linear. The maximum value of the electrical conductivity measured at room temperature for the P-1 composition was $10^{-2.75}$ $S.m^{-1}$. When working temperature was raised to 80 ºC, the conductivity values increased noticeably. The maximum conductivity measured at this temperature was $10^{-2.26}$ $S.m^{-1}$ and the conductivity versus porosity relationship was somewhat linear for all the percentages of humidity. As the PMMA content increased to 2.5 wt%, the linearity of the conductivity versus the porosity curves disappeared and an exponential relationship was dominant for all the percentages of humidity. The maximum conductivity measured for the P-3 composition was $10^{-2.5}$ $S.m^{-1}$ and at lower percentages of humidity, i.e 20%, the conductivity increased sharply with porosity especially at 40% of porosity. At intermediate humidity levels, the linearity of conductivity versus porosity curves was more evident. For the P-3 composition when the working temperature was increased to 80 ºC, the conductivity reached a maximum value of $10^{-2.06}$ $S.m^{-1}$ and as can be seen from Fig. 3. d., the conductivity versus porosity curve of the P-3 composition became more linear with an increase in the working temperature.

The humidity sensitivity versus porosity of porous barium titanate ceramics are given in Fig. 4. All the conductivity graphs showed an exponential tendency with porosity. At lower percentages of porosity, the conductivities obtained at various percentages of humidity were close to each other. As the porosity increased, the conductivity curves became more diverse. The maximum humidity sensitivity measured at room temperature for the P-1 composition was 2.45 meaning that at higher percentages of humidity, the conductivity increased by 100-1000 times of the value in air. The minimum sensitivity determined at room temperature for the most porous sample was 1.29. At lower levels of humidity, the humidity sensitivity versus porosity curves were more linear. When the working temperature was raised to 80×C, the maximum value of the sensitivity reached 2.94 and the minimum sensitivity was measured to be 1.35 for the most porous sample. As the PMMA content was increased to 2.5 wt.%, the maximum sensitivity increased to 2.72. The humidity sensitivity had a maximum value when the working temperature was raised to 80 ºC for the P-3 composition which was 2.93. It was concluded that the humidity sensitivity increased noticeably with porosity and working temperature in a range of 20-80 ºC.

Conclusions

Porous barium titanate based ceramics were succesfully fabricated by the addition of PMMA. Grain size variations

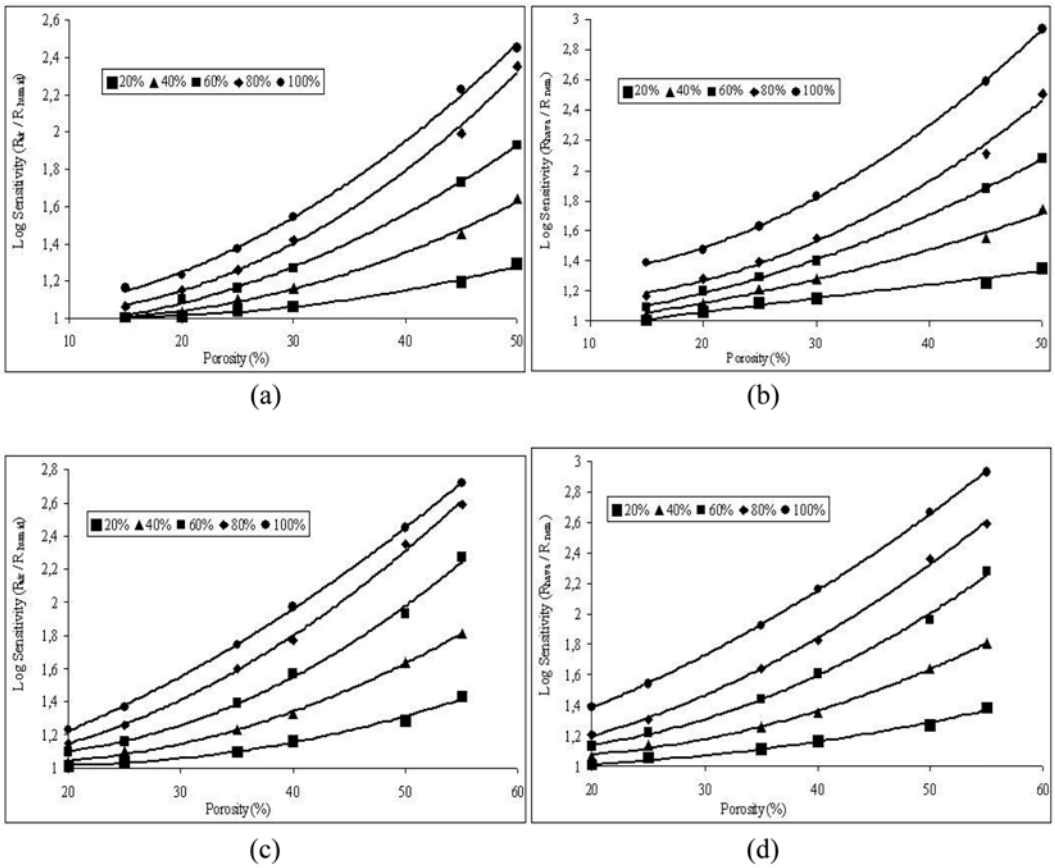

Fig. 4. Humidity sensitivity versus porosity for P-1 at (a) 20 ºC, (b) 80 ºC and P-3 (c) 20 ºC, (d) 80 ºC.

and microstructural features were affected by the pore-forming agent. There was a grain size refinement with the addition of PMMA. The electrical conductivity and humidity sensitivity properties of samples were investigated as a function of porosity. In general, it was observed that the humidity sensitivity of porous barium titanate ceramics was controlled by the content of porosity and the working temperature. Fabricated ceramics were determined to be adequate for humidity sensing applications.

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