Barium titanate thick films prepared by screen printing technique

Mirjana M. Vijatović[1], Jelena D. Bobić[1], Biljana D. Stojanović[1], Barbara Malič[2]

[1]*Institute for Multidisciplinary Research, University of Belgrade, Kneza Višeslava 1, Belgrade, Serbia*
[2]*Institute Jozef Stefan, Jamova 9, Ljubljana, Slovenia*

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Abstract

The barium titanate ($BaTiO_3$) thick films were prepared by screen printing technique using powders obtained by soft chemical route, modified Pechini process. Three different barium titanate powders were prepared: i) pure, ii) doped with lanthanum and iii) doped with antimony. Pastes for screen printing were prepared using previously obtained powders. The thick films were deposited onto Al_2O_3 substrates and fired at 850°C together with electrode material (silver/palladium) in the moving belt furnace in the air atmosphere. Measurements of thickness and roughness of barium titanate thick films were performed. The electrical properties of thick films such as dielectric constant, dielectric losses, Curie temperature, hysteresis loop were reported. The influence of different factors on electrical properties values was analyzed.

Keywords: *$BaTiO_3$, thick film, screen printing, electrical properties*

I. Introduction

Microelectronics technology expands continually through the integration of different types of electronic components into multilayer ceramic packages. Due to its high dielectric constant and low dielectric losses characteristics barium titanate has found extensive application in electronic industry as a dielectric in ceramic capacitors and also in multilayer capacitors [1]. Large number of different dopants can be accommodated in the $BaTiO_3$ lattice, therefore, doping of $BaTiO_3$ ceramics is very important to obtain required characteristics for its applications in semiconductors, PTC thermistors etc [2].

Screen printing technique is one of the oldest forms of graphic art reproductions and involves the deposition of paste (or ink) onto a base material (substrate) through the use of a finely-woven screen with the desired geometry. The process is commonly used for the production of graphics and text onto items such as T-shirts, mugs, textiles and is very similar to that used for microelectronic thick films. Nowadays, thick films are not only used in hybrid circuits as a resistors, conductors and dielectrics, they can be also used in advanced solid state sensors and actuators. This process is useful to accommodate the demands of miniaturization, circuit complexity and multilayer assembles [3].

* Corresponding author: tel: +381 11 208 5039,
fax: +381 11 208 5062, e-mail: *miravijat@yahoo.com*

In this work, $BaTiO_3$ thick films were prepared by screen printing technique. The microstructure and electrical properties of pure and doped thick films were analyzed.

II. Experimental

2.1 Powder and paste preparation

Barium titanate ($BaTiO_3$ - BT) powders were prepared by the polymeric organometallic precursor method (Pechini process-PPM) using barium and titanium citrates. For doping barium titanate, lanthanum nitrate hexahydrate solution was added ($La(NO_3)_3 \cdot 6H_2O$, Alfa Aesar, 99.99 %) with 0.3 mol% La (BTL) and antimony acetate ($Sb(CH_3COO)_3$) with 0.3 mol% Sb (BTS). The details of the process used have been described elsewhere [4,5].

Three main components in a thick film paste are: i) the functional component (barium titanate powder), ii) low temperature melting glass (63 wt.% PbO - 25 wt.% B_2O_3 - 12 wt.% SiO_2) and iii) organic binder (butyl carbitol). The main functions of added glass are bonding of functional component particles together and enabling good adhesion of paste and substrate. On the other hand, organic binder is used for getting correct viscosity of the paste for screen printing. Ratio between organic material and barium titanate based powder was 30:70. The electrodes were prepared from the

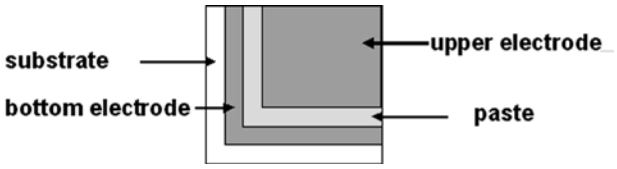

Figure 1. Barium titanate thick film surface

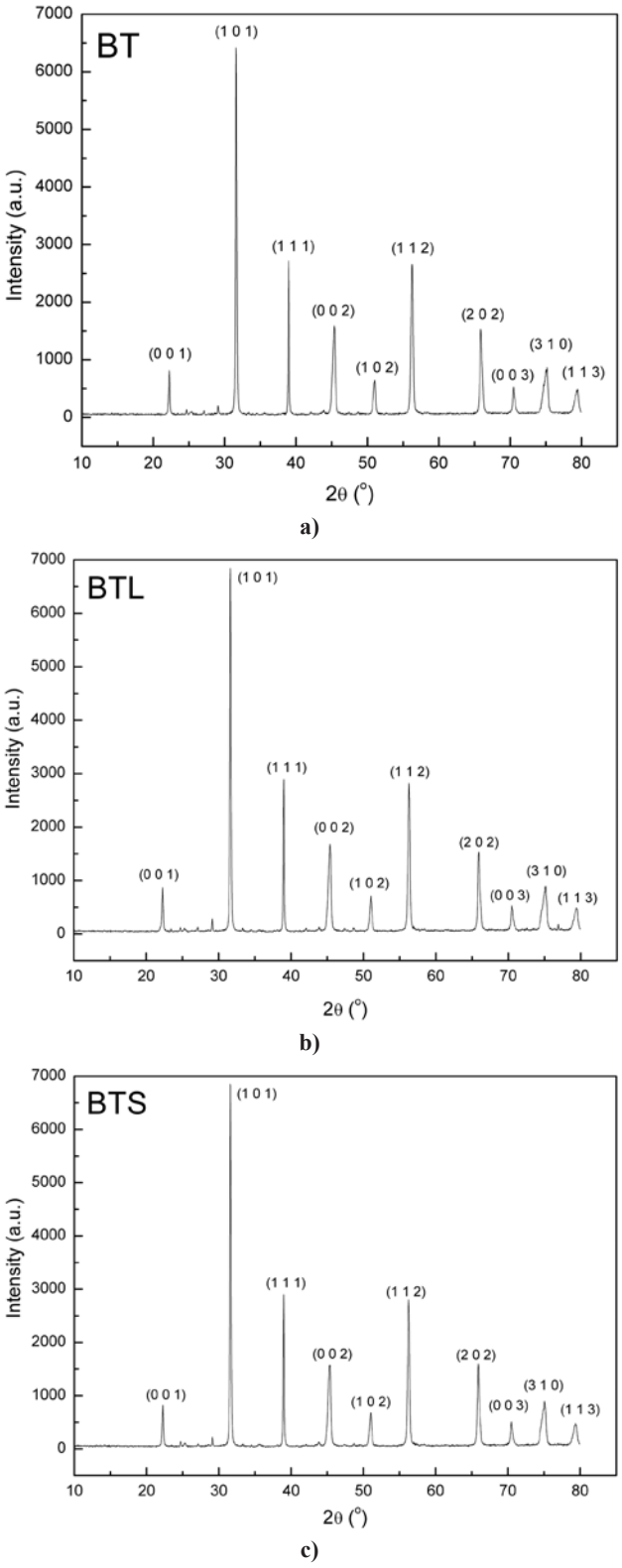

Figure 2. XRD diffraction for (a) pure, (b) doped with lanthanum and (c) doped with antimony thick films

silver/palladium mixture (Ag/Pd - 70/30). The viscosity of obtained paste was in the range 0.6–1.1×10^2 mPas for shear rate 10 s^{-1} [3,6].

2.2 Thick film preparation

Thick films were prepared by screen printing technique. The bottom electrode, silver/palladium mixture (Ag/Pd - 70/30), was deposited on the Al_2O_3 support, in the middle was screen-printed dielectric layer of: i) BT, ii) BTL or iii) BTS and on the top was deposed the upper electrode (Fig. 1). Sintering was performed at 850°C during 1 h in moving belt furnace in air flow atmosphere [6,7]. Obtained films presented thickness of about 50 μm.

2.3 Characterization

Different methods of analysis were used for the characterization of barium titanate thick films. The microstructure and morphology of nanopowders and thick films were investigated using X-ray diffraction (Model Phillips PW1710 diffractometer) and scanning electron microscope (Tescan VEGA TS 5130MM).

Thickness and roughness of barium titanate thick films (BT, BTL and BTS) were measured using profilometer (Solarius Vocanyon Technology DS-51224). Two types of measurements were performed: i) where the probe traces along a straight line and ii) where it scans the film surface. From this measurements roughness parameters R_a (arithmetic average of the roughness profile 2D) and S_a (arithmetic average of the 3D roughness) were obtained.

Electrical measurements such as dielectric constant, dielectric losses and measurement of hysteresis loop were carried out using Impedance Analyzer (HP 4192A). Dielectric measurements were performed in the frequency range from 10–1000 KHz and temperature range from 25–200°C. Measurements of ferroelectric properties were performed at frequency of 50 Hz and amplitude was in the range 20–300 V.

III. Results and discussion

It is well known that electrical properties, such as dielectric constant and dielectric losses, evaluate potential application of films. Therefore, it is very important to control all processing parameters because during the preparation of thick films many factors could affect its final electrical properties. Some of the main factors are: choice of substrate and electrodes, properties of the paste ingredients, viscosity of the paste as well as the deposition process and time-temperature-atmosphere conditions during firing.

In the investigated case, the thick films were deposited on alumina substrates which is the most common material used as substrate due to its chemical stability, mechanical strength, thermal shock resistance and good chemical compatibility with film.

Silver electrodes are usually used as an electrode material in thick films. However, due to silver tendency to

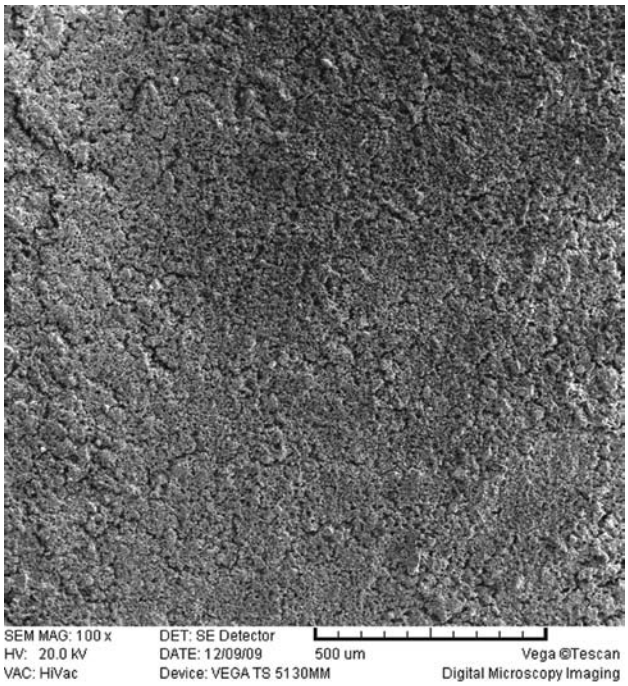

Figure 3. SEM micrograph of barium titanate thick film surface

migrate in the presence of moisture and an electric field, in our case 30% Pd was added to reduce the migration of electrode material into a film. Platinum can also be alloyed with silver and those electrodes could solve migration problems but choice between Ag/Pd and Ag/Pt is usually made on the basis of economics [3,7,8].

The XRD results for all $BaTiO_3$ powders show the formation of well crystallized cubic crystal structure (JCPDS 31-0174). The particle size analysis of powders obtained by polymeric precursor method indicates rounded shape particles of about 25–40 nm.

Fig. 2. shows the XRD results for $BaTiO_3$ pure and doped thick films. The formation of tetragonal structure can be detected in all samples (JCPDS 05-0626). A small amount of secondary phase was found and it was assumed to be residue of organic materials from the paste.

SEM micrograph presented on Fig. 3 indicates rather high porosity and inhomogeneous surface of barium titanate thick film.

Roughness parameters R_a (arithmetic average of the roughness profile 2D) and S_a (arithmetic average of the 3D roughness) were obtained from roughness measurements. Those results indicate that the roughness of all films is rather high. In the Table 1 the results for thickness of measured films and their roughness parameters are presented.

Generally, the pastes exhibit pseudoplastic behaviour and the viscosity varies with the applied shear force. This is main property of paste because it must have minimum viscosity to ensure transfer through the screen, but it also must become more viscous after printing to provide a good definition of the film and to disable its leakage from the substrate. Therefore, to obtain smoother surface of the film, the paste viscosity has to be optimized as well as the openings of the screen which define the amount of paste that is being deposited on substrate [3]. This will be the subject of future work.

The dielectric properties of barium titanate thick films are presented in Fig. 4. It can be noticed a characteristic peak for structural transition from cubic paraelectric to tetragonal ferroelectric structure that occur in barium titanate at Curie temperature. Generally, in the BT coarse ceramics phase transformation peak was found to be sharp [9,10]. In investigated case, phase transition peak is broaden and this behaviour was observed by other authors [3,11,12] in BT films, as well. It was assumed that small grain size causes the peak broadening and flattering. Curie temperature peak at 136°C was observed in all obtained BT thick films. The value of dielectric constant (Table 2) is much lower than that reported for bulk BT, BTL and BTS materials. Results given on Fig. 4 also point out that dielectric constant decreases with doping by lanthanum and antimony [13,14]. The reason for low dielectric constant could be diffusion of electrode material through

Table 1. Thickness (d) and roughness expressed as R_a (arithmetic average of the roughness profile 2D) and S_a (arithmetic average of the 3D roughness) of BT, BTL and BTS films

Sample	ε (at 25°C)	ε (at T_c)	P_r [μC/cm²]	E_c [kV/ cm²]
BT	112	131	0.173	11.45
BTL	78	92	0.237	17.35
BTS	38	71	0.160	17.27

Table 2. Dielectric permittivity (ε) measured at 25°C and at Curie temperature, remnant polarization (P_r) and coercive field (E_c) of BT, BTL and BTS films

Sample	d [μm]	R_a [μm]	S_a [μm]
BT	48.70	2.10	5.35
BTL	50.63	1.60	4.56
BTS	46.20	2.20	4.82

intergranular pores which enables the formation of conductive film, as well as small grain size. Similar behaviour was noticed by other authors in thin films and bulk materials [7,12]. This problem could be probably solved by using the circular electrodes instead of deposition of electrodes on whole film surface and by increasing the sintering temperature for 50–100°C. Slight shifting of dielectric constant with frequency was also observed.

Dielectric losses (Fig. 5) have low values, from 0.02 at room temperature to 0.009 at Curie temperature measured at 1 MHz. Different authors concluded that the values of dielectric losses depend also on the number of layers. They noticed that as the dielectric layer gets thinner the higher dielectric loss is. In their works dielectric losses decrease in all temperature range and it is in agreement with results obtained in our study [6,15]. However, the details about this kind of behaviour were not found and that will be subject of our future investigation.

The reason for evident diminution of dielectric properties found in investigated case and some literature data could be because the films were not sintered to full density [6,15]. It can be assumed that the reduction of grain size, high porosity and defects have more pronounced effect on dielectric properties than diffusion of electrode material in dielectric layer.

The hysteresis loops of all thick films are presented on Fig. 6 and they have shown a nonsaturating *P-E* relationship. Values of remnant polarization (P_r) and coercive field (E_c) are given in the Table 2.

Typically, ceramics have lower remnant polarization and higher coercive field compared to single crystal [10]. The coercive field for $BaTiO_3$ single crystal at room temperature when the loop is developed at 50 Hz is 1 KV/cm and remnant polarization about 25 μC/cm^2. Lower P_r and higher E_c were observed in investigated case, as well as in $BaTiO_3$ thick film obtained from powder prepared by mechanochemical synthesis [7].

This nonsaturating loop behaviour had been also observed for BT thin films obtained by polymeric precursor method and flash evaporation method [16,17]. The assumption of this behaviour is complex process of conduction due to the contamination of films by diffusion of electrode material or inhomogeneous surface of films.

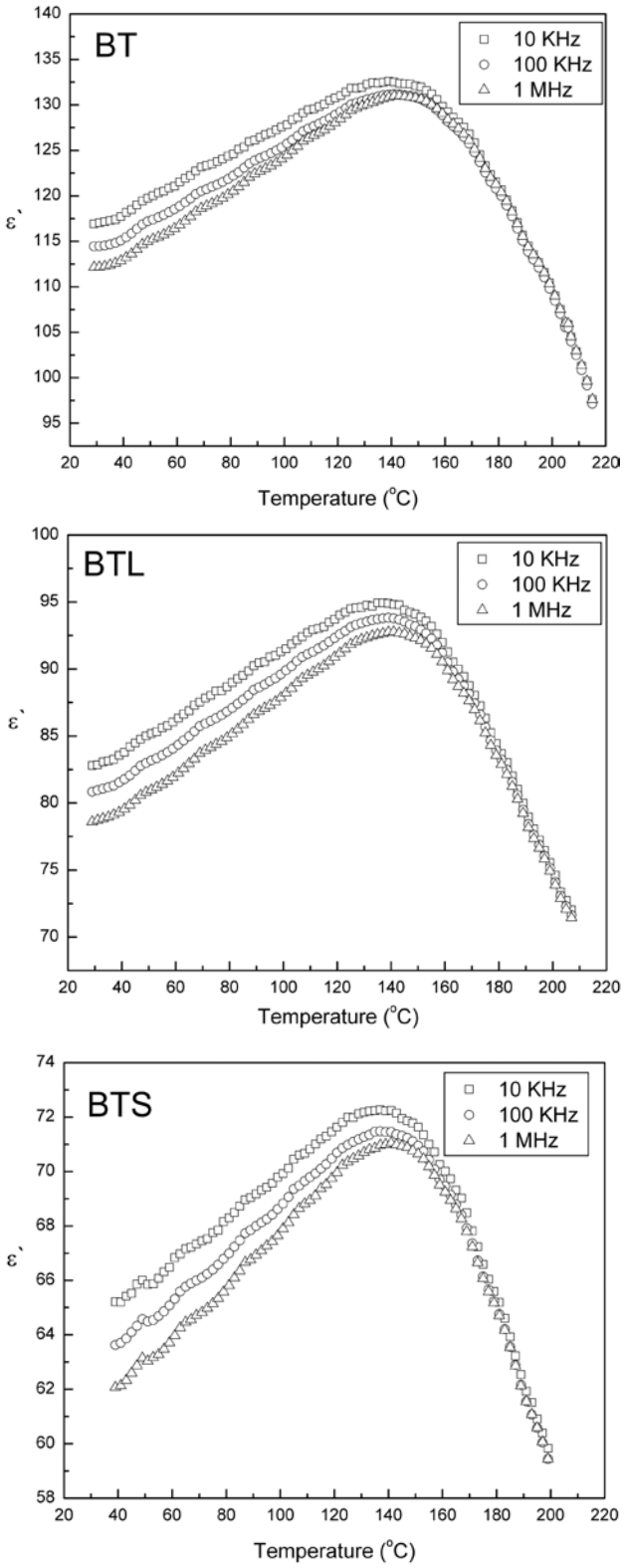

Figure 4. Dielectric constant vs. temperature of pure and doped thick films

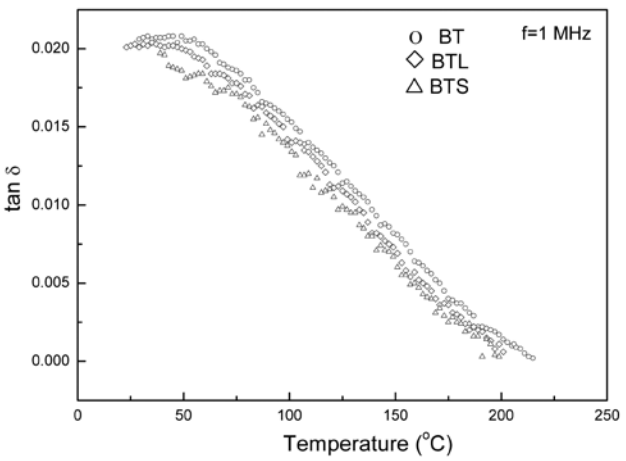

Figure 5. Dielectric losses vs. temperature for all thick films

IV. Conclusions

Barium titanate powders were prepared by polymeric precursor method starting from citrate solutions. Three different types of powders were prepared: i) pure, ii) doped with lanthanum and iii) doped with antimony. Obtained powders had small and rounded particles with dimensions of about 25–40 nm and they were used as a functional component for paste preparation.

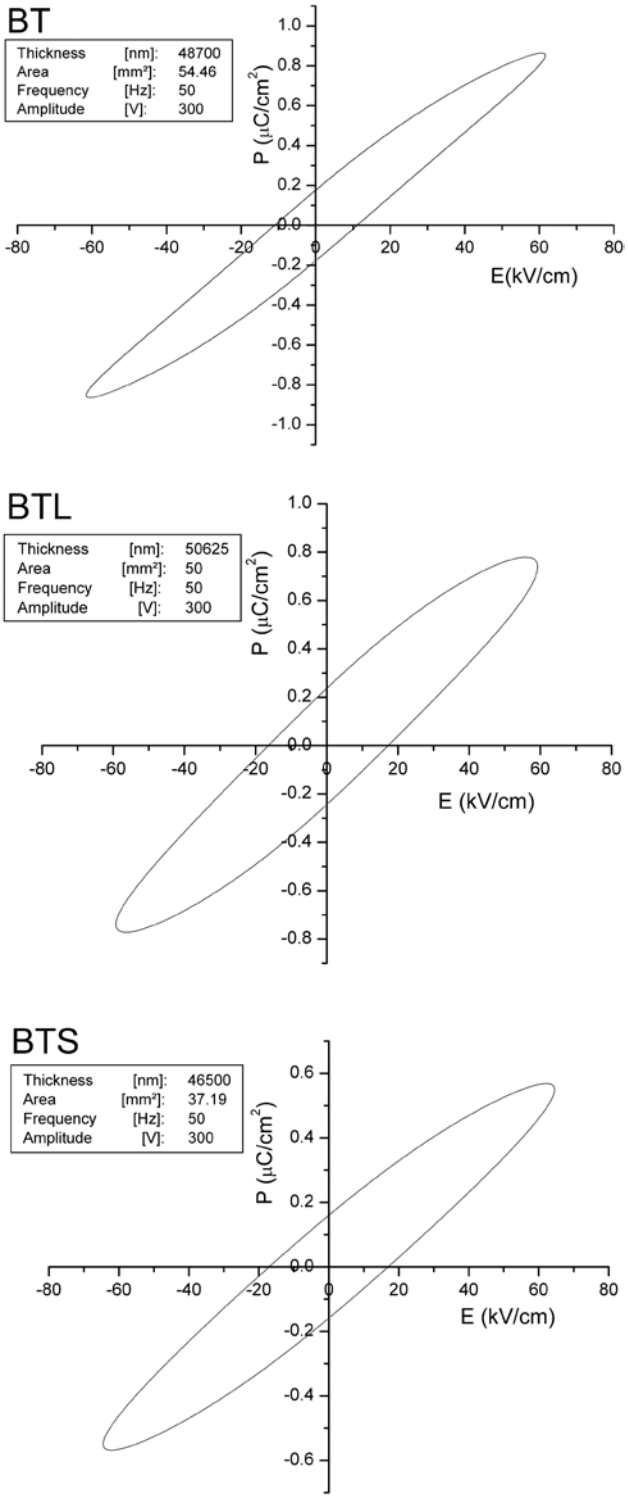

Figure 6. Hysteresis loop of pure and doped $BaTiO_3$ thick films

Barium titanate films with average thickness of about 50 μm were obtained by screen printing technique. Tetragonal crystal structure and high roughness of all three types of films were detected.

The influence of electrode material, porosity and small grain size on thick films electrical properties was analyzed. Changing of electrode material or using circular electrodes could probably solve the problem of its incorporation in the thick film. Increasing of sintering temperature could increase grain growth and eliminate porosity of film, so it will be possible to obtain thick films with better electrical properties.

Therefore, screen printed barium titanate thick films could be a potential candidate for applications such as multilayer capacitors or sensors.

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