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15:30 – 19:00, TUE **GB - 17 - P**

INVESTIGATION OF $(Ba_{1-x}Ca_yY_z)TiO_3$ PTCR-CERAMICS BY ESR METHOD

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With the purpose of controlling the temperature interval of PTCR-effect in the ceramics based on barium titanate one can use the method of partial isovalent substitution. The partial isovalent substitution results in the reduction of both the varistor effect value and the range of donor dopant concentration corresponding to the limits in which PTCR-effect appears. With the purpose of clearing up the charge compensation mechanism, which occurs when partially substituting calcium for barium, the ESR investigation was carried out. It has been ascertained, that the additional Y^{3+}-T^{3+} centers appear in PTCR ceramics in which the partial isovalent substitution of barium by calcium was carried out: $(Ba_{1-x}Ca_yY_z)TiO_3$. It has been shown, that the intensity of ESR spectra of Y^{3+}-T^{3+} centers – according to the concentration of donor dopants - correlates with the electrophysical properties of researched samples. This fact allows the explanation of observed regularities in the variation of electrophysical parameters in PTCR-ceramics.

15:30 – 19:00, TUE **GB - 18 - P**

PTCR EFFECT IN UNDOPED $BaTiO_3$ CERAMICS ANNEALED IN A FLUORINE CONTAINING ATMOSPHERE

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The PTCR effect originates in temperature-dependent potential barriers at the grain boundaries of $BaTiO_3$ ceramics, these barriers are formed by the creation of acceptor states at the surfaces of n-type semiconducting, ferroelectric grains. Normally, the acceptor states are formed during a controlled reoxidation of the donor-doped $BaTiO_3$ ceramics. Alternatively, fluorine can act as an effective acceptor when adsorbed at the grain boundaries. Alles et al. [1] reported the PTCR effect in undoped atmospherically reduced $BaTiO_3$ ceramics exposed to a fluorine-containing atmosphere. In contrast to the acceptor nature of the fluorine adsorbed at the grain boundaries, the fluorine incorporated into the $BaTiO_3$ perovskite structure at the oxygen sites acts as a donor dopant.

Pellets of $BaTiO_3$ ceramics, sintered in air, were annealed in a fluorine containing atmosphere at high temperatures (500-1100 °C). Insulating, air-sintered, $BaTiO_3$ ceramics became semiconducting after the treatment in the fluorine-containing atmosphere, whereas the PTCR effect has not been observed. However, the PTCR effect has appeared after reoxidation of fluorinated ceramics by reoxidation in air at high temperatures (1200 °C). The results strongly suggest that the fluorine was incorporated as a donor-dopant in $BaTiO_3$.

The electrical properties of the ceramics have been related to chemical reactions between $BaTiO_3$ and the fluorine containing atmosphere.

[1] A. B. Alles, V. R. W. Amarakoon, V. L. Burdick, J. Am. Ceram. Soc., 72 [1] 148-51 (1989)