Potential barriers in PTC barium titanate observed by EFM

S. M. GHENO*, H. L. HASEGAWA
Department of Materials Engineering, Federal University of Sao Carlos, São Paulo, Brazil

V. L. PIMENTEL
Brazilian Synchrotron Light Laboratory (LNLS), Campinas, SP, Brazil

P. I. PAULIN FILHO
Department of Materials Engineering, Federal University of Sao Carlos, São Paulo, Brazil

Published online: xx xx

PTC thermistors based on doped barium titanate are ferroelectric materials that show commercial interest due to a large variation in electrical resistance with temperature. The PTC effect in ceramics based on semiconducting barium titanate is due to formation of electric potential barriers in grain boundaries, increasing the electrical resistance [1]. Barium titanate ceramics when doped shows an electric behavior, which consists of an abrupt increase of resistivity with the temperature, close to Curie temperature (T_c). This effect happens in barium titanate during the change of cubic to tetragonal phase when cooled to temperatures below 130 °C [2, 3]. The models more accepted attributes the PTC effect to the formation of potential barriers in grain boundaries, increasing the resistivity when temperatures above 130 °C are reached [4]. Being basically a grain boundaries effect the PTC behavior depends strongly on microstructure [2–5]. The electric properties of ceramic PTC can be observed through the nature of the grains boundaries, and the levels of energy involved in their process were not well explained [4, 5]. The formation of potential barriers on barium titanate doped with yttrium were investigated using electrostatic force microscopy (EFM) with electric field gradient applications and surface potential images shows the formation of potential along grain boundary at applied voltage of 10 V.

Semiconducting barium titanate was obtained by mixing 0.3% of yttrium in the nitrate form with BaTiO3 powder (TAM ceramics). The mixing was made in aqueous solution and after drying, the powder was dispersed and pellets were obtained by compaction with a uniaxial press. Sintering was done at 1350 °C by 2 hr and grains were reveled by thermal attack at 1250 °C for 1 min. EFM images were obtained using an atomic force microscope (Nanoscope IIIa) operating in electrostatic force mode (EFM) using a silicon probe (NSC15). The images of surface potential were done with applications of 0, 4 and 10 V, *in situ*.

Fig. 1a show the AFM topographic image of 0.3Y-$BaTiO_3$ reveling microstructure where grains and grain boundaries are clearly defined. Fig. 1b show an EFM image without applied voltage showing no features. Figs. 1c and 1d shows EFM images with 4 and 10 V applied to the samples, respectively. At 4 V the grain contour starts to appear and at 10 V the grain contour are clearly visible and in agreement with the topographic image showed in Fig. 1a. In Fig. 1d, dark regions are associated to semiconducting material showing that the grains are current conductors and bright regions are insulating regions, associated to grain boundaries. These images are formed because as the voltage increase the probe start to be repelled at the grain boundaries regions.

The 3D image of Fig. 2 is referring to Fig. 1d of grains and grain boundaries barrier. This image is in agreement with theories developed to explain the PTC behavior observed in doped barium titanate. This figure shows that PTC effect is related to the barrier formed at grain boundaries due to segregation of acceptor and donor dopants. Electronic trapping due to vacancies and acceptor depends on dopant segregation which depends on thermal treatment of samples. Defects and diffusion effects suggest that the potential barriers originated at grain boundaries are due to barium vacancies rich regions that are electrically compensated by electron donors (oxygen diffusion along grain boundaries). However, acceptor dopants and donor dopants are assumed to be uniformly distributed through the grains and grains boundaries and the acceptors effects are due to their activation energies. Activation energies depend of polarization in ferroelectric region and formation of high electrical resistance region at grain boundaries results in potential barriers. Space charge is developed at grain boundaries vicinity due to the electron flux from the conducting grains to vicinity of high resistance area (grain boundaries) [1, 4, 5].

Chemical defects and diffusion studies suggested [4, 5] that the potential barriers in grain boundaries are originated due to layers with barium rich vacancy or areas which form grain neighborhoods during the cooling from high temperatures. It is assumed that in these layers the donors are completely compensated

* Author to whom all correspondence should be addressed.

0022-2461
DOI: xxxx

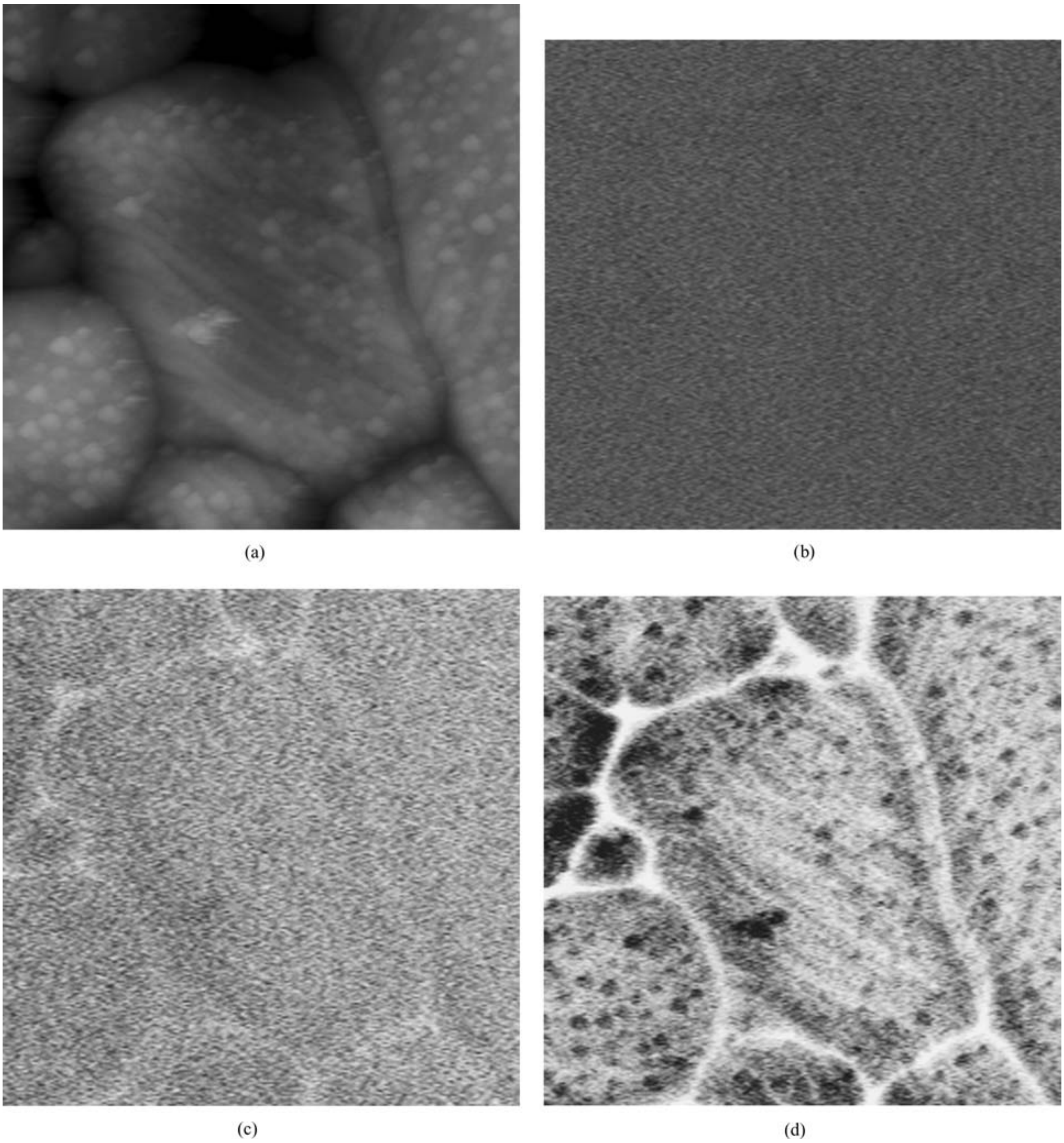

Figure 1 Micrographics images of barium titanate doped with yttrium (0.3Y-$BaTiO_3$) (3×3 μm): topographic (AFM) (a); 0 V (EFM) (b); 4 V (EFM) (c); 10 v (EFM)(d).

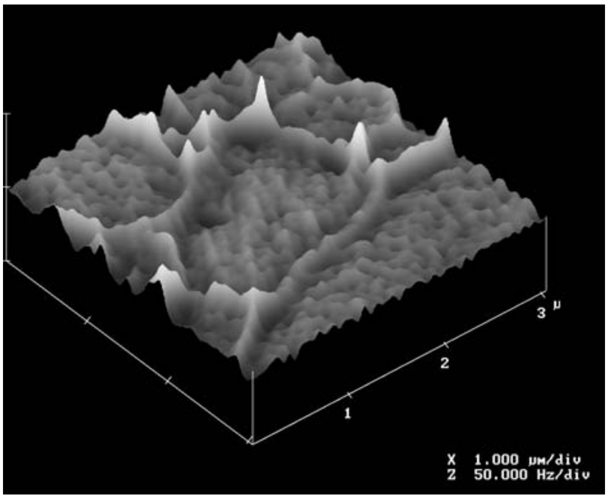

Figure 2 3D image profile of barium titanate doped with yttrium (0.3Y-$BaTiO_3$) obtained by EFM with 10 V of applied voltage.

by barium vacancies. However, the dopant donors or acceptors are uniformly distributed through grains and grain boundaries and the acceptors effect is only interpreted through your energy levels. The activation energy can be expressed as function of the polarization in the ferroelectrics area. If the traps in the grain boundary are activated, some of the carriers contributed by the donor atoms in the grain may be trapped at the grain boundaries, thus producing a space region of the opposite polarity. The thickness and resistivity of the space charge region, and the grain-boundary resistive region, can then limit the conductivity of the sample. The results obtained here with EFM are in agreement with Desu and Payne's theory [4, 5]. Also formation of high resistivity areas in the grain contour surrounding semiconductors grains result in potential barrier due to balance of Fermi levels [3]. Space loads are developed in neighborhoods of grains limit due of the electrons flow, starting from the interior of grains semiconductors to high resistivity regions in the neighborhoods of the grains. This transition has been explained in terms of layer thickness of the space load and grain size.

In conclusion these results give a strong support to explanation of PTC effects in $BaTiO_3$ ceramics showing potential barrier formed at grains boundaries regions and the formation of a resistivity layer associated with space charge regions.

Acknowledgements

The authors would gratefully acknowledge CNPq (Brazil) for its financial support of this research and the Brazilian Synchrotron Light Laboratory (LNLS).

References

1. W. HEYWANG, *J. Am. Ceram. Soc.* **47**(10) (1964) 484.
2. C. A. PUTMAN *et. al.*, *J. Appl. Phys. Lett.* **64** (1994) 2454.
3. K. UMEMURA et. al., *ibid.* **32** (1993) L1711.
4. S. B. DESU and D. A. PAYNE, *J. Am. Ceram. Soc.* **73**(11) (1990) 3416.
5. S. B. DESU and D. A. PAYNE, *J. Am. Ceram. Soc.* **73**(11) (1990) 3398.

Received 18 May
and accepted 19 May 2005