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RECENT TRENDS IN DESIGN OF ELECTROCALORIC ACTIVE FERROELECTRIC CERAMICS

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To protect the environment from destruction of ozonosphere and from increase of the concentration of greenhouse gases, freon should be abolished in the very near future and it is very urgent to search for substituting materials and to develop new refrigeration techniques, such as adiabatic depolarization cooling of ferroelectrics. The lead scandium tantalate $Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) and its solid solutions exhibit remarkable electrocaloric (EC) properties between known ABO_3 perovskites. The strong EC effect (temperature change of dielectrics under applied electric field and adiabatic conditions) observed in highly ordered PST materials at the induced phase transformation is due to a substantial structural rearrangement at field induced Fm3m to R3m phase transition (significant change of entropy and unit cell volume $\Delta V = 0.078$ Å^3). Degree of ordering of three- and pentavalent ions in the B sublattice varies depending on thermal treatment of initially (long-range ordering parameter Ω=0.85 - 0.88) hot-pressed PST ceramics. The long-range ordering was calculated from the intensities ratio of I_{111}/I_{200} X-ray diffraction lines measured by powder diffractometer DRON UM1. As Ω decreases, the EC effect drops significantly under 0.2 K. The highest known value of $\Delta T_{EC} = 1.8 \div 2.3$ K at field intensities up to 50 kV/cm in the vicinity of the field-induced phase transition is obtained in highly ordered PST samples after specific long time thermal treatment at 1480°C for 20 h and slow cooling of hot pressed ceramic samples. The corresponding phase transition temperature drops down to 2–8°C and the density reduces to 96.2% suggesting the presence of Pb vacancies in A sublattice. Highly ordered PST ceramics with Pb vacancies with extreme high ECE at room temperature is possibly one more state of the material, in addition to 3 known PST states: stoichiometric highly ordered, disordered and disordered with Pb vacancies. Multilayer capacitor technologies have allowed to obtain $\Delta T_{EK} > 3$ K due to high field intensities (150 kV/cm at layer thickness of 40–70 mkm).

Possible alternative ferroelectric materials without the expensive Sc are checked. Lead magnesium niobate $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) – lead titanate $PbTiO_3$ (PT) solid solutions were studied under different processing conditions for obtaining ceramics with sufficient high $\Delta T_{EC} \sim 1$K near room temperature. PMN crystal undergoes a field-induced first order phase transition from randomly mean cubic phase Pm3m to a macroscopically ferroelectric R3m phase in vicinity its Curie temperature $T_k \sim -15$°C. Therefore it is expected that (1-x)PMN – xPT ferroelectric ceramics will possess significant electrocaloric effect near room temperature. An original method has been used to obtain PMN-PT ceramics of 100% perovskite structure from overstoichiometric MgO mixture. Conventional sintering and firing as well as hot

pressing technique were checked. The technology is in the conceptual stage of new product development.