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The structure and PTCR effects of Mg-doped $ZnTiO_3$ ceramics

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Abstract

Zinc titanate doped with magnesium was produced by a conventional solid state reaction technique using metal oxides. The X-ray powder diffraction pattern showed a single phase of $ZnTiO_3$. The magnesium can replace the zinc ions and form a solid solution in the $ZnTiO_3$ phase, and the intensities of the $ZnTiO_3$ peaks decreased with increasing addition of Mg. The materials thus produced are semiconductors, with a positive temperature coefficient of resistivity. Increased addition of magnesium decreases the electrical resistivity. In addition, the sintered density and c/a ratio also rise with the increasing addition of Mg, while the open porosity decreases. Moreover, the Curie temperature (T_c) of the $(Zn_{1-x}Mg_x)TiO_3$ materials can be shifted to a higher temperature by increasing the Mg^{2+} concentration.

Keywords: C. Dielectric properties; C. Electrical properties; Ceramics; Oxides; X-ray diffraction

1. Introduction

Donor doped ABO_3 ceramics sintered in an oxidizing atmosphere exhibit an anomalous increase in electrical resistivity near the ferroelectric Curie temperature [1–5]. This behavior is referred to as the positive temperature coefficient of resistivity (PTCR) effect, and is a grain-boundary related phenomenon. Ceramics which exhibit specific PTCR properties are commonly employed in a wide range of applications, including temperature sensors, protection circuits, flowmeters, self-regulating heating elements, and degaussing components in color televisions sets. It has been reported that porous ABO_3 can be prepared by the incorporation of graphite, polyvinylalcohol (PVA), polyvinylbutyral (PVB), borides, silicides and carbides to the ceramics. Porous semiconducting ABO_3 ceramics have been reported to exhibit large PTCR effects. Oxygen can be adsorbed at the grain boundaries due to the presence of pores in the ceramics, which are better than ordinary dense ceramics for the formation of a surface acceptor state [6]. Porous thermistors show better heat resistance than dense ones, and thus can be used for overcurrent protectors in electric circuits [7].

Several theoretical models have been proposed to explain the anomalous increase in the resistivity of these materials [8–11]. The most widely accepted explanation for the PTCR phenomenon was originally proposed by Heywang [8]. The main idea of this model is based on the presence of grain boundary depletion layers consisting of two-dimensional surface acceptor states, e.g. adsorbed oxygen atoms or segregated acceptor ions that are present as impurities [10,11]. $ZnTiO_3$ is a perovskite type oxide structure that is a potential useful candidate for use in microwave resonator materials [12] and as a paint pigment [13]. Recent reports indicate that doped and undoped $ZnTiO_3$ have the V-type resistivity-temperature characteristics and possess the typical PTCR properties above the transition point [14,15], but to date there are few studies examining the PTCR of doped and undoped $ZnTiO_3$. In this paper, the authors attempt to synthesize $ZnTiO_3$ doped with different amounts of Mg, and the structure, physical properties, and relationships between the PTCR effect and porosity of the resulting $(Zn_{1-x}Mg_x)TiO_3$ were examined.

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2. Experimental procedures

2.1. The preparation of samples

$(Zn_{1-x}Mg_x)TiO_3$ samples with $x = 0$–0.1 were prepared by a conventional solid-state reaction method using ZnO, TiO_2 and MgO powders. The starting materials with a purity of 99.99% were supplied from Aldrich Chemical Company, Inc. and Acros Organics. The starting materials were mixed in ethanol by ball milling for 24 h with zirconia balls in polyethylene jars and dried at 120 °C. The mixed powders were calcined at 800 °C for 24 h to form the $ZnTiO_3$ phase and milled again for 24 h with zirconia balls in polyethylene jars. Three wt% of polyvinyl alcohol (PVA) solution was added as a binder to the ground powders thus obtained, and these were then dried at 120 °C, and pressed into discs 10 mm in diameter and 5 mm thick (using a pressure of about 5 MPa), with the weight of the discs fixed at 1.6 g. Cold isostatic pressing of about 200 MPa for 20 min in rubber bags was then applied to the discs, which were subsequently sintered at temperatures of 800–940 °C for 24 h in order to obtain the $ZnTiO_3$ phase. The $ZnTiO_3$ will decompose into α-Zn_2TiO_4 and rutile phases when the sintering temperature is above 945 °C.

2.2. Characterization

The samples were analyzed by X-ray diffractometry (XRD, Rigaku) using Cu-Kα radiation to identify the possible phases formed after heat-treatment. The surface morphology was examined by high resolution scanning electron microscopy (HR-SEM, S4200, Hitachi). Both sides of the specimens were finished to a mirror surface, and electrodes were attached to the surfaces using ohmic silver paste and gold wires. Temperature dependence of the dielectric constant was measured with an inductance–capacitance–resistance (LCR) meter (Hewlett-Packard, HP-4284A) at 1 kHz, and the electric resistivity was measured between 0 and 40 °C using a multimeter (Hewlett-Packard, HP-3457A) during the heating and cooling of the sample at 4 °C/min. The sintered density and open porosity was calculated using the Archimedes method given by the equation [16]:

$$Density = \frac{D}{W - B} \quad (1)$$

$$Open\ porosity = \frac{W - D}{W - B} \times 100\% \quad (2)$$

where B is the weight of the samples measured in water, D is the weight of the samples measured after drying at 100 °C for 24 h and W is the weight measured after removing the water from the surface of the samples.

3. Results and discussions

3.1. Phases in samples

Fig. 1 shows the XRD profiles of $ZnTiO_3$ pellets doped with (a) 0, (b) 1, (c) 3, (d) 5 and (e) 10 at% Mg sintered at 900 °C for 24 h in air. The figure indicates that the $(Zn_{1-x}Mg_x)TiO_3$ samples with $x = 0$–0.1 had a single phase of $ZnTiO_3$. Because both $ZnTiO_3$ and $MgTiO_3$ have hexagonal symmetry with a space group of R3, the smaller ionic radius of Mg^{2+} (0.66 Å) compared to that of Zn^{2+} (0.74 Å) readily induces the solid solution of (Zn,Mg)TiO_3. The intensities of the $ZnTiO_3$ peaks decreases with increasing Mg content. The results of our earlier study [15] also indicated that the intensities of $(Zn_{1-x}Mg_x)TiO_3$ decreased with increasing Mg content. When ions smaller than the Zn^{2+} ones are added to $ZnTiO_3$, the lattices of the $(Zn_{1-x}Mg_x)TiO_3$ crystals are slightly distorted [17], and this leads to a decrease in their intensities and traces of the second phase (α-Zn_2TiO_4 and rutile) forming at high concentrations of Mg. The lattice parameters were investigated to determine the effects of the substitution of zinc by magnesium on the crystal structure of $(Zn_{1-x}Mg_x)TiO_3$ solid solution. The lattice parameters of $ZnTiO_3$ doped with different amounts of Mg sintered at 900 °C are shown in Fig. 2. The unit cell volumes were calculated from the a- and c-axes parameters based on the hexagonal symmetry. The a-, c-axes and cell volume of the (Zn,Mg)TiO_3 unit cell decrease with increasing the amounts of Mg, and these results are similar to the those reported in Kim et al. [12].

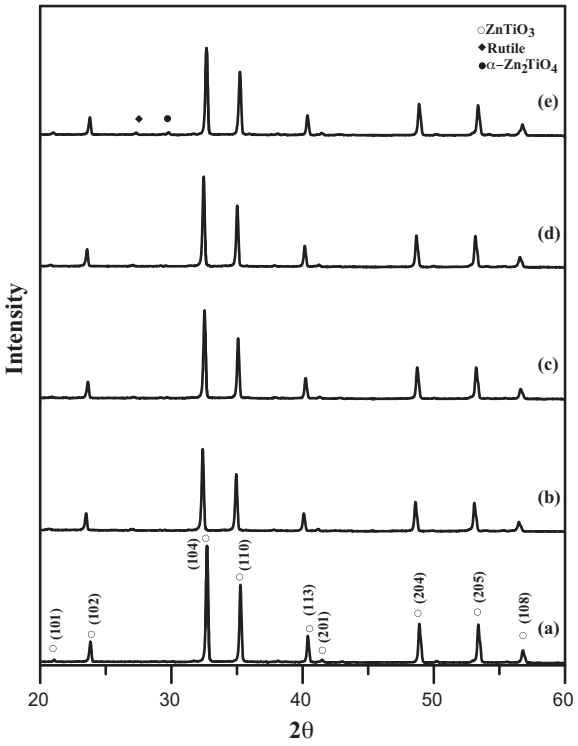


Fig. 1. XRD profiles of $ZnTiO_3$ pellet doped with (a) 0, (b) 1, (c) 3, (d) 5 and (e) 10 at% Mg sintered at 900 °C for 24 h in air.

3.2. Microstructures

Fig. 3 shows the SEM micrographs of $ZnTiO_3$ doped with (a) 1, (b) 3, (c) 5 and (c) 10 at% Mg sintered at 900 °C for 24 h in air. The sizes of the spherical particles (about 1 μm) seem to be uniform and open pores were formed. There are no differences in the surface morphology as the Mg content increases, and this

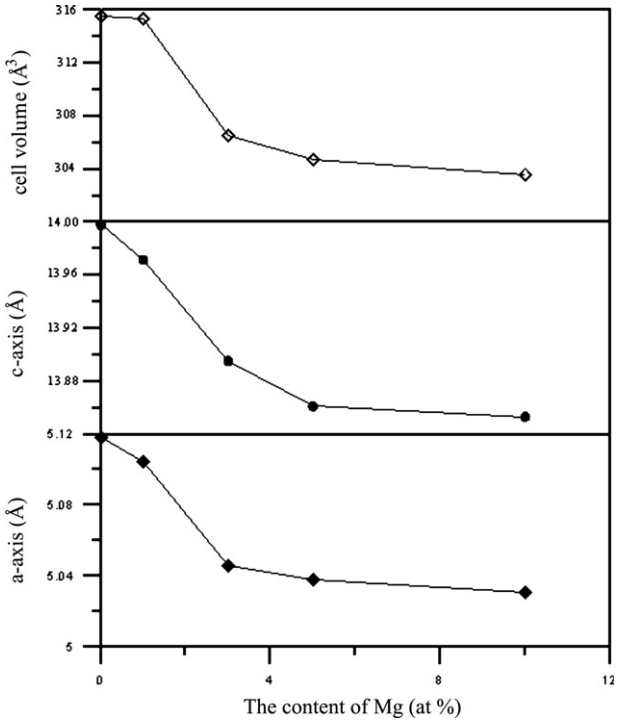


Fig. 2. The lattice parameters of the unit cell.

might be due to the formation of a solid solution. Fig. 4 shows the TEM bright field image for (a) $ZnTiO_3$, (b) $(Zn_{0.97}Mg_{0.03})TiO_3$ sintered at 900 °C for 24 h, and (c) EDS analysis of grain α in (b). The TEM image shows that the grain sizes decrease for the $ZnTiO_3$ doped with Mg ions, and they form a solid solution. It has been reported that porous ABO_3 can be prepared by the incorporation of polyvinylalcohol (PVA). Table 1 shows the parameters of the $(Zn_{1-x}Mg_x)TiO_3$ system sintered at 900 °C for 24 h in air. Table 1 indicates that the open porosity decreased (or density increased) with increasing Mg content, while the c/a value increased. A plausible reason for this is that during the substitution of Mg^{2+} the smaller Mg^{2+} ions make the unit cells smaller, and cause the atoms to be arranged more densely, thus decreasing the porosity. Furthermore, the shorter distances between the center ion and its nearest neighbors not only lead to a distortion of the octahedron, but also cause an increase in the c/a ratio [18].

3.3. The Curie temperature (T_c)

Fig. 4 shows the temperature dependence of the dielectric constant for $ZnTiO_3$ doped with different amounts Mg sintered at 900 °C in air. The Curie temperature (T_c) increased with the increasing Mg content, and had a maximum value of about 25 °C at the 10 at% Mg. As discussed earlier, the smaller Mg^{2+} ions make the unit cells smaller and the crystals more compact. A shorter distance between the center ion and its nearest neighbors causes a distortion of the octahedron and an increase in the c/a ratio, thus inducing a rise in the Curie temperature [18]. The region around the dielectric peak broadens with the increasing Mg content. This broadening of the transition has been attributed to the disorder [19] that affects various ion radii in the arrangement of the cations at the A-sites, leading to microscopic heterogeneities in the composition, and thus in the distribution of different local Curie points (Fig. 5).

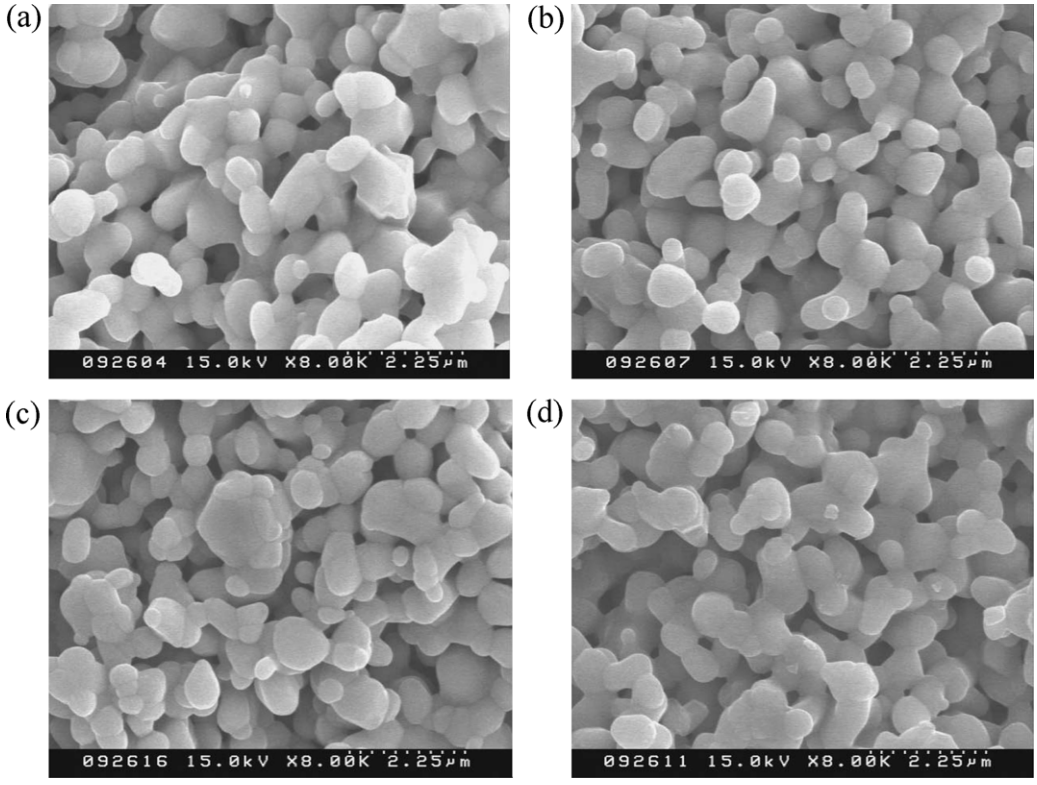
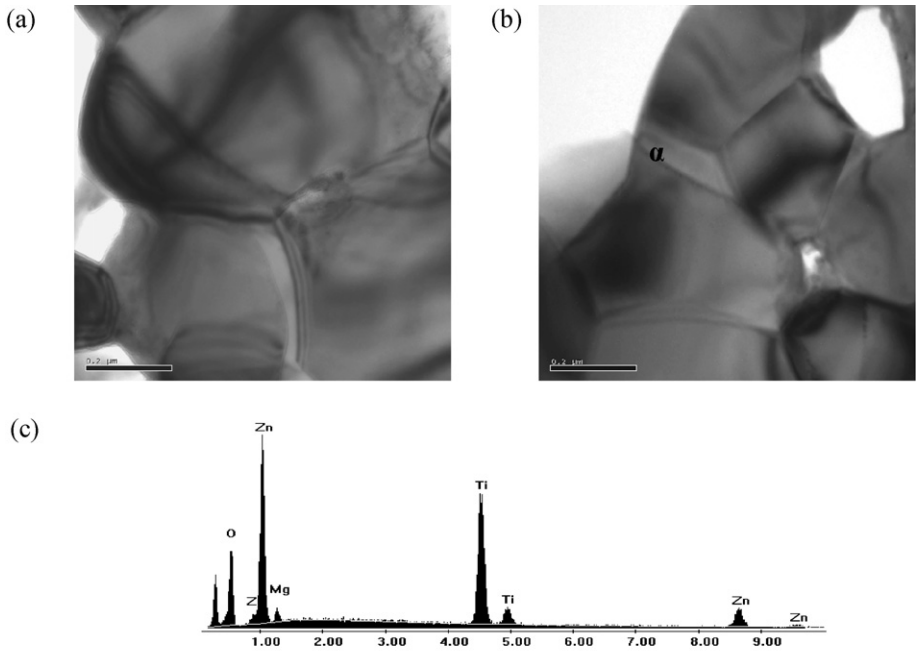


Fig. 3. SEM micrographs of $ZnTiO_3$ doped with (a) 1, (b) 3, (c) 5, and (d) 10 at% Mg sintered at 900 °C for 24 h in air.



Element	Wt. %	At. %	K-ratio	Z	A	F
O K	23.13	50.23	0.0505	1.1383	0.1917	1.0005
Mg K	2.04	2.91	0.0078	1.0863	0.3508	1.0003
Ti K	36.57	26.52	0.3482	0.9065	0.9844	1.0071
Zn K	38.26	20.33	0.3498	0.9200	0.9938	1.0000
Total	100.00	100.00				

Fig. 4. The TEM bright field image for (a) $ZnTiO_3$, (b) $(Zn_{0.97}Mg_{0.03})TiO_3$ sintered at 900 °C for 24 h, and (c) EDS analysis of grain α in (b).

3.4. PTCR effect

The results of earlier studies showed that some ABO_3 structure materials have a V-type resistivity-temperature characteristic [20,21], which is believed to be intrinsic to semiconducting structure ceramics with this structure. Fig. 6 shows the electrical resistivity as a function of temperature between 0 and 40 °C for $ZnTiO_3$ doped with different amounts of Mg sintered at 900 °C. It can be seen that the semiconductor behavior occurs in the low temperature region, and that the materials have the typical PTCR characteristics above the transition point. At high temperatures above the Curie point, T_c, and in absence of spontaneous polarization, the height of the potential barrier is controlled by the dielectric permittivity, which in turn depends on the temperature T. However, when T is lower than T_c, the potential barrier may be compensated by the charge arising from the spontaneous polarization, and this will render the whole material conductive [10]. According to the Heywang's model [8], a two-dimensional surface state with

Table 1
The parameters of the $(Zn_{1-x}Mg_x)TiO_3$ system.

Sample	Porosity (%)	Sintered density (g/cm^3)	T_c (°C)	c/a
$ZnTiO_3$	34.62	3.37	~5	2.7349
$(Zn_{0.99}Mg_{0.01})TiO_3$	33.31	3.49	~10	2.7369
$(Zn_{0.97}Mg_{0.03})TiO_3$	31.70	3.50	~12	2.7469
$(Zn_{0.95}Mg_{0.05})TiO_3$	30.50	3.53	~22	2.7501
$(Zn_{0.90}Mg_{0.10})TiO_3$	27.90	3.61	~25	2.7537

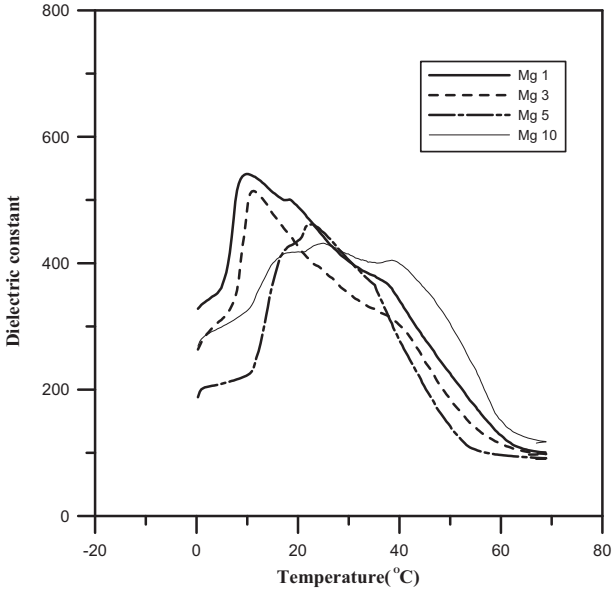


Fig. 5. Temperature dependence of dielectric constant for $(Zn_{1-x}Mg_x)TiO_3$ sintered at 900 °C for 24 h in air.

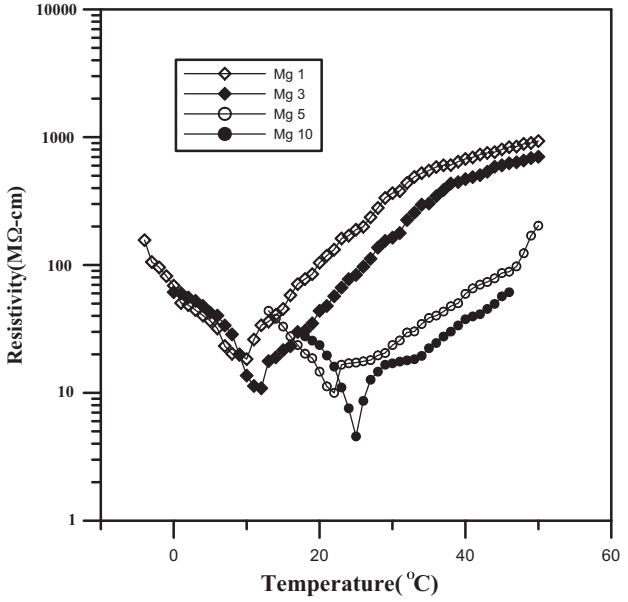


Fig. 6. Variation in electrical resistivity with temperature for $ZnTiO_3$ doped with different at% Mg sintered at 900 °C.

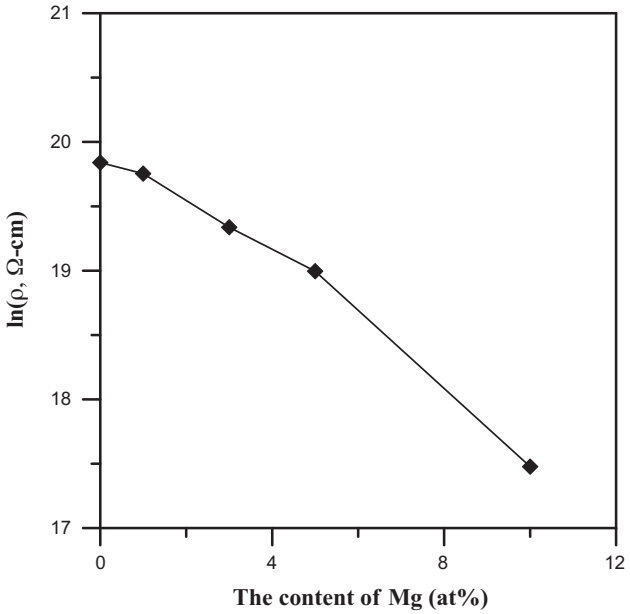


Fig. 7. The relationship between $\ln(\rho_{RT})$ versus the dopant concentration of Mg.

acceptor characteristics present at grain boundaries causes a built-in potential that reduces the probability of electrons passing through the grain boundaries. On the basis of this theory, the resistivity is controlled by the potential barrier height Φ, such that:

$$\rho(T) = \rho_0 \exp\left(\frac{e\Phi}{kT}\right) \tag{3}$$

where ρ_o is a constant, e the electronic charge, k the Boltzmann constant, T the temperature and Φ are given by:

$$\Phi = \left(\frac{eN_S^2}{\varepsilon_0 \varepsilon_L N_d}\right) \tag{4}$$

where N_s is the surface state acceptor density, ε_o the permittivity of free space, N_d the donor concentration and ε_L is the relative permittivity of the material within the barrier, and is described by the Curie–Weiss law as

$$\varepsilon_L = \frac{C}{T - T_C} \tag{5}$$

where C is the Curie constant. Substituting Eqs (4) and (5) into Eq (3) yields

$$\rho(T) = \rho_0^{'} \exp\left(\frac{-\alpha T_C}{T}\right) \tag{6}$$

where

$$\alpha = \frac{e^2 N_S^2}{\varepsilon_0 N_d k C} \tag{7}$$

and the pre-exponential factor ρ'_0 is given by

$$\rho_0' = \rho_0 \exp(\alpha) \tag{8}$$

Examining Eq. (5), it is found that above T_c, ε_L decreases sharply with temperature, as normally observed in ferroelectric materials. The resistivity $\rho(T)$ above T_c to increase sharply with T can be observed. The variation in the room temperature resistivity ρ_{RT} with the investigated donor concentration of Mg is shown in Fig. 7. The room temperature was set at 25 °C. The ρ_{RT} decreases as the dopant concentration rises, and this is because an increase in the donor N_d leads to a reduction in the potential barrier height Φ [22]. Therefore, the decrease in ρ_{RT} that can be seen in Fig. 7 may be due to a reduction in the potential barrier height as a result of increasing the donor concentrations.

4. Conclusions

Doped $ZnTiO_3$ with different amounts of Mg have been synthesized successfully using a conventional solid state reaction. The materials form a solid solution, but the intensities of the $(Zn_{1-x}Mg_x)TiO_3$ peaks decrease as the Mg content increases, and this is because the lattice of the $(Zn_{1-x}Mg_x)TiO_3$ series is slightly distorted. The results of the investigations carried out in this work show that the materials have the typical PTCR characteristics above the transition point, which was observed when the temperature dependence of the dielectric constant was measured. The effects of the Mg content on the properties can be attributed to the change in the bulk porosity. With an increase in the Mg content, smaller ions relative to the Zn^{2+} ones lead to increases in the Curie temperature (T_c), density and c/a value. The decrease in electrical resistivity with increasing amounts of Mg is also attributed to the decrease in porosity.

Acknowledgments

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