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ADVANCED ELECTROCERAMIC MATERIALS FOR ELECTROTECHNICAL APPLICATIONS

C. Miclea, C. Tanasoiu, C. F. Miclea, V. Tanasoiu

National Institute for Materials Physics
Str. Atomistilor 105 bis, 76900 Bucharest – Magurele, P.O. Box MG 7, Romania

Advanced electroceramics have played a critical role in the development of new and modern technologies such as computers, telecomunications and aerospace and they will continue to play the leading role in the technology of the future. The present report presents and discusses a number of advanced electroceramic materials with special references to their specific properties that make them indispensable in a large area of applications. The materials discussed include cobalt-mangan oxides used as negative temperature coefficient thermistors, semiconducting doped barium titanate used for positive temperature coefficient thermistors with large applications in thermal protections and piezoelectric electroceramics of PZT type, which find new application as ceramic transducers and sensors in biomedical and aerospace industries or as simply buzzers, filters, igniters, ultrasonic cleaners, towed array sonars, medical imaging system, ink-jet printing heads, camera shuttlers, positioners for optical systems, micromotors and actuators. Such advanced electroceramic materials are extremely useful for the future sophisticated technologies such as heads for magnetic recording, scanning tunneling microscope, sensors for antilock braking systems, ultrasonic bone-healing devices and some other biomedical applications.

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1. Introduction

Though the ceramic materials originate somewhere in the ancient times, it may be stated that the beginning of them is connected with the fabrication of bricks and pottery. It is therefore understandable that unsophisticated products first come to mind when most people think of ceramics. Nowadays it would be impossible to think our life and achievements without ceramic materials.

In all their application ceramics are valuable primarily for their ability to withstand heat and chemical attack, virtues that stem from the strong bonds that hold their constituent atoms in place.

Recent advances in ceramics have provided greater control over aspects of composition and microstructure that govern physical properties. Such control makes it possible to tailor ceramics to fulfill special chemical, thermal, mechanical, and electrical requirements no other material can satisfy. Indeed, advanced ceramics have played critical roles in the development of new technology such as computers and telecommunications and they will continue to play a leading role in the technologies of the future. Generally, a ceramic material may be simply considered a material resulting from the high temperature burning of a mixture of oxides. Therefore, it gives them chemical stability, manifested as imperviousness to environmental degradation and makes further oxidation impossible. On the other hand the atomic bond in ceramics endows them with a high melting point, hardness and stiffness so that ceramics maintain their shape under stress until a certain threshold is exceeded.

All the properties stated briefly so far make ceramics invaluable materials for our life. Therefore, anywhere in the world, great efforts are being made to make better and sophisticated ceramic materials.

The present report is aimed at presenting some main results of our investigation, concerning a number of advanced electroceramic materials and their application in various fields.

2. Experimental

2.1. The preparation technology

The process of making advanced ceramics is remarkably similar in principle to the traditional clay artifacts that are made today. For our electroceramics we used oxides, carbonates as raw materials, of high purity, generally over 99,5%, which become available at industrial prices and quantities. This fact is of great significance since it has made the very existence of the electronic ceramic industry possible and also has had beneficial effects in the refractories fields.

The ceramic technique we used to fabricate high quality electroceramics implies the following main steps.

a) *Mixing*, acomplished by planetary ball mills using water, alcohol, acetone or other organic fluids for a better homogenization.

b) *Calcination* of the mixed powder at temperatures ranging between 800-1100 ^{o}C, in order to effect the thermochemical reaction among the constituent oxides and to form the desired solid solution. The temperature of calcination was chosen high enough to cause complete reaction but also low enough to permit easy subsequent grinding.

c) *Grinding*, accomplished by means of a planetary ball mill using different vessels and balls so as to avoid as much as possible any further contamination of the initial composition. The most usual vessels we used were made of stainless steel, tungsten steel and agate. Generally it was chosen a grinding medium that suffers very little wear or that have wear products compatible with the composition being ground.

d) *Forming* by pressing the powders in steel dies of different shapes using polyvinyl alcohol solution or water as binders.

e) *Firing* at a given high temperature, or a narrow temperature range, for maturation where the densification reaches a maximum and the properties reach their optimum. Thus barium titanate matures around 1450 ^{o}C [1], the piezoelectric ceramics between 1200 and 1300 ^{o}C while some other oxidic ceramics, such as manganites, mature around 1200 ^{o}C [2]. These temperatures may be changed, some time drastically, when modifiers are added to the initial composition without affecting too much the basic properties [3-8].

3. Results and discussions

During the last decades we prepared and investigated a great number of ceramic materials of various compositions showing remarkable properties and numerous spectacular applications. We shall present only a few of them.

3.1. Cobalt manganites

This class of materials has the following chemical composition:

$$Mn_xCo_y(Me_z)O_4 \tag{1}$$

where $x + y + z = 3$ and *Me* stands for *Cu*, *Ni*, *Al*, *Ti* or *Li*.

The most interesting property of these ceramics is the behavior of their electrical resistance against temperature which is described by the following relationship:

$$R_T = R_\infty \exp(B/T) \tag{2}$$

where R_T is the value of electrical resistance at a temperature T, R_∞ is the value of electrical resistance at infinite temperature, and *B* a material constant expressed in Kelvin degrees.

The nominal electrical resistance R_{25} was easily modified by changing the nature of *Me* and the value of *z* from (1), within a large interval between 0.5 and 500 kΩ.

The most direct and important applications of this type of ceramics was the fabrication of Negative Temperature Coefficient (NTC) thermistors both as discs of different diameters and mostly as bead thermistors for temperature control and measurements [9-13].

While disc thermistors are generally made at industrial scale by the usual ceramic technique the bead thermistors cannot be made but manually by specific technology consisting in making a rather liquid-viscous intimate mixture of grinded calcined oxidic powder and polyvinyl alcohol solution which was next manually applied in minute droplets onto two parallel thin platinum. After drying in an oven they are sintered at high temperature, then cut so as to have two platinum terminals and sealed and encapsulated in a thin glass tube as can be seen in Fig. 1.

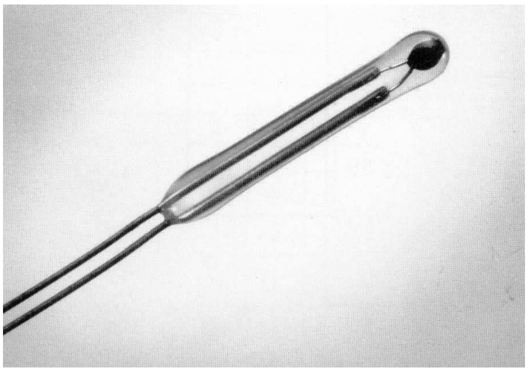

Fig. 1. Glass encapsulated bead NTC thermistor.

Such bead thermistors were designed for temperature measurements and control applications. They feature small size and provide maximum stability up to 300 ^{o}C. In addition they are ideally suited for the most stringent military, aerospace, oceanographic and industrial electronic application such as humidity detection, fire detection, measurement of fluids speed, levelmeters and so on.

3.2. Barium titanate

Barium titanate was the first performant electroceramic material with numerous application in the fields of electronics and ultrasonic transducers. It can be easy manufactured by ceramic technique and has a wider temperature range of operation.

Dielectric, piezoelectric and semiconducting properties of barium titanate are of utmost importance when applications are concerned but here we shall limit ourselvs to its semiconducting properties.

The extraordinary semiconducting properties of doped $BaTiO_3$ ceramics were discovered early in fifties and they are nowadays utilized in nonlinear Positive Temperature Coefficient (PTC) thermistors as well as in barrier-layer capacitors and intergranular capacitors [10-15].

Semiconducting barium titanate shows at least two very interesting features. One is that extremely low dope concentration (around 1 % at) are necessary to convert it from an isolator with resistivity of about 10^{12} Ω·cm to a semiconducting material with a resistivity of a few Ω·cm at room temperature. The second one is that by this doping a remarkably high resistivity appears above the Curie point. This anomalous increase of the resistivity is known as the PTCR effect and is used for Positive Temperature Coefficient (PTC) thermistors. A satisfactory interpretation of this effect was given by Haywang [11] and Jonker [12] by assuming the existence of a depletion layer at the grain boundaries of ceramic particles, whose height is controlled by the dielectric constant and spontaneous ferroelectric polarization of the particles. The literature trying to explain this effect is very wealthy [16-31] but many questions remained still unanswered. Anyhow, there was experimentally established a number of facts that can be summarized as follows.

1. The PTCR effect is linked directly to the occurrence of ferroelectricity. Any change in the Curie point leads to a corresponding shift of the temperature of which the specific resistivity changes abruptly [32].

2. $BaTiO_3$ single crystals do not exhibit any PTCR effect [33].

3. In undoped $BaTiO_3$ ceramics no PTCR effect has been detected. Specimens subjected to a reducing treatment do conduct well but their resistivity shows no anomaly at the Curie point.

4. The PTCR effect occurs only in donor-doped $BaTiO_3$ ceramics, the magnitude of the effect being determined largely by the condition of preparation (composition, sintering temperature, sintering atmosphere). Above all the cooling conditions and the after treatments in different atmospheres exert much influence on the PTCR properties [17, 20, 22, 34-36].

5. Very small additions of acceptors which, however, amount to only a fraction of the donor dopes are able to modify the PTCR effect considerably [36, 37].

The fabrication technology become an essential approach for the presence of the PTCR effect in doped barium titanate ceramics so that the quality of PTC thermistors depends on the skill of the producers.

In the present work we have fabricated a great number of PTC thermistor starting with the following general chemical formula:

$$Ba_{1-x-y}Sr_xPb_yY_{0,01}TiO_3 \tag{3}$$

The isovalent substitutions of barium by Sr or Pb bring about structural modifications whose effect is a shift of the tetragonal-cubic transition temperature i.e. of the Curie point. Sr decreases and Pb increases the Curie point respectively as can be see in Fig. 2.

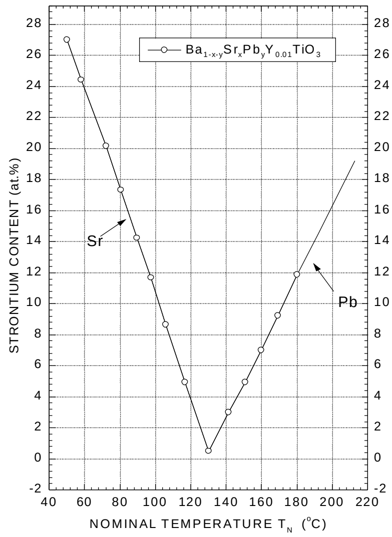

Fig. 2. The nominal temperature of PTC thermistors as a function of composition.

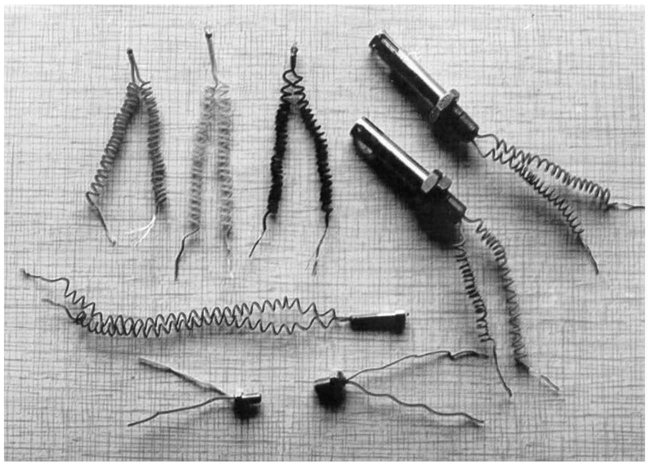

Fig. 3. Different types of PTC transducers fot thermal protections.

The main application for such thermistors is thermal protection. Constructively such a PTC thermistors consists of a disc, about 4 mm in diameter and 1-1.2 mm thickness, having ohmic contacts on the paralel faces on which two therminal wires are connected. A protection of shrinkable tube is applied on the thermistor. For different types of thermal protections the thermistors may be incorporated in different metallic cases as cam be see in Fig. 3.

3.3. Lead titanate-zirconate (PZT) type materials

This new class of piezoelectric materials was discovered in the sixties [38], and they show very strong and stable piezoelectric effects. Such ceramics are used in the consumer-automotive, medical and aerospace industries with application ranging from low-cost buzzers and filtres through high performance transducers for ultrasonic imaging systems and towed array sonars. Relatively new uses of piezoelectric ceramics include actuators, micromotors and transformers. The promise of developing "smart" materials, providing both sensing and actuating functions, has increased the focus on development of piezoelectric active materials.

Our research activity on piezoelectric ceramics was focused towards developing new performant piezoelectric materials with special properties able to be used both for domestic application and for the most recent ones such as actuators and micromotors.

The compositions we were working on were as follows:

1. A "soft" type piezoelectric material with the following chemical formula:

$$Pb \quad Nb_{0,002}Li_{0,007}Zr_{0,51}Ti_{0,463}O_3 \tag{4}$$

generally used for transducers for sound and ultrasounds and

2. A "hard" type piezoelectric material with the following chemical formula:

$$Pb_{0,98}Sr_{0,02}Mn_{0,017}Sb_{0,033}Zr_{0,48}Ti_{0,47}O_3 \tag{5}$$

generally used as high power, high voltage ultrasonic generators.

Apart from these two types of piezoceramic materials some other compositions were studied using different dopings, especially transitional metals, in order to improve some basic constants, such as dielectric constant, for special applications in the field of actuators and micromotors.

We succeeded in making materials with high piezoelectric characteristics as can be seen in Table 1.

Table 1. The experimental values of the main piezoelectric parameters for the four piezoceramics materials investigated.

Property and symbol	Soft piezomater. MPT	Hard piezomater. MPG	Special mat.1 MPS-1	Special mat.2 MPS-2
Density ρ (g/cm^3)	7.66	7.60	7.68	7.70
Relative dielectric const. ε_r	1500	1200	5000	7000
Loss tangent $tg\delta$	0.016	0.003	0.005	0.006
Planar coupling coeff. k_p	0.60	0.56	0.61	0.62
Mechanical quality factor Q_m	80	1800	60	70
Charge constant d_{33} $(10^{-12} m/V)$	340	290	722	790
Voltage constant g_{33} $(10^{-3} Vm/N)$	25.9	27.0	20.2	22.3

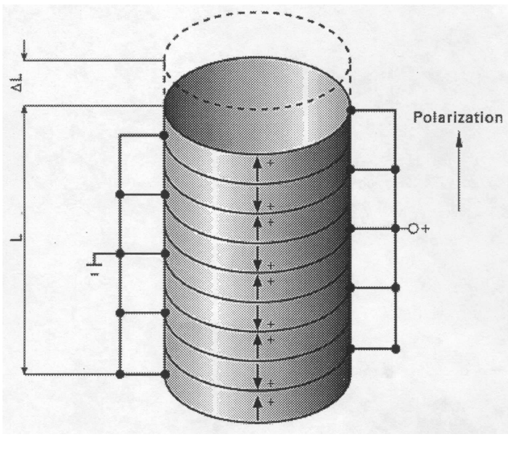

Fig. 4. Schematic view of a stack construction of piezo-actuator.

While the MPT and MPG ceramics are currently used for application in the field of ultrasonic transducers, the MPS-1 and MPS-2 are specially designed for actuators and micromotors due to their high dielectric and charge constants.

A piezoactuators is a layered construction (stack) of thin piezoceramic samples, with electric contacts in between, and sealed together by means of an adhesive as can be seen in Fig. 4.

The total displacement ΔL is given by:

$$\Delta L = d_{33} \cdot n \cdot U \tag{6}$$

where d_{33} is the dielectric charge constant of the piezoceramic elements expressed in m/V; n is the number of piezoceramic layers and U is the operating voltage. One can see that the higher d_{33} the larger ΔL. The usual construction of actuators may provide maximum displacements of the order of 200 μm.

For piezoelectric motors [39-52] the active element consists of a rather thin piezoceramic ring, completely electroded on one side and with a special electrode configuration on the other as can be seen in Fig. 5 and sequentially poled. This makes possible that one group of segments (system 1) excites the sine mode and the second group (system 2) excites the cosine mode. The piezoceramic ring being polarized in its thickens direction the bending vibrations of the stator are excited by the in-plane expansion and contraction so that an elliptic motion of the point of the surface of the stator is generated by the proper superposition of the two orthogonal bending modes resulting in a traveling bending wave in the stator.

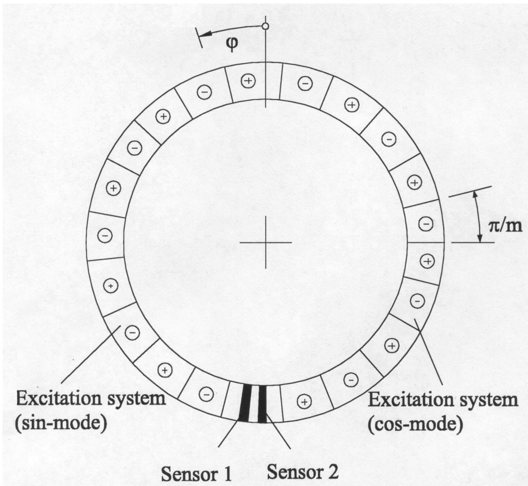

Fig. 5. Schematic view of a piezoceramic active element for piezoelectric motors.

The piezoelectric motors offer several positive features over any other type of motors, which make them extremely attractive for a lot of application. These features are:

- Much higher torque compared to the conventional drives of the same volume.
- Generation of low speeds, adjustable down to zero, without the need for gearing.
- No loss of troque at high or low speed.
- Large holding torgue at rest without additional energy supply.
- Extremely high dynamics and excelent controlability.
- Completely lack of inertia and practically instantaneous moving in any direction.
- Quiet running in the audibly range.
- Compact design and high degree of miniaturization.
- Simple mechanical components.
- No magnetic field and hence no electromagnetic disturbance.

Consequently, the piezoelectric motors are extremely well suited for fast positioning systems such as cars, office technology and consumer goods, but also in satellites, aerospace vehicles, or high technology medical equipment. Also window winders, gearless window wipers, seat adjusters, drives for paper feeders and writing, head adjustment of printers and lens focus motors in cameras or videocameras are just another some examples of first applications.

4. Conclusions

A number of advanced electroceramic materials were prepared by ceramic technology and their properties were investigated.

The materials include cobalt manganites used to fabricate NTC thermistors for temperature measurement and control, semiconducting barium titanate used to fabricate PTC thermistors for thermal protection and lead titanate zirconate PZT solid solution used for piezoelectric transducers. Various applications of all these materials have been presented and discussed.

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