

We expect that electronic devices used in our daily life will become smaller, lighter, faster, more reliable, multifunctional, environment friendly. To achieve these objectives, it is necessary to search for both new more effective materials and new methods which would ensure progress in the miniaturization, integration scale and reliability of electronic components.

In LTCC technology (*low temperature cofired ceramics*), several layers applied as screen printing thick films and as green ceramic tapes (with various functions assigned in an electronic system, e.g. as conductive paths, resistors, capacitors, inductors) form a multilayer module that after lamination is co-fired in a common process. This relatively simple and inexpensive technology enables miniaturization and easy integration of passive components. Thus, it is utilized among others for production of commonly used multilayer ceramic chip capacitors.

Modern electronic systems become more sensitive to interferences and damages caused by overvoltages related to temporary increase in voltage above the maximal allowed value. Besides atmospheric discharges, switching of high power devices and electrostatic discharges can also be the sources of overvoltages. Varistors are widely used for protection against high voltage surges. Varistors are ceramic variable resistors which exhibit current-voltage characteristics strongly dependent on voltage. The application range of varistors is very broad, comprising power supply networks, telecommunication, computers, systems for measurement and control, consumer electronics, lighting systems, automobile electronics.

Conventional varistors are manufactured as bulk elements based on ceramics containing ZnO, SiC, SnO₂, TiO₂, SrTiO₃. Varistor ceramics is composed of large semiconducting grains characterized by a relatively high electrical conductivity, surrounded by thin highly resistive films. The nonlinear behavior of these materials is attributed to the formation of potential barriers at grain boundaries. In the low voltage (pre-breakdown) region, the varistor resistance is very high and its current-voltage characteristic is almost ohmic. Above the breakdown voltage (switch voltage) the potential barrier at grain boundaries is overcome and a rapid decrease in resistance takes place. This leads to suppressing of overvoltage and the voltage is kept at a lower acceptable level. Large current flows through the varistor which can dissipate the absorbed energy of the transient pulse.

Permanent demand for the miniaturization and enhanced integration scale in electronics and the growing application range of low voltage devices stimulates development of multilayer varistors obtained in LTCC technology. These varistors are manufactured by co-sintering of the laminates composed of several layers of tape cast green varistor tapes with screen printed electrodes connected in parallel. Multilayer varistors are utilized in integrated circuits, hybrid circuits, surface mount circuits for low voltage protection against overvoltages caused, e.g. by electrostatic discharge. Today, many electronic devices have their own independent supply source and work at low voltages. For their surge protection, multilayer varistors are the most suitable choice.

The project objective is development and characterization of the properties of a group of new materials (single component and composite) based on perovskites of CaCu₃Ti₄O₁₂-type and on doped zinc oxide, and multilayer varistor elements made of these materials and fabricated in LTCC technology.

Perovskites is the common name for a broad group of natural and artificially produced compounds of the general composition ABX₃ that crystallize in the structure of rare mineral CaTiO₃. In this structure, each cation B is surrounded by six anions X to form octahedra connected by the corners, and the A cations occupy spaces between octahedra. Due to great composition and structure flexibility, there is remarkable variety of properties shown by perovskites. For example, among these materials are excellent insulators, as well as good electrical conductors, and even superconductors. Consequently, very vast is the application range of these materials in electronics, e.g. as ferroelectrics, piezoelectrics, pyroelectric elements, thermistors, varistors, multiferroics, microwave ceramics, and more recently as cheap, flexible solar cells (in this case involving organic cations). Some of the perovskites have an established position in electronics, for example the most popular dielectric for capacitors - barium titanate BaTiO₃, or the well-known piezoelectric material - lead zirconate titanate PZT (Pb (ZrTi)O₃).

The proposed group of materials of CaCu₃Ti₄O₁₂ structure is poorly understood and scarcely used, in spite of very promising capacitor and varistor properties. The perovskite structure of these compounds is more complex (with two types of cations in the position A), and with strong deformation of oxygen octahedra. The unique feature of these materials is the spontaneous formation of insulating layers at grain boundaries leading to the formation of potential barriers responsible for the varistor effect. In traditional varistors to achieve the desired properties of grain boundaries, it is necessary to apply the relevant carefully selected additives and heat treatment conditions. In addition to the simplicity of the manufacturing process, an important advantage of the proposed materials is also the lack of content of bismuth, vanadium and lead oxides - volatile during heat treatment and harmful components of conventional varistors.

In the proposed project, the authors plan to explain the varistor effect mechanism in the newly developed group of materials. Formation of potential barriers at grain boundaries responsible for varistor properties is a complex interplay of several phenomena strongly dependent on composition and conductivity of grains and grain boundaries regions, applied dopants, intrinsic crystal lattice defects, reactions at phase boundaries. Basic studies aimed at elucidation of this effect will be performed in two areas. The first one concerns investigations of electrical conduction and dielectric relaxation by impedance spectroscopy, DC conductivity, current-voltage characteristics and thermoelectric effect measurements. The second equally important area of the studies will comprise characterization of microstructure by transmission (TEM) and scanning (SEM) electron microscopy, and composition analysis by X-ray energy dispersive spectroscopy (EDS), electron diffraction in TEM, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

Impedance spectroscopy is an excellent tool to study the electrical properties of heterogeneous materials, such as varistors, in which the regions of grain boundaries differ strongly from the interiors of the grains. The method is based on an analysis of the electrical response of the sample to a small excitation AC signal over a wide frequency range. It gives the opportunity to determine the resistance and capacitance of different electrically active regions in the sample and provides information on the processes of electrical conduction and polarization (movement of charged particles within the material caused by an external electric field).

Scanning and transmission electron microscopy (SEM, TEM), along with X-ray energy dispersive spectroscopy (including EDS in TEM) will allow for micro- and nanostructure observations at very high magnifications and precise elemental composition microanalysis of grain interiors, grain boundaries regions and electrode-ceramic interphases. X-ray photoelectron spectroscopy (XPS) studies will enable determination of the chemical composition and oxidation states of the elements on the surface of cross-

sectioned samples and will provide information about conductance mechanism of the materials under investigation.

The pioneering nature of the proposed project will consist in explanation of the varistor effect mechanism in a group of novel materials (single component and composite) based on perovskites, derived from the correlation of the results of electrical properties studies with those resulting from advanced investigation of the micro- and nanostructure, and chemical composition. It should be underlined that the varistor effect in multilayer LTCC structures based on $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and relative materials so far has not been studied neither in Poland nor abroad.