ABSTRACT

Nanoferroelectric ceramics attract considerable scientific interest because of their unusually improved physical properties having widespread utility in telecommunications, medical imaging, dielectric, ultrasonic devices, non-volatile memories, etc. In order to predict the unique property of nanocrystalline materials, which is a combination of the property of crystallite and intercrystalline region, it is essential to understand precisely how the structure of the crystalline and intercrystalline region, varies with a decrease in crystallite size. The present study aims to investigate crystallite size effect on the structural, dielectric, impedance, electrical conductivity and mechanical properties of nanocrystalline lead zirconate titanate (PZT) based systems.

The ferroelectric $Pb(Zr_{0.53}Ti_{0.47})O_3$ (PZT), $Pb_{0.92}Sm_{0.08}(Zr_{0.53}Ti_{0.47})_{0.98}O_3$ (PSZT), $Pb_{0.92}Gd_{0.08}(Zr_{0.53}Ti_{0.47})_{0.98}O_3$ (PGZT), $Pb_{0.92}Nd_{0.08}(Zr_{0.53}Ti_{0.47})_{0.98}O_3$ (PNZT) and, $Pb_{0.92}Zn_{0.08}(Zr_{0.53}Ti_{0.47})O_3$ (PZZT) samples has been prepared by mechanical alloying of individual oxides. The unmodified and modified PZT in Pb site by Sm^{+3}, Gd^{+3}, Nd^{+3}, and Zn^{+2} samples synthesized by mechanical alloying are nanocrystalline with single phase cubic structure at room temperature. The phase stability of the cubic crystal structure of nanocrystalline samples has been investigated by sintering the compacted pellets at different sintering temperatures (400-1200^{0}C). The cubic phase formed by mechanical alloying transforms to tetragonal phase at higher sintering temperature. The temperature of the phase transition is lower for the modified PZTs. The phase transition between cubic and tetragonal phase is driven by crystallite size. Cubic phase appears to be stable below 50nm and tetragonal phase above it. SEM micrographs demonstrate particle coarsening with increase in sintering temperature. TEM studies confirm the formation of nanocrystalline PZT in both unmodified and modified PZT samples. The average crystallite size estimated using x-ray data, after eliminating the instrumental broadening and strain contribution, works out to be ≈ 15 nm in all the cases. This estimate has also been confirmed by transmission electron microscopy studies.

The broadening of the dielectric peak and the decrease in the ε_{max} is not only due to the structural disorder but also due to the decrease in the crystallite size. The ferroelectric-paraelectric phase transition temperature T_c decreases with increase in crystallite size/sintering temperature. Dielectric constant maximum ε_{max} increases with increase in sintering temperature and loss tangent decreases with increase in sintering temperature. Modification of PZT by Sm^{+3}, Gd^{+3}, Nd^{+3}, and Zn^{+2} causes more disordering in the systems.

Electrical properties of the nanoceramic have been studied using impedance spectroscopy technique. An impedance spectrum shows that the electrical properties of these samples are strongly dependent on crystallite size/sintering and a good correlation can be established with the sample microstructure in different temperature ranges. The impedance spectroscopy data of nanocrystalline samples show a semicircle in the high frequency region corresponding to the grain properties of ceramic samples, followed by a second and more depressed semicircle attributed to the grain boundary properties. The bulk resistance decreases with rise in temperature. Nanocrystalline unsintered samples have more grain boundary resistance than sintered ones. Negative temperature coefficient of resistance (NTCR) behavior in the materials indicates semiconducting nature of the studied materials. It was found that relaxation time is decreases with decrease in crystallite size.

It has been found that conductivity of nanocrystalline ceramics shows strong dependence on crystallite size, and conductivity increases with decrease in crystallite size. Polaronic related charge-hopping mechanism is responsible for charge-carrier transportation in these nanoferroelectric ceramics. Hopping and dc activation energies are found to be maximum for higher sintering temperature. The activation energy shows minimum with a maximum of corresponding minimum hopping distance (R_{min}) and critical percolation radius (R_P).

The mechanical properties of these samples were evaluated from nanoindentation data. Nanodisplacement increases with decrease in crystallite size. Hardness and Young's modulus are found to be higher for the tetragonal phase. Nonlinearity increases with decrease in crystallite size.

It was observed that nanosize affects the physical properties of ferroelectric nanoceramics and hence these nanoferreoelectrics are promising for the 21st century.