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Ferroelectrically Active Sublattices and Phase Transitions in Perovskite Type Crystals

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Data which support the division of the ABO_3 perovskite type ferroelectrics and antiferroelectrics into 2 groups in terms of their ferroelectrically active sublattices (A or B) are given. The interconnection between the type of the ferroelectrically active sublattice in ABO_3 at the sequence of phase transitions and the character of dielectric properties has been demonstrated. The data obtained suggest an antiferroelectric mechanism of "puckering" transitions in perovskites. The dependence of Curie temperature on various factors is discussed.

§1. Introduction

There are fundamental problems in ferroelectricity. However, the key problem within the scope of the ferroelectricity is determination of possible types of ferroelectrically active (FA) sublattices and their number. The purpose of this paper is to present some basic ideas developed by the author in his studies on the subject.[1-5]

§2. Ferroelectrically Active Sublattices

Already in some early studies (see, for example, ref. 6) FE properties of $BaTiO_3$ (ABO_3) were connected with the geometrical loosness of its unit cell. It was concluded that Ti cations (B type) have some "freedom" in its cubic unit cell and are FA. Lately anomalous dielectric properties were found in $PbTiO_3$[7] and $PbZrO_3$[8,9] and it has been concluded that these sabstances are completely analogous to $BaTiO_3$ on their geometry. If the structural micromechanism of spontaneously polarized state (SPS) were identical in $BaTiO_3$ and $PbTiO_3$, then the phase diagrams of solid solutions of either of them would be expected to be similar. Yet on substitution of Zr for Ti in $BaTiO_3$ and $PbTiO_3$ the phase diagram of system $BaTiO_3$-$BaZrO_3$ (I)[10] exhibits distinct dissimilarity from that of the system $PbTiO_3$-$PbZrO_3$ (II).[11] This points clearly to the difference in structural micromechanism of SPS origination in $BaTiO_3$ and $PbTiO_3$. This conclusion combined with other observations allows a classification of FE and AFE perovskite compounds in terms of FA sublattice (A or B),[1] for more detail see Table I.

The validity of the above division of perovskites into two groups is supported by the experimental results obtained by other investigators[12-17] with the use of various techniques.

Publication[12] describes Mössbauer study of $BaTiO_3$ (I) and $PbZrO_3$ (II), doped with 1 at.% of radioactive $Sn^{119\,m}$. Among other things, data on so-called low temperature anharmonicity (or size disparity anharmonicity) caused by the geometrical loosness of the unit cell are obtained. It is concluded that the vibration anharmonicity of B sublattice exists in (I) but not in (II).

Authors[5] used X-ray technique to study the vibration anharmonicity of crystal lattices of some perovskites. They obtained the function $F(T)=\lambda^2/\sin^2\theta\cdot\ln I_T/I_{T_0}$ for each perovskite. All investigated perovskites were divided in the following two groups: 1) $BaTiO_3$, $KNbO_3$; 2) $PbTiO_3$, $SrTiO_3$, $PbZrO_3$ versus the character deviation of this function from a harmonic (linear) dependence.

X-ray study of the temperature dependences of the meansquare amplitudes $\langle\mu^2\rangle$ of the vibration of the atoms in $BaTiO_3$ and $SrTiO_3$ has been carried out too.[5,13] This investigation has shown the vibrations of Ti sublattice (B type) in $BaTiO_3$ and Sr sublattice in $SrTiO_3$ (A type) to be markedly anharmonic. The same is true for O sublattice in both cases. These results are in good agreement with data on $BaTiO_3$ reported in ref. 14.

According to ref. 15, $BaTiO_3$ and $KNbO_3$

Table I. Classification of ABO_3 perovskite ferroelectrics and antiferroelectrics in terms of ferroelectrically active sublattice (A or B).

FE, AFE, FIE	Ferroelectrically active sublattice	ABO_3	t*	T_c K	Distortion of the unit cell at 300 K
FE	B $(t > I)$	$RbTaO_3$	1.07	T_{decom}**	C
		$BaTiO_3$	1.03	393	T
		$KNbO_3$	1.00	708	M
	A $(t < 1)$	$KTaO_3$	1.00	13	C
		$PbTiO_3$	0.98	763	T
		$(K_{1/2}Bi_{1/2})TiO_3$	0.95	653	T
		$BiFeO_3$	0.92	1123	Rh
FE AFE		$SrTiO_3$	0.92	110	C
		$(Na_{1/2}Bi_{1/2})TiO_3$	0.90	593	Rh
AFE FIE		$PbZrO_3$	0.90	503	M
		$PbHfO_3$	0.90	488	M
		$NaNbO_3$	0.86	913	M
		$CdTiO_3$	0.86	>1450	M
		$CaTiO_3$	0.86	>1500	M

* $t=(R_{A(C.N.12)}+R_O)/\sqrt{2}\,(R_B+R_O)$

** A decomposition temperature of $RbTaO_3$ sinthesized under a high pressure.

*** C, T, Rh, M-cubic, tetragonal, rhombohedral, monoclinic, respectively.

both exhibit anisotropic overdamped soft modes in the cubic phase, whereas in $KTaO_3$, $PbTiO_3$ and $SrTiO_3$ these modes are underdamped and isotropic. The ESR data on a number of $ABO_3{:}Fe^{3+}$ perovskites[16)] are consistent with the above mentioned classification of perovskites. The all investigated perovskites are divided on the same 2 groups in dependence on the measured octahedral $^6S_{5/2}$ state splitting a of Fe^{3+} ions.

§3. Phase Transition Sequences and Dielectric Properties

It was mentioned above that the type of FA sublattice determines both the phase transition sequence and the character of dielectric properties (FE or AFE). Table I demonstrates that all perovskites having a FA sublattice of B type ($t>1$) are FE. These perovskites have as a rule 3 phase transitions: T→PM→Rh is observed as the temperature decreases. Structural analysis shows that the FA cations are shifted according to the sequence: $C_4 \rightarrow C_2 \rightarrow C_3$.

Perovskites having a FA sublattice of A type ($t<1$) exhibit either FE properties (in case of T or Rh distortions of their unit cells) or AFE properties (monoclinic distortion). Here the sequence of the shifts is somewhat different, namely: $C_4 \rightarrow C_3 \rightarrow C_2$ and involves the successive transitions T→Rh→PM as the temperature decreases.

The same sequence ($C_4 \rightarrow C_3 \rightarrow C_2$) is observed for perovskite compounds and solid solutions with $t<1$ when t decreases. There is no distinct boundary between t values for FE compounds and these for AFE compounds with $t<1$. $SrTiO_3$ ($t=0.92$) and $Na_{1/2}Bi_{1/2}TiO_3$ ($t=0.90$) can exhibit either FE or AFE properties depending on temperature. It is worth to note that $PbZrO_3$ ($t=0.90$), which was earlier thought of as a "model" AFE compound, has actually the t-values characteristic of the intermediate region. This accounts for the fact that high electric fields can induce FE properties in this compound. Of course, one can't expect the induced AFE-FE transitions of perovskites having smaller t values (such as $CaTiO_3$ with $t=0.86$). However, our recent results seem to suggest an AFE mechanism for "puckering" transitions.[4, 5)]

For example, it has been assumed that $CdTiO_3$ is SPS only below 50 K, but our investigations[18)] show that the substitution of Sr ions for a small fraction of Cd ions produces a distinct peak of ε ($\varepsilon_{\max}$) at elevated temperatures (383 K), with the characteristic of ferrielectrics, FIE (such as dielectric hysteresis loops, pyroeffect etc.) being observed below $T_{\varepsilon_{\max}}$. The drastic increase in $T_{\varepsilon_{\max}}$ can be understood if one assumes that at $T > 50$ K the AFE properties are inherent in the "puckered" crystal structure of $CdTiO_3$ and that the influence of small additions of Sr reduced mainly to the transition of AFE state to FIE one below 383 K. The results obtained with the $(Na_{1/2}Bi_{1/2})TiO_3$ (I)–$CdTiO_3$ (II) system are quite interesting.[5,19)] At first $T_{\varepsilon_{\max}}$ drops to nearly 270 K as the content of (II) increases. Then $T_{\varepsilon_{\max}}$ starts increasing and reaches 475 K at approximately 60 mol.% of (II). Again, this can be understood if T_c of the component (II) is assumed to be high (>770 K) and the component itself is AFE at $T > 50$ K (with little or no dielectric anomalies).

It has been reported by several investigators that $SrTiO_3$ undergoes a "puckering" structural transformation at 110K. At the same time our investigation of the system $KTaO_3$ (I)–$SrTiO_3$ (II) shows that T_c increases over the range 12.5–110 K.[20)] These data are in good agreement with those reported by Little,[21)] who observed a monotonous decrease in the unit cell volume of $SrTiO_3$ over 10–110 K. This phenomenon is undoubtedly caused by electrostriction characteristic of both FE and AFE states.

In this context, two more facts merit consideration. First, perovskites with "puckered" crystal structures, perovskite mineral $CaTiO_3$ itself among them, have superstructures owing to the antiparallel shift of ions of the same sort. Second, high inner electric fields affect all ions in $CaTiO_3$, with the exception of Ti-ions[22)] which occupy center-symmetric positions. And the existing electric dipoles form a AFE configuration.

All the above mentioned facts lead us to conclude that the "puckering" transitions in perovskites are essentially AFE in nature.

§4. Curie Temperature

In several reports[23-26)] the drastic strengthening of covalency of the bond B-O in ABO_3 is believed to be the driving force of FE transitions. However our precise Mössbauer study of $BaTiO_3:Sn^{119\,m}$ did not lead to detecting any noticeable change in the chemical shift at T_c.[12)] Therefore, there is no particular reason why T_c should be connected with any change in the nature of B-O bond. This conclusion agrees well with that made in a theoretical work,[27)] the author of which does not consider it possible to explain the origination of SPS in perovskites on the basis of the covalent admixture model. The data available in literature concern also the factors affecting T_c (see ref. 21).

In an earlier publication[2)] we suggested a new approach to the problem of T_c. As is stated above, the successive phase transitions in ABO_3, including that at T_c, is determined by the type of corresponding FA-sublattice or, to be more exact, by the FA-sublattice energy connected mainly with dipole-dipole interaction. In case of a tetragonal crystal the product $P_{\alpha i} \cdot E_i$ can be used as an approximate estimation of this energy ($P_{\alpha i}$-electronic dipole moment of the FA-cation-A or B; E_i-strength of the inner field affecting the i-cation, $i =$ A, B). The corresponding values of $P_{\alpha i}$ and E_i were obtained for a number of FE and AFE compounds. An influence of different parameters on $P_{\alpha i}$ and E_i have been studied (see, for instance, data on $BaTiO_3$[28,29)]). In calculation we made use of the electrostatic model of point dipoles and point charges similar to that employed by other investigators.[30,31)] Its efficiency is proved in particular by the similarity of the results obtained on the basis of a "shell" model.[32)]

Both the theoretical estimation and the treatment of experimental data enabled us to establish the following schematic dependence for ABO_3 compounds (see also refs. 2 and 3)

$$T_c \sim A_i, \alpha_i, e_i, \frac{I}{V}, N_{\mathrm{upe}}, N_{\mathrm{J-T}} \cdot \, . \, . \; ;$$

where: A_i–degree of the FA sublattice vibration anharmonicity, which depends itself on the geometrical looseness of FA polyhedron (BO_6 or AO_{12}), degree of the covalency of B-O or A-O bond etc.; α_i and e_i—the electronic polarizability and the charge on a FA cation, respectively, V—volume of the cubic unit cell, N_{upe}—the number of cations with an unshared pair of electrons (Pb^{2+}, Bi^{3+}, . . .), $N_{\mathrm{J-T}}$—the number of Jahn-Teller's cations (Cu^{2+}, Mn^{3+}, . . .), which also favour the origination of the SPS.[33, 34]

The above expression lists the most important factors determining T_c. The exact form of it has not yet been established. This general dependence of T_c from different factors can be regarded as basically new though it has observed some results obtained by other investigators (see ref. 2).

§5. Complex Perovskite Compounds

In the case of the $(A^{I}_{2-x}A^{II}_{x})(B^{I}_{2-y}B^{II}_{y})O_6$ perovskites with the orderly arranged B^{I} and B^{II} cations, the FA sublattice is always B type (B^{I} or B^{II}) and constructed of small cations of high valency.[3] It is quite clear that their T_c will depend on the same factors and in the same manner as in the case of a simple perovskite (see refs. 4, 35). When a unit cell is subject to T or Rh distortion, FE properties are observed. When it is subject to M distortion, AFE properties are observed. The complex perovskites can exhibit either FE or AFE properties even though their unit cells retain essentially cubic form below T_c.[5, 36]

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