05.1-12 JAHN-TELLER CO- OPERATIVE EFFECT AND FERROELECTRIC PHASE TRANSITIONS OF COMPLEX METAL OXIDES WITH PEROVSKITE-TYPE STRUCTURE.
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A question of principle in a problem of ferroelectricity is the one about factors which are favorable for the origination of spontaneously polarized state (SPS). In particular it is very important to study the effect of Jahn-Teller cations (Cu^{2+}, Mn^{3+}, Cr^{2+}) present in oxygen octahedra of complex perovskites (A',A'',...)(B',B'',...)O_3 on SPS. Different investigators made opposite conclusions about the character of the effect discussed.
The report contains some well-known data (Yu.N.Venev, E.D.Politova and S.A.Ivanov . Ferro- and Antiferroelectrics of Barium Titanium Family, Moscow, Chemistry, I985, 256 p.) and our new data, which concerned Cu-containing perovskites (in this case Jahn-Teller effect is expressed very strongly), namely:
I. Results of improving crystal structures of the Ba_2CuWO_6 perovskite (electron microdiffraction technique) and Sr_2CuTeO_6 perovskite (powder sample, neutron diffraction, Rietveld method) according to which the structures of these compounds are noncentrosymmetric and there are parallel shifts of ions of the same kin. These facts are characteristic of ferroelectrics.
2. An existence of cubic-tetragonal phase transitions which are accompanied with dielectric anomalies in the Cu-containing perovskites. These data also indicate the ferroelectric nature of the above-mentioned transitions.
3. Some solid solution systems based on Cu-containing perovskites were studied. In particular, in the case of the $PbZrO_3$(I)-Sr_2CuWO_6 (II) system the increasing Curie temperature was established versus concentration of the component II.
4. The Mn-containing compound $Pb(Mn_{0,5}Nb_{0,5})O_3$ was investigated and well-known data on some solid solutions on its base were analyzed. It was concluded that this substance is an antiferroelectric with Curie temperature equal I40°C. Moreover in the case of the $(Bi_{0,5}Sr_{0,5})MnO_3$ solid solution with the perovskite-type structure the unit cell volume is decreased slightly to the certain temperature, evidently due to electrostriction which takes plase in ferro- and antiferroelectrics.
Above mentioned results allow us to make a definite conclusion that:
I. Jahn-Teller co-operative effect favours the origination of spontaneously polarized state in complex metal oxides with perovskite-type structure.
2. Cu-containing perovskites are ferroelectrics - ferroelastics with high Curie temperatures.
3. Mn-containing perovskites studied are antiferroelectrics-ferroelastics.

05.1-13 INVESTIGATION OF LOW TEMPERATURE CATION ORDERING ZrO_2-TiO_2-SnO_2 SOLID SOLUTIONS. by
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Zirconium titanate is the basis of a family of useful dielectric compositions, characterized by extremely low dielectric loss at microwave frequencies (Q > 10,000) and a unique composition dependence of the temperature coefficient of the dielectric constant (Tcκ).

Solid solution compositions in the system ZrO_2-TiO_2-SnO_2 are most commonly employed as microwave dielectrics, Tcκ being tuneable through the nature and degree of the tin substitution in the stoichiometric formula

$$Zr_xTi_ySn_zO4 \quad \text{where } x+y+z=2$$

The single phase region, lattice parameters and dielectric properties of these solid solutions as conventionally fired ceramics (1300-1350°C) were determined in early characterization studies (G. Wolfram and H. E. Gobel, Mat. Res. Bull., 1981, 16, 1455-63). It was later demonstrated that the high-low phase transition observed in undoped zirconium titanate was suppressed in the SnO_2-doped material, suggesting that the excellent dielectric properties of the solid solution compositions were characteristic of the high temperature phase (A. E. McHale and R. S. Roth, Comm. Amer. Ceram. Soc., 1983, 66, C18-C20).

Further work into the nature of the "transition" in zirconium titanate has shown it to be an unusual, continuous transformation coupling both structure and chemistry from the Zr:Ti ≈ 1:1 (random cations in α-PbO_2 structure) in the high temperature phase to Zr:Ti≈ 1:2 (ordered cations, fersmite-like structure) in the stable low temperature phase. Intermediate solid solutions are formed which show degrees of incommensurate cation ordering in the temperature range of the "transition" (1100-1200°C) and which, for kinetic reasons, persist at lower temperatures on cooling. The type of observed incommensurate ordering and its kinetic stability may be dependant on the nature of the ternary solid solution system (A. E. McHale and R. S. Roth, J. Amer. Ceram. Soc., 1986, 69, 827-32). Formation of the low temperature phase, $ZrTi_2O_6$, was possible only through the use of chemically homogeneous coprecipitated compositions.

We will present a reinvestigation of the system ZrO_2-TiO_2-SnO_2 in the temperature region of the phase transition, 1000-1300°C, using chemically prepared compositions to facilitate low temperature structural equilibration. Crystal structure data and cation ordering parameters will be correlated where possible with previously published dielectric property measurements for these compositions. The data will be used to quantify the structural role of tin in these solid solutions and to estimate the magnitude of the effect of cation ordering on the microwave dielectric properties.