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Dielectric properties of manganese and cobalt doped lead iron tantalate ceramics

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Abstract

This paper reports the results of synthesis and sintering studies as well as dielectric properties of $Pb(Fe_{1/2}Ta_{1/2})O_3$ (PFT) relaxor ferroelectric ceramics. Influence of doping with MnO_2 and Co_3O_4 (0.1–1 mol%) on resistivity and dielectric characteristics were investigated. The dielectric permittivity and dissipation factor of the ceramics were determined as a function of temperature in the range from −55 to 500 °C at frequencies 10 Hz to 1 MHz. DC resistivities of the samples were measured in the temperature range 20–500 °C. Two maxima in dielectric permittivity versus temperature curves were observed, dependent on frequency and the content of dopants. The investigated PFT ceramics were characterized by high dielectric permittivity of 3500–6700 at the transition temperature and 900–17,000 at the second maxima.

Keywords: Ceramics; Dielectric properties

1. Introduction

Interesting dielectric, piezoelectric, pyroelectric and optical properties of lead-based relaxor ferroelectrics of general formula $Pb(B'B'')O_3$ have attracted great attention during the last two decades. Advantageous features predestinating these materials for applications in capacitors are: high dielectric permittivity, broad maxima of dielectric characteristics, relatively low sintering temperature and low electrical field dependence of capacitance. Although there are many publications devoted to various relaxors, literature data concerning $Pb(Fe_{1/2}Ta_{1/2})O_3$ are not numerous.[1–11]

Lead iron tantalate has a disordered perovskite-type structure and exhibits the diffuse paraelectric–ferroelectric transition at about −30 °C. PFT belongs to a group of relaxors difficult to synthesize. However, relatively low sintering temperature (about 1050 °C), high dielectric permittivity and high resistivity make PFT a promising material for capacitor dielectrics.

In this work the conditions of synthesis and sintering of $Pb(Fe_{1/2}Ta_{1/2})O_3$—undoped and doped with MnO_2 and Co_3O_4 were studied and dielectric properties of the ceramics were investigated as a function of temperature, frequency and the content of dopants. The addition of the dopants was supposed to improve resistivity and suppress dissipation factor of PFT ceramics.

2. Experimental procedure

Two-step “wolframite” method developed for relaxors by Swartz et al.[12] was used to synthesize $Pb(Fe_{1/2}Ta_{1/2})O_3$. First, Fe_2O_3 was mixed with Ta_2O_5, ball-milled in alcohol, dried, pelletized and calcined at 1000 °C for 4 h. The reaction product $FeTaO_4$ was mixed with PbO and MnO_2 (0.1, 0.3, 0.6, 0.8 and 1 mol%) or Co_3O_4 (0.2, 0.5, 1 mol%) and then calcined at 850 °C for 4 h. Such a synthesis procedure enhances the efficiency of the formation of the desired perovskite phase $Pb(Fe_{1/2}Ta_{1/2})O_3$ and confines the creation of detrimental pyrochlore-type phases. Starting materials were weighed in stoichiometric proportions, no PbO excess was introduced. Small amounts of the dopants were added over stoichiometry.

The synthesized PFT-based powders were ball-milled, mixed with 3% water solution of polyvinyl alcohol, granulated, pressed into discs and sintered in the temperature range 900–1100 °C for 2 h. The pellets were placed in closed alumina crucibles and covered with $PbZrO_3$ powder enriched with PbO in order to restrict lead oxide evaporation.

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Phase compositions of the synthesized powders and the sintered samples were studied by means of a Philips X'Pert diffractometer.

Resistivity of PFT ceramics was measured in the temperature range 20–500 °C using a 6517A Keithley electrometer and a Philips resistance meter. Dielectric permittivity and dissipation factor of the ceramic samples were determined during heating in the temperature range from −55 to 500 °C at frequencies from 10 Hz to 1 MHz using a LCR QuadTech meter.

A Jeol scanning electron microscope and a Link Isis X-ray microprobe were used for characterization of the microstructure and the distribution of elements in the obtained ceramics.

3. Results and discussion

The X-ray diffraction analysis has shown that PFT is the main phase formed as a result of the synthesis. Small amounts of another phase with the composition $Pb_{1.34}Ta_2O_{6.34}$, close to that of the regular pyrochlore $Pb_3Ta_4O_{13}$, were also detected. The quantity of this phase after sintering was lower than that after the calcination step. This indicates that the undesired pyrochlore phase had transformed into the perovskite one at higher reaction temperatures.

In this work firing at 1050 °C for 2 h was established as the optimal sintering condition. The samples fired at lower temperatures (900–1000 °C) were not sufficiently densified and those sintered at 1100 °C did not exhibit any noticeable improvement in dielectric properties.

The microstructure of the sintered PFT ceramics was dense and fine-grained. Fig. 1 illustrates the scanning electron micrograph of a fracture of a PFT sample, with average grain size of 0.5–2 μm. The rounded shapes of the grains suggest sintering in the presence of a liquid phase. Microprobe analysis indicated that the distribution of elements in the ceramics was uniform and no Pb-rich phases occurred at the grain boundaries.

The PFT-based ceramics exhibited broad maxima in dielectric permittivity versus temperature plots, as well as strong dependencies of permittivity and dissipation factor on frequency. In Figs. 2–6 the relative electrical permittivity (ε_r) for an undoped PFT and for PFT samples with 0.1 and 1 mol% MnO_2, 0.2 and 1 mol% Co_3O_4, are shown as a function of temperature at frequencies 10 Hz to 1 MHz. The first maximum of permittivity corresponding to the diffuse ferroelectric–paraelectric transi-

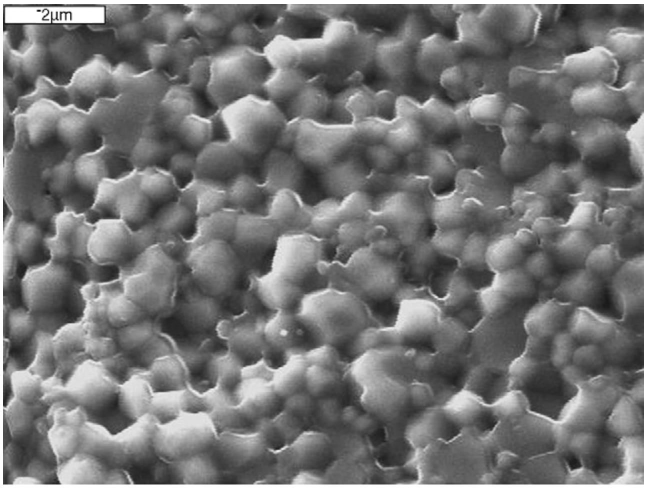

Fig. 1. SEM micrograph of the fracture of a PFT sample sintered at 1050 °C.

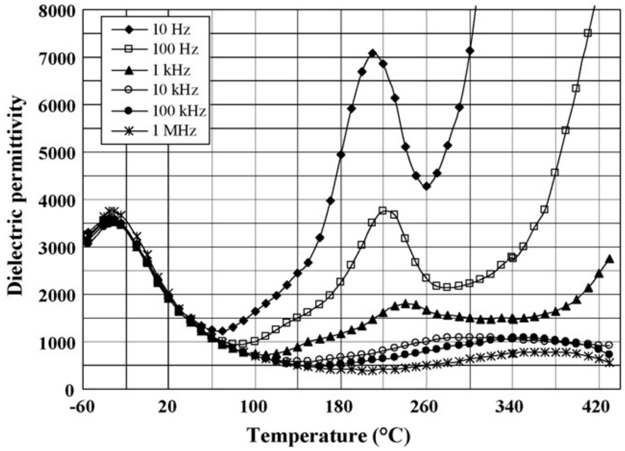

Fig. 2. Temperature dependence of dielectric permittivity for PFT ceramics without dopants.

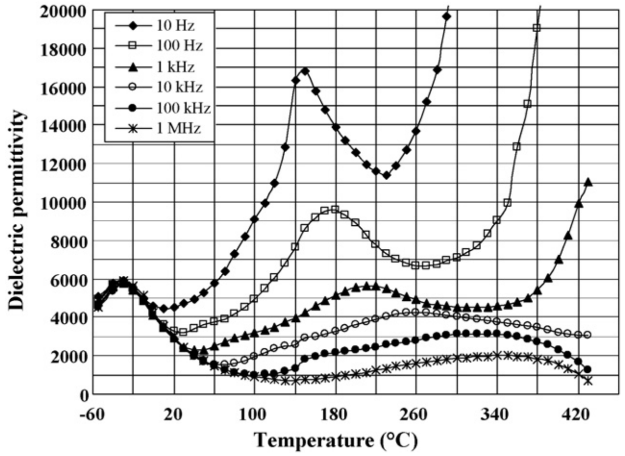

Fig. 3. Temperature dependence of dielectric permittivity for PFT ceramics with 0.1 mol% MnO_2.

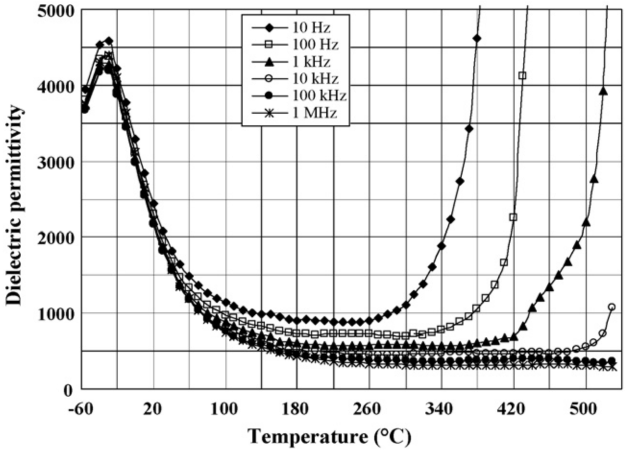

Fig. 4. Temperature dependence of dielectric permittivity for PFT ceramics with 1 mol% MnO_2.

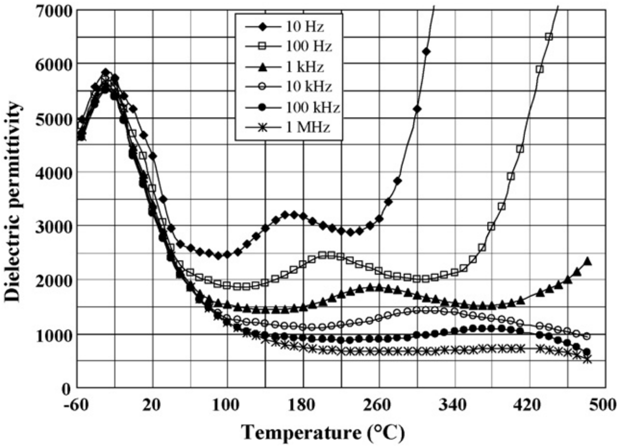

Fig. 5. Temperature dependence of dielectric permittivity for PFT ceramics with 0.2 mol% Co_3O_4.

tion was observed at about −30 °C. The maximum ε_r values were 3500–6700, depending on frequency and dopant content. This value is close to those determined by Uchino and Nomura[2] (4500 at 100 kHz) and lower than that reported by Nomura et al.[1] (9500) and Zhu et al.[11] (17,500 at 100 Hz). The latter authors have suggested that the obtained high permittivity values were related to the applied calcination procedure which had led to a disordered state for the B-site cations.

The dielectric permittivity maximum attributed to the ferroelectric–paraelectric transition was not the only one at a given frequency in the examined temperature range. As illustrated in Figs. 2–6, at higher temperatures (in the range 150–470 °C) a second set of peaks in $\varepsilon_r = f(T)$ plots was present, related to the relaxation process. These peaks were shifted towards higher temperatures with increasing frequency. The maximum permittivity values decreased as frequency was raised. Above the peak temperature a monotonous increase in the ε_r values caused by electrical conduction was observed, rapid at low frequencies. Dielectric properties of the examined PFT ceramics sintered at 1050 °C are given in Table 1.

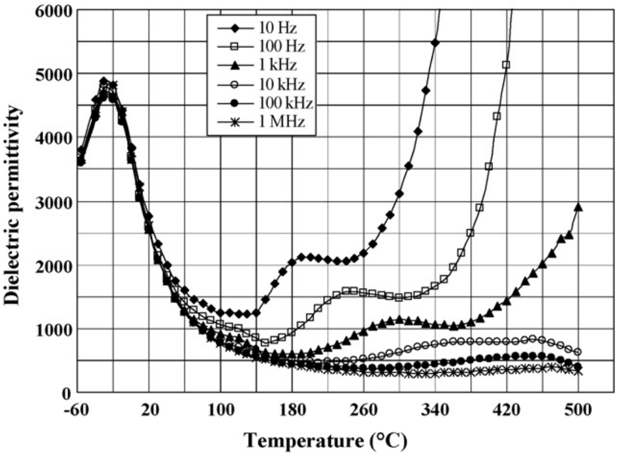

Fig. 6. Temperature dependence of dielectric permittivity for PFT ceramics with 1 mol% Co_3O_4.

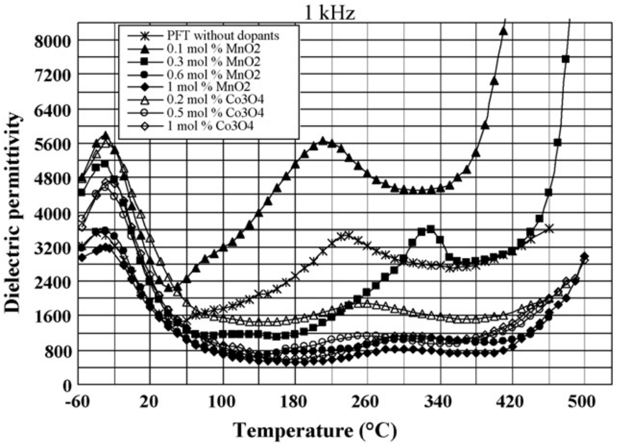

Fig. 7. Comparison of temperature dependencies of dielectric permittivity at 1 kHz for PFT ceramics with various contents of MnO_2 and Co_3O_4 dopants.

In Fig. 7 the plots of the dielectric permittivity at 1 kHz versus temperature are compared for various concentrations of dopants. The PFT doping with 0.1–1 mol% MnO_2 or 0.2–1 mol% Co_3O_4 did not influence significantly the temperature of the ferroelectric–paraelectric transition. Only a slight shift from −35 °C for undoped ceramics to −30 °C for doped ones, as well as a small broadening of peaks with increasing MnO_2 content were observed. Broadening of dielectric constant curves was also reported by other authors, e.g. for PZN-BT ceramics doped with 0.1–0.4% MnO_2,[13] PFW doped with 0.1–2 at.% Mn,[14] PFW doped with 1–5 at.% Co,[15] PFT doped with 0.3 mol% La_2O_3.[10]

The influence of the dopants was found to be distinct in the case of maximum values of first dielectric permittivity peak related to the ferroelectric phase transition. The highest values of ε_r were observed for the low doping level of 0.1–0.3 mol% MnO_2 and 0.2–0.5 mol% Co_3O_4 (Table 1, Figs. 3 and 5). The effect of Co_3O_4 doping on the enlargement of maximum dielectric permittivity values was more marked than that for MnO_2. It is supposed that incorporation of small amounts of additional manganese or cobalt ions in B-sites of the perovskite could enhance chemical microinhomogeneity of the relaxor, thus entailing an increase in ε_r values. An increase in maximum dielectric permittivity was also revealed by Zhu et al.[10] for lead iron tantalate ceramics slightly doped with 0.3 mol% La_2O_3. However, other authors have stated an opposite tendency—lowering of maximum dielectric permittivity for Mn and Co doped relaxor ceramics,[13–15] although this effect was either slight or observed for contents of additives higher (>1%) than those applied in this work.

It was found that the influence of dopant content was also significant for the position and the values of the second maxima in $\varepsilon_r = f(T)$ plots. Comparing Figs. 2 and 3 with Fig. 4 it can be seen that the peaks, although distinct for the undoped and slightly doped samples, became more flat for the ceramics doped with 1 mol% MnO_2. These differences were not so distinct in the case of doping with Co_3O_4. The increase in frequency caused for all compositions a shift of the second ε_r maxima towards higher temperatures and lowering of their values.

Table 1
Dielectric properties of PFT ceramics sintered at 1050 °C

Composition	Curie temperature (°C)	$\varepsilon_{\mathrm{r\,max}}$ at the transition temperature (10 Hz to 1 MHz)	Temperature of the second ε_{r} peaks (10 Hz to 1 MHz) (°C)	$\varepsilon_{\mathrm{r\,max}}$ at the second peaks (10 Hz to 1 MHz)	tan δ at 20 °C (1 kHz)
PFT without dopants	−35	3500–3800	200–370	800–7100	0.013
PFT with 0.1 mol% MnO_2	−30	5700–5900	150–350	2000–16800	0.044
PFT with 0.3 mol% MnO_2	−30	5100–5200	270–460	660–4700	0.033
PFT with 0.6 mol% MnO_2	−30	3500–3700	230–460	570–1400	0.012
PFT with 1 mol% MnO_2	−30	4200–4600	220–460	320–900	0.012
PFT with 0.2 mol% Co_3O_4	−30	5500–5800	170–420	730–3200	0.04
PFT with 0.5 mol% Co_3O_4	−30	6300–6700	230–430	950–6400	0.007
PFT with 1 mol% Co_3O_4	−30	4600–4900	200–470	390–2100	0.007

It was found that up to 20 °C the tan δ values in the frequency range 100 Hz to 1 MHz were relatively low (up to 0.007–0.04). The highest dissipation factor values were observed for the samples with 0.1–0.3 mol% MnO_2 and 0.2 mol% Co_3O_4, the lowest for those with 0.5–1 mol% of dopants. In Fig. 8 the dissipation factor of PFT ceramics doped with 1 mol% MnO_2 at frequencies changing in the range 10 Hz to 1 MHz is plotted as a function of temperature. There occurred some humps in these curves, shifting towards higher temperatures and increasing their height with raising frequency. In the higher temperature range the dissipation factor of PFT ceramics rapidly increased due to electric conduction. The temperature at which a violent enhancement of tan δ took place increased with increasing dopant level. The influence of MnO_2 on depressing dissipation factor, especially at low frequencies, is correlated with the observed effect of resistivity reduction.

As depicted in Fig. 9, the logarithm of the reciprocal of frequency at the second maximum in dielectric permittivity, corresponding to relaxation time, is approximately a linear function of inverse temperature for the investigated ceramics. The activation energies determined on the basis of Arrhenius plots were about 1.1–1.6 eV. The highest values were observed for the undoped samples and those with 0.6–1 mol% MnO_2, the lowest for PFT ceramics doped with 1 mol% Co_3O_4. The lowest relaxation times (10^{-2} to 10^{-8} s in the temperature range 170–450 °C) were found for the PFT samples doped with 0.1 mol% MnO_2 and 0.2 mol% Co_3O_4, as well as for undoped ones. The ceramics with 0.5–1 mol% of dopants exhibited at a given temperature higher relaxation times in the range 10^{-6} to 10^{-2} s.

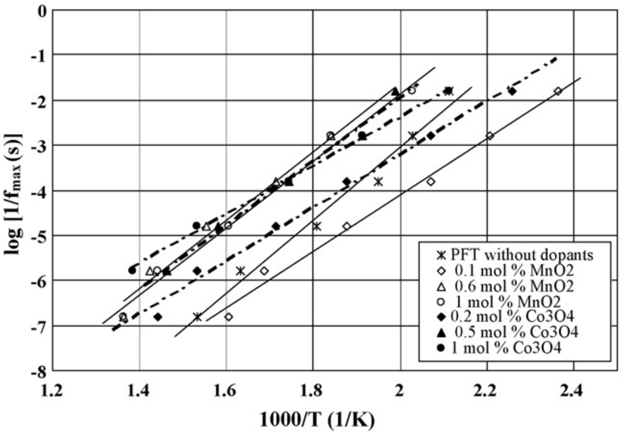

Fig. 9. Logarithm of dielectric relaxation time as a function of temperature for PFT ceramics.

In Table 2 the resistivities of PFT ceramics at room temperature are listed. All compositions showed relatively high resistivity of 10^9 to 10^{12} Ω cm. As follows from Fig. 10 and Table 2, doping with MnO_2 in the range 0.1–1 mol% and with Co_3O_4 in the range 0.2–0.5 mol% increases resistivity of pure PFT (2–20

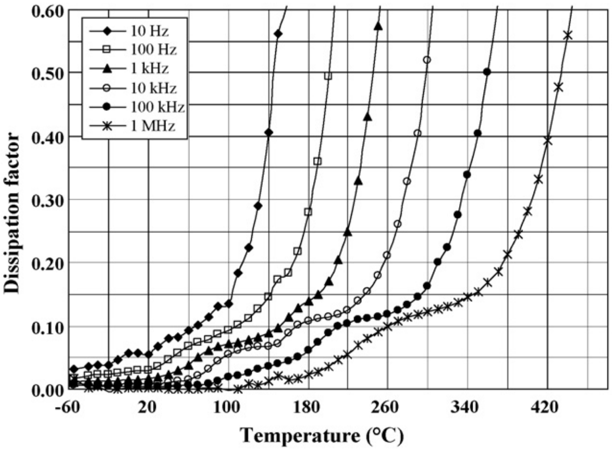

Fig. 8. Temperature dependence of dissipation factor for PFT ceramics with 1 mol% MnO_2.

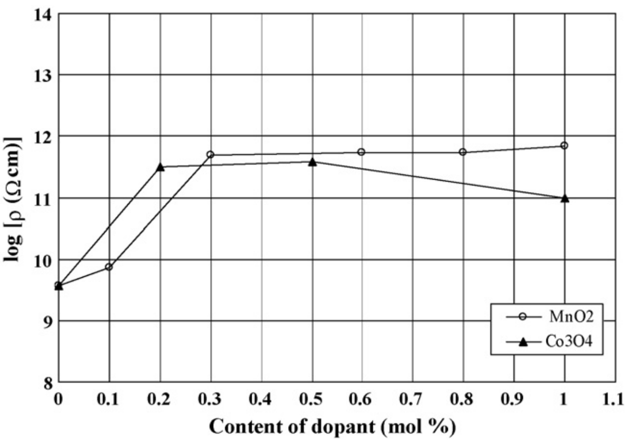

Fig. 10. Relationship between resistivity at 20 °C and content of MnO_2 and Co_3O_4 in PFT ceramics.

Table 2
Resistivities at 20 °C and activation energies of electrical conduction for PFT ceramics

Composition	Resistivity at 20 °C (Ω cm)	Activation energy (eV)
PFT without dopants	3.8×10^9	0.55 (20–100 °C), 0.74 (100–500 °C)
PFT with 0.1 mol% MnO_2	7.5×10^9	0.65 (20–90 °C), 0.76 (90–500 °C)
PFT with 0.3 mol% MnO_2	1.7×10^{11}	0.67 (20–100 °C), 0.95 (100–500 °C)
PFT with 0.6 mol% MnO_2	5.5×10^{11}	0.53 (20–130 °C), 1.01 (130–500 °C)
PFT with 1 mol% MnO_2	6.8×10^{11}	0.44 (20–140 °C), 0.96 (140–500 °C)
PFT with 0.2 mol% Co_3O_4	3.2×10^{11}	0.69 (20–100 °C), 0.90 (100–500 °C)
PFT with 0.5 mol% Co_3O_4	3.9×10^{11}	0.66 (20–120 °C), 0.90 (120–500 °C)
PFT with 1 mol% Co_3O_4	9.7×10^{10}	0.64 (20–170 °C), 0.88 (170–500 °C)

times). This increase is significant only up to 0.3 mol% MnO_2 and 0.2 mol% Co_3O_4. The PFT ceramics doped with 1 mol% Co_3O_4 exhibited slightly decreased resistivity in comparison with the sample containing 0.5 mol% of this dopant. The effect of doping on the increase of resistivity and the suppression of dissipation factor was more evident for manganese than for cobalt ions.

The MnO_2 and Co_3O_4 were introduced to PFT in small amounts (0.1–1 mol%), remaining below the solubility limits, according to the studies of other authors for similar compounds, like PFW, PZT.[14,16] Accordingly, the dopants were expected to enter the lattice substitutionally. The lack of second phases in doped PFT ceramics was confirmed by X-ray studies and microprobe analysis. Mn^{4+}, Co^{2+}, Co^{3+} as ions with smaller radii than Pb^{2+} (0.53, 0.65 and 0.55 Å, respectively) should favour B-sites in ABO_3 perovskite structure, although occupation of A-sites is not excluded.[16]

Tetravalent manganese ions are supposed to act as donors and contribute electrons to the conduction process. Recombination of electrons with holes leads to diminishing of the predominant p-type conduction in relaxor ceramics. However, the mechanism of resistivity increase is not clear for Co_3O_4. Cobalt cations may serve as an acceptor additive, compensating for the lead vacancies, formed during the sintering process. It ought to be stressed that manganese, cobalt and iron may be present in the lattice as ions with different valances and ionic radii (Mn^{2+}, Mn^{3+} and Mn^{4+}, Fe^{2+} and Fe^{3+}, Co^{2+} and Co^{3+}). Hopping of electrons between Fe, Mn and Co ions in different oxidation states is supposed to contribute to electrical conduction of the examined ceramics.

In Fig. 11 the results of conductivity measurements carried out in the temperature range 20–500 °C, are presented as $\log \sigma = f(1000/T)$ for PFT ceramics with various MnO_2 and Co_3O_4 dopant contents. The dependencies obeyed the Arrhenius law, although two sections of plots with different slopes can be distinguished, indicating that some changes in the conduction mechanism occur in the examined temperature range. As shown in Fig. 11 and Table 2, the slopes of Arrhenius plots were lower for all samples in the temperature range from 20 to 100–170 °C, with the activation energies changing from 0.44 to 0.69 eV. At higher temperatures the activation energies were higher—in the range 0.74–1.01 eV. This could result from the increased role of intrinsic conductivity at higher temperatures due to higher concentration and mobility of thermally activated electrons and holes. The conduction at lower temperatures is supposed to be determined by processes not so much activated thermally, related to the presence of dopants, impurities, lattice defects.

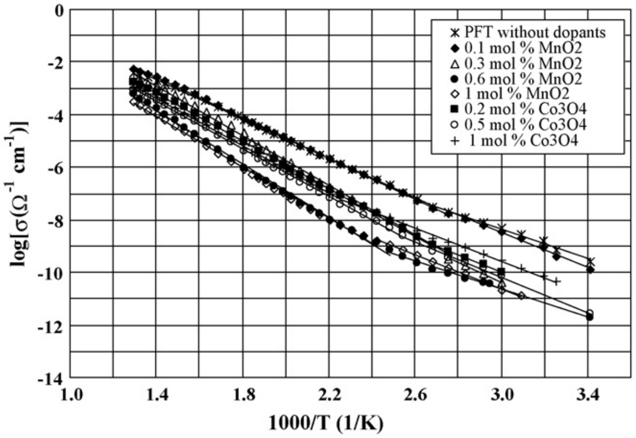

Fig. 11. Electrical conductivity as a function of temperature in the range 20–500 °C for PFT ceramics with various contents of MnO_2 and Co_3O_4 dopants.

As can be seen from Table 2, the PFT ceramics with MnO_2 showed smaller differences between activation energies in lower and higher temperature regions for undoped and slightly doped (0.1–0.3 mol%) samples as compared with those with 0.6–1 mol% of the additive. The slopes of Arrhenius plots for PFT doped with Co_3O_4 in both temperature regions were similar for all compositions.

4. Conclusions

The PFT relaxor ceramics sintered at 1050 °C showed relatively high dielectric permittivity (about 3500–6700 at transition temperature). Two sets of broad maxima were observed in dielectric permittivity versus temperature plots—the first one at about −30 °C, corresponding to the ferroelectric–paraelectric transition, and the second one in the temperature range 150–470 °C, related to dielectric relaxation, the latter being strongly dependent on frequency. The highest values of dielectric permittivity, both at transition temperature and at the temperature corresponding to a second peak, were observed for the low doping level of 0.1–0.3 mol% MnO_2 and 0.2–0.5 mol% Co_3O_4. Doping with 0.1–1 mol% MnO_2 and 0.2–0.5 mol% Co_3O_4 caused an increase in resistivity of undoped PFT ceramics. The most effective suppression of dissipation factor and increase in resistivity was found for 1 mol% MnO_2 content.

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