Capacitor and resonator ceramics with low sintering temperature

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A complex-composition ceramic condenser material based on barium titanate and a ceramic resonator material based on barium-neodymium titanate are obtained and investigated. Developed are glass technological additions which introduction into the raw material lowers the ceramics sintering temperature by 200–250°C, increases the density and diminishes the porosity of the ceramics samples, their electrophysical parameters remaining unchanged.

Получен и исследован керамический конденсаторный материал сложного состава на основе титаната бария и керамический резонаторный материал на основе титаната бария-неодима. Разработаны стекловидные технологические добавки, введение которых в шихту снижает температуру спекания керамики на 200–250°C, увеличивает плотность и уменьшает пористость керамических образцов без ухудшения их электрофизических параметров.

As a rule, condenser ceramics with high values of permittivity is obtained on the base of barium titanate which belongs to class 2 according to the temperature coefficient of capacitance (TCC).

However, many technical applications call for materials with higher temperature stability, i.e. TCC class 1 compounds. Among the latter, there should be mentioned the materials based on complex rare-earth titanates which perovskite-like structure is stabilized by rare-earth metal ions, e.g. barium-neodymium titanate $BaNd_2Ti_5O_{14}$ [1].

The main difficulty at the obtaining of ceramic condenser materials on the base of barium titanate and barium-neodymium titanate is a high sintering temperature (1350°C and more). At the same time, available in the literature are the data on the possibility to lower the sintering temperature by introducing fusible technological additions, which form liquid phase on the grain surface [2–4].

The goal of the present work is to investigate the technological conditions of the obtaining of ceramic condenser materials on the base of barium and barium-neodymium titanate with low sintering temperatures.

The technological procedures providing an essential decrease of the sintering temperature were worked out on barium-neodymium titanate (BNT) and the industrial composition consisting of barium titanate (BT) 89 mass % with the additions of calcium, zirconium, neodymium, niobium, zinc, yttrium oxides.

The samples to be investigated were obtained using the conventional ceramic technique by solid-phase synthesis of the mixtures of metal oxides and carbonates taken in stoichiometric proportion.

The conditions of synthesis and sintering were chosen from the results of thermogravimetric, dilatometric and X-ray investigations. Differential thermal analysis was realized on MOM OD-103 derivatograph in the temperature range from 20°C to 1300°C at 5–10°C/min heating rates. Dilatometric measurements were carried out on NETZCH 402 ED dilatometer at the same temperatures and heating rates. X-ray investigations were realized on D-500 SIEMENS dif-

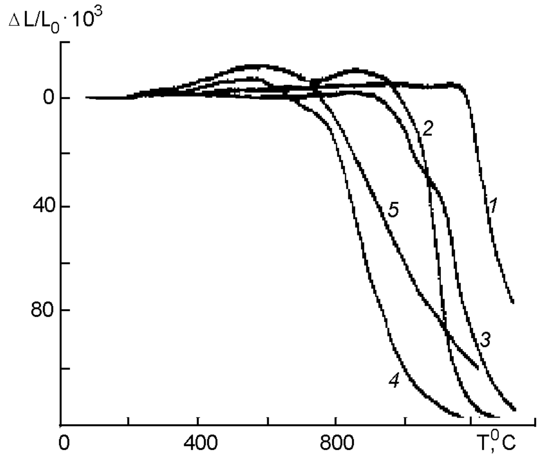

Fig. 1. Dilatometric curves for BT-based materials synthesized at 1300°C. Additions: *1* — without, *2* — LiF and B_2O_3, *3* — SiO_2 and B_2O_3, *4* — GA-1, *5* — GA-2.

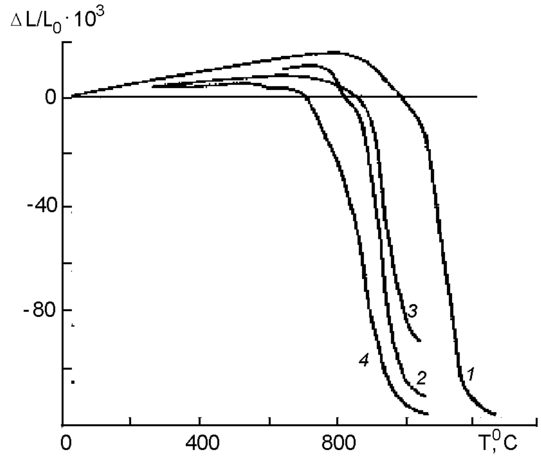

Fig. 2. Dilatometric curves for BNT materials synthesized at 1330°C. Additions: *1* — without, *2* — GA-1, *3* — GA-2, *4* — GA-3.

fractometer in filtered Cu K_α radiation. The samples' microstructure was studied using the microscope ISM-820 with microanalysis means.

The sintering temperature was chosen from the results of dilatometric investigation, the quality of the sintered samples was controlled by X-ray method and compared with the results of density and porosity measurements. The samples were sintered in modernized furnaces, the temperature being maintained to an accuracy of ±2°C.

The values of open porosity and density were measured by the method of hydrostatic weighing.

To determine dielectric properties, the ceramic disks were coated with electrodes by firing silver paste on their surface at 700°C.

Synthesis of BT- and BNT-based ceramic materials was carried out in the temperature range from 950 to 1300°C and from 1300 to 1330°C, respectively. According to the data of X-ray phase analysis, for BT the system of X-ray patterns which corresponds to the perovskite-like crystal structure of barium titanate is observed only after synthesis at 1300°C. The optimum temperature for the synthesis of BNT material (with a content of the main substance not smaller than 96 %) is 1330°C.

To determine the optimum sintering temperature, dilatometric shrinkage curves were obtained for BT material synthesized at 1300°C (Fig. 1, curve 1) and for BNT material synthesized at 1330°C (Fig. 2, curve 1). As seen from these figures, without using technological additions BT- and BNT-based ceramic samples can be sintered at a temperature not lower than 1300°C and 1350°C, respectively.

To decrease the sintering temperature of the ceramic samples, we tested different technological additions. In particular, complex additions containing LiF, SiO_2 and B_2O_3 were introduced into synthesized BT material. The dilatometric curves are shown in Fig. 1 (curves 2,3). As is seen, these additions allow to lower the sintering temperature down to 1100–1150°C. At the next stage of our investigation the technological additions decreasing the sintering temperature were introduced in the form of specially prepared glasses on the base of LiF, ZnO, Bi_2O_3, B_2O_3.

Presented in Fig. 1 (curve 4) is the dilatometric curve obtained while introducing the glass addition LiF–B_2O_3–Bi_2O_3 (GA-1) into synthesized BT material. As seen from this dependence, the process of sintering takes place at 1000°C, the degree of sintering shrinkage reaches 12 %, the density of the ceramic samples at the said temperature runs into 97 % of the theoretical value. In the case when the same glass addition is introduced into synthesized BNT material (Fig. 2, curve 2), the ceramic sample is sintered at a temperature higher than 1100°C, the degree of shrinkage being 10 %.

Shown in Fig. 1 (curve 5) and Fig. 2 (curve 3) are the dilatometric curves obtained for BT and BNT materials containing the glass addition B_2O_3–Bi_2O_3–ZnO (GA-2) conventionally used in ceramic condensers based on barium titanate for lowering the

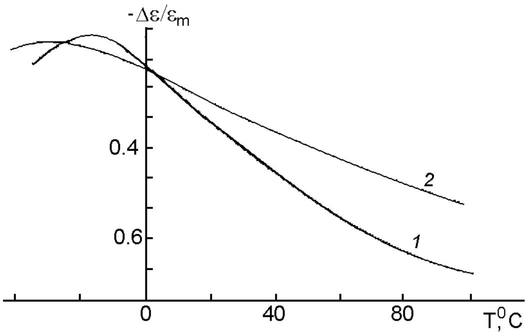

Fig. 3. Temperature dependences of relative permittivity for the industrial BT-based material (curve *1*) and for BT ceramics with low sintering temperature (curve *2*).

sintering temperature. The presented dependences show that for BT ceramics such an addition also allows to decrease the sintering temperature down to 1000°C, whereas for BNT this temperature cannot be lower than 1100–1150°C.

On the base of the above-mentioned oxides we synthesized a glass addition containing alkali earth elements (GA-3). Its introduction into BNT (Fig. 2, curve 4) allowed to obtain a ceramic material sintered at 1050°C. Its degree of sintering shrinkage is 12 %, the density is maximal (95 % of the theoretical value), the porosity being minimal.

Microstructure investigations show that the introduction of glass additions favors the formation of needle-like grains of BNT ceramics and diminution of their size, whereas BT ceramics shows a closely packed structure without visible pores.

Presented in Fig. 3 are relative changes in permittivity for one of the capacitor materials we have developed on the base of BT with a low sintering temperature (curve 2). For comparison, similar data are shown for industrial BT-based material (curve 1). As is seen, the developed material has better temperature characteristics.

The permittivity of the developed ceramic material based on BNT with a low sintering temperature is equal to 150 (MPO group of the ε temperature coefficient).

Obtained is a complex-composition condenser material based on BT and a resonator ceramic material based on BNT. The introduction of glass additions into sintered BT and BNT materials leads to improvement of their producibility, in particular, to an essential decrease of the sintering temperature, widening of the temperature interval of sintering, increase of the density and diminution of the porosity of the ceramic samples.

References

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Конденсаторна та резонаторна кераміка з низькою температурою спікання

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Одержано та досліджено керамічний матеріал на основі титанату барію та керамічний резонаторний матеріал на основі титанату барію-неодиму. Розроблено скловидні технологічні домішки, додавання яких у шихту знижує температуру спікання кераміки на 200–250°С, збільшує густину та пористість керамічних зразків без погіршення їх електрофізичних параметрів.