Current trends in the development of high dielectric permittivity ceramics

Lyuben Lakov\(^1\), Mihaela Aleksandrova\(^1\), Vladimir Blaskov\(^1\)

\(^1\)Institute of Metal Science, Equipment and Technologies with Hydro- and Aerodynamics Centre “Acad. A. Balevski”, Bulgarian Academy of Sciences, Shipchenksi Prohod Blvd. 67, 1574 Sofia, Bulgaria, e-mail: mihaela.krasimirova@mail.bg

Abstract: The proposed review looks at some aspects concerning ferroelectrics that are characterized by high dielectric constant at/ or near Curie temperature. Particular attention has been paid to the doping of BaTiO\(_3\) with rare earth elements because they prove to be very promising for the production of supercapacitors. It is pointed out that the preparation of ceramic materials with high dielectric permittivity by sol-gel method is of huge interest due to the numerous advantages inhered to this technology.

Keywords: BaTiO\(_3\), CERAMIC MATERIALS, HIGH PERMITTIVITY, RARE EARTH ELEMENTS

1. Introduction

In recent years, interest in the development of new ceramic materials has increased significantly. A directive from the European Union has been introduced to restrict the import and production of lead-containing materials. [1] According to the norms presented, lead should not be contained in dielectric materials that are part of integrated circuits or discrete semiconductor devices. This is how ideas for the creation of high quality lead-free ceramic materials are born. [2]

For a number of simple electronic applications such as ceramic multilayer capacitors (MLCC), they have quite low thermal stability. The dielectric permittivity characteristics of these MLCCs generally meet the temperature specification “YSV” of the “Electrical Industry Association” (EIA). The ‘YSV’ specification for condenser materials operates in the temperature range from -30°C to + 85°C. Capacity will not increase above 22% and will not decrease below 82% of its nominal value. In the field of electronic components, there is a continuing trend of miniaturization, involving multi-layer capacitors of chips. Therefore, the rapidly expanding market for surface mounted technology chips requires higher and higher compact MLCCs, i.e. greater volume capacity. The required increase in specific capacity is realized in two ways:

- Increasing the relative dielectric permittivity.
- Reducing the thickness of the dielectric layer. [3]

“YSV” dielectric materials typically use the maximum transmittance arising at the Curie point (Tc). The temperature characteristics of “YSV” materials generally correspond to a simple, wide dielectric close to room temperature. The most commonly used base material for MLCCs is BaTiO\(_3\), showing a Tc of 130°C and a relative dielectric permittivity \(\varepsilon_r = 2000\). The maximum dielectric constant is shifted to room temperature by chemical modification of the ceramic material. [4]

BaTiO\(_3\) is a well-known ecological material, one of the lead-free materials with a perovskite structure that is widely used in the electronics industry [5,6]. BaTiO\(_3\) pertains to compounds with the general formula ABO\(_3\), where B ions take the place of A and Ti occupy the B places [5,6]. The doping of such ABO\(_3\) ceramics has been studied for many years in order to improve its electrical and dielectric properties. [5]

2. Influence of modifiers

In recent years, particular attention has been paid to the production of high dielectric permittivity (\(\varepsilon_r\)) ceramic materials (ferroelectrics) by doping of BaTiO\(_3\) with ions of various metals in order to apply them as supercapacitors. A significant feature of high dielectric permittivity is also the Curie temperature (Tc) which pertains to the phase transition from ferroelectric to paraelectric state. The combination of high dielectric permittivity with the appropriate Curie temperature (close to room temperature if possible) is crucial for the application of ferroelectric materials to various technological applications (including as supercapacitors). Therefore, this review pays particular attention to the two mentioned characteristics.

Very high dielectric permittivity is registered for BaTiO\(_3\) doped with trivalent ions of rare earth elements, which induces a significantly increase in the dielectric permittivity [7,8], thus improving the performance of relevant energy storage devices. It has been found that the permittivity depends very strongly on the crystallites sizes and with size decreasing it initially enhances but then diminishes, i.e. a maximum is observed [9]. The permittivity of the rare earth element (RE) doped BaTiO\(_3\) is also determined by the crystal lattice distortion and the presence of point defects in the newly formed perovskite structure. If the radius of the (RE) doping ion is smaller than that of Ba\(^{2+}\) and of Ti\(^{4+}\) the substitution is realized in A sites. This is observed at Nd\(^{3+}\), La\(^{3+}\), Sm\(^{3+}\) and the doping ions improve the dielectric properties of the ferroelectrics. At a larger (RE) radius than Ba\(^{2+}\) and Ti\(^{4+}\) the doping ions substitute in B sites, in the intermediate case, as in Y\(^{3+}\) and Er\(^{3+}\), both A and B are replaced at the same time. [10] In general, both the Ba and the oxygen-compensating vacancies are formed. [10] Characteristic of all ferroelectrics obtained by doping BaTiO\(_3\) with rare earth elements (except Er) is that the temperature of the ferroelectric - paraelectric phase transition can be lowered to room temperature. [11]

Using the doping of BaTiO\(_3\) with rare earth elements, a number of authors have prepared ferroelectrics with high \(\varepsilon_r\) values. The dielectric permittivity of ferroelectrics obtained by the addition of neodymium to barium titanate has been found to depend very strongly on the size of the crystallites, passing through the maximum. At room temperature (Tc) it reaches a surprisingly high value of \(\varepsilon_r = 550000\) [10]. The Sm doped BaTiO\(_3\) exhibits dielectric permittivity 6400 at Tc 50°C [9]. A very high Er = 10130 was registered at Tc equal to 22°C for Ce doped barium titanate. [12] Ferroelectric Ba\(_0.95\)La\(_{0.05}\)TiO\(_3\)-x with surprisingly high permittivity 800000 room (Tc) has been synthesized by adding La to BaTiO\(_3\) [13] There is evidence in the literature for the preparation of Gd substituted BaTiO\(_3\) by the hydrothermal method and subsequent heating in a nitrogen atmosphere. [14] The material exhibited a high relative dielectric constant of 20000 at room Tc.

High dielectric permittivity ceramic materials have been prepared by doping of BaTiO\(_3\) with elements that do not belong to the rare earths, thus a ferroelectric with \(\varepsilon_r = 2500\) at room Tc is synthesized by doping of barium titanate with Sr. [15] When Zr is added to BaTiO\(_3\), the resulting Ba\(_{2-x}\)Sr\(_x\)Ti\(_3\)O\(_7\) ferroelectric exhibit a dielectric permittivity of 10586 at room Curie temperature [16] Another Zr substituted barium titanate with a formula Ba\(_{Ti}\)\(_{1-x}\)Zr\(_{0.5}\)O\(_3\) has a dielectric permittivity of 5000 at room Tc [17].

The direct metal substitution in BaTiO\(_3\) has been also applied in order to prepare ceramics with high dielectric permittivity. As a rule the synthesis proceeds in a reducing medium. Thus Fe-doped BaTiO\(_3\) ferroelectric with a surprisingly high \(\varepsilon_r = 66500\) at room Tc was synthesized.[18] The codoping of BaTiO\(_3\)
with Sm and Mn was also successfully used to synthesize dielectric ceramics with $\varepsilon_r$ 13,000 at $T_c$ 20.4°C [19]

3. Preparation

A very effective approach for the synthesis of high dielectric permittivity is sol-gel technology. This method belongs to the methods of “soft” chemistry, i.e. the preparation of the materials is carried out at relatively low temperatures and atmospheric pressure, without the need for expensive apparatus (peculiar to the physical methods). Other positive features of this technology are (i) possibility for the production of a very large number of materials and compounds and with complex structure and phase composition (including hybrids, composites); (ii) effective stoichiometry control of the of the materials obtained, as well as the use of both inorganic and organic precursors [11]. The synthesized samples are distinguished by their homogeneity. The use of sol-gel technology allows the synthesis of high $\varepsilon_r$ ferroelectrics at significantly lower temperatures than the most commonly used solid phase synthesis. This results in materials with much smaller grain sizes, high homogeneity, and to preparation of high relative dielectric permittivity ceramics at low Curie temperatures and proves to be very effective for the preparation of various ferroelectric materials suitable for high-capacity devices. The sol gel technology was successfully applied to obtain Ce doped BaTiO$_3$ [12], Sr doped BaTiO$_3$. [15]

Suitable for the synthesis of ferroelectrics, with surprisingly impressive dielectric permeability is the sol-hydrothermal method applied by Sun et all [13]. It can be considered as a variant of sol-gel technology. The method allows the synthesis of a pure phase composed of nanoparticles with a narrow size distribution, which proves to be extremely favorable for the production of ceramic materials with high dielectric permittivity.

The most commonly applied method for preparation of ferroelectrics with high dielectric permittivity is conventional solid-phase synthesis. Thus, BaTiO$_3$ is doped with Zr,[16,17] Gd, Y, Yb,[14] Nd,[20,21] Sn and Mn [18] etc. The preparation by solid state reactions requires as a rule higher temperatures in order to obtain doped BaTiO$_3$ than sol-gel technology.

Recently, the production of dielectric ceramics with high $\varepsilon_r$ by direct doting of BaTiO$_3$ with metal has also aroused interest. Fe-doped barium titanate was thus synthesized [19]. The drawback of the method is the compulsory use of a reducing atmosphere.

The synthesis of high dielectric permittivity such as La doped BaTiO$_3$ [13] has also been accomplished through some physical methods such as spark plasma. Physical methods, however, require expensive and complex apparatus as opposed to the sol-gel method.

4. Conclusions

The dielectric ceramics prepared by rare-earth element(s) doped BaTiO$_3$ (RE: BaTiO$_3$) has been considered as one of the most suitable materials for ferroelectric capacitors, because of its high $\varepsilon_r$. This high dielectric permittivity of RE: BaTiO$_3$ is intimately related to the structural distortion and chemical defects surrounding the dopants. The sol-gel method is considered to be very suitable for preparation of high permittivity ferroelectrics due to its advantages: (i) to obtain homogeneous ceramic materials, (ii) the low temperature of synthesis and sintering, (iii) to synthesize materials and compounds with complex structure and phase composition and small grain sizes.

Acknowledgements

The authors are grateful to the financial support of Bulgarian National Science Fund at the Ministry of Education and Science, Contract No KI-06-H 37/26 18.12.2019.

References:


17. Z.i Yu, Ch. Ang, R. Guo, and A. S. Bhalla; Ferroelectric-relaxor behavior of Ba(Ti0.7Zr0.3)O₃ ceramics; J. Appl. Phys. 92, (2002) 2655-2657; doi: 10.1063/1.1495069


