A comparative study has been made of the processes involved in the consolidation of nanosized barium titanate powders by nonisothermal sintering at a linear heating rate, by rate-controlled sintering, and high-pressure sintering (up to 5 GPa). The use of linear heating and high-pressure has been found to be ineffective for obtaining nonporous ceramics (residual porosity of about 2%) and for minimizing grain growth. The application of external pressure does not prevent coalescent grain growth controlled by surface diffusion. When rate-controlled sintering is employed a densification/grain growth optimum can be attained with a relative density of 99.9% of the theoretical value and a grain size of about 100 nm.

Keywords: nanocrystalline barium titanate, nonisothermal sintering, rate-controlled sintering, high-pressure sintering, structure.

Because of its dielectric properties barium titanate is used extensively as a material for multilayer capacitors, thermistors, varistors, integrated electronic devices, etc. Manufacturing technology is known to have a strong effect on the structure and properties of barium titanate ceramics: the size and shape of grains and pores, the domain size, and the atomic structure of grain boundaries. Miniaturization of electronic devices is of high priority: the main trend is to make polycrystalline layers thinner, which requires finer powders. Today’s fabrication techniques produce powders with a particle size of \( \sim 100 \) nm and dielectric layers just a few microns thick. The next step in the development of the technology will be the production of powder with a particle size of \( \sim 10 \) nm with a corresponding dielectric layer thickness of under 1 \( \mu \)m. Thin-film technologies are inappropriate because the ferroelectric obtained has a small dielectric constant.

An experimental dependence of the dielectric constant \( \varepsilon \) on the grain size in compact barium titanate (Fig. 1), was described by Arlt and Hennings [1]. That relation indicates that the maximum (\( \varepsilon = 5500-6000 \) at room temperature) corresponds to polycrystalline ceramics with a grain size of 0.7-0.8 \( \mu \)m. As the grain size decreases relative to the extremum, \( \varepsilon \) rapidly decreases and is 2000 for ceramics with a grain size of 0.3 \( \mu \)m. However, Arlt and Hennings constructed the relation by using specimens obtained by different methods: sintering for ceramics with grains larger than 0.5-0.6 \( \mu \)m, and hot pressing for ceramics with larger grains, since grain growth could not be suppressed during isothermal sintering. High-pressure sintering (up to 8 GPa) was used to obtain nanocrystalline barium titanate with a density of 98% of the theoretical value, grain size of 70 nm, and a dielectric constant of about 2000 at room temperature [2], which is roughly triple the value predicted by extrapolation of the Arlt curve in the region of grain sizes less than 100 nm (Fig. 1).

As shown in [2], with a mean grain size of 40 nm barium titanate still maintains its ferroelectric properties, which opens up the prospect of miniaturization of multilayer capacitors. Comparison of the dielectric properties of specimens obtained by different methods revealed differences which apparently are due to structural differences, primarily in the grain distribution by size and quality of their boundaries. The optimal grain size and optimal consolidation methods should be found, therefore, to ensure that the grain structure and boundaries are of the requisite quality. One possible solution to this problem has been proposed in parts V and VI of this work.
Rate-controlled sintering (RCS) can produce a compact polycrystalline ceramics with a grain size of more than 70 nm [3]. The concept of RCS was developed by Palmour and Jonson [4]. They postulated that if the compaction rate is controlled, the temperature and heating rate become shrinkage-dependent variables, which can be controlled by a negative feedback between the compaction rate and the instantaneous temperature. This method of organizing sintering is contrary to the traditional approach, where the compaction rate depends on the temperature and the heating rate set by the experimenter. Palmour and Jonson developed a universal heating regime in three stages. The first stage has a high linear compaction rate, up to 72.5% of the theoretical density. In that stage the high heating rate causes the surface diffusion to decrease and as a result grains become larger without any appreciable shrinkage. The second stage has a much lower compaction rate up to 85% of the theoretical density to maintain an open porosity, which is a brake for grain boundaries. The third stage has a low compaction rate, which decreases according to a logarithmic law [5]. Such a complicated regime, however, is not a dogma and can be modified flexibly, as is shown in this work in comparison with high-pressure isothermal sintering.

Rate-controlled sintering, therefore, can be used to obtain compact ceramics with differ grain size distributions just by a single method of compaction of the same initial powder with similar grain boundary parameters and also to study the grain size dependence of the dielectric constant of barium titanate. Using high-pressure sintering, we obtain an object for a comparative study of structure and properties. Optimization of the sintering of nanocrystalline barium titanate powder in order to obtain a polycrystalline ceramics with different grain sizes and, hence, different dielectric properties is the subject of this work.

Method of Investigation

Barium titanate powders were obtained by a new technology of nonisothermal decomposition of barium titanyl-oxalate tetrahydrate \( \text{BaTiO(C}_2\text{H}_4\text{)}_2\cdot4\text{H}_2\text{O} \), making it possible to control the morphology and size distribution of particles in the powder [6-10]. The characteristics of the powders were determined by scanning and transmission electron microscopy, x-ray diffraction analysis, and the BET method (thermal desorption of nitrogen).

Specimens for sintering were prepared by two-sided pressing in a steel compression mold, using a plasticizer. The compacting pressure varied from 50 to 300 MPa. The plasticizer used, polyvinyl butyral (8 mass %), was sublimated in air by heating to 400°C at a rate of 30 deg/h.

For sintering in air with a variable temperature we continuously monitored the compaction of the specimens under heating by using a precision dilatometric setup developed at the Institute for Problems of Materials Science, National Academy of Sciences of Ukraine. The preliminary nonisothermal sintering consisted of two heating stages: rapid, at a rate of 60 deg/h to 700°C (the temperature at which linear shrinkage begins) and slow, at a constant rate in the range 6-60 deg/min to 1300°C without isothermal soaking. The cooling rate was the same for all specimens, 12 deg/min. From the results of sintering with a constant compaction rate for all powders we constructed kinetic response fields and on that basis we calculated the optimal temperature-time controlled-rate sintering regimes. The relative error of measurement of the lengths of