

Influence of MnO_2 and Co_3O_4 dopants on dielectric properties of $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ ceramics

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Abstract

Dielectric properties of $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ ceramic doped with 0.05–1 mol% of MnO_2 or Co_3O_4 were investigated in a wide temperature range from -160 to 450 °C at frequencies 10 Hz–1 MHz. Besides the maxima corresponding to the ferroelectric–paraelectric transition, at higher temperatures other peaks in temperature dependencies of relative electrical permittivity and dissipation factor were observed, attributed to dielectric relaxation. The location and height of these peaks are strongly related to frequency and the dopant level. Both MnO_2 and Co_3O_4 addition caused a significant increase in the resistivity of PFW ceramic—from 10^6 Ω cm for undoped samples to 10^{11} Ω cm for those with 1 mol% of a dopant. The activation energies of relaxation calculated on the basis of dielectric measurements are very close to the conduction activation energies determined in similar temperature range.

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1. Introduction

Recently much attention has been paid to relaxor ferroelectrics with perovskite structure which show excellent dielectric, piezoelectric, electrostrictive and pyroelectric properties. In this family, lead iron tungstate $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ (PFW) has the lowest firing temperature—below 900 °C. This makes it an attractive material for some applications, e.g. thick film capacitors. An advantageous feature of this compound is also a relatively high tolerance factor (1.007)¹ causing that the obtainment of pure perovskite phase without formation of detrimental pyrochlore phases is not as difficult as in the case of some other relaxors. PFW has a disordered perovskite-type structure in which two kinds of ions are distributed randomly in octahedral positions. Diffuse phase transition of this compound takes place near -90 °C. The low Curie temperature of lead iron tungstate can be easily shifted upwards by addition

of lead titanate PbTiO_3 , with the transition temperature at 490 °C.²

Many publications have been devoted to $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$,^{2–21} although not so numerous as in the case of other relaxors. Poor resistivity and high dissipation factor are serious disadvantages of PFW ceramic. However, these parameters can be improved by introduction of some additives. The principal aim of this work was to investigate the influence of MnO_2 and Co_3O_4 dopants on dielectric properties of $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ ceramic.

2. Experimental

$\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ was synthesized by the two-step “columbite” method, developed by Swartz and ShROUT.^{22,23} Fe_2O_3 and WO_3 were weighted in stoichiometric proportions, ball milled in alcohol and calcined at 1000 °C for 4 h. Then the mixture of the reaction product Fe_2WO_6 with PbO and MnO_2 or Co_3O_4 was milled, dried and calcined at 800 °C for 4 h. Phase composition of the powders after the

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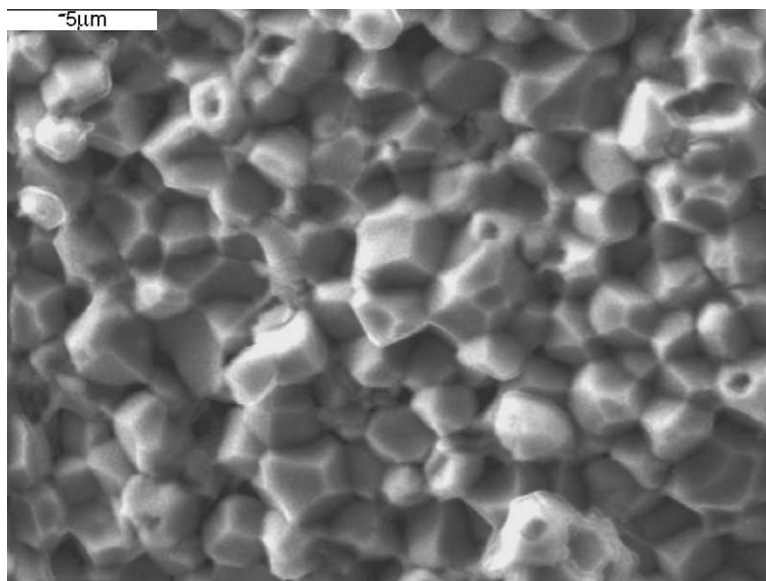


Fig. 1. SEM micrograph of PFW ceramic sintered at 870 °C.

synthesis was controlled by X-ray analysis using a Philips X'Pert diffractometer. $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ based powders were mixed with 3% water solution of polyvinyl alcohol, granulated, pressed into discs and sintered at 870 °C during 2 h in closed crucibles.

Microstructure and chemical composition of the obtained ceramics were examined using a Joel scanning electron microscope 5400 and a Link Isis X-ray microprobe 300.

Silver electrodes were deposited on both sides of the samples. Dc resistivity of the ceramics was measured in the temperature range 20–500 °C by means of a 6517A Keithley electrometer and a Philips resistance meter.

Capacitance and dissipation factor of the samples were determined during heating in the temperature range from –160 to 450 °C at frequencies 10 Hz–1 MHz by the use of a 7600B LCR QuadTech meter.

3. Results and discussion

The X-ray diffraction analysis has shown that as a result of the applied synthesis procedure the monophasic $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ was obtained. The PFW samples sintered at 870 °C are characterized by a dense fine-grained microstructure, illustrated in Fig. 1. The average grain size is 2–4 μm.

The studies by Vilarinho et al.² concerning the changes in resistivity caused by nitrogen annealing and the Hall effect³ have indicated that PFW ceramic exhibits p-type conductivity resulting from lead losses during the sintering process and formation of cation vacancies and electron holes, according to the equations:



where V_{Pb} , V'_{Pb} , and V''_{Pb} denote neutral, singly ionized and doubly ionized lead vacancies, respectively, and h^{\bullet} is the electron hole.

In the case of PFW one can also expect formation of defects related to a change in the degree of Fe oxidation. As a result of partial reduction of Fe^{3+} ions to Fe^{2+} , the creation of electron holes is supposed leading to increased p-type conductivity, exceeding that exhibited by other relaxors.

In this work it was found that the content of MnO_2 and Co_3O_4 dopants had a great influence on the resistivity of the $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ ceramic. Fig. 2 presents the relationship between the resistivity and the concentration of MnO_2 and Co_3O_4 in PFW. It can be seen that the resistivity increases violently in the range 0–0.5 mol% and then does not show any significant change up to 1 mol%. The val-

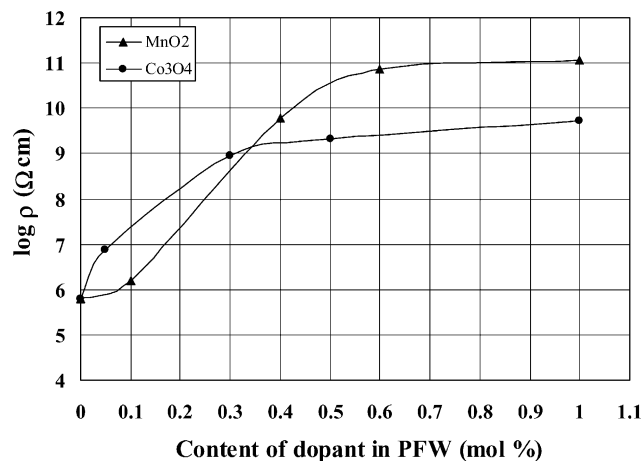


Fig. 2. Relationship between resistivity at 20 °C and content of MnO_2 and Co_3O_4 in PFW ceramics.

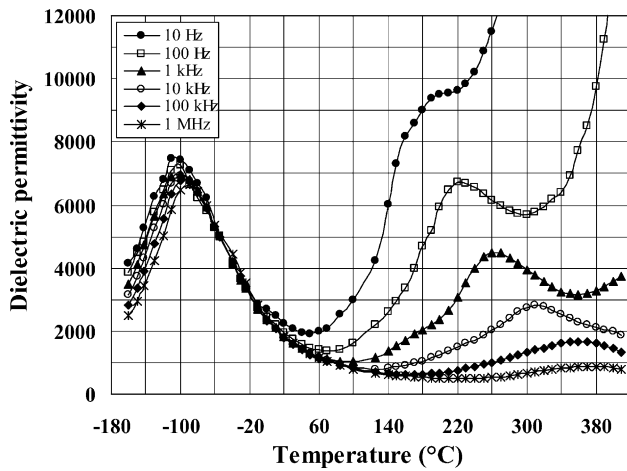


Fig. 3. Temperature dependence of dielectric permittivity for PFW ceramic with 1 mol% MnO₂.

ues of resistivity grow even 5 orders of magnitude—from 10⁶ Ω cm for the pure PFW to 10¹¹ Ω cm for the samples with 1 mol% MnO₂.

The observed great increase in resistivity of PFW ceramic after the introduction of MnO₂ or Co₃O₄ was probably the effect of simultaneous influence of two factors—the restricted tendency to reduction of iron ions and the formation of oxygen vacancies as a result of partial substitution of Pb²⁺ (or Fe³⁺) by Mn⁴⁺ or Co³⁺ ions.

The ionization of oxygen vacancies leads to the formation of free electrons according to equations:



where V_O, V_O[•], V_O^{••} are neutral, singly and doubly ionized oxygen vacancies, respectively, and e⁻ is the free electron. Recombination of electrons with holes results in the decrease of the dominant p-type conductivity.

The PFW ceramic exhibits relaxor-like behavior—a broad maximum in dielectric constant versus temperature plots and strong dependencies of permittivity and dissipation factor on frequency. In Fig. 3 the relative electrical permittivity for a

PFW sample with 1 mol% MnO₂ is presented as a function of temperature in the range from -160 to 420 °C at frequencies 10 Hz–1 MHz. The maximum ε_r value of about 7000, corresponding to the ferroelectric–paraelectric transition, was observed at -100 °C.

It was found that the dielectric constant peak related to this transition is not the only one at a given frequency in the examined temperature range. At higher temperatures another maximum of electrical permittivity was observed related to relaxation process. This peak is shifted towards higher temperatures with increasing frequency. Dielectric permittivity maximum decreases as frequency is raised and the temperature dependence of the frequency corresponding to a peak does not change exponentially. This behavior is illustrated in Fig. 3. Above the peak temperature the ε_r values start to increase rapidly due to electrical conduction. The rate of this increase diminishes with increasing frequency. The data gathered in Table 1 indicate that the second permittivity peaks for the investigated compositions and frequencies occur in the temperature range 20–400 °C.

The influence of the applied dopants on the location and the values of dielectric permittivity at the maximum corresponding to the ferroelectric–paraelectric transition was not discernible on the basis of the data obtained in this work. This is not consistent with the results reported by Miranda et al.⁴ who have revealed that Co doping of PFW at the level of 1–10 at.% caused a decrease in the dielectric permittivity maximum and shifted the transition temperature to higher temperatures. This discrepancy could arise from much lower dopant contents used in this work.

As presented in Table 1, the influence of the applied MnO₂ and Co₃O₄ dopants in the case of the second peaks related to dielectric relaxation. The changes in the courses of dielectric permittivity versus temperature plots at 1 kHz for various concentrations of dopants are shown in Fig. 4. It can be seen that the maximum value of ε_r decreases with the increasing content of both MnO₂ and Co₃O₄ and generally shifts slightly towards higher temperatures.

The presence of second peaks in the case of the dissipation factor versus temperature plots was observed in temperature range from -50 to 330 °C and only for the PFW

Table 1

Temperatures of the second maxima in permittivity and dissipation factor vs. temperature plots, determined at frequencies 10 Hz–1 MHz

| Composition | Temperature (°C) | | | | | | | | | | | |
|---|-----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | ε _r = f(t) | | | | | | tg δ = f(t) | | | | | |
| | Frequency (Hz) | | | | | | Frequency (Hz) | | | | | |
| | 10 | 10 ² | 10 ³ | 10 ⁴ | 10 ⁵ | 10 ⁶ | 10 | 10 ² | 10 ³ | 10 ⁴ | 10 ⁵ | 10 ⁶ |
| PFW | 20 | 90 | 140 | 210 | 230 | 240 | | | -40 | -10 | 30 | 90 |
| PFW with 0.05 mol% Co ₃ O ₄ | 40 | 100 | 160 | 240 | 280 | 280 | -30 | -10 | 20 | 40 | 80 | 150 |
| PFW with 0.5 mol% Co ₃ O ₄ | 150 | 190 | 240 | 300 | 350 | 370 | 60 | 90 | 130 | 180 | 240 | 330 |
| PFW with 1 mol% Co ₃ O ₄ | 170 | 230 | 260 | 290 | 340 | 360 | | | Lack of peaks | | | |
| PFW with 0.1 mol% MnO ₂ | 170 | 190 | 220 | 260 | 290 | 310 | | -50 | -30 | 0 | 40 | 100 |
| PFW with 0.4 mol% MnO ₂ | 180 | 210 | 240 | 260 | 320 | 320 | 40 | 60 | 90 | 125 | 180 | 240 |
| PFW with 0.6 mol% MnO ₂ | 200 | 230 | 280 | 320 | 360 | 400 | | | Lack of peaks | | | |
| PFW with 1 mol% MnO ₂ | 180 | 220 | 260 | 310 | 360 | 370 | | | Lack of peaks | | | |

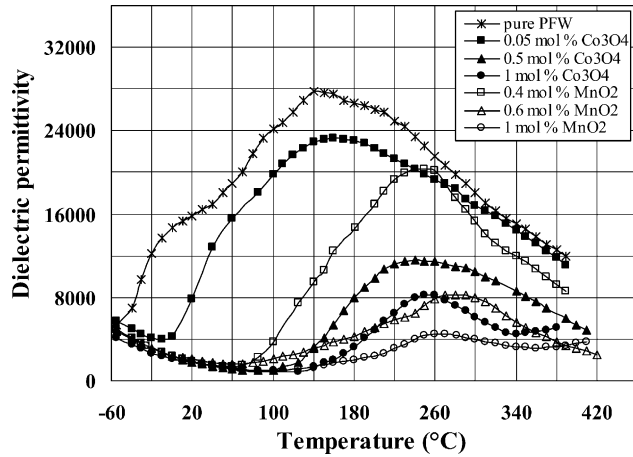


Fig. 4. Comparison of temperature dependencies of dielectric permittivity at 1 kHz for PFW ceramics with various contents of MnO_2 and Co_3O_4 dopants.

samples with a small addition of dopants (0–0.4 mol% MnO_2 and 0–0.5 mol% Co_3O_4). These samples are characterized by lower resistivity (10^6 to $10^9 \Omega \text{ cm}$). The temperatures at which the second maxima in $\text{tg } \delta = f(t)$ plots occur are listed in Table 1 for frequencies between 10 Hz and 1 MHz. In Fig. 5 the temperature dependence of dissipation factor for a sample doped with 0.4 mol% MnO_2 is shown, illustrating the presence of a set of peaks. Dissipation factor maxima increase and are shifted towards higher temperatures with increasing frequency.

When the dopant content was raised to the level ensuring higher resistivity, the second $\text{tg } \delta$ peaks attributed to dielectric relaxation disappeared. In Table 1 it is shown that for the ceramics with 0.6 and 1 mol% of MnO_2 or 1 mol% of Co_3O_4 these maxima do not occur. This effect is depicted in Fig. 6 for a sample with 1 mol% MnO_2 . The only distinct dissipation factor peaks visible in this figure are those related to the ferroelectric–paraelectric transition at low temperatures. Such a behavior would indicate that the existence of the second $\text{tg } \delta$ maxima depends on the concentration of electron

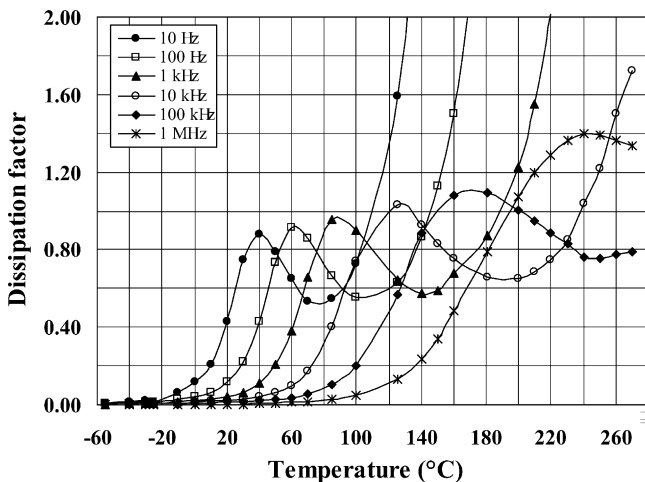


Fig. 5. Temperature dependence of dissipation factor for PFW ceramic with 0.4 mol% MnO_2 .

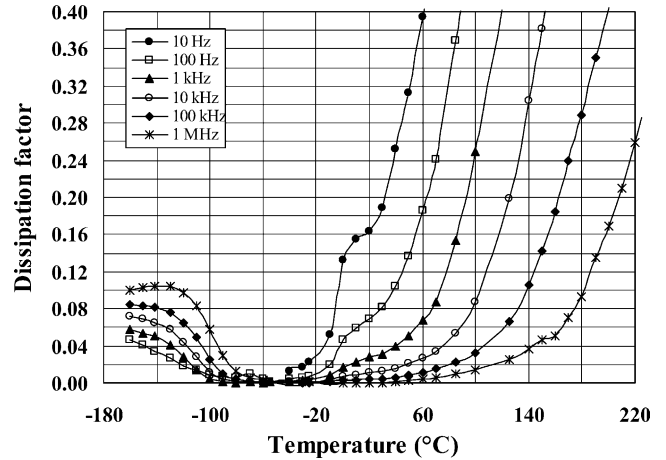


Fig. 6. Temperature dependence of dissipation factor for PFW ceramic with 1 mol% MnO_2 .

holes—a decrease in electron hole concentration resulting from Mn^{4+} or Co^{3+} doping entails vanishing of these peaks. As can be seen from Table 1, the location of dissipation factor maxima for a given frequency strongly depends on the dopant concentration, shifting towards higher temperatures with increasing content of MnO_2 or Co_3O_4 . For example, the $\text{tg } \delta$ peak at 1 kHz for 0.05% Co_3O_4 is situated at 20 °C and for 0.5% Co_3O_4 at 130 °C.

A maximum of dissipation factor occurs when the condition $2\pi f\tau = 1$ is fulfilled, where f is frequency and τ is the relaxation time. Since the relaxation time is known to decrease with increasing temperature, consequently the frequency of dissipation factor peak must increase.

In Fig. 7 the logarithm of relaxation time is plotted as a function of $1000/T$ for PFW ceramics with various contents of MnO_2 and Co_3O_4 dopants. The linear nature of these plots indicates that the relaxation time τ obeys well the Arrhenius law:

$$\tau = \tau_0 \exp \frac{E_\tau}{k_B T} \quad (5)$$

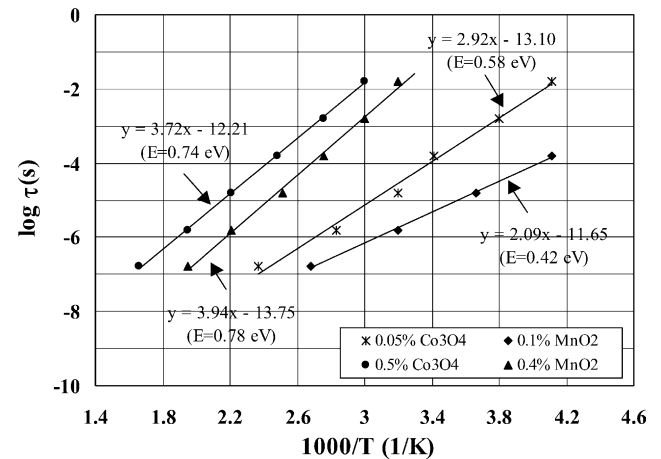


Fig. 7. Logarithm of relaxation time as a function of temperature for PFW ceramics doped with MnO_2 and Co_3O_4 .

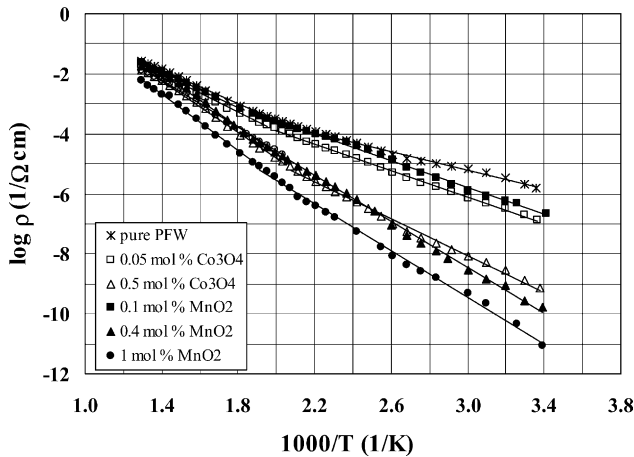


Fig. 8. Temperature dependence of electrical conductivity for PFW ceramics with various contents of MnO_2 and Co_3O_4 dopants.

where E_τ is the activation energy of dielectric relaxation; k_B —Boltzmann constant; T —temperature.

It was found that the activation energy of relaxation increases with increasing dopant concentration. The E_τ values were 0.42 eV and 0.78 eV for 0.1% and 0.4% of MnO_2 , and 0.58 eV and 0.74 eV for 0.05% and 0.5% of Co_3O_4 , respectively. The relaxation times at a given temperature increase significantly with increasing dopant level, as illustrated in Fig. 7. For example, at 60 °C the relaxation times change from 10^{-6} to 10^{-5} s for PFW with low dopant concentration (0.05–0.1 mol%) to 10^{-3} to 10^{-2} s for the samples containing 1 mol% of MnO_2 or Co_3O_4 .

The presence of a second set of permittivity and dissipation factor peaks was also observed by Vilarinho et al.² for $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ – PbTiO_3 solid solutions in the temperature range 77–327 °C. These authors have observed the disappearance of the second peak sets for the samples after annealing in nitrogen, which caused a significant increase in their resistivity. The same effect was obtained in this work as a result of PFW doping with MnO_2 and Co_3O_4 . The activation energies of relaxation reported by Vilarinho et al. (between 0.50 eV and 0.63 eV) are close to the values determined in this work.

In Fig. 8 the results of conductivity measurements carried out in the temperature range 20–500 °C, presented as $\log \sigma = f(1000/T)$, are compared for the pure PFW ceramic and the materials doped with MnO_2 or Co_3O_4 .

The temperature dependence of electrical conductivity σ for the examined samples fulfils well the Arrhenius relationship:

$$\sigma = \sigma_0 \exp \frac{E_\sigma}{k_B T} \quad (6)$$

where E_σ is the activation energy of electrical conduction; k_B —Boltzmann constant; T —temperature.

In Table 2 the resistivity values at 20 °C and activation energies calculated on the basis of Eq. (6) are listed. Two linear regions of Arrhenius plots characterized by different slopes were observed, indicating that some changes in conduction mechanism have taken place in the examined temperature range. As can be seen from Table 2 and Fig. 8 for all PFW based samples in the temperature range from 20 to 170–250 °C, the slopes of $\log \sigma = f(1/T)$ are lower, with the activation energies in the range 0.31–0.77 eV. At higher temperatures the slopes are steeper and the activation energies increase to 0.6–0.94 eV. The samples of pure PFW or those with only a small dopant addition (0.05–0.1 mol%) show the activation energies lower in the whole examined temperature range as compared with those for the ceramics containing 0.4–1 mol% of MnO_2 or Co_3O_4 . The steeper slopes of Arrhenius plots could be ascribed to the enhanced role of intrinsic conductivity at higher temperatures due to the increased concentration and mobility of thermally activated electrons and holes. At lower temperatures the conduction is supposed to be determined by processes not so strongly thermally activated, related to the presence of dopants, impurities, lattice defects.

MnO_2 was found to be more effective than Co_3O_4 as a dopant increasing resistivity for higher contents of these oxides in PFW (>0.4 mol%). From Table 2 it can be seen that for the ceramic with 1 mol% MnO_2 both the resistivity at 20 °C and the conduction activation energies are higher than these values for the samples doped with 1 mol% Co_3O_4 .

In Fig. 9 the Arrhenius plots for the relaxation time and the dc electrical conductivity determined in the similar temperature range are compared for a PFW sample containing 0.4 mol% MnO_2 and that with 0.5 mol% Co_3O_4 . It could be stated that the slopes of both plots and consequently the relevant activation energies are quite similar (0.78 eV and 0.78 eV for the ceramic with 0.4 mol% MnO_2 and 0.72 eV and 0.74 eV for the ceramic with 0.5 mol% Co_3O_4 , respectively). This

Table 2

Resistivities and activation energies of electrical conductivity for PFW ceramics with various MnO_2 and Co_3O_4 content

| Composition | Resistivity (at 20 °C) (Ω cm) | Activation energy of electrical conductivity (eV) |
|--|---------------------------------------|---|
| PFW | 6×10^5 | 0.31 (20–200 °C) 0.60 (200–500 °C) |
| PFW with 0.05 mol% Co_3O_4 | 7×10^6 | 0.44 (20–240 °C) 0.66 (240–500 °C) |
| PFW with 0.5 mol% Co_3O_4 | 2×10^9 | 0.59 (20–170 °C) 0.86 (180–500 °C) |
| PFW with 1 mol% Co_3O_4 | 5×10^9 | 0.54 (20–220 °C) 0.79 (220–500 °C) |
| PFW with 0.1 mol% MnO_2 | 4×10^6 | 0.45 (30–260 °C) 0.60 (260–460 °C) |
| PFW with 0.4 mol% MnO_2 | 6×10^9 | 0.76 (20–220 °C) 0.88 (220–500 °C) |
| PFW with 0.6 mol% MnO_2 | 7×10^{10} | 0.77 (20–210 °C) 0.94 (210–500 °C) |
| PFW with 1 mol% MnO_2 | 10^{11} | 0.77 (20–250 °C) 0.94 (250–500 °C) |

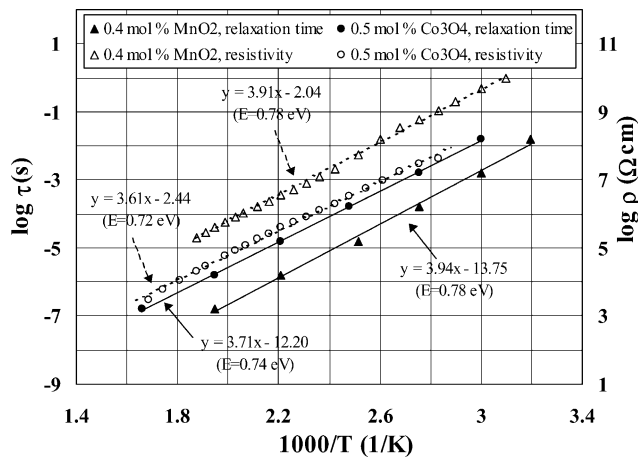


Fig. 9. Comparison of logarithms of relaxation time and electrical resistivity vs. temperature for PFW ceramics with 0.4 mol% MnO₂ and 0.5 mol% Co₃O₄.

would suggest that both the mechanisms of electrical conduction and dielectric relaxation are related to the concentration of the same charge carriers, i.e. electron holes.

4. Conclusions

The addition of small amounts of MnO₂ or Co₃O₄ (0.05–1 mol%) have resulted in a significant increase in the resistivity of Pb(Fe_{2/3}W_{1/3})O₃ ceramic, reaching 5 orders of magnitude for 1 mol% of a dopant.

The permittivity and dissipation factor peaks corresponding to the ferroelectric–paraelectric transition are not the only ones in the examined temperature range. At higher temperatures another maxima were observed attributed to relaxation process. Their location strongly depends on frequency and the dopant concentration. The increase in resistivity resulting from the appropriate level of doping with MnO₂ or Co₃O₄ causes vanishing of the second dissipation factor peaks.

The activation energies of the dielectric relaxation were found to be very close to those of the dc conduction. This suggests that the mechanisms of both processes can be related to the same charge carriers, i.e. holes.

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