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Preparation and Properties of Some Novel Perovskite-Type Ferroelectrics

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A number of solid solutions in $PbTiO_3$ and $BaTiO_3$ of the types

$$PbNb_{2/3-x}Ti_{x/2}W_{x/2}Mg_{1/3}O_3 \quad \text{and} \quad BaFe_xW_{x/2}Ti_{1-3/2x}O_3$$

were prepared and characterized as to structural and dielectric parameters. Substitution of smaller ions, which diminished cell constants, invariably resulted in reduction of the Curie temperature. The importance of proper valence compensation in developing high dielectric constant materials was demonstrated.

Introduction

After the original discovery (*1*) of the ferroelectric properties of the perovskite-type compound $BaTiO_3$ (point group P4/mmm for the polar, Pm3m for the nonpolar phase) in 1946, there have been intensive studies of the dielectric behavior of other ABO_3 oxides. The ferroelectric properties of $PbTiO_3$, for instance, were first described by Shirane *et al.* (*2*); and subsequently other perovskite-type compounds such as $KNbO_3$ (*3*), $NaNbO_3$ (*4*), $CdTiO_3$ (*5*) and $LiNbO_3$ (*6*) were also found to be ferroelectric. Of these materials, $LiNbO_3$ has recently achieved particular prominence in the form of massive single crystals which are used as modulators to generate the second harmonic of laser beams. After the dielectric characterization of simple ABO_3 compositions, numerous studies were carried out on substitutions of either the A or the B ion in the $BaTiO_3$ or $PbTiO_3$. Typical examples would be the $Ba_{1-x}Sr_xTiO_3$, $BaTi_{1-x}Sn_xO_3$ or $Pb_{1-x}Ca_xTiO_3$ systems. These types of substitutions generally decrease the lattice parameters of the base composition and show an associated drop of the Curie temperature. This was originally taken as evidence for the hypothesis that ferroelectricity is due to the "rattling" of Ti ions in the octahedral oxygen cage of pure $BaTiO_3$ and $PbTiO_3$, and shrinking of the cell volume would tighten the Ti–oxygen dipoles and therefore reduce the Curie temperature. Most of these substitutions are still being used for the practical purpose of increasing the dielectric constant by bringing the Curie temperature into the vicinity of room temperature; the substitution level is generally only a few mole percent. More substantial substitutions, particularly in $PbTiO_3$, have been carried out by Bokov (*7*) and Smolenski (*8*) and resulted in such compounds as $PbZn_{1/3}Ta_{2/3}O_3$, $PbYb_{1/2}Nb_{1/2}O_3$ and $PbMg_{1/3}Nb_{2/3}O_3$. These compounds are all ferroelectric and have Curie temperatures far below the 490C reported for pure $PbTiO_3$. The structural evidence for $PbMg_{1/3}Nb_{2/3}O_3$ points toward a random distribution of Mg^{+2} and Nb^{+5} without ordering and the subsequent formation of a superstructure. More recently, Bonner *et al.* (*9*) succeeded in preparing large single crystals of $Pb_3MgNb_2O_9$ ($PbMg_{1/3}Nb_{2/3}O_3$) and measuring the quadratic electro-optic coefficients. They also used this compound as a modulator for the 1.06 μ emission from a Nd:YAG laser. Since WO_3 itself (*10*) is known to be a ferroelectric and since the highly-polarizable characteristics of Ti^{+4} in an octahedral oxygen environment had already been established, it was of interest to attempt a IV/VI substitution for Nb^{+5} in $PbMg_{1/3}Nb_{2/3}O_3$ and study the dielectric properties of the resulting $PbMg_{1/3}W_{1/3}Ti_{1/3}O_3$ compound as well as of related compositions. Similar studies on the

$$PbMg_{1/3}W_{1/3}O_3\text{–}PbTiO_3$$

system were carried out by Krainik (*11*).

Sample Preparation and Results

All compounds described in this paper were prepared by the standard solid state techniques of prereacting the stoichiometric constituents at an intermediate temperature of 800–1000C, ball-milling in agate mills, pressing into disks, and final firing at 1000–1200C. The chemicals used were of the best commercially available purity and were not given any further purification treatments. In the case of PbO-containing compositions, the final firing of ceramic disks was carried out in a PbO-atmosphere established by maintaining the samples in a covered crucible above a PbO melt. This eliminated any loss of PbO from the samples.

Although it is recognized that

$$PbMg_{1/3}Ti_{1/3}W_{1/3}O_3$$

is only one specific example of the more general series $PbTi_{1-x}Mg_{x/2}W_{x/2}O_3$, this specific composition was studied first. In its polar ferroelectric room temperature state, $Pb(MgTiW)_{1/3}O_3$ crystallizes in the tetragonally distorted perovskite structure with the following parameters:

$$a_t = 3.912\ \text{Å}$$
$$c_t = 3.994\ \text{Å}$$
$$c/a = 1.02$$
$$\text{Cell volume} = 61.123\ \text{Å}^3$$
$$\text{X-ray density} = 9.25_2\ \text{g}\cdot\text{ml}^{-1}$$

The c/a ratio places this compound intermediate to $BaTiO_3$ (1.01) and $PbTiO_3$ (1.06). The dielectric constant at 1 kHz of a ceramic disk of >80% density was 1173 with an associated dissipation factor of 0.2%.

The dielectric constant vs. temperature curve shows a peak at 120C, which is taken as the Curie temperature. Using Ag as electrodes, ferroelectricity of the compound was further demonstrated by observing a rather square E-D loop on an oscilloscope tracer. The peak-to-peak voltage per 18 mils of sample was 2500 V, such that the saturation polarization P_s of 2.45 μ coulomb/cm^2 is probably not a truly saturated value. P_r was 1.31 μ coulomb/cm^2. Capacitance change and dissipation factor for a printed capacitor as a function of temperature are shown in Figs. 1 and 2, respectively. For comparison, the equivalent behavior of $BaTiO_3$ is also included in the plot. The maximum dielectric constant observed for this printed form of $Pb(MgWTi)_{1/3}O_3$ was only about 400, indicating a significant loss in dielectric polarizability over the ceramic disk. This loss is attributed to a partial interaction with the glass used in printing the capacitor on an Al_2O_3 substrate. Table I summarizes the results obtained on ceramic disks with other compositions of the $PbTi_{1-x}Mg_{x/2}W_{x/2}O_3$ system.

TABLE I

Dielectric Constants vs. x for the $PbTi_{1-x}Mg_{x/2}W_{x/2}O_3$ System

x	Composition	Dielectric Const. k, at 300K
0.2	$PbTi_{0.80}Mg_{0.10}W_{0.10}O_3$	180
0.4	$PbTi_{0.60}Mg_{0.20}W_{0.20}O_3$	442
0.6	$PbTi_{0.40}Mg_{0.30}W_{0.30}O_3$	841
0.8	$PbTi_{0.20}Mg_{0.40}W_{0.40}O_3$	558
1.0	$PbMg_{0.5}W_{0.5}O_3$	173

These data indicate a maximum dielectric constant in the vicinity of equal distribution of ions over the B-site. This is in good agreement with Krainik's data who observed the highest k value for 40 mole percent $PbTiO_3$ in $PbMg_{1/2}W_{1/2}O_3$. A similar study

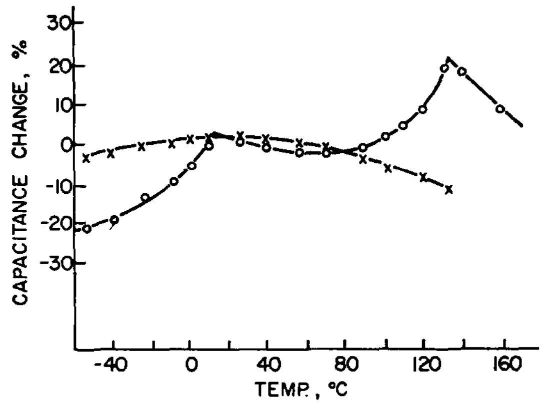

Fig. 1. Capacitance Change vs. Ambient Temperature for $BaTiO_3$ (o) and $PbTi_{1/3}Mg_{1/3}W_{1/3}O_3$ (×).

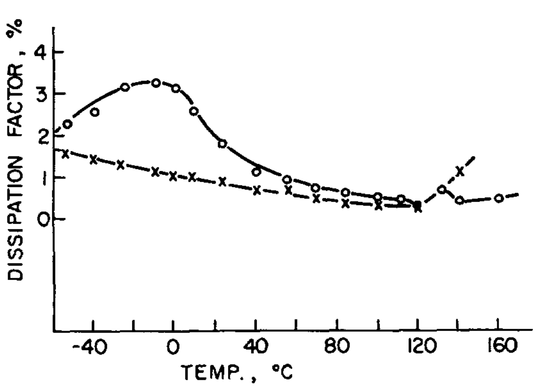

Fig. 2. Dissipation Factor (at 1 kHz) vs. Ambient Temperature for $BaTiO_3$ (o) and $PbTi_{1/3}Mg_{1/3}W_{1/3}O_3$ (×).

TABLE II

LATTICE PARAMETERS AND DIELECTRIC CONSTANTS OF THE $PbNb_{2/3-x}Ti_{x/2}W_{x/2}Mg_{1/3}O_3$ SYSTEM

x	a, (Å)	c, (Å)	c/a	Dielectric Const. k at 300K
0.1	4.038	—	—	1860
0.2	4.033	—	—	1920
0.3	4.023	—	—	3370
0.4	4.010	4.013	1.0006	1800
0.5	3.992	4.000	1.0020	1750
0.6	3.989	3.998	1.0022	1837
0.62	3.986	3.996	1.0025	1672
0.66	3.982	3.994	1.0030	1124

was carried out for the $PbZr_{1-x}Mg_{x/2}W_{x/2}O_3$ system but the dielectric values were found generally lower.

Attempts to grow single crystals of

$$Pb(MgTiW)_{1/3}O_3$$

by the Czochralski technique failed; the composition melts incongruently at 1100C.

In connection with this work, it was of interest to see what a partial substitution of the Ti^{+4}/W^{+6} combination in $Pb(MgTiW)_{1/3}O_3$ would do. This resulted in an investigation of the system $PbNb_{2/3-x}Ti_{x/2}Mg_{1/3}O_3$. The observed Curie temperature for various compositions are given in Fig. 3 and the structural parameters are summarized in Table II.

Although the composition with $x = 0.3$ is listed as cubic in the table, it was in fact very slightly distorted and ferroelectric with a Curie temperature near room temperature. This would, of course, explain the high dielectric constant which has been measured near the peak of k vs. T. The extrapolated value of the Curie temperature for $x = 0$ ($PbMg_{1/3}Nb_{2/3}O_3$) would give a value of −25C (in fair agreement with Bokov's (l.c.) value of −10C) and the extrapolated parameter of 4.043 Å is in good agreement with the 4.041 Å parameter given by Ismailzade (*12*). Further substitutional studies were concerned with such systems as $Pb_{1-x}Ba_x(MgTiW)_{1/3}O_3$,

$$Pb_{1-x}Y_xMg_{1/3}Ti_{1/3}W_{1/3-x}Nb_xO_3$$

and $Pb_{1-x}K_xMg_{1/3}Ti_{1/3}W_{1/3-x}Nb_xO_3$. None of these exhibited interesting structural or dielectric behavior; therefore, the data are not discussed in detail.

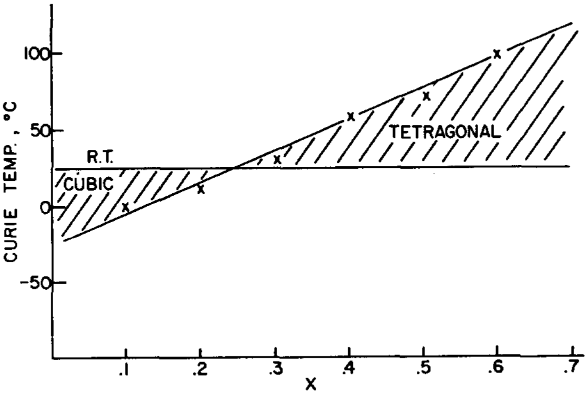

FIG. 3. Curie Temperature vs. Composition for the System $PbNb_{2/3-x}Ti_{x/2}W_{x/2}Mg_{1/3}O_3$.

Of the III/VI substituted compositions based on $PbTiO_3$, the compound $PbFe_{2/3}W_{1/3}O_3$ is of particular interest since it contains Fe^{+3}. It has been studied by Agranovskaya (*13*) and a Curie temperature of −90C is reported. Solid solutions with $PbTiO_3$ of the type $PbFe_xW_{x/2}Ti_{1-3/2x}O_3$ constituted another interesting system for study of dielectric behavior as a function of composition. The results are summarized in Table III. With increasing substitutional level, the cell volume as well as the c/a ratio shrink, resulting in a concordant drop of Curie temperature as well as the measured room temperature dielectric constant. The k values for $x = 0.4$ and 0.5 are rather meaningless since they were associated with excessive dissipation factors (>10%). The significantly increased electrical conductivity of these samples (last column) readily accounts for this excessive loss factor. The electrical resistivities of a few selected examples from this series over a limited temperature range are shown in Fig. 4. All exhibit semiconducting behavior with a strong negative temperature coefficient, which increases with decreasing substitutional level. It appears that the electrical resistivity of all compositions converge into a common value of about 10 ohm-cm at 700–800C. Again, similar equivalent substitutions with Al^{+3} or Ga^{+3} in place of Fe^{+3} did not give any noteworthy results.

The $BaFe_xW_{x/2}Ti_{1-3/2x}O_3$ system is of interest, particularly since one end-member of this series of solid solutions, $BaFe_{2/3}W_{1/3}O_3$ (*14*), has the hexagonal barium titanate structure, and one could therefore expect two structural transitions as the composition was systematically varied. From the data in Table IV, the tetragonal, ferroelectric region is limited to the rather narrow composition range of $x = 0$–0.03. For this reason, $BaFe_{2/3}W_{1/3}O_3$ is a

TABLE III

CURIE TEMPERATURE, DIELECTRIC CONSTANT

x	Composition	a, (Å)	c, (Å)	c/a	T_c (C)	k	Resistivity, ohm-cm, 300K
0	$PbTiO_3$	3.897	4.144	1.063	490	—	—
0.01	$PbFe_{0.01}W_{0.005}Ti_{0.985}O_3$	3.898	4.127	1.058	480	130	3.0×10^{12}
0.05	$PbFe_{0.05}W_{0.025}Ti_{0.925}O_3$	3.900	4.071	1.044	400	162	6.0×10^{12}
0.10	$PbFe_{0.10}W_{0.05}Ti_{0.85}O_3$	3.903	4.062	1.040	360	174	1.0×10^{12}
0.20	$PbFe_{0.20}W_{0.10}Ti_{0.70}O_3$	3.910	4.052	1.036	200	337	2.0×10^{12}
0.30	$PbFe_{0.3}W_{0.15}Ti_{0.55}O_3$	3.960	—	1.000	~RT	543	5.0×10^9
0.40	$PbFe_{0.4}W_{0.2}Ti_{0.4}O_3$	3.974	—	—	<RT	1611	3.0×10^6
0.50	$PbFe_{0.5}W_{0.25}Ti_{0.25}O_3$	3.985	—	—	<RT	5300	4.5×10^5

highly effective solid solution component for reducing the Curie temperature of $BaTiO_3$. This is best illustrated in Fig. 5 where it is compared to two other commonly used modifiers for $BaTiO_3$. While almost 30 mole percent of $SrTiO_3$ is required to suppress T_C to 300K, 3 mole percent of

$$BaFe_{2/3}W_{1/3}O_3$$

will have essentially the same effect.

Ferric ion by itself has been used as an additive to modify the dielectric properties of $BaTiO_3$. Without simultaneous addition of other ions, valence compensation must occur by generation of oxygen vacancies in the system, $BaFe_x^{+3}Ti_{1-x}^{+4}O_{3-x/2}\varnothing_{x/2}$. This type of valence compensation, however, appears detrimental to the dielectric properties of $BaTiO_3$, as shown in Table V, which also compares the properties of the fully coordinated, properly

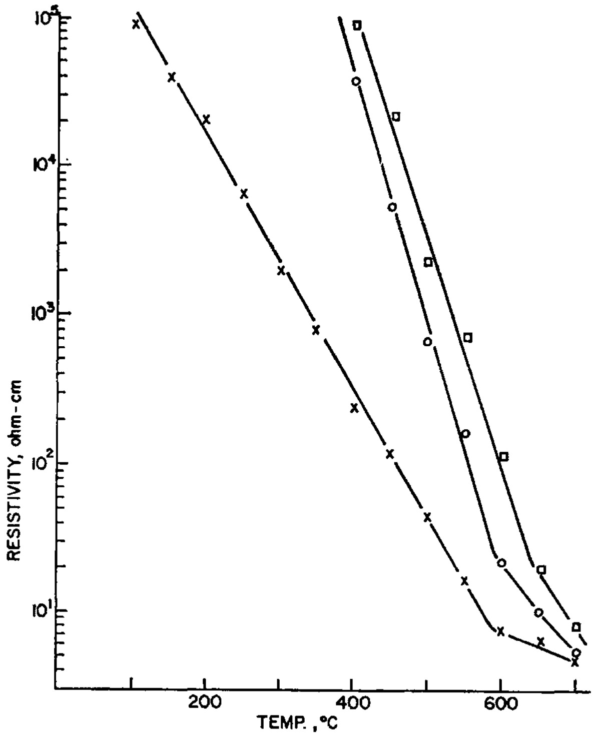

FIG. 4. Electrical Resistivity as a Function of Temperature for $PbFe_{0.5}Ti_{0.25}W_{0.25}O_3$ (×), $PbFe_{0.2}Ti_{0.7}W_{0.1}O_3$ (o), and $PbFe_{0.1}Ti_{0.85}W_{0.05}O_3$ (□).

TABLE IV

STRUCTURAL AND DIELECTRIC PARAMETERS OF THE $BaFe_xW_{x/2}Ti_{1-3/2x}O_3$ SYSTEM

x	Composition	a, (Å)	c, (Å)	c/a	Curie temp. (C)
0	$BaTiO_3$	3.986	4.026	1.010	120
0.01	$BaFe_{0.01}W_{0.005}Ti_{0.985}O_3$	3.998	4.030	1.008	70
0.03	$BaFe_{0.03}W_{0.015}Ti_{0.955}O_3$	4.000	4.030	1.005	30
0.04	$BaFe_{0.04}W_{0.02}Ti_{0.94}O_3$	4.0057	—	1.000	<RT
0.05	$BaFe_{0.05}W_{0.025}Ti_{0.925}O_3$	4.0065	—	1.000	−40
0.10	$BaFe_{0.10}W_{0.05}Ti_{0.85}O_3$	4.0087	—	1.000	−80
0.20	$BaFe_{0.20}W_{0.10}Ti_{0.70}O_3$	4.0135	—	1.000	<−80
0.30	$BaFe_{0.30}W_{0.15}Ti_{0.55}O_3$	4.0183	—	1.000	
0.40	$BaFe_{0.40}W_{0.20}Ti_{0.40}O_3$	5.763	13.994	2.428	
0.50	$BaFe_{0.5}W_{0.25}Ti_{0.25}O_3$	5.948	13.820	2.323	

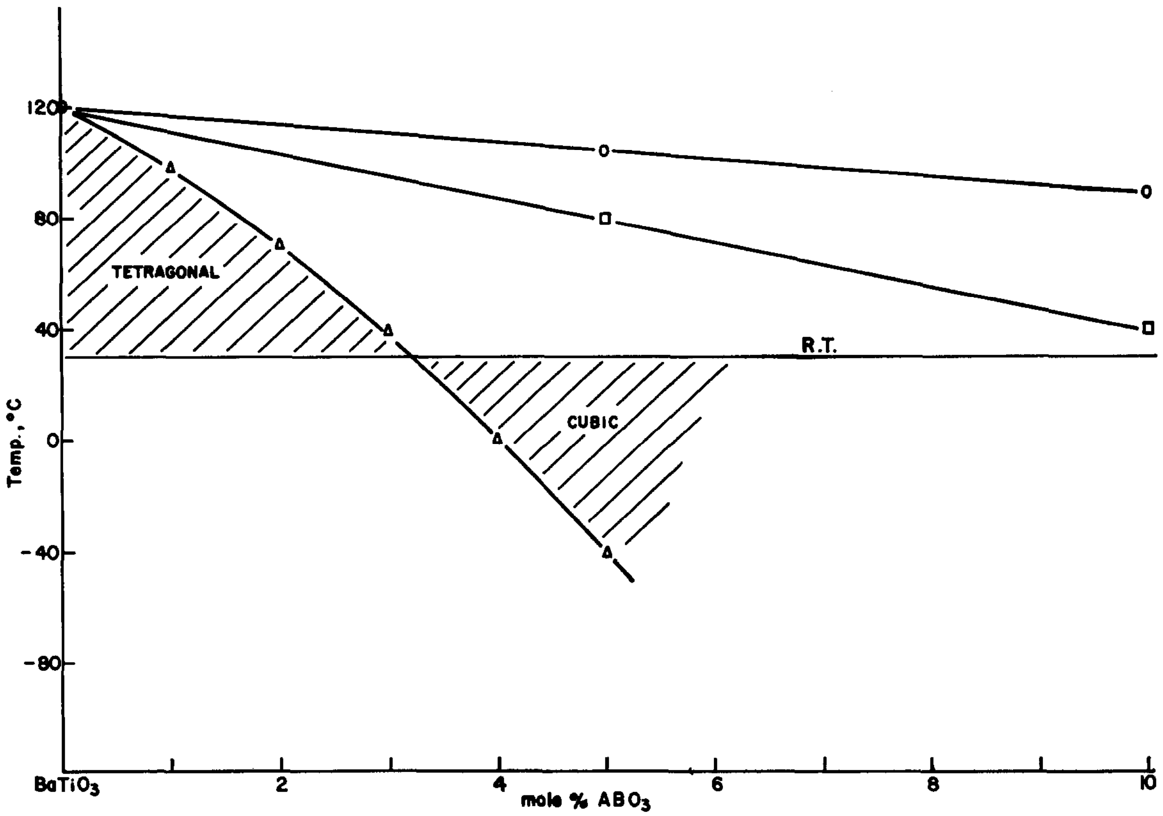

FIG. 5. Influence on the Curie Temperature of Various ABO_3 Compounds in Solid Solution with $BaTiO_3$. $BaSnO_3$ (□), $SrTiO_3$ (o), $BaFe_{2/3}W_{1/3}O_3$ (△).

TABLE V

COMPARISON OF DIELECTRIC PROPERTIES FOR VACANCY TUNGSTEN AND NIOBIUM COMPENSATED Fe^{+3} SUBSTITUTIONS IN $BaTiO_3$

	$BaFe_xTi_{1-x}O_{3-x/2}\varnothing_{x/2}$		$BaFe_xTi_{1-2x}Nb_xO_3$		$BaFe_xTi_{1-3/2x}W_{x/2}O_3$	
x	Dielectric Constant, *k*	Dissipation factor, *dF*	Dielectric Constant, *k*	Dissipation factor, *dF*	Dielectric Constant, *k*	Dissipation factor, *dF*
0	1316	1.7	1316	1.7	1316	1.7
0.005	262	3.5	1648	1.1	1619	1.0
0.01	195	4.0	1875	2.5	1910	1.0
0.015	122	4.5	2155	4.1	2413	1.5
0.02	80.4	5.0	2587	4.2	2616	1.6
0.025	69.2	6.0	2947	8.9	2908	1.7
0.030	61.9	7.0	3446	9.5	3241	1.7
0.035	60.0	11.5	3390	15.0	2531	4.0
0.04	45.0	15.0	3199	27.0	1994	6.9

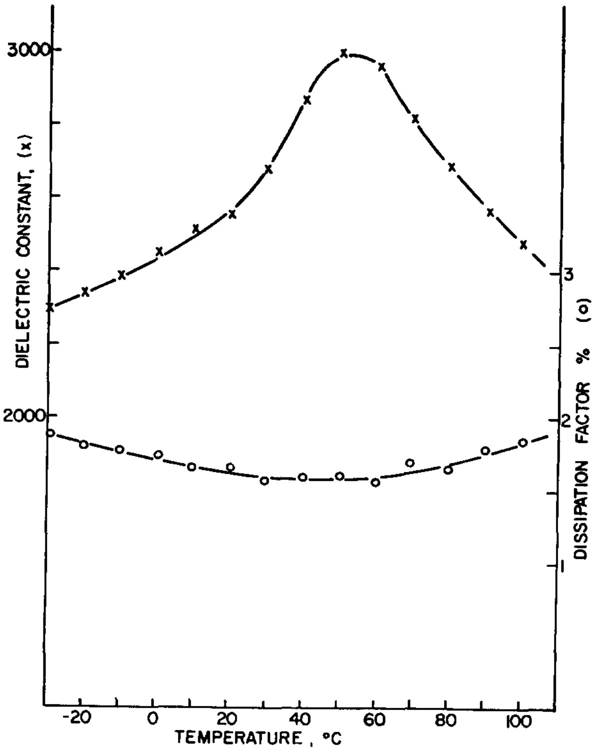

FIG. 6. Dielectric Constant (×) and Dissipation Factor (o) as a Function of Temperature for $BaFe_{0.20}W_{0.01}Ti_{0.97}O_3$.

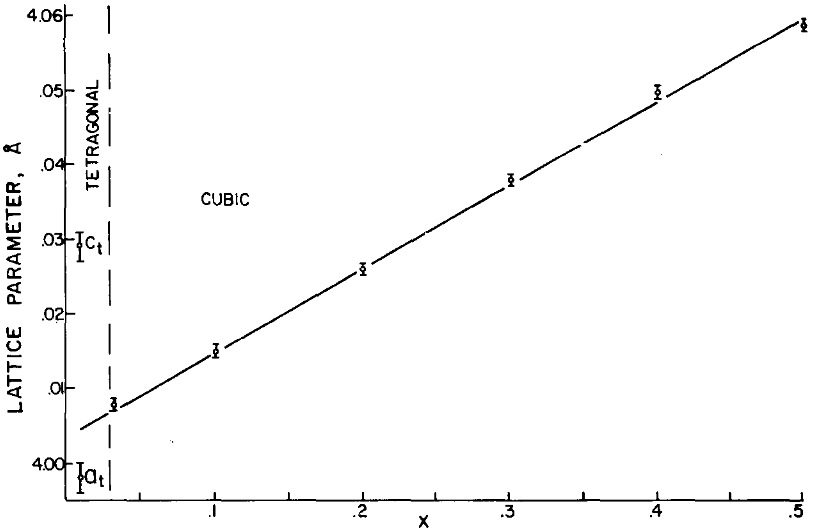

FIG. 7. Lattice Parameters as a Function of Composition for the $BaNb_xFe_xTi_{1-2x}O_3$ System.

compensated compounds prepared under identical conditions.

These data clearly demonstrate the importance of valence compensation, since it is evident that the addition of Fe^{+3} to $BaTiO_3$ without such secondary additives decreases rather than increases k. Figure 6 shows the dielectric constant and the dissipation factor for a ceramic disk of the composition with $x = 0.02$.

In a final study of solid solutions with $BaTiO_3$, the $BaFe_xNb_xTi_{1-2x}O_3$ system was investigated. Since $BaNb_{1/2}Fe_{1/2}O_3$ (*15*) is an undistorted cubic perovskite, a less complicated structural situation could be expected, and indeed only a tetragonal/cubic transition was found, as shown in Fig. 7. In the cubic region, true Vegard's law behavior without deviation from a straight line was found. The dielectric behavior was similar, but not superior, to that of the $BaFe_xTi_{1-3/2x}W_{x/2}O_3$ system, as can be seen from the data in Table V. Dissipation factors in particular were worse than for the equivalent W^{+6} compensated system.

Summary

Study of a number of solid solutions of complex perovskite-type compositions with $PbTiO_3$ and $BaTiO_3$ has demonstrated that substituents with generally smaller ionic radii than the host ion can effectively lower the Curie temperature of these two ferroelectrics. Lowering of Curie temperature was invariably associated with a reduction of the lattice parameters due to the indicated size differences. Knowledge of the dependence of T_C on composition permits the custom synthesis of dielectrics with predictable properties, within the limits imposed by the behavior of the unsubstituted perovskites.

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References

1. A. VON HIPPEL, R. G. BRECKENRIDGE, F. G. CHESLEY, AND L. TISZA, *Ind. Eng. Chem.* **38**, 1097 (1946).
2. G. SHIRANE AND K. SUZUKI, *J. Phys. Soc. Japan* **6**, 265 (1951).
3. B. T. MATHIAS, *Phys. Rev.* **75**, 1771 (1949).
4. B. T. MATHIAS AND J. P. REMEIKA, *Phys. Rev.* **82**, 727 (1951).
5. G. A. SMOLENSKI, *Doklady Akad. Nauk. S.S.S.R.* **70**, 405 (1950).
6. K. NASSAU, H. J. LEVINSTEIN, AND G. M. LOIACONO, *J. Phys. Chem. Solids* **27**, 983 (1966).
7. V. A. BOKOV AND I. E. MYLNIKOVA, *Sov. Phys. Solid State* **2**, 2428 (1961).
8. G. A. SMOLENSKI, A. I. AGRANOVSKAYA, S. N. POPOV, AND V. A. ISUPOV, *Sov. Phys. Tech. Phys.* **3**, 1981 (1958).
9. W. A. BONNER, E. F. DEARBORN, J. E. GEUSIC, H. M. MARCOS, AND L. G. VAN UITERT, *Appl. Phys. Letters* **10**, 163 (1967).
10. B. T. MATHIAS, *Phys. Rev.* **76**, 430 (1949).
11. N. N. KRAINIK AND A. I. AGRANOVSKAYA, *Sov. Phys. Solid State* **2**, (1) 63 (1960).
12. I. G. ISMAILZADE, *Sov. Phys. Cryst.* **5**, 292 (1960).
13. A. I. AGRANOVSKAYA, *Bull. Acad. Sci. USSR, Phys. Ser.* **24**, 1271 (1960).
14. G. BLASSE, *J. Inorg. Nucl. Chem.* **27** (1965).
15. F. GALASSO AND J. PYLE, *J. Am. Chem. Soc.* **81**, 820 (1959)