

**CHARACTERIZATION OF SAMARIUM COPPER TANTALATE - A NEW PEROVSKITE
MATERIAL WITH HIGH DIELECTRIC PERMITTIVITY**

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Abstract

A permanent progress in miniaturization of electronic capacitive elements requires development of new materials exhibiting a high dielectric constant. The paper reports on synthesis and sintering conditions and dielectric properties of a new ceramic material with the composition $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$. This material has a complex perovskite structure analogous to that of $\text{Cu}_2\text{Ta}_4\text{O}_{12}$. Its high dielectric permittivity reaching 10^5 could be attributed to spontaneous formation of internal barrier layer capacitors (IBLC). Complex impedance spectroscopic studies carried out at frequencies of 10 Hz – 2 MHz and in a wide temperature range from -55 to 700°C reveal two types of dielectric response of the ceramic samples. A high-frequency and low-temperature response is related to grains, whereas a low-frequency and high-temperature response is attributed to grain boundaries. Scanning electron microscope images and energy-dispersive X-ray microanalysis confirmed the existence of semiconducting grains and more resistive grain boundaries in the investigated ceramic material.

Key words: samarium copper tantalate, perovskite ceramic, dielectric properties, internal barrier layer capacitor

1. INTRODUCTION

Development of new materials exhibiting high dielectric permittivity is important to attain progress in miniaturization of capacitive electronic components. Among candidates are members of a family of nonferroelectric materials with a complex perovskite structure and the composition of $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ ($\text{A}=\text{Ca}, \text{Bi}_{2/3}, \text{Nd}_{2/3}, \text{Sm}_{2/3}, \text{Gd}_{2/3}, \text{Dy}_{2/3}$) [1-9] and $\text{ACuTa}_4\text{O}_{12}$ ($\text{A}=\text{Cu}, \text{Bi}_{2/3}, \text{Nd}_{2/3}, \text{Sm}_{2/3}, \text{Gd}_{2/3}, \text{Dy}_{2/3}$) [10-15].

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ which is the best known representative of these materials, shows a very high dielectric constant of 10^5 being stable over a wide frequency and temperature range. Formation of internal barrier layer (IBL) and surface barrier layer (SBL) capacitors has been suggested to be the most plausible reason for this dielectric behavior.

In contrast to a complex multistage fabrication procedure of conventional barrier layer capacitors based on BaTiO_3 and SrTiO_3 , for $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{ACuTa}_4\text{O}_{12}$ materials such capacitors are formed spontaneously in a one step sintering process in air.

In ABO_3 perovskite structure of the considered compounds, there occurs strong tilting of TiO_6 or TaO_6 octahedra and four-fold coordination of small Cu ions in A sites [1, 10, 12]. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is a stoichiometric compound, but most of other members of the family have partly unoccupied A sites. In the case of $\text{Cu}_2\text{Ta}_4\text{O}_{12}$, a half of A sites remains unoccupied [10, 12].

The present work describes fabrication procedure and dielectric properties of a new material with the composition $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ ceramic with the structure analogous to $\text{Cu}_2\text{Ta}_4\text{O}_{12}$.

2. EXPERIMENTAL

The $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ material was synthesized by a conventional solid state reaction method. Starting oxides Sm_2O_3 , CuO and Ta_2O_5 were weighed in stoichiometric proportions, mixed and ball-milled for 8 h in isopropyl alcohol, then dried, pelletized and calcined at 1180°C for 25 h. The reaction product was ball-milled for 8 h, pressed into pellets and sintered at $1180\text{--}1220^\circ\text{C}$ for 12–25 h. A X'Pert Philips diffractometer was used to determine phase composition of the obtained material.

A FEI scanning electron microscope and an EDAX Genesis EDS system were utilized to examine the microstructure and chemical composition of the ceramic samples. Impedance spectroscopic studies using a LCR QuadTech meter were carried out in the temperature range from -55 to 700°C at frequencies 10 Hz - 2 MHz. Dc conductivity of the investigated material was measured in the temperature range $20\text{--}800^\circ\text{C}$.

3. RESULTS AND DISCUSSION

Figs. 1–6 present the results of the impedance spectroscopic studies of $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ ceramic samples sintered at 1220°C for 25 h. In Fig. 1a and Fig. 1b the frequency dependencies of the real and the imaginary parts of impedance are plotted as a function of frequency in log-log coordinates. Fig. 2 shows log-log plots of the imaginary versus the real part of impedance in the whole investigated temperature range from -55 to 700°C . In Fig. 3 the complex impedance data are depicted for a few selected temperatures in the range from -55 to 700°C .

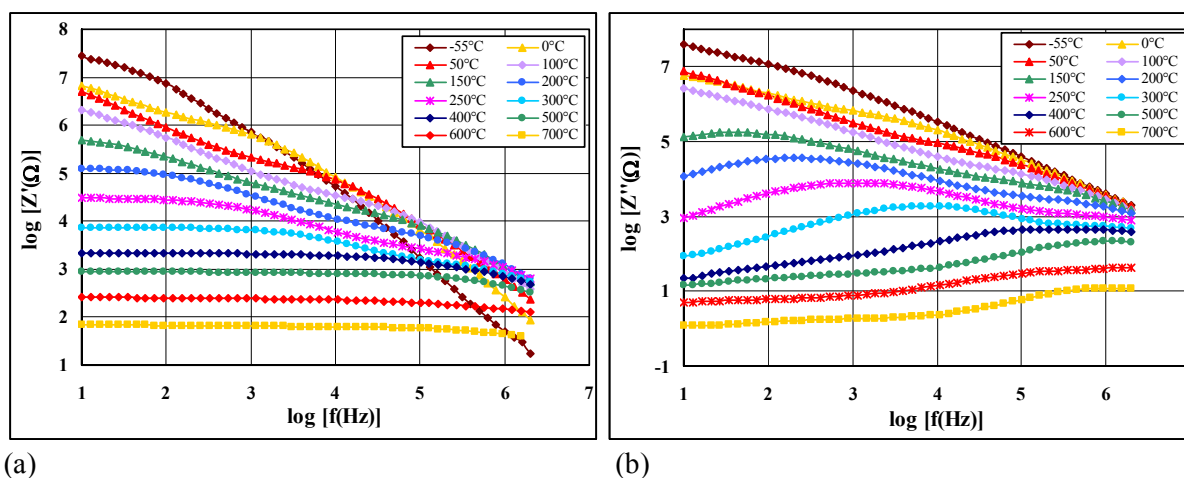


Fig. 1. Frequency dependence of the real (a) and the imaginary (b) parts of impedance in a temperature range from -55 to 700°C for $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ ceramic sintered at 1220°C .

The impedance data reflect two main kinds of the dielectric response. At low temperatures and high frequencies, a response related to grains can be distinguished. This response is represented by a flat maximum in Z'' versus frequency plot (Fig. 1b) and a small incomplete arc in Z'' versus Z' plots (Fig. 3a). Above 100°C , a dominant response is that attributed to grain boundaries. At a given temperature, a distinct maximum is visible in Z'' versus frequency plot (Fig. 1b) corresponding to a plateau in Z' versus frequency curve (Fig. 1a).

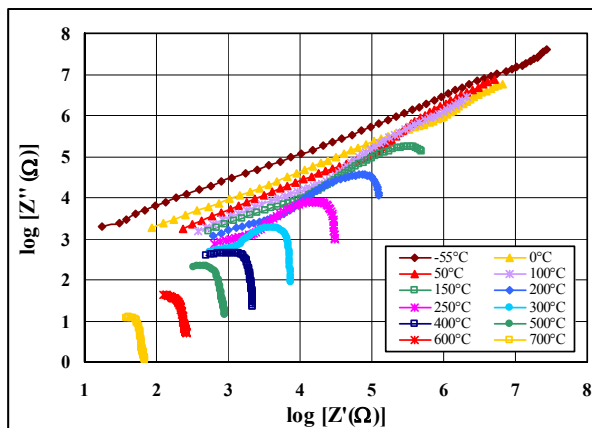


Fig. 2. Log-log plot of the imaginary versus the real part of impedance in the temperatures range from -55 to 700°C for $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ ceramic

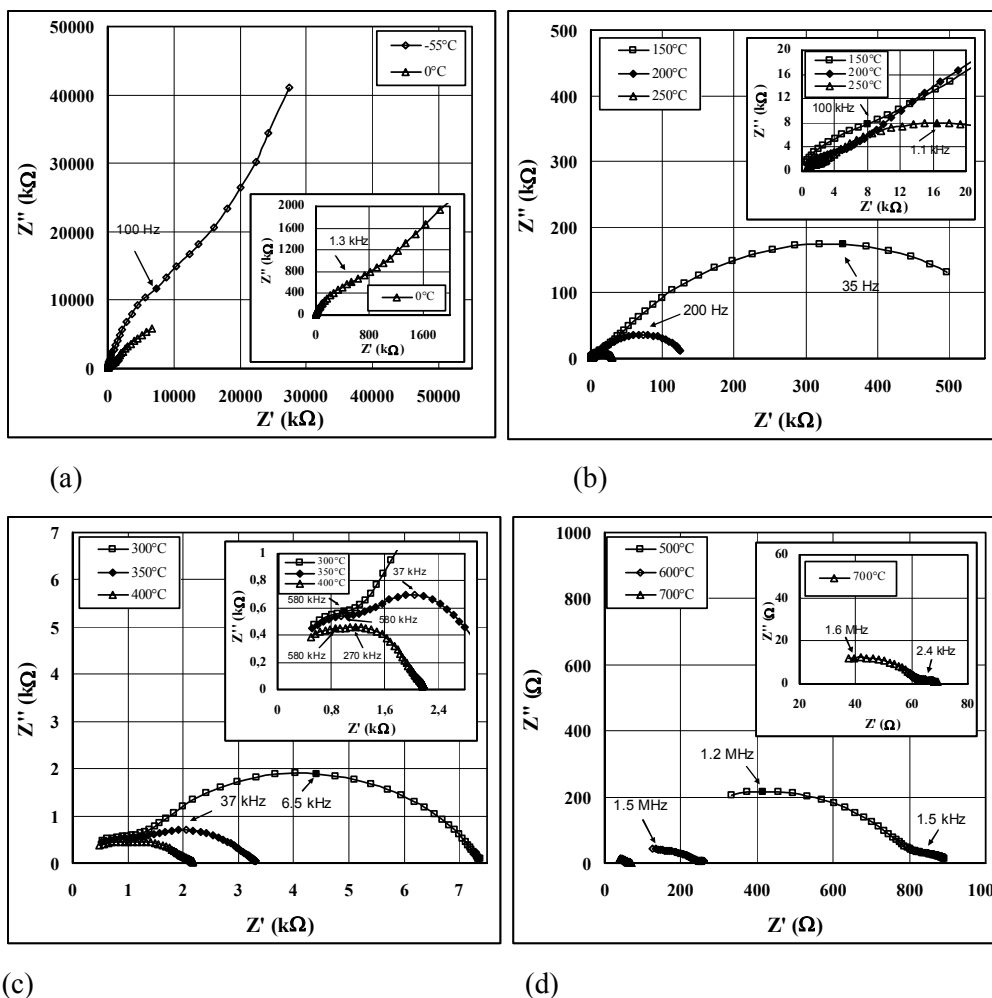


Fig. 3. (a)-(d) Complex plane impedance plots for different temperatures in a range from -55 to 700°C for $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ ceramic

In the complex impedance plots ($Z''=f(Z')$) the response of grain boundaries is reflected by a large arc (Fig. 3b,c,d). Below 200°C and above 400°C this arc is incomplete at the low- or high-frequency side, respectively. The additional right-side (low-frequency) very small and depressed arc which can be observed at the highest investigated temperatures (above 600°C) and at the lowest frequencies (Fig. 3d), can be ascribed to the electrode-sample interface.

In Fig. 4a the resistances of grains and grain boundaries determined from the complex impedance plots are shown as a function of reciprocal temperature. Fig. 4b displays the temperature dependence of the relaxation times τ of dielectric relaxation of grains and grain boundaries calculated from the relationship $2\pi f_{\max}\tau = 1$ (where $f_{\max}$ is frequency corresponding to a maximum in the complex impedance plot). The activation energies determined from the slopes of the Arrhenius plots are 0.35 eV and 0.77 eV for resistances of grains and resistances of grain boundaries, respectively. The activation energies of relaxation times are 0.29 eV and 0.68 eV for grains and grain boundaries, respectively. The values of activation energies for resistance and dielectric relaxation are close. This indicates that electrical conduction and dielectric relaxation processes are controlled by transport of the same charge carriers. Below 150°C, the resistances of grain boundaries are more than one order higher than those of grains.

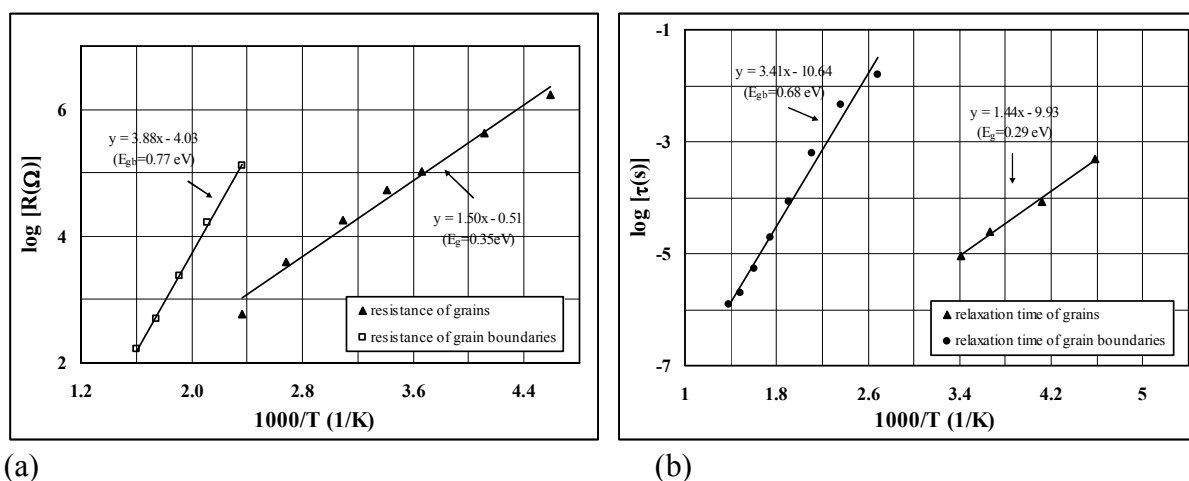


Fig. 4. (a) Resistances of grains and grain boundaries versus reciprocal temperature (b) dielectric relaxation times of grains and grain boundaries versus reciprocal temperature for $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ ceramic

In Fig. 5a and Fig. 5b the log-log plots of frequency dependencies of the real part of permittivity ϵ' and the imaginary part of electric modulus M'' are displayed in a wide temperature range. The ϵ' plots tend to converge at the high-frequency and low-frequency sides. The high frequency low-temperature step at a level of about 40 is related to intrinsic properties of grains. The low-frequency, high-temperature step corresponding to the values exceeding 10^3 - 10^5 is attributed to the response of grain boundaries.

The frequency dependence of M'' reveals large maxima which shift to higher frequencies with increasing temperature. These M'' peak values, which are proportional to the capacitances of grains, are almost the same for all temperatures in the range from -55 to 300°C. The humps with the heights 2-3 orders lower than those of maxima can be attributed to the capacitances of grain boundaries.

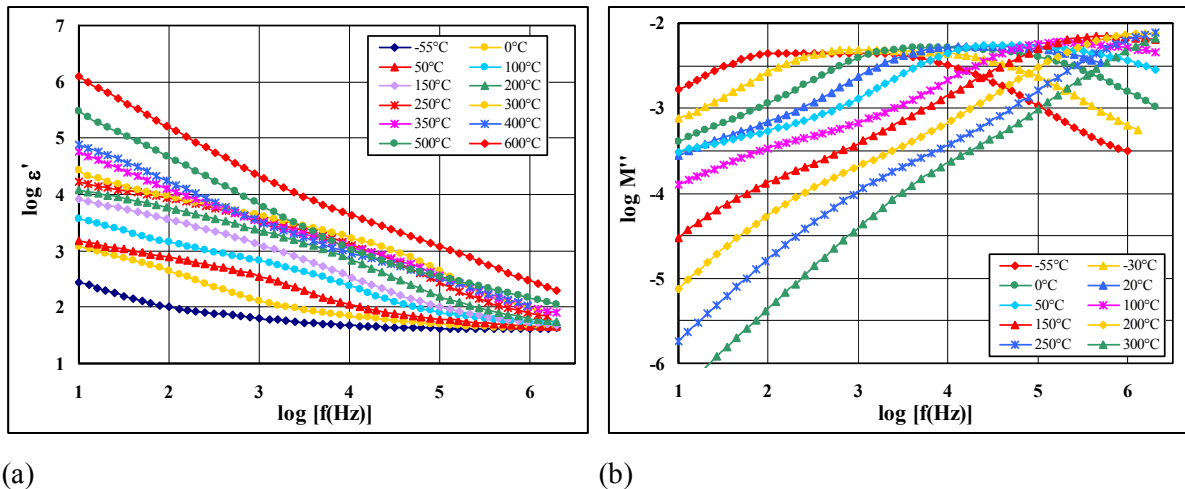


Fig. 5. Frequency dependence of (a) the real part of permittivity in a temperature range from -55 to 600°C, (b) the imaginary part of electric modulus in a temperature range from -55 to 300°C (b) for $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ ceramic

In Fig. 6 the logarithm of dc electrical conductivity of $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ ceramic in the temperature range 20-800°C is plotted as a function of reciprocal temperature. The activation energies determined from the slopes of linear parts of the plot are 0.49, 0.74 and 0.77 eV in different temperature ranges shown in Fig. 6. The activation energy of dc conduction in the temperature range 420-800°C is close to that of resistance of grain boundaries (0.77 eV), determined from the impedance data.

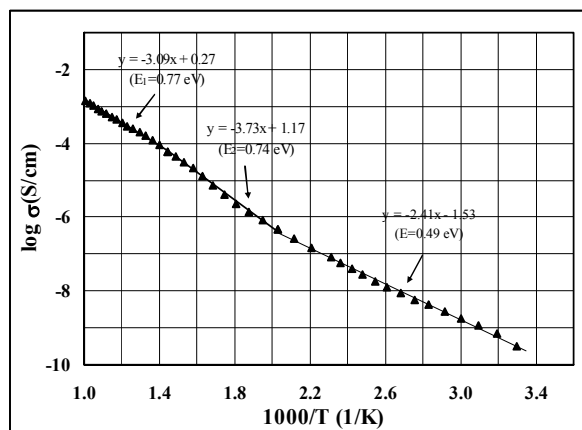


Fig. 6. Logarithm of dc electrical conductivity as a function of reciprocal temperature

The microstructure observed using scanning electron microscope is fine-grained although the grain sizes are not uniform changing in the range from 0.5 to 5 μm . The energy dispersive spectroscopy method (EDS) reveals a higher content of oxygen at grain boundaries than in grain interiors.

4. CONCLUSIONS

On the basis of impedance spectroscopic data two main dielectric responses were recognized in $\text{Sm}_{2/3}\text{CuTa}_4\text{O}_{12}$ ceramics. A low-temperature, high-frequency response can be attributed to grains, whereas a high-temperature low-frequency response to grain boundaries. The resistances and capacitances of grains are more than one order lower than those of grain boundaries. The microanalysis by the EDS method reveals that the content of oxygen at grain boundaries is higher than that in grain interiors. The fabricated material seems to be an IBL capacitor with internal barriers spontaneously formed at grain boundaries of semiconducting grains.

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REFERENCES

1. Subramanian, M.A., Li, D., Duan, N., Reisner, B.A., Sleight, A.W. (2000) High Dielectric Constant in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{ACu}_3\text{Ti}_3\text{FeO}_{12}$ Phases. *J. Solid State Chem.* **151**, pp. 323-325.
2. Sinclair, D.C., Adams, T.B., Morrison, F.D., West, A.R. (2002) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$: One-step internal barrier layer capacitor. *App. Phys. Lett.* **80**, pp. 2153-2155.
3. Shao, S.F., Zhang J.L., Zheng, P., Wang, C.L. (2007) Effect of Cu-stoichiometry on the dielectric and electric properties in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *Solid State Commun.* **142**, pp. 281-286.
4. Prakash, S.B., Varma, K.B.R. (2007) The influence of the segregation of Cu-rich phase on the microstructural and impedance characteristics of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics. *J. Mater. Sci.* **42**, pp. 7467–7477.
5. Wu, L., Zhu, Y., Park, S., Shapiro, S., Shirane, G. (2005) Defect structure of the high-dielectric-constant perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. *Phys. Rev. B* **71**, 014118.
6. Bueno, P.R., Tararan, R., Parra, R., Joanni, E., Ramirez, M.A., Ribeiro, W.C., Longo, E., Varela, J.A. (2009) A polaronic stacking fault defect model for $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ material: an approach for the origin of the huge dielectric constant and semiconducting coexistent features. *J. Phys. D: Appl. Phys.* **42**, 055404.
7. Liu J., Duan, C.G., Yin, W.G., Mei, W.N., Smith, R.W., Hardy, J.R. (2004) Large dielectric constant and Maxwell-Wagner relaxation in $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$. *Phys. Rev. B* **70**, 144106.
8. Szwagierczak, D. (2009) Dielectric behavior of $\text{Bi}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramic and thick films. *J. Electroceram.* **25**, pp. 56-61.
9. Szwagierczak, D., Kulawik, J. (2012) Application of High Permittivity Bismuth Copper Titanate in Multilayer Capacitors. *Acta Phys. Pol. A* **121**, pp. 119-121.
10. Ebbinghaus, S.G. (2007) Influence of composition and thermal treatment on the properties of $\text{Cu}_{2+x}\text{Ta}_4\text{O}_{12+\delta}$. *Prog. Solid State Chem.* **35**, pp. 421-431.
11. Renner, B., Lunkenheimer, P., Schetter, M., Loidl, A., Reller, A., Ebbinghaus, SG. (2004) Dielectric behavior of copper tantalum oxide. *J. Appl. Phys.* **96**, pp. 4400-4404.
12. Vincent, H., Bochu, B., Aubert, J.J., Joubert, J.C., Marezio, M. (1978) Crystal structure of CuTa_2O_6 . *J. Solid State Chem.* **24**, pp. 245-253.

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13. Szwagierczak, D., Kulawik, J. (2008) Sintering and Dielectric Properties of $\text{Cu}_2\text{Ta}_4\text{O}_{12}$ Ceramics. J. Eur. Ceram. Soc. **28**, pp. 2075-2083.
14. Szwagierczak, D., Kulawik, J. (2010) Dielectric properties of high permittivity ceramics based on $\text{Dy}_{2/3}\text{CuTa}_4\text{O}_{12}$. J. Alloys Compd. **491**, pp. 465-471.
15. Szwagierczak D. (2012) Internal Barrier Layer Capacitance Effects in Neodymium Copper Tantalate Ceramics. Acta Phys. Pol. A **121**, pp. 205-207.