

Investigations of properties of ceramic materials with perovskite structure in chosen electronic applications

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Abstract. In this work synthesis, sintering processes and properties of three groups of perovskite-type ceramics utilized in chosen electronic applications are briefly described. The first group includes high permittivity dielectrics based on relaxor ferroelectrics and new leadfree ceramics, destined for bulk and thick film capacitors. The second group comprises ceramics for low and high temperature thermistors and the third one nonstoichiometric conducting compounds containing doped SrMnO_3 and SrCoO_3 , tested as electrode materials for solid state cells.

Key words: perovskite, dielectric, thermistor, ceramic electrodes.

1. Introduction

Complex metal oxides of perovskite structure due to their various physical and chemical properties are widely utilized in electronics – in the production of capacitors, infrared detectors, thermistors, electromechanical transducers, resonators, oscillators, filters (also microwave ones), gas sensors, electrodes of electrochemical cells, lithium batteries and in many other applications.

Perovskite structure of the general formula ABO_3 contains two cation sublattices and an anion sublattice. One of the cation sublattices is formed by “A” cations with coordination number 12, situated between oxygen octahedra, while the second sublattice is built-up by the “B” cations with coordination number 6, occupying appropriate sites inside the octahedra.

The subject of this paper is a short presentation of fabrication methods and properties of three groups of the developed perovskite-type ceramics used as: capacitor dielectrics, thermistors and electrodes of solid state cells.

Relaxor ferroelectrics $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$ ($\text{B}' = \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Fe}^{3+}, \text{Ni}^{2+}, \text{In}^{3+}, \text{Sc}^{3+}$; $\text{B}'' = \text{Nb}^{5+}, \text{Ta}^{5+}, \text{W}^{6+}$) has been intensively studied for several years [1,2]. These compounds are applied as dielectrics in capacitors, as well as piezoelectric, electrostrictive and pyroelectric components. The advantageous features of relaxors predestining them to be used as dielectrics in type II capacitors are: very high dielectric permittivity, broad maximum of permittivity versus temperature, weak dependence of capacitance on electrical field and relatively low sintering temperature. Dielectric materials based on five relaxor ferroelectrics are briefly described in this paper.

Recently, there has been an increasing tendency to confine the application of compounds containing lead in electronic products industry. This involves searching for new substances which could replace lead containing

compounds like: $\text{Pb}(\text{ZrTi})\text{O}_3$, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, now commonly used in piezoelectric elements and capacitors. An increasing number of papers concerning leadfree materials characterized by high dielectric permittivity have been published lately [3,4]. This work presents the results of investigations of six compounds with perovskite structure, in which calcium or bismuth and copper ions were substituted for lead.

NTC thermistors (thermal sensitive resistors of negative temperature coefficient), known from many years, are typically complex oxides of transition metals with spinel structure. Disadvantages of these materials are poor stability and aging at temperatures higher than 200°C. An interesting alternative to the spinel thermistor ceramics are some materials with perovskite structure [5]. The main features determining their usability are: high values of temperature coefficient of resistance, monophasic, chemically uniform composition, stability of electrical parameters in time and at high temperatures, as well as a possibility to tailor the resistance by a proper composition change. In this work the results obtained for five investigated thermistor materials destined for low and high temperature applications are presented.

As a consequence of the rapidly growing demand for alternative, renewable and environmentally friendly energy sources, potential materials for solid state fuel cells have been recently intensively studied. Due to the high price of platinum, poor mechanical strength and evaporation of porous platinum layers at high temperatures, search for alternative electrode materials is an important challenge. Such promising materials, exhibiting high mixed electronic conductivity and very good thermal and mechanical stability, are some complex oxides with perovskite structure [6,7]. A group of materials based on cerium, lanthanum and samarium doped SrMnO_3 and SrCoO_3 , presented in

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this paper, owing to a lowered lanthanides content as compared with conventional electrode perovskite compositions, is characterized by reduced fabrication costs resulting both from lower costs of starting materials and from lower sintering temperatures of the ceramics.

2. Experimental

Synthesis of capacitor ceramics was carried out by a two-step method, ensuring formation of the perovskite phase, this process consisting in reaction of B' and B'' cations prior to the reaction with a cation from "A" position. Starting oxides were ball-milled in appropriate stoichiometric proportions and calcined at 1000°C and at 800 - 850°C during the first and the second synthesis step, respectively. Ceramic samples were sintered in the temperature range 870 - 1300°C for 1 - 2 h.

Syntheses of thermistor and conducting samples were performed by calcination at 1200 - 1350°C. The sintering temperature range was 1350 - 1430°C and 1200 - 1440°C for thermistor and electrode materials, respectively.

Thick film pastes were prepared by mixing of perovskite powders with organic vehicle - solution of ethyl cellulose in terpineol. Capacitor thick films were fired in a BTU VI-zone furnace in the temperature range 850 - 950°C. Glassfree electrode layers were sintered in a chamber furnace at 1000 - 1100°C and at 1050 - 1250°C, for the pastes based on cerium doped SrCoO₃ and the pastes based on cerium, lanthanum and samarium doped SrMnO₃, respectively.

Phase composition of the samples was controlled by X-ray analysis using a Philips X'Pert diffractometer. Microstructure, grain size, distribution of phases and cooperation of electrodes with a substrate were studied using a Jeol scanning electron microscope and a Link Isis electron microprobe.

Resistivity of the developed materials was measured in the temperature range 20 - 500°C for capacitors, -55 to 800°C for thermistors and 20 - 820°C for conductive ceramics and thick films. A Philips resistance meter and a Hioki meter were used for measuring of high and low resistivities, respectively. Capacitance and dissipation factor of plate and thick film capacitors were determined by means of a LCR Quadtech meter at frequencies changing from 10 Hz to 1 MHz in the temperature range from -55 to 500°C. Changes in resistivity of thermistors were measured after stability tests carried out at 180°C for 500 h.

Performance of the perovskite layers as electrodes was studied by measurements of electromotive force of oxygen concentration cell with yttria stabilized zirconia as solid electrolyte.

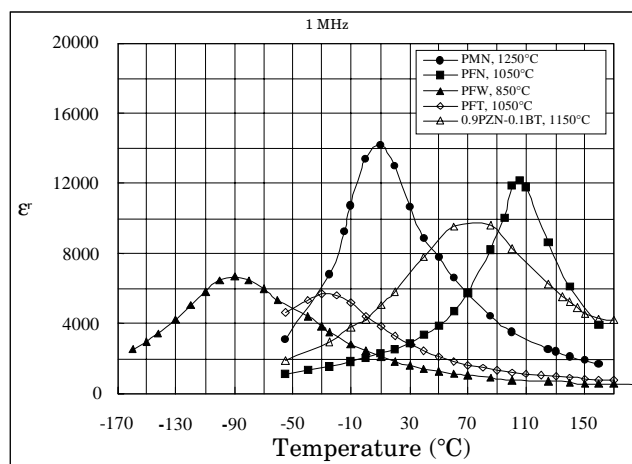
3. Materials for type II capacitor dielectrics

3.1. Properties of relaxor ceramics and thick films.

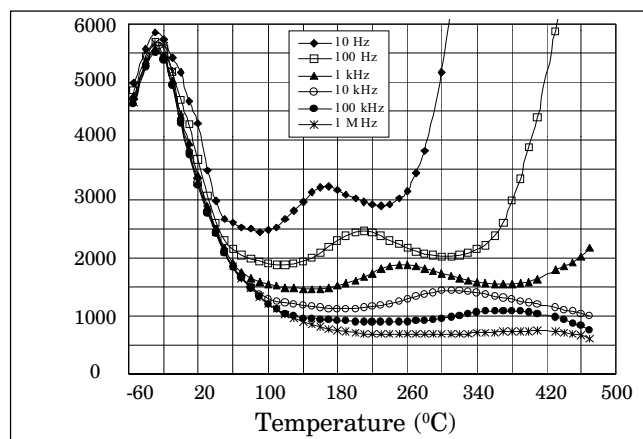
Dielectric properties of multicomponent materials based on five relaxor ferroelectrics: Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN), Pb(Zn_{1/3}Nb_{2/3})O₃ (PZN), Pb(Fe_{1/2}Nb_{1/2})O₃ (PFN), Pb(Fe_{1/2}Ta_{1/2})O₃

(PFT) and Pb(Fe_{2/3}W_{1/3})O₃ (PFW) with addition of normal ferroelectrics: BaTiO₃ and PbTiO₃ were investigated in wide temperature and frequency ranges.

Unlike a sharp peak at Curie temperature, characteristic for normal ferroelectrics, a broad maximum of dielectric permittivity versus temperature occurs for relaxor ferroelectrics (Fig. 1). This effect results from diffuse phase transition related to disordered distribution of cations in B sites of perovskite structure.



(a)



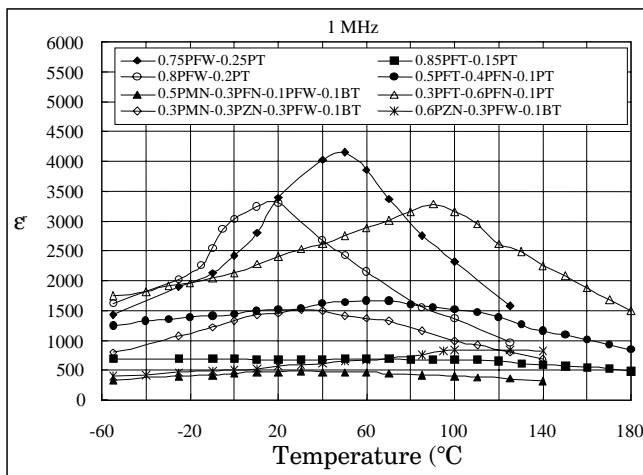
(b)

Fig. 1. Temperature dependence of dielectric permittivity for relaxor ceramics with various compositions at 1 MHz (a) and for PFT ceramics in the frequency range 10 Hz - 1 MHz (b)

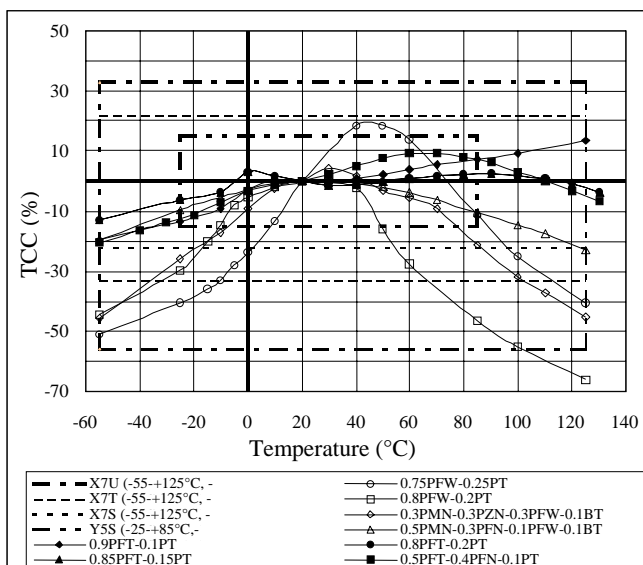
The relaxor materials investigated in this work exhibited high dielectric permittivity with maximum values of 3000 to 22000 at Curie temperature. For PFN, PFT and PFW relaxors in the examined temperature range at a given frequency, besides maxima of dielectric permittivity and dissipation factor related to ferroelectric-paraelectric transition, a second set of peaks was observed at higher temperatures, ascribed to relaxation processes (see Fig. 1b). These peaks were shifted towards higher temperatures and their height decreased with increasing frequency and content of MnO₂ and Co₃O₄ dopants (in the range of 0.1 - 1 mol %).

In the case of the dielectrics containing PMN and/or PZN, dissipation factor was rather high below Curie temperature and then violently decreased to the level of 0.005 – 0.02 above T_c . This behaviour is typical of dielectric losses caused by spontaneous polarization in ferroelectrics. For the materials containing PFN, PFW and PFT, dissipation factor rapidly increased with decreasing frequency, indicating the contribution of losses due to electrical conduction.

Flattening of $\epsilon_r = f(T)$ curves and a desired Curie temperature were attained by a proper choice of compositions containing relaxors and normal ferroelectrics with various transition temperatures. Lowering of sintering temperatures to the level of 900 – 1100°C resulted from an addition of PFW and PFN. The improvement of resistivity and dissipation factor was achieved by the introduction of PMN and PZN relaxors characterized by a high resistivity and by doping with small amounts of MnO_2 or Co_3O_4 .



(a)



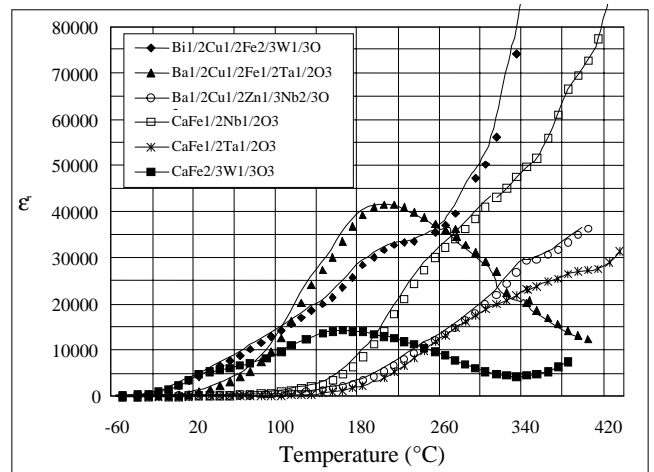
(b)

Fig. 2. Comparison of dielectric permittivity at 1 MHz (a) and temperature change of capacitance (b) for thick films based on relaxor ceramics sintered at 880°C

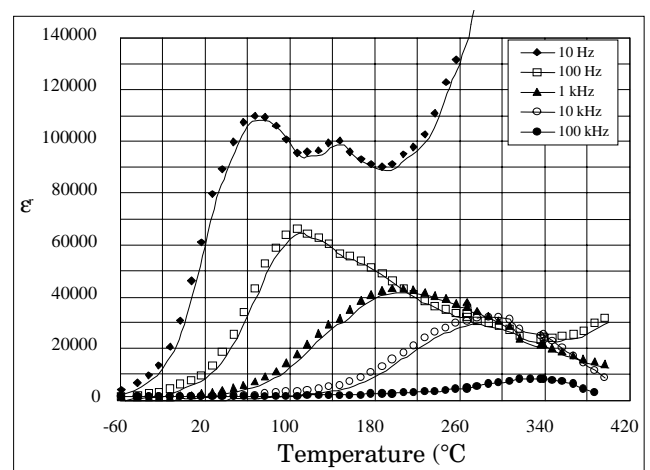
On the basis of the obtained ferroelectric materials glassfree pastes were prepared, destined for dielectric layers in thick film type II capacitors. The main components of these pastes were PFW, PFN and PFT relaxors, chosen in view of their low sintering temperatures. The layers made of the developed pastes exhibited a high dielectric permittivity at the level of 500 – 4000 (Fig. 2a).

Among the investigated thick films, the layers with composition 0.5PFT-0.4PFN-0.1PT, fired at 880°C, were characterized by the most advantageous features, such as: high resistivity ($10^{12} \Omega \text{ cm}$), high dielectric permittivity (1600 - 2200 at Curie temperature) and low temperature change of capacitance at frequencies ranging from 100 Hz to 1 MHz (from -20% to 9% in the temperature range from -55 to 125°C) (see Fig. 2b).

3.2. Properties of leadfree ceramics. The paper presents the properties of six leadfree materials with perovskite structure: $Ca(Fe_{2/3}W_{1/3})O_3$ (CFW), $Ca(Fe_{1/2}Nb_{1/2})O_3$ (CFN), $Ca(Fe_{1/2}Ta_{1/2})O_3$ (CFT), $Bi_{1/2}Cu_{1/2}(Fe_{2/3}W_{1/3})O_3$



(a)



(b)

Fig. 3. Temperature dependence of dielectric permittivity of leadfree ceramics with various compositions at 1 kHz (a) and BCFT ceramics in the frequency range 10 Hz – 1 MHz (b)

(BCFW), $\text{Bi}_{1/2}\text{Cu}_{1/2}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (BCFT) and $\text{Bi}_{1/2}\text{Cu}_{1/2}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BCZN).

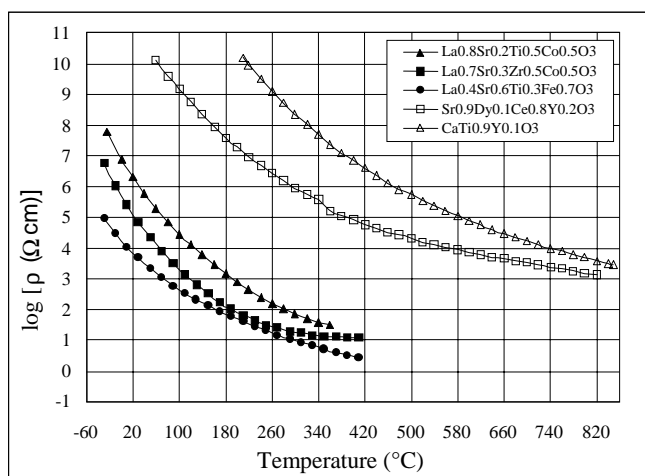
In the investigated temperature range the obtained materials exhibited broad maxima or humps on the plots of temperature dependence of dielectric permittivity, related to dielectric relaxation (Fig. 3). Their location shifted towards higher temperatures with increasing frequency. The maximum ϵ_r values diminished significantly with increasing frequency. Flattening of $\epsilon_r = f(T)$ curves took place both in the low temperature region and at high frequencies. At higher temperatures dielectric permittivity increased in monotonic way due to rising electrical conductivity. The developed ceramics were characterized by very high maximum values of dielectric permittivity in the range 25 000 – 100 000. Maxima or humps occurred in the temperature range 70 – 440°C. There were also found maxima on the dissipation factor versus temperature plots, increasing and shifting towards higher temperatures with rising frequency. Above the peak temperature the dielectric losses started to grow monotonically due to electrical conduction.

Shapes of the dielectric dependencies determined for CFW, BCFT and BCFW were close to those observed for other nonferroelectric materials with perovskite structure [3, 4]. The course of dielectric characteristics for these compounds could be attributed to the formation of internal barrier layer capacitors and/or to Maxwell-Wagner polarization caused by electrical inhomogeneity.

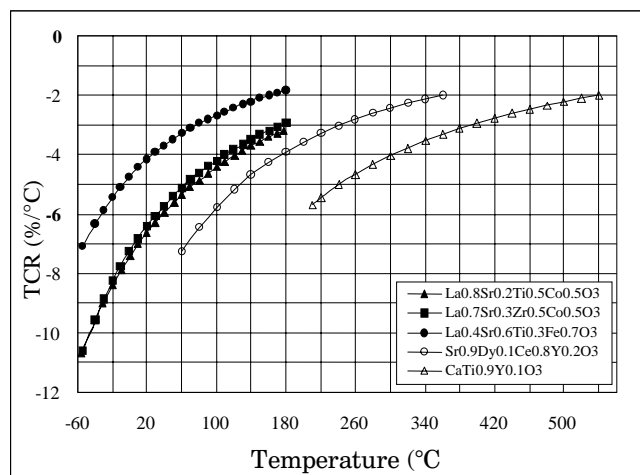
4. Thermistor ceramics

The paper presents the results for NTC thermistor materials with compositions $\text{La}_{0.7}\text{Sr}_{0.3}\text{Zr}_{0.5}\text{Co}^{2+}_{0.2}\text{Co}^{3+}_{0.3}\text{O}_3$, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ti}_{0.5}\text{Co}^{2+}_{0.3}\text{Co}^{3+}_{0.2}\text{O}_3$ and $\text{La}_{0.4}\text{Sr}_{0.6}\text{Ti}_{0.3}\text{Fe}_{0.7}\text{O}_3$ destined for low temperature applications, and with compositions $\text{CaTi}_{0.9}\text{Y}_{0.1}\text{O}_3$ and $\text{Sr}_{0.9}\text{Dy}_{0.1}\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_3$ for high temperature applications (Fig. 4).

The obtained materials exhibited high negative temperature coefficients of resistivity changing from -10.7 to -1.6%/°C in the temperature range from -55 to 180°C



(a)



(b)

Fig. 4. Temperature dependence of logarithm of resistivity (a) and TCR (b) for thermistor ceramics

for compositions destined for low temperature applications, from -7.2 to -2%/°C in the temperature range 70 - 360°C for $\text{Sr}_{0.9}\text{Dy}_{0.1}\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_3$ ceramics and from -5.7 to -2%/°C in the temperature range 210 - 540°C for $\text{CaTi}_{0.9}\text{Y}_{0.1}\text{O}_3$ ceramics.

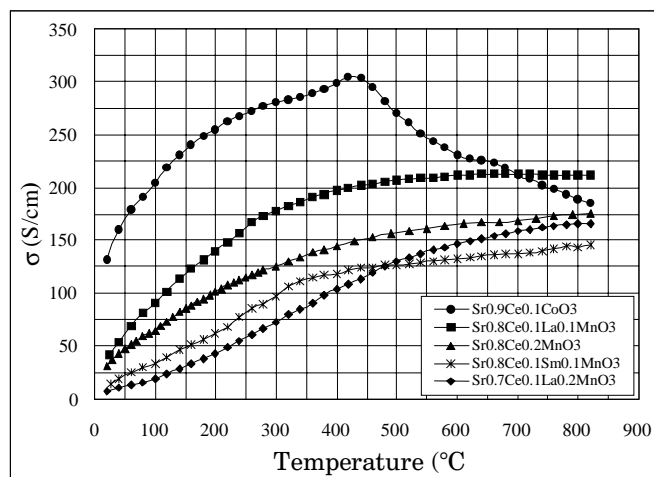
The developed thermistors did not show any discernible resistance changes after storing at room temperature for 4 months. Changes after stability tests (500 h at 180°C) were small (0.1 – 1.6 %). X-ray diffraction analysis confirmed single phase composition of the investigated ceramics.

5. Electrode materials for solid state cells

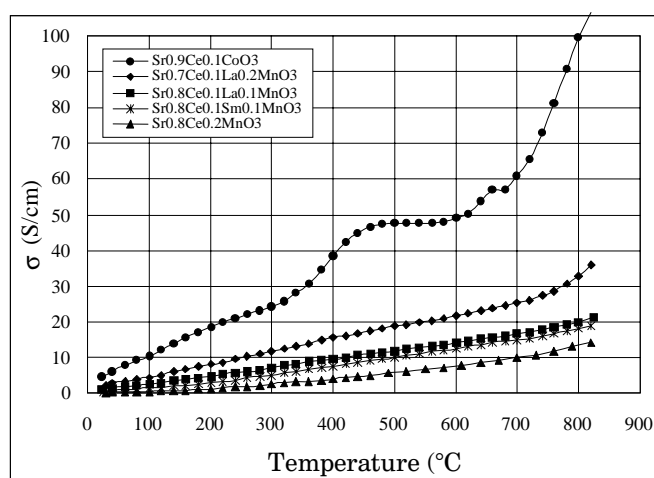
The synthesized $\text{Sr}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$, $\text{Sr}_{0.8}\text{Ce}_{0.1}\text{La}_{0.1}\text{MnO}_3$, $\text{Sr}_{0.8}\text{Ce}_{0.1}\text{Sm}_{0.1}\text{MnO}_3$ and $\text{Sr}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ complex oxides are nonstoichiometric compounds with perovskite structure. At temperatures higher than 800°C the sintered ceramic samples with these compositions exhibited the electrical conductivity not lower than 150 S/cm. In the case of oxides with manganese content, the observed small changes in conductivity with increasing temperature above 400°C (Fig. 5(a)) would indicate that the conductivity type tends to change from semiconducting to semimetallic one.

The highest values of conductivity, exceeding 300 S/cm at 420°C, were found for the ceramics based on cobalt oxide. For $\text{Sr}_{0.9}\text{Ce}_{0.1}\text{CoO}_3$ a distinct transition from semiconducting to metallic character of conduction was observed, entailing a decrease in conductivity with increasing temperature above 420°C (Fig. 5a).

Conductivity of the electrode thick films with manganese was about one order of magnitude lower than that of the sintered ceramics, ranging from 10 to 36 S/cm. The layers with cobalt exhibited a much higher conductivity, of the order of 100 S/cm at 800°C. The good conductivity of the investigated materials resulted from the intentionally introduced nonstoichiometry. Disproportionation reaction of manganese and cobalt ions takes place at high temperatures. $\text{Mn}^{3+}/\text{Mn}^{4+}$ or $\text{Co}^{3+}/\text{Co}^{4+}$



(a)



(b)

Fig. 5. Temperature dependence of electrical conductivity of conductive perovskite ceramics (a) and thick films (b)

ions are supposed to form in the crystal lattice and, consequently, an increase in the concentration of charge carriers and the electrical conductivity occurs [6,7].

The developed electrode materials were successfully tested in an oxygen concentration cell. At temperatures above 750°C a very good agreement between the experimental and theoretical values of electromotive force of the cell with solid electrolyte $ZrO_2 - 8 \text{ mol}\% Y_2O_3$ was observed (see Fig. 6). The electrode compositions presented in this paper could compete on price with the commercially available powders, based on complex manganese, cobalt, iron, lanthanum and strontium oxides, which contain even up to 85 mol% of the expensive lanthanum.

6. Conclusions

Since the substitution of various cations, as well as deformation of the ideal perovskite crystal lattice and formation of defects take place easily, there is a possibility to obtain very broad variety of compositions and properties

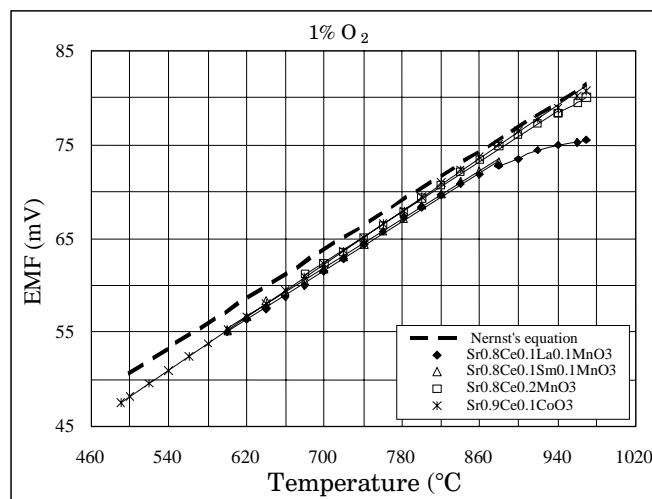


Fig. 6. Temperature dependencies of electromotive force of the oxygen concentration cell (gas mixture – nitrogen with 1% oxygen, reference gas – air) with $ZrO_2 - 8\% Y_2O_3$ solid electrolyte and perovskite electrodes. For comparison theoretical line calculated from the Nernst's equation is shown

of compounds with this structure. The presented paper reports on some experimental results concerning perovskite-type materials destined for chosen electronic applications. The examples were given for capacitor dielectrics, semiconducting thermistors and electrode materials being mixed electronic and ionic conductors. For each of the presented group of materials, good properties appropriate for a particular application have been achieved, with the perspective of further improvement of the parameters by changing the composition and processing of the ceramics and thick films.

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