Size effect on ferroelectric behavior of dense nanocrystalline $BaTiO_3$ ceramics

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Barium titanate, $BaTiO_3$, has extensive use in electronics as dielectric/piezoelectric ceramic material. The present endeavour in the microelectronics is the miniaturisation of the ferroelectric components which imposes a corresponding reduction of grain size. The study of size-dependent properties in the nanometric range is thus of fundamental importance for optimising the performances of the ferroelectric components. In this study, crystal structure, phase transitions and permittivity of dense $BaTiO_3$ ceramics with grain size of 50-1200 nm have been investigated. The nanocrystalline ceramics were prepared by spark plasma sintering at temperatures of 800-1000 °C using powders obtained by a chemical aqueous method. The final relative density was ≥97%. The tetragonality of the ferroelectric phase (c/a-1, where c and a are the unit cell edges) gradually decreases from 0.8% (1200 nm) to 0.25% (50 nm). The heat of transition corresponding to the tetragonal/cubic transformation is also remarkably affected by grain size and the value measured for the 50 nm ceramic is only 20% of that of the coarse ceramic. Extrapolation of the experimental trends indicates that the critical grain size corresponding to the disappearance of ferroelectric behaviour in dense $BaTiO_3$ ceramics at room temperature is of the order of 10-30 nm. The dielectric constant is strongly depressed by the grain size effect and the Curie point is gradually shifted to lower temperatures. Above the Curie temperature, the behaviour is well described by the Curie-Weiss law. A strong lowering of the Curie-Weiss temperature with decreasing grain size (1200 nm: 100 °C; 50 nm: –50 °C) has been observed. The grain size effect will be qualitatively discussed in the framework of the Landau-Ginsburg-Devonshire theory of ferroelectrics. The possible influence of a non-ferroelectric grain boundary layer on the effective permittivity of the nanocrystalline ceramics in the paraelectric state will be also considered.