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THE ELECTRICAL CONDUCTIVITY OF PMN-PT CERAMICS

PRZEWODNICTWO ELEKTRYCZNE CERAMIKI PMN-PT

The results of investigations of d.c. and a.c. conductivity are presented for PMN-PT ceramics obtained by two step sol-gel method. A.c. conductivity has been calculated from dielectric measurements for frequencies 100Hz-20kHz. It has been stated that the activation energy calculated from d.c. conductivity is much higher than calculated from a.c. conductivity. The analysis based on Jonsher's power law is also presented.

Keywords: ceramics, electrical conductivity, PMN-PT, relaxor

W pracy przedstawiono wyniki badań przewodnictwa stałoprądowego i zmiennoprądowego dla ceramiki PMN-PT otrzymanej dwustopniową metodą zol-żel. Przewodnictwo zmienno prądowe było obliczane na podstawie pomiarów dielektrycznych w przedziale częstotliwości 100Hz-20kHz. Stwierdzono, że energia aktywacji obliczona z pomiarów przewodnictwa stałoprądowego jest znacznie wyższa, niż obliczona z przewodnictwa zmiennoprądowego. Przedstawiono również analizę w oparciu o uniwersalne prawo potęgowe Jonshera.

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is a well known relaxor material with T_m, temperature ~270K. Solid solutions with $PbTiO_3$ i.e. (1-x)PMN-xPT exhibit higher T_m temperatures at the range from ~270K for x=0 up to ~500K for x=0.5. At the same time with increasing x the transition from the relaxor to the normal ferroelectrical properties takes place. Usually compositions near to 0.9PMN-0.1PT are considered as a boundary between relaxor and normal ferroelectrical properties at the room temperature.

In this paper we present the results of investigations of d.c. and a.c. electrical conductivity v.s. temperature.

2. Samples and experiment

Investigated by us ceramic samples of (1-x)PMN-xPT with 0< x <0.37 have been obtained by two step coloumbite sol-gel technology (SG) similar to described in [1]. The dielectric and electromechanical properties of our PMN-PT samples were described earlier in [2].

3. Results

We investigated d.c. conductivity as a function of temperature by measuring current after constant voltage. The minimum value of applied voltage which allowed the measurements in wide temperatures range was 10^4V/m. This value was about 10 times higher than amplitude of a.c. field used to investigations of a.c. conductivity. The main investigations for d.c. conductivity was ln as a function of 1/T to obtain the plot presented schematically in Fig.1 based on equations for carriers concentration (1) and electric conductivity (2).

$$n = N_0 \cdot e^{-\frac{E_a}{kT}} \quad (1)$$

$$\sigma(T) = \sigma_\infty \cdot e^{-\frac{E_A}{kT}}. \quad (2)$$

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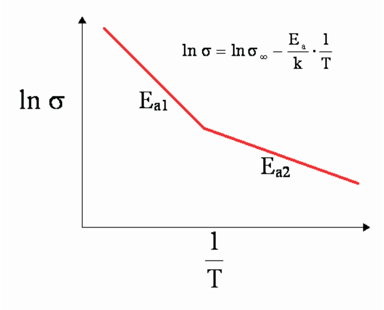
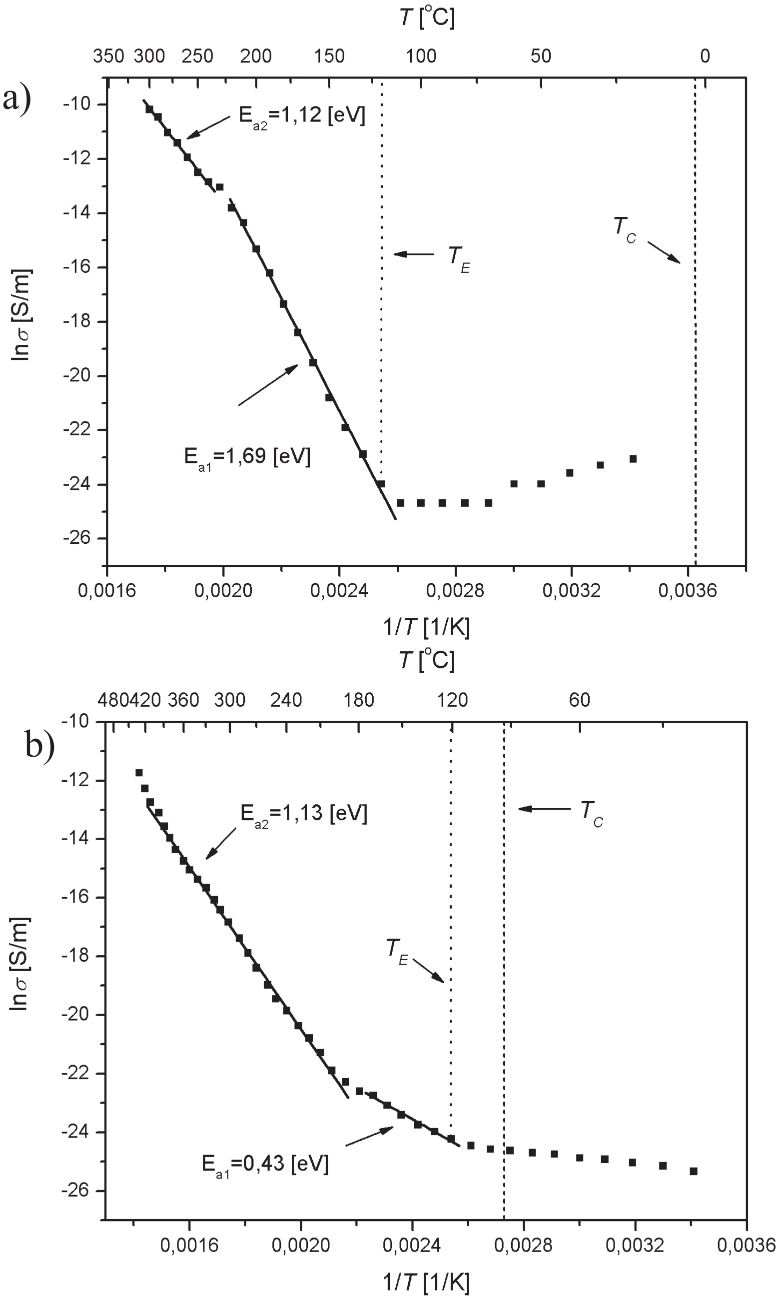


Fig. 1. Schematically presented Arrhenius plot for d.c. conductivity

The results obtained for investigated PMN-PT ceramics are presented in Fig.2.



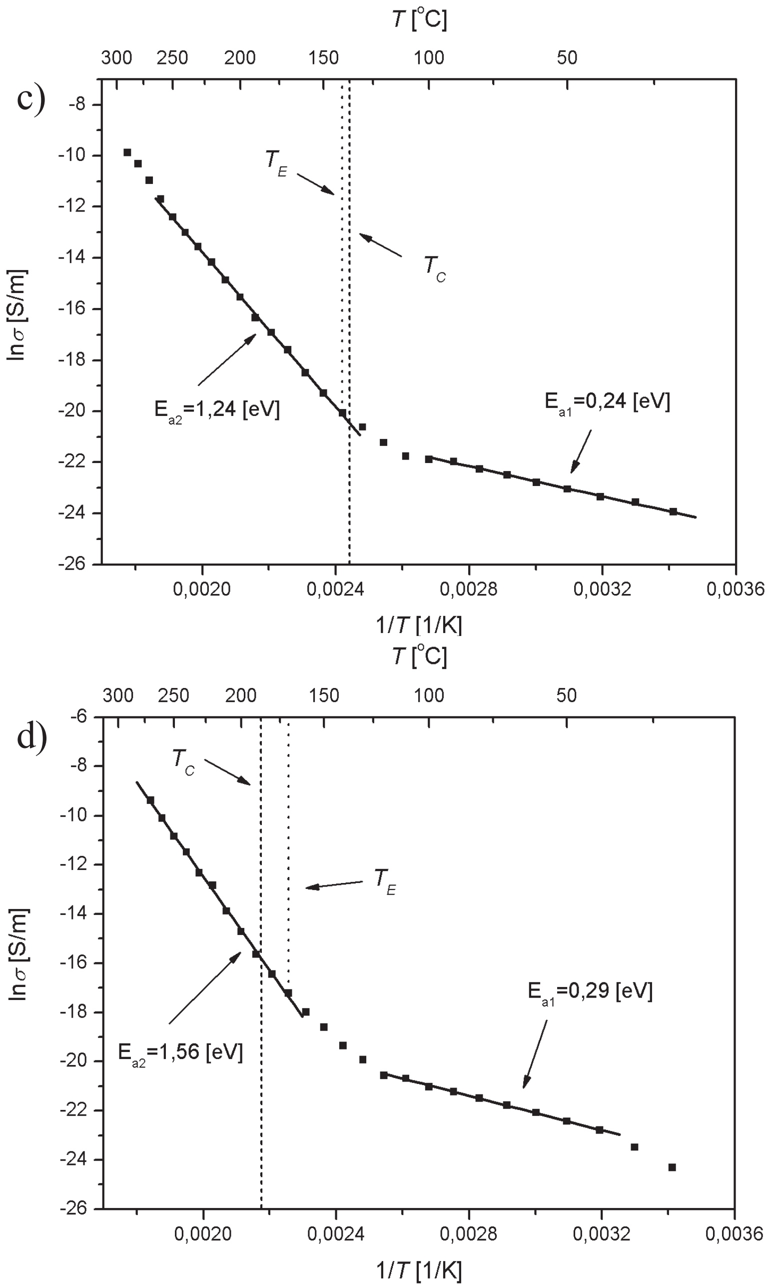
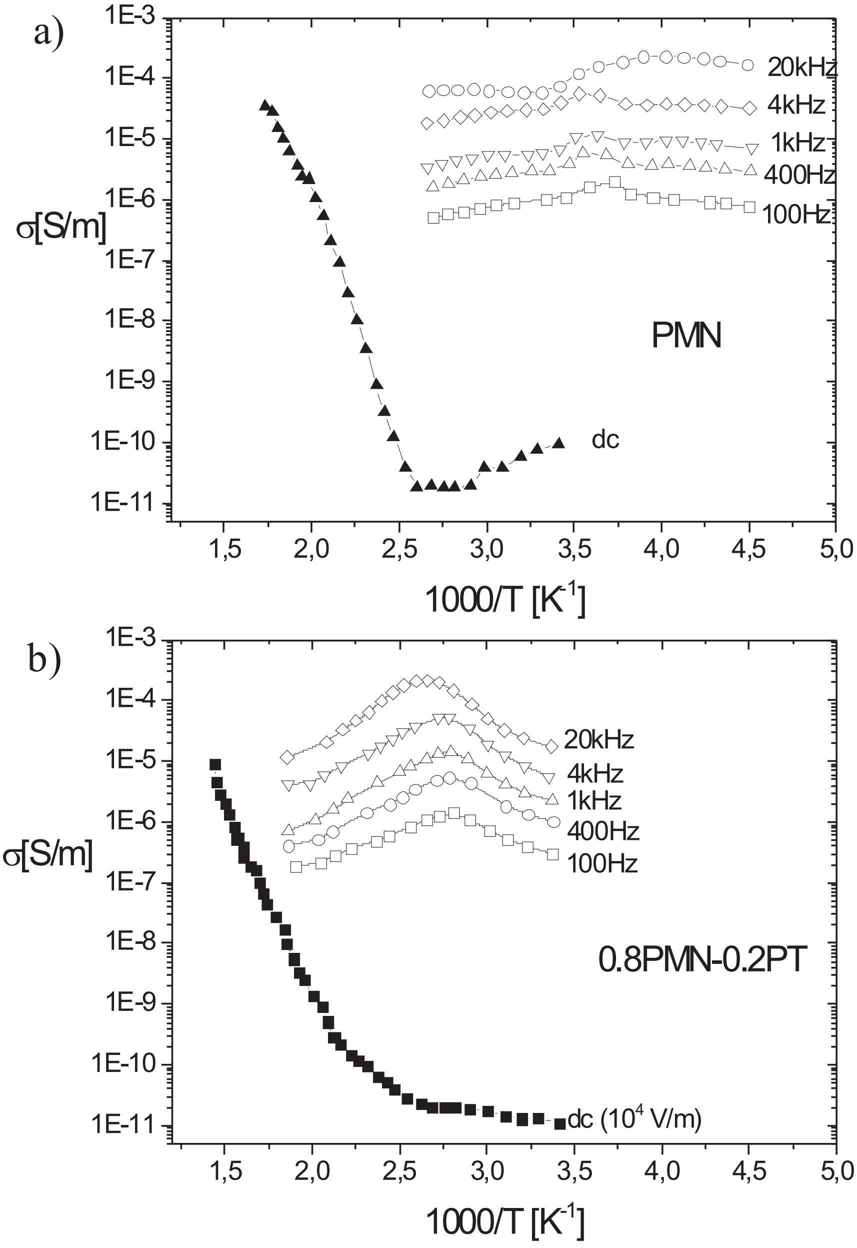


Fig. 2. Dependencies lnσ=f(1/T) for a – PMN; b – 0.8PMN-0.2PT; c – 0.72PMN-0.28PT; d – 0.63PMN-0.37PT

A.c. conductivity has been calculated from dielectric measurements for frequencies 100Hz-20kHz. Formula (3) was used for calculations of σ_{AC}. Results are presented in Fig.3

$$\tan\delta = \frac{\sigma_{AC}}{\omega\varepsilon_0\varepsilon_r} \quad \Rightarrow \quad \sigma_{AC} = \tan\delta \cdot \omega \cdot \varepsilon_0 \cdot \varepsilon'. \qquad (3)$$


a)
σ[S/m]
1E-3
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
1E-10
1E-11
20kHz
4kHz
1kHz
400Hz
100Hz
PMN
dc
1,5
2,0
2,5
3,0
3,5
4,0
4,5
5,0
1000/T [K-1]
b)
σ[S/m]
1E-3
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
1E-10
1E-11
20kHz
4kHz
1kHz
400Hz
100Hz
0.8PMN-0.2PT
dc (10^4 V/m)
1,5
2,0
2,5
3,0
3,5
4,0
4,5
5,0
1000/T [K-1]

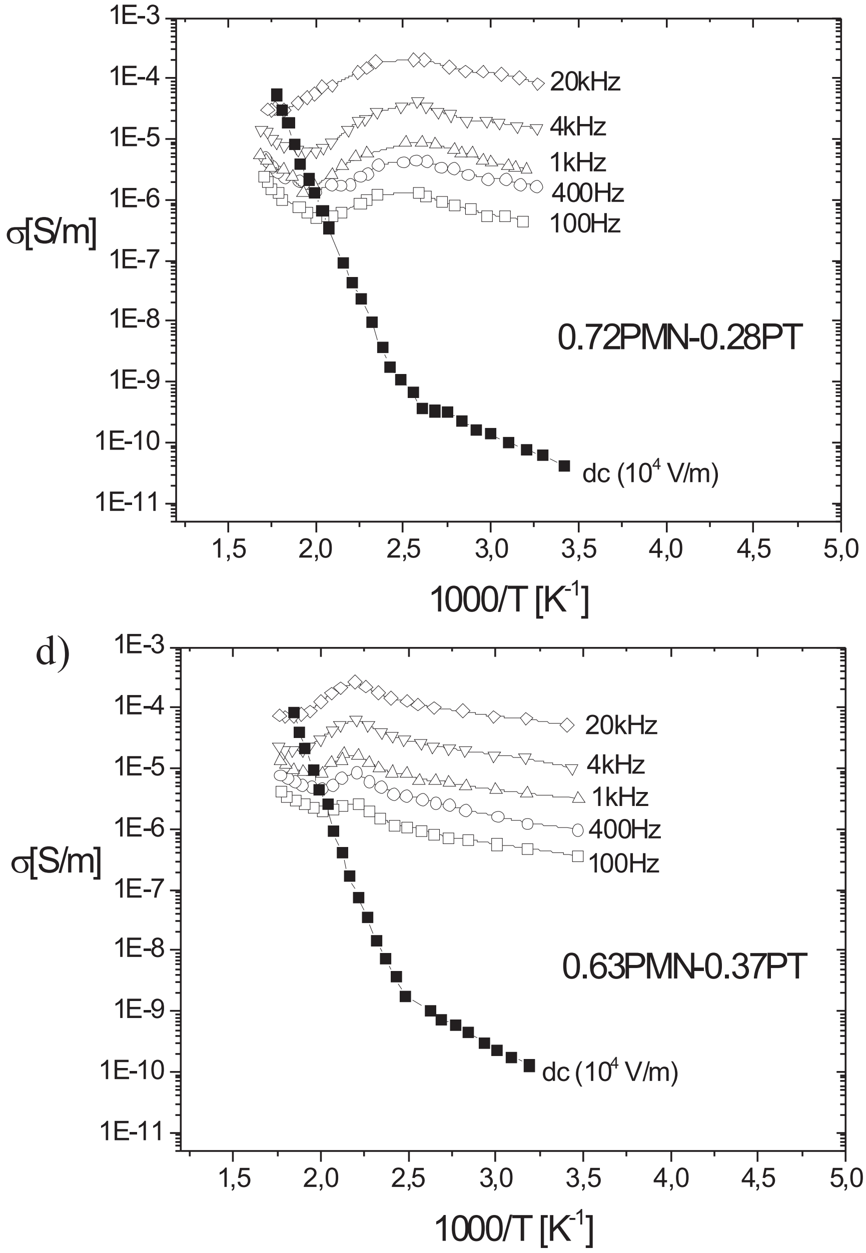


Fig. 3. Dependencies logσ_{AC}=f(1/T) and logσ_{DC}=f(1/T) for a – PMN; b – 0.8PMN-0.2PT; c – 0.72PMN-0.28PT; d – 0.63PMN-0.37PT

4. Discussion

Analyzing results presented in Fig.2 it has been possible to compare the temperature $T_C = T_m$ at which the maximum of dielectric permittivity take place, with the temperature T_E at which the change of activation energy take place. Results are presented in Table 1.

TABLE 1

E_a, T_E, T_c calclated from Fig.2

Composition	E_{a1} [eV]	E_{a2} [eV]	T_E [°C]	T_m [°C]	T_R -T_C[K]
PMN	1.69	1.12	119.8	2.5	117.3
0.8PMN-0.2PT	0.43	1.13	120.8	93.2	27.6
0.72PMN-0.28PT	0.24	1.24	140.2	136.7	3.5
0.63PMN-0.37PT	0.29	1.56	170.1	187.0	-16.9

Investigations of a.c. conductivity presented in Fig.3 shown the difference between relaxor sample PMN and other samples with ferroelectric properties.

The dependencies of a.c. conductivity on frequency are good described by universal Jonscher's power law [3]

$$\sigma_{AC} = \sigma_{DC} + A\omega^n \quad 0 < n < 1 \tag{4}$$

All obtained $\sigma(f)$ data at all temperatures can be fitted to eq. (4). Examples of results of fitting are presented in Fig.4 and in Tables 2 and 3.

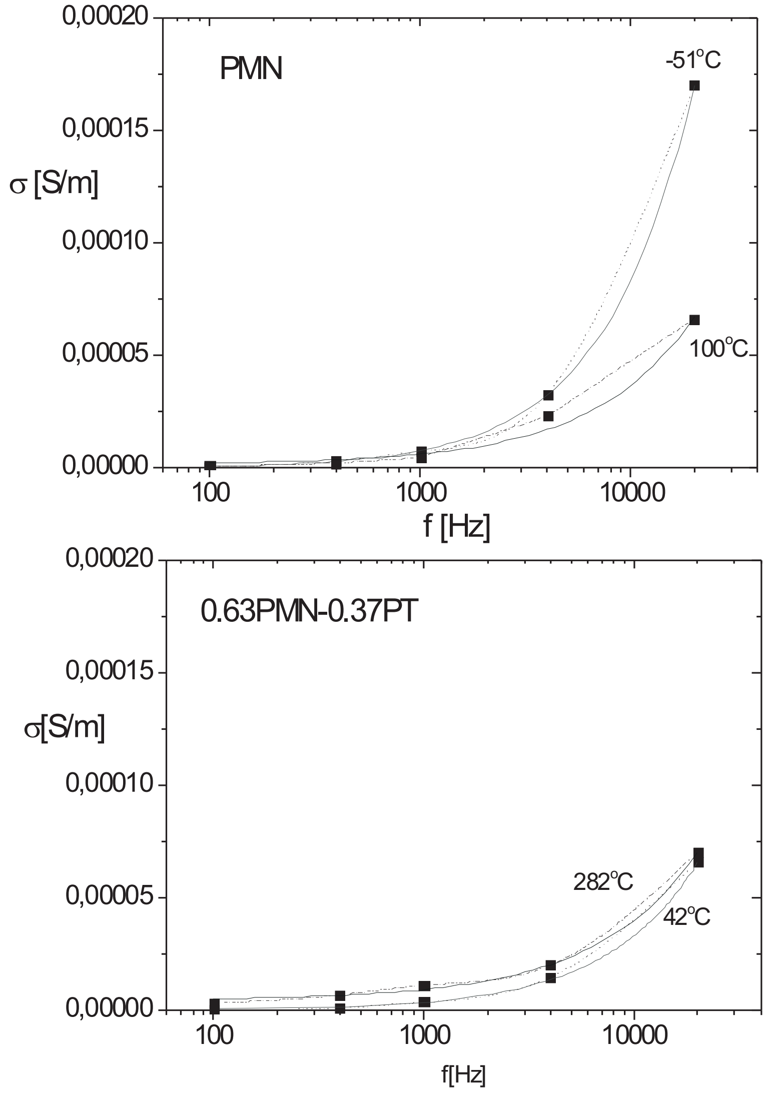


Fig. 4. Results of fitting $\sigma(f)$ data to eq. (4)

TABLE 2

Results of fitting experimental data to equation (4) for PMN

	$^{\sigma}\mathrm{DC}$ $^{[\mathrm{S/m}]}$	A	n
-51[°C]	$-1.65 \cdot 10^{-7}$	$9.53 \cdot 10^{-10}$	1.03
282[°C]	$1.65 \cdot 10^{-6}$	$1.64 \cdot 10^{-9}$	0.90

TABLE 3

Results of fitting experimental data to equation (4) for 0.63PMN-0.37PT

	$^{\sigma}\mathrm{DC}$ $^{[\mathrm{S/m}]}$	A	n
42[°C]	$4.15 \cdot 10^{-7}$	$6.17 \cdot 10^{-10}$	0.98
282[°C]	$4.76 \cdot 10^{-6}$	$2.08 \cdot 10^{-9}$	0.88

At high temperatures a.c. conductivity weaker depends on frequency. However d.c. conductivity is not the boundary value as predict formula (4) and the activation energy calulated from d.c. conductivity is much higher than calculated from a.c. conductivity. It can be probably related to the following reasons:

i – surface d.c. conductivity
ii – higher value of electric field used for d.c. measurements than the attitude of a.c. field
iii – the influence of near electrode layers. Parallel RC circuit on which is based formula (4) may be not good for such situation.

In [4] similar investigations allow authors to find divide line between relaxor, diffused ferroelectric, ferroelectric and dielectric. The results of our investigations shown also that there are the differences between relaxor PMN and ferroelectric PMN-PT however the divide line is not so sharp.

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REFERENCES

[1] Z. Jiwei, S. Bo, Z. Liangying, Y. Xi, Preparation and dielectrical properties by sol-gel derived PMN-PT powder and ceramic, Materials Chemistry and Physics **64**, 1-4 (2000).

[2] R. Skulski, P. Wawrzała, D. Bochenek, K. Ćwikiel, Dielectrical and electromechanical behaviors of PMN-PT ceramic samples, Journal Of Intelligent Material Systems And Structures **18**, 1049-1056 (2007).

[3] A. K. Jonscher, A new understanding of the dielectric relaxation of solids, J. Mater. Sci. 16 (6), 2037 (1981).

[4] I. Rivera, Ashok Kumar, N. Ortega, R. S. Katiyar, S. Lushnikov, Divide line between relaxor, diffused ferroelectric, ferroelectric and dielectric, Solid State Communications **149**, 172-176 (2009).