

PTCR EFFECT IN COMPOSITE CERAMICS

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Abstract: An anomalous PTCR effect (positive temperature coefficient of electrical resistivity) was observed in composite ceramics in the ZnO-MO (M = Ni, Mg), ZnO-Ln₂O₃ (Ln = Nd, Sm) systems. The composite ceramics exhibiting the PTCR effect are composed of a low resistivity phase and a high resistivity phase with different linear thermal expansion coefficients. The origin of the PTCR effect could be attributed to a large difference between electrical and thermal properties of the constituent phases.

PTCR efekt v kompozitni keramiki

Ključne besede: keramika kompozitna, PTCR koeficienti temperaturni pozitivni upornosti električne, PTCR efekti, upornost električna, raztezki termični linearni, upornost električna specifična mala, upornost električna specifična velika, koeficienti razteznosti termični linearni, lastnosti električne, lastnosti termične

Povzetek: V kompozitni keramiki na osnovi sistemov ZnO-MO (M = Ni, Mg) in ZnO-Ln₂O₃ (Ln = Nd, Sm) smo proučevali anomalijo električne upornosti - PTCR efekt (pozitivni temperaturni koeficient električne upornosti). Kompozitna keramika je bila sestavljena iz faze z majhno specifično upornostjo in faze z veliko specifično upornostjo in z večjim linearnim termičnim koeficientom razteznosti. Izvor PTCR efekta kompozita smo pripisali relativno velikim razlikam med električnimi in termičnimi lastnostmi obeh osnovnih faz, ki sestavljata kompozit. Pri sobni temperaturi tvori faza z manjšo specifično upornostjo v kompozitu prevodni skelet, ki se pri višjih temperaturah prekine zaradi večjega raztezka faze z večjo specifično upornostjo. Omenjen fenomen tj. relativno hitro povišanje električne upornosti s porastom temperature polprevodnega kompozita označujemo kot PTCR efekt.

1. Introduction

An anomalous positive temperature coefficient of electrical resistivity (PTCR effect) was first observed in donor-doped BaTiO₃ /1, 2/. Other known materials exhibiting a PTCR effect are polymer composites /3/, ceramic composites /4, 5/, and compounds based on V₂O₃ /2, 6/. Some of these materials are employed as PTCR thermistors for temperature sensors and regulators, overcurrent protection, fluid-flow sensors, TV de-gaussers etc.

Polymer composites exhibiting a PTCR effect are composed of a conductive phase, in the form of a metal /7, 8/ or other highly conductive powder /9, 10/, and an insulating polymer phase. The conductive phase forms a conductive network in a conductive composite at room temperature. At elevated temperatures the polymer expands abruptly at the temperature near to its melting point and disconnects the conductive network which leads to an increase of resistivity, i.e. the PTCR effect. Similar behaviour is observed also for SiC-SiO₂ /4/ and graphite-SiO₂ /5/ ceramic composites where the volume expansion of the insulating phase is attributed to the SiO₂ phase transition at around 260-270°C.

Kirkpatrick et al. /11/ reported about a PTCR effect in ZnO-NiO-TiO₂ three phase ceramics, composed of ZnO_{SS} and NiO_{SS} solid solutions and of a spinel phase (Zn,Ni)₂TiO₄. Zajc and Drofenik /12/ observed a PTCR effect also in ZnO-NiO two phase ceramics composed from solid solutions of ZnO_{SS} and NiO_{SS}. According to our previous studies, a large difference in resistivity and in linear thermal expansion of the ZnO_{SS} and NiO_{SS} constituent phases may cause a PTCR effect in

ZnO-NiO two phase ceramics /13, 14/. A ZnO_{SS} low resistivity network is present in ZnO-NiO two phase ceramics at room temperature. The ZnO_{SS} network could be disconnected at elevated temperatures due to a larger linear thermal expansion coefficient of the high resistivity NiO_{SS} phase, which results in a resistivity increase in this ceramics during heating, i.e. a PTCR effect.

Accepting the explanation proposed for the ZnO_{SS} - NiO_{SS}⁽¹³⁾ system that the main conditions necessary for such oxide systems to exhibit the PTCR effect are: the number of constituent phases must be ≥ 2 , the constituent phases must be thermodynamically stable in the temperature range where the composite is sintered, at least one of the constituent phase must differ in its linear temperature expansion coefficient and at least one of the constituent phases must exhibit an appreciably higher conductivity in the temperature range considered, one can apply the same concept for other systems which fulfil the demanded conditions.

In this manuscript results of our studies on the ZnO-MgO and ZnO-Ln₂O₃ (Ln = Nd, Sm) systems are reported. The ZnO-MgO system was selected for these due to its similarity with the studied ZnO-NiO system, regarding electrical and thermal properties /15/, crystal structure and their phase compatibility with ZnO /16-18/. On the other hand the phases Nd₂O₃ and Sm₂O₃ exhibit a large linear thermal expansion coefficient and a higher resistivity than ZnO /15/, and no intermediate phases were reported to form between ZnO and Nd₂O₃ or Sm₂O₃ /19, 20/ during the heating of binary compositions. So one is justified in expecting a PTCR effect in these investigated systems.

2. Experimental procedure

Samples were prepared from ZnO (Pharma A), MgO (Merck), Nd₂O₃ (Reacton, Johnson Matthey Company) and Sm₂O₃ (Alfa Produkte) by a classical ceramic route. In the ZnO-MgO system samples with 10, 28, 42, 45, 55, 70, 81, and 96 mol.% of ZnO, in the ZnO-Nd₂O₃ system samples with 20, 40, 50, 60, 70, 80 and 90 wt.% of ZnO and in the ZnO-Sm₂O₃ system samples with 20, 40, 45, 50, 55, 60, 70, 80 wt.% of ZnO were examined. The ZnO-MgO mixtures were first calcinated at 1100°C for 24h and afterwards milled in SiO₂ media, while ZnO-Ln₂O₃ powder mixtures were sintered after homogenisation and the preparation of pellets. Pellets from powder mixtures were pressed at 70 MPa and sintered at 1450°C for 2h, and in the case of the ZnO-MgO system, at 1350°C for 24h.

An In-Ga electrode introduced by rubbing both flat surfaces of the pellets was used for the electrical measurements. Resistance versus temperature measurements were obtained by a Hewlett Packard Multimeter 3457A. Some samples exhibited resistance higher than $3 \times 10^9 \Omega$ (the upper limit of the instrument) and therefore their resistance versus temperature behaviour was not measured. Since the density of the ZnO-Ln₂O₃ ceramics was quite high (>95% of theoretical), the probability of water adsorption was rather low. In spite of this the resistivity versus temperature dependence of the samples was measured immediately after sintering and samples were kept in an exicator. No degradation of the samples several months old was observed.

Microstructure of the ceramics was investigated by a scanning electron microscope Jeol JXA 840A and phase composition was semiquantitatively determined by EDS (energy dispersive spectroscopy) microanalysis.

3. Results and discussion

3.1 ZnO-MgO system

Resistivity versus the temperature dependence of the ZnO-MgO composite ceramics with different mol.% of ZnO is shown in Fig. 1. Ceramics with less than 45 mol.% exhibit room temperature resistance beyond the upper limit of the instrument, i.e. higher than $3 \times 10^9 \Omega$. The PTCR effect was observed in the case of the ceramics with 42-81 mol.% of ZnO. The maximum resistivity was observed at around 450°C.

Microstructures of the ZnO-MgO two phase ceramics exhibiting PTCR effect are shown in Fig. 2. Both phases in the composite samples were analysed by EDS microanalysis and were identified as (Mg_{1-y}Zn_y)O and a (Zn_{1-x}Mg_x)O solid solution. As already mentioned the ZnO-MgO system was studied due to its similarity with the ZnO-NiO system including the mutual solid solubility of phases. Rigamonti /21/ explained much lower solid solubility of MgO and /or NiO in ZnO than that of ZnO in MgO and/or NiO with respect to the crystal structure. ZnO and its solid solutions have a zincite crystal structure with a hexagonal unit cell, while MgO (and also NiO) and their solid solutions have a rocksalt crystal structure with a cubic unit cell. In general, solubility of cubic

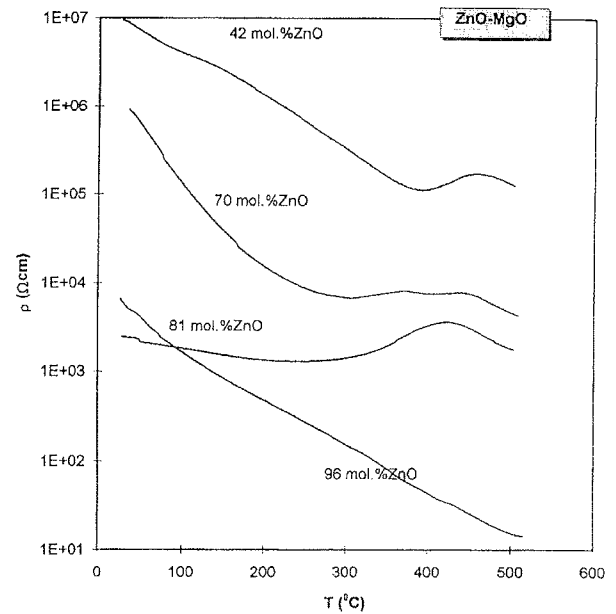


Fig. 1: Resistivity versus temperature behaviour of the ZnO-MgO composite ceramics with different composition.

oxides, with a smaller cation than Zn²⁺, in a ZnO lattice is much smaller than vice versa because a hexagonal cell is less flexible than a cubic one. Thus, it was assumed that the (Zn_{1-x}Mg_x)O lattice with the zincite structure has a smaller linear thermal expansion coefficient than that of the (Mg_{1-y}Zn_y)O phase with the rocksalt structure and this is associated with the difference in the crystal structure. A similar phenomenon was reported for the ZnO-NiO system /14/.

Fig. 2a shows the microstructure of the ceramics with 42 mol.% of ZnO. As can be seen the (Mg_{1-y}Zn_y)O phase predominates in the microstructure, while in the ceramics with 70 mol.% of ZnO, (Fig. 2b), the (Zn_{1-x}Mg_x)O phase predominates. From Fig. 1 where the R(T) dependence for various composite samples is shown one can see that the resistivity of the samples decreases with the overall percentage of ZnO in samples. According to the phase equilibria of the system ZnO-MgO and microstructural observation of the samples considered one can assign the lower resistivity of the samples to the higher content of ZnO and/or consequently to a higher amount of low ohmic phase (Zn(1-x)Mg_x)O in the samples.

It is well known that MgO exhibits a much higher resistivity than ZnO ($>10^{15} \Omega\text{cm}$ and 1-20 Ωcm at 20°C, respectively /15/). Therefore resistivity should decrease with an increasing amount of ZnO. A slightly higher resistivity of the ceramics containing 96 mol.% of ZnO than that of the ceramics with 81 mol.% of ZnO could be attributed to their density. The density of the ZnO-MgO ceramics is decreasing with the increasing amount of ZnO which can also be seen in Fig. 2 since the ceramic containing 70 mol.% of ZnO is much more porous than the one containing 42 mol.% of ZnO.

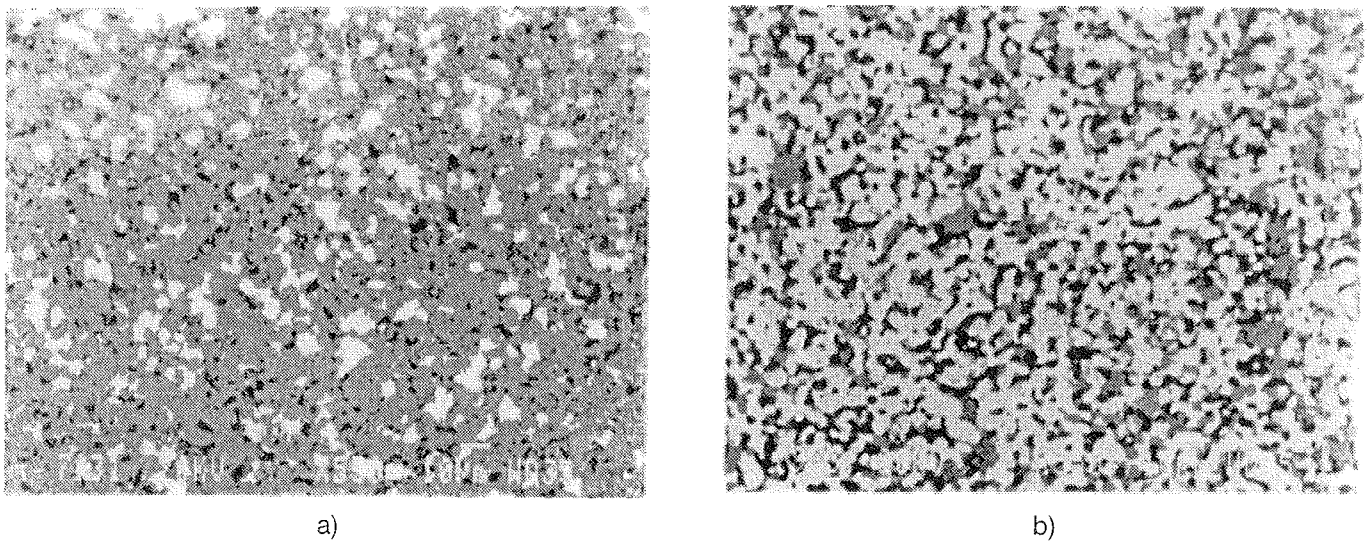


Fig. 2: SEM micrographs of the polished ZnO-MgO ceramics, sintered at 1450°C for 2h containing: a) 42 mol.% of ZnO and b) 70 mol.% of ZnO. White and dark phases are the $(Zn_{1-x}Mg_x)O$ and $(Mg_{1-y}Zn_y)O$ solid solutions.

Further, on the basis of the $R(T)$ dependence and on the literature data as well as on the experimental results which show that both constituent phases exhibit different linear thermal coefficients of expansion, one might conclude that the origin of the observed PTCR effect could be explained in terms of the disconnection of the low resistivity network composed of $(Zn_{1-x}Mg_x)O$ phase due to the larger linear thermal expansion of the high resistivity phase $(Mg_{1-y}Zn_y)O$.

Thus, on the basis of the present investigation one can conclude that the ZnO-MgO ceramic composite composed of two constituent phases $(Zn_{1-x}Mg_x)O$ and $(Mg_{1-y}Zn_y)O$ exhibits a noticeable PTCR effect for the same reason as that identified in the ZnO-NiO system /13/.

3.2. ZnO-Ln₂O₃ (Ln = Nd, Sm) system

In Fig. 3a the resistivity versus temperature behaviour of the ZnO-Nd₂O₃ ceramics with different composition is shown. The resistivity of the ZnO-Nd₂O₃ ceramic with 20 wt.% of ZnO was beyond the upper limit of the instrument, therefore its resistivity versus temperature behaviour was not measured. However the composite samples with 40-80 wt.% of ZnO exhibited the PTCR effect with a maximum resistivity at around 400°C.

In Fig. 3b the resistivity versus temperature behaviour of the ZnO-Sm₂O₃ ceramics with different compositions is shown. The PTCR effect in these ceramics was in general smaller than that found in ceramics prepared from the ZnO-Nd₂O₃ system. The highest PTCR effect was found in the composite samples with 55 wt.% of ZnO. In general, a higher PTCR effect was observed in

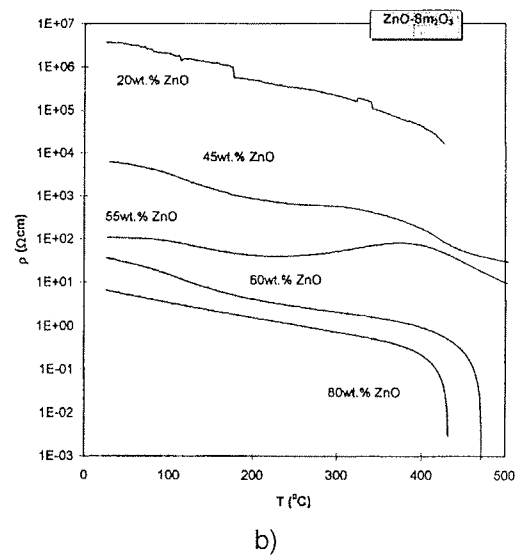
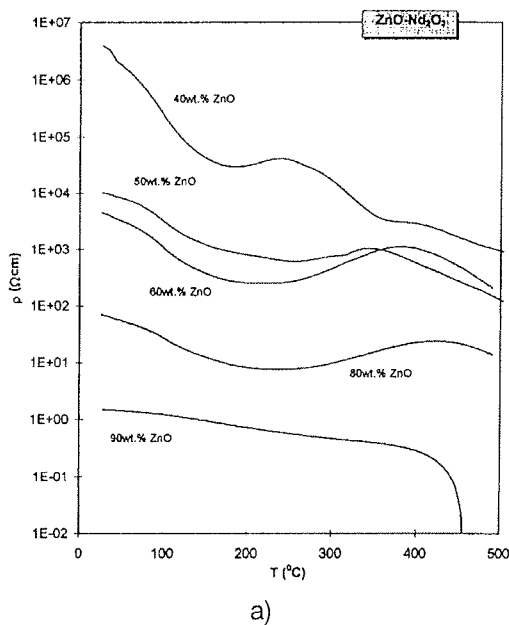


Fig. 3: Resistivity versus temperature behaviour of the a) ZnO-Nd₂O₃ and b) ZnO-Sm₂O₃ composite ceramics with different compositions

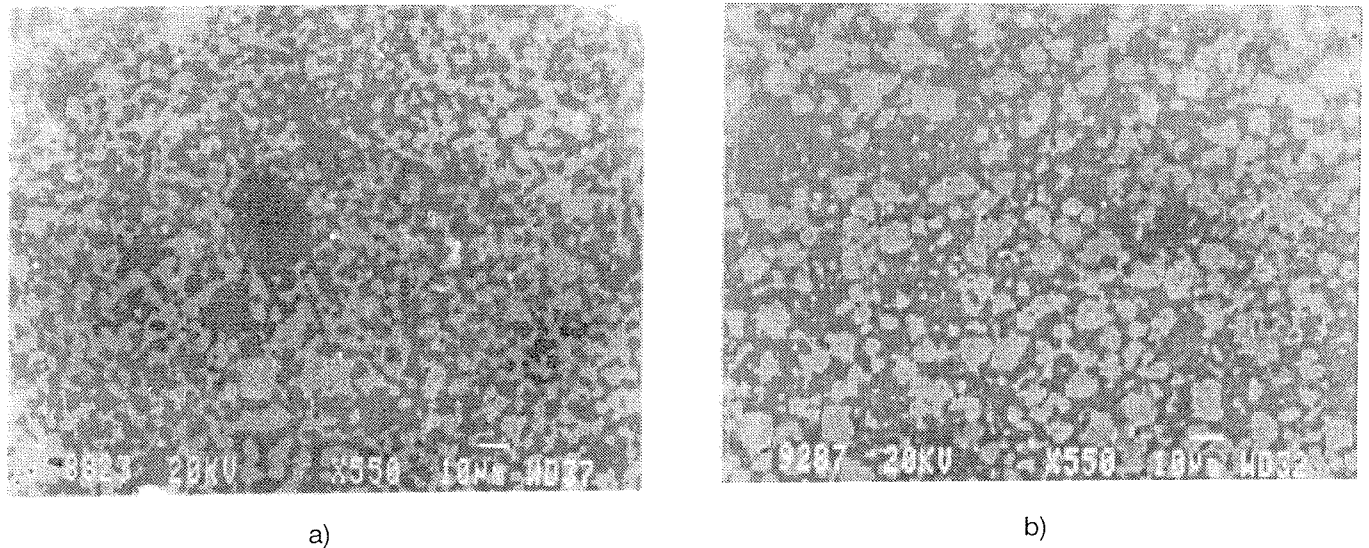


Fig. 4: SEM micrographs of the polished composite ceramics, sintered at 1350°C for 24h: a) ZnO-Ln₂O₃ containing 50 wt.% of ZnO and b) ZnO-Sm₂O₃ containing 55 wt.% of ZnO. Dark phase is ZnO and the white phase is Nd₂O₃-rich phase (a) or Sm₂O₃-rich phase (b).

samples prepared from the composites with the composition within the ZnO-Nd₂O₃ system than those prepared from the ZnO-Sm₂O₃ ceramics. One of the reasons for this could be a larger resistivity difference between the constituent phases in the ZnO-Nd₂O₃ than that of the ZnO-Sm₂O₃ ceramics which is indicated by a more significant influence of the composition on the resistivity of the ZnO-Nd₂O₃ ceramics. We believe that a more important reason for this might be a bigger thermal mismatch between the constituent phases in the ZnO-Nd₂O₃ than in the ZnO-Sm₂O₃ ceramics, since Nd₂O₃ has a larger linear thermal expansion coefficient than Sm₂O₃ /15/.

A microstructure of the ZnO-Ln₂O₃ (Ln = Nd, Sm) ceramics exhibiting a PTCR effect is shown in Fig. 4. It can be seen that the ceramics consists of two phases. As was determined by EDS microanalysis, the first phase could be pure ZnO, while in the other phase some solid solubility of ZnO in Ln₂O₃ was detected, i.e. 7-13 mol.% of ZnO in Nd₂O₃ and 8-16 mol.% of ZnO in the Sm₂O₃-rich phase. The work of Godzhieva and co-workers /19, 20/, did not report any solid solubility between ZnO and Ln₂O₃ (Ln = Nd, Sm).

When we compare the PTCR effect in the NiO-ZnO system⁽¹³⁾, which can serve as a model system, with the PTCR effect in these two types of composite, based on the systems ZnO-Ln₂O₃ considered here, one can notice that the PTCR effect in these systems is noticeably smaller than one would expect due to the difference in the linear thermal expansion coefficient of pure constituent phases, ZnO and Ln₂O₃ respectively. The linear thermal expansion coefficient of Nd₂O₃ and Sm₂O₃ is about three times larger than that of ZnO in the temperature range 20-500°C /15/. For approximately the same thermal mismatch a larger PTCR effect was observed in the ZnO-NiO system /13, 14/. We believe that the formation of solid solubility during heat treatment in the com-

posites studied here, decrease the difference in linear thermal expansion between both constituent phases due to the formation of the solid solution which is usually more rigid than that of the pure oxide.

On the other hand this partial solubility of ZnO in the rare earth oxide used and the formation of Nd₂O₃- and Sm₂O₃-rich constituent phases, does not significantly effect the resistivity difference, which is still large. As can be seen in Fig. 3, the resistivity increases significantly with a decreasing amount of ZnO indicating that Nd₂O₃- and Sm₂O₃-rich phases have much higher resistivities than ZnO.

Taking into account all of this, it could be concluded that the ZnO-Ln₂O₃ (Ln = Nd, Sm) composite ceramics, composed of low resistivity ZnO constituent phase and the high resistivity Ln₂O₃ phase exhibits a noticeable PTCR effect due to a difference in the linear thermal expansion coefficient between the constituent phases.

4. Conclusions

It was observed that ZnO-MgO and ZnO-Ln₂O₃ (Ln = Nd, Sm) composite ceramics exhibits three important features:

1. Two constituent phases,
2. A significant resistivity difference between the constituent phases and
3. A significant thermal mismatch between the constituent phases.

Thus, the origin of the PTCR effect in these ceramics could be explained using the proposed explanation in the ZnO-NiO composite ceramics⁽¹³⁾.

In general, the PTCR effect in all composite ceramics whose constituent phases exhibit a significant resistivity difference and thermal mismatch could be explained as

follows: The low resistivity network present in the ceramics at room temperature can be disconnected at elevated temperatures due to the larger linear thermal expansion of the high resistivity phase.

5. References

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