SOVIET PHYSICS JETP VOLUME 21, NUMBER 5 NOVEMBER, 1965

NEW MAGNETIC FERROELECTRICS

Yu. E. ROGINSKAYA, Yu. N. VENEVTSEV, and G. S. ZHDANOV

L. Ya. Karpov Physico-chemical Institute

Submitted to JETP editor November 24, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 48, 1224-1232 (May, 1965)

Ten new perovskite compounds of complex composition were synthesized and their electric and magnetic properties studied. In certain temperature ranges, six of the compounds exhibited antiferromagnetic or ferrimagnetic properties combined with ferroelectric or antiferroelectric properties. In the remaining four compounds, ferroelectric and antiferroelectric properties coexisted with paramagnetic properties. An investigation of these magnetic ferroelectrics yielded data indicating an interrelationship of their electric and magnetic dipole structures.

1. INTRODUCTION

THE ability to prepare complex perovskites of the composition $A(B'B'')O_3$ makes it much easier to obtain magnetic ferroelectrics, i.e., substances combining the properties of ferroelectrics and magnetic materials. In such perovskites there are, in principle, considerable opportunities to increase the content of paramagnetic B ions at the octahedral sites by varying their composition and to achieve finally the appearance of the magnetic dipole structure. It is also known that the presence of easily polarized ions of type A (Pb^{2+}, Bi^{3+}, etc.) favors the appearance of the electric dipole structure.

In the present study, a series of new lead-bearing perovskites was synthesized and their properties were investigated. A brief communication about the preparation of these and several other complex perovskites was published earlier.[1] In the present paper, the emphasis is on the results of an investigation of their properties.

2. CONDITIONS OF PREPARATION OF THE SAMPLES AND THE METHOD OF INVESTIGATION

The compounds were prepared by the ceramic method. The initial substances were PbO, $MnCO_3$, Mn_2O_3, Co_2O_3, Fe_2O_3, $CdCO_3$, and Nb_2O_5 of analytic purity grade, MnO_2, WO_3 (very pure), W and Re (spectroscopically pure). ReO_3 was obtained from Re_2O_7 by the method described in[2]. Re_2O_7 was prepared by dissolving metallic Re in concentrated HNO_3, forming the acid $HReO_4$, and subsequently decomposing it in air. W^{5+} and Re^{5+} were obtained in the synthesis of the corresponding perovskite compounds using the method described in[3,4]. To retain the valence of the transition metal ions in the synthesized compounds, the firing was carried out in an appropriate atmosphere. The temperatures and atmospheres in both firings are listed in the table (T_{mo} and T_{eo} are, respectively, the temperatures of magnetic and electric ordering).

An x-ray diffraction phase analysis was carried out after each firing, in cameras 57.3 mm in diameter, using Cu radiation. The nature of the distortion and the parameters of the perovskite cells were determined using x-ray diffraction patterns obtained in RKU-114 cameras using Cr and Fe radiation and the method described in[9].

The temperature dependence of the permittivity was investigated in the temperature range from −180 to +400°C using a type MPP-300 bridge at 200 kc. The high-temperature investigations were carried out on samples whose conductivity did not exceed $10^{-6}\ \Omega^{-1} \cdot cm^{-1}$ at 20°C; when the conductivity rose with temperature to $10^{-4}\ \Omega^{-1} \cdot cm^{-1}$, the measurements were stopped. The determination of the phase-transition points of the compounds with higher conductivities (such as the compounds 2, 3, and 11 listed in the table) was carried out by x-ray exposure at high temperatures using a type URS-50 IM ionization apparatus. The temperature dependence of the magnetic susceptibility of the compounds 1—9 was determined in the temperature range −175—400°C using the method described in[10].

3. RESULTS OF THE INVESTIGATIONS AND DISCUSSION

All the compounds listed in the table have the perovskite structure and are unary (single-phase)

Some properties of the new perovskites

No.	Composition	Preparation conditions	Factor t**	Unit cell parameters***	Conductivity at 20°C, $\Omega^{-1}\cdot cm^{-1}$	T_{mo}, °C	T_{eo}, °C	Ferroelectric and magnetic properties
1	$PbMn_{2/3}W_{1/3}O_3$	700, 750, N_2	0,96	$a = c = 4.098$ Å, $b = 4,014$ Å, $\beta = 90°23'$	$2\cdot10^{-9}$	—70	200	afe + afm
2	$Pb_2Mn^{+2}Re^{+6}O_6$	630, 680, vacuum	0,94	$a = c = 4.043$ Å, $b = 4.012$ Å, $\beta = 90°33'$	$1\cdot10^{-3}$	—170	120	afe + fim
3	$Pb_2Mn^{+3}Re^{+5}O_6$		—	$a = c = 4,039$ Å, $b = 4,004$ Å, $\beta = 90°49'$	$1\cdot10^{-3}$	—150	95	afe + fim
4	Pb_2CoNbO_6	730, 780, O_2	0,98	$a_{cub} = 8.084$ Å	$1\cdot10^{-7}$	—60	11	fe + afm
5	$PbMn_{1/2}Nb_{1/2}O_3$	780, 830, N_2	0,97	$a_{pseudocub} = 4.004$ Å	$8\cdot10^{-7}$	—	~20	fe + fm
6	$Pb_2Fe^{+3}W^{+5}O_6$		—	$a_{cub} = 8,030$ Å	$5\cdot10^{-5}$	—	—	—
7	$Pb_2Mn^{+2}W^{+6}O_6$		0,92	$a = c = 4.063$ Å, $b = 4,033$ Å, $\beta = 90°12'$	$8\cdot10^{-10}$	—	150	afe + pm
8	$Pb_2Mn^{+3}W^{+5}O_6$	750, 800, N_2	—	$a = c = 4.070$ Å, $b = 4.019$ Å, $\beta = 90°18'$	$1\cdot10^{-9}$	—	165	afe + pm
9	$PbFe_{1/2}Mn_{1/4}W_{1/4}O_3$	750, 800, N_2	0,99	$a_{cub} = 4,037$ Å	$5\cdot10^{-10}$	—130	—8	fe + fim
10	$PbCd_{1/4}Mn_{1/4}Nb_{1/2}O_3$	730, 780, O_2	0,95	$a_{cub} = 4.060$ Å	$1,2\cdot10^{-6}$	—	20	fe(afe) + pm
11	$PbCd_{1/3}Mn_{1/3}W_{1/3}O_3$	700, 750, O_2	0.94	$a = c = 4,137$ Å, $b = 4,069$ Å, $\beta = 90°56'$	$2\cdot10^{-5}$	—	300	afe + pm
	$BiFeO_3$*			$a = 3,962$ Å, $\alpha_{Rh} = 89°24'$		370	850	fe + afm
	$PbFe_{2/3}W_{1/3}O_3$			$a_{cub} = 4,02$ Å		110	—95	fe + afm
	$PbFe_{1/2}Nb_{1/2}O_3$			$a = 4,014$ Å, $\alpha_{Rh} = 89°54'$		—130	114	fe + afm
	$YMnO_3$ [5]			hexagonal cell $a = 6.125$ Å, $c = 11.41$ Å		—227 [6]	660 [7]	fe + afm
	$YbMnO_3$			hexagonal cell $a = 6,062$ Å, $c = 11,37$ Å		—	710 [7,8]	fe + afm

*The compounds which are not numbered are the magnetic ferroelectrics, with the perovskite or other structure, known before the present study.

**The geometrical factor $t = [R_A \text{ (coord. no. 12)} + R_0]/\sqrt{2}(R_B + B_0)$ is calculated on the assumption of a random distribution of type B ions of various kinds over the octahedral sites.

***The perovskite subcell parameters are listed for the compounds having a superstructure, due to the ordering of the B ions, and those having the monoclinic distortion of the subcells.

Notation: fe – ferroelectric, afe – antiferroelectric, afm – antiferromagnet, fm – ferromagnet, fim – ferrimagnet, pm – paramagnet. 700, 750, N_2 – denote the temperature of the first and second firing in °C and the firing atmosphere.

with the exception of $Pb_2Fe^{3+}W^{5+}O_6$, whose x-ray diffraction pattern shows lines characteristic of the spinel structure. The conditions necessary to obtain W^{5+} produce a considerable number of Fe^{2+} ions, and consequently Fe_3O_4 is formed. Attempts to obtain samples of the composition $PbMn^{3+}_{1/2}Nb^{5+}_{1/2}O_3$ with the perovskite structure have been made previously.[11,12] However, in that work, the samples did not consist of a single phase because they were synthesized in air, and contained, apart from the perovskite phase, a considerable amount of the pyrochlore phase. In our samples, prepared in an atmosphere of N_2, the pyrochlore phase was absent.

Superstructure lines, characteristic of an ordered distribution of type B ions, are present in the x-ray diffraction patterns of the compounds 2–4 and 6–8 (cf. the table). The compounds Pb_2CoNbO_6 and $Pb_2Fe^{3+}W^{5+}O_6$ have undistorted cubic structures at room temperature and ordering leads to the doubling of the period compared with the usual perovskite cell and to the doubling of the formula to $A_2B'B''O_6$. In the compounds 2, 3, 7, and 8, the usual perovskite cell is distorted monoclinic with $b/a < 1$ and $\beta > 90°$, and the unit cell is more complex than the unit cells of the compounds Pb_2CoNbO_6 and Pb_2FeWO_6. However, this problem was not investigated further. We restricted ourselves to the determination of the perovskite subcell parameters in the compounds 2, 3, 7, and 8.

The compounds 9–11, which have three types of ion in the B positions, may be regarded as combinations of binary solid solutions: $PbFe_{2/3}W_{1/3}O_3$, $PbCd_{1/3}Nb_{2/3}O_3$, Pb_2CdWO_6 with $PbMnO_3$ respectively, where the first three compounds, but not $PbMnO_3$, have the perovskite structure. In fact, the compositions of the solid solutions of the system Pb_2CdWO_6—$PbMnO_3$, close to the "compound" $PbCd_{1/3}Mn_{1/3}W_{1/3}O_3$ also have the perovskite structure. Therefore, the composition 11 may be regarded as a solid solution of these components. However, in the case of the compositions 9 and 10, perovskite samples consisting completely of a single phase are obtained under the stoichiometric conditions expressed by the coefficients in the compounds 9 and 10. A slight deviation from these

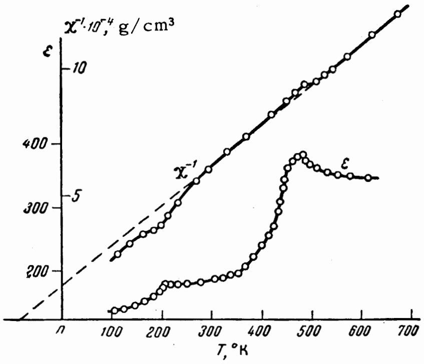

FIG. 1. Temperature dependences of the permittivity ε and the reciprocal magnetic susceptibility χ^{-1} of the compound $PbMn_{2/3}W_{1/3}O_3$.

compositions leads to the appearance of the pyrochlore phase. Thus, these compositions may be regarded as complex perovskite compounds.

We shall now deal in greater detail with the results of investigations of individual compounds.

1. **$PbMn_{2/3}W_{1/3}O_3$.** Figure 1 shows the temperature dependences of the permittivity ε and of the reciprocal magnetic susceptibility χ^{-1} for the compound $PbMn_{2/3}W_{1/3}O_3$. The maximum in the ε(T) curve together with the monoclinic distortion of the perovskite cell and the value of the geometrical factor t = 0.96 may be regarded[13] as indicating the existence of antiferroelectric properties in this compound. The temperature dependence $\chi^{-1}(T)$ above −70°C obeys the Curie-Weiss law $\chi = C/(T - \Theta_p)$ with a negative value of the constant $\Theta_p = -75$°K. Near −70°C, there is a departure from the linear dependence $\chi^{-1}(T)$ and at −70°C a kink is observed in the curve. The negative value of Θ_p, the absence of a spontaneous moment at temperatures below −70°C and the kink in the $\chi^{-1}(T)$ curve may indicate the existence of antiferromagnetic properties in $PbMn_{2/3}W_{1/3}O_3$ at −70°C. The increase in the magnetic susceptibility at temperatures below −70°C (which we assumed to be the Néel temperature) is obviously associated, as in the case of $PbFe_{2/3}W_{1/3}O_3$,[14] with the fact that quite a large number of diamagnetic W^{6+} ions is located in the B positions. Therefore, some Mn^{3+} ions do not take part in the indirect exchange and behave as in a normal paramagnet. The antiferroelectric phase transition is reflected by a small inflection of the $\chi^{-1}(T)$ curve. The appearance of the magnetic ordering causes some anomaly in the ε(T) curve of the antiferroelectric phase.

2. **$Pb_2Mn^{2+}Re^{6+}O_6$ and $Pb_2Mn^{3+}Re^{5+}O_6$.** Figure 2 shows the temperature dependence of the subcell parameters of $PbMn^{2+}_{1/2}Re^{6+}_{1/2}O_3$ and the results of the magnetic measurements for the same compound.

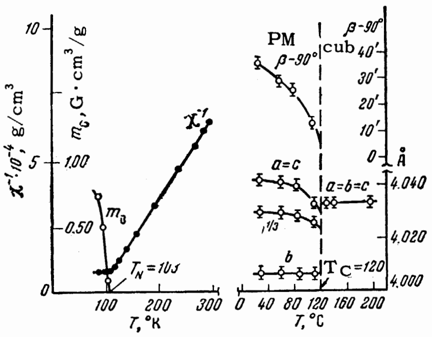

FIG. 2. Temperature dependences of the perovskite subcell parameters (on the right-hand side: PM – the pseudomonoclinic modification, cub – the cubic modification), of the reciprocal magnetic susceptibility χ^{-1}, and of the spontaneous magnetic moment m_0 (on the left-hand side) of the compound $Pb_2Mn^{2+}Re^{6+}O_6$ (T_N – the Néel point, T_C – the antiferroelectric Curie point).

At 120°C, the monoclinic distorted modification of this compound is transformed into cubic. By analogy with the antiferroelectrics Pb_2CoWO_6[15,16] and Pb_2YbNbO_6,[16] which have the same ordering of the B ions as $PbMn^{2+}Re^{6+}O_6$ and similar monoclinic distorted subcells, and in which the antiferroelectric Curie point corresponds to the phase transition of the monoclinic modification to the cubic one, we may assume the phase transition at 120°C in $Pb_2Mn^{2+}Re^{6+}O_6$ to be the antiferroelectric transition and the temperature of 120°C to be its Curie point.

According to the magnetic measurements, a spontaneous magnetic moment appears at −170°C in $Pb_2Mn^{2+}Re^{6+}O_6$ and a kink is observed there in the temperature dependence of χ^{-1}. The linear temperature dependence of χ^{-1} with a positive value of $\Theta_p = 85$°K, right up to the appearance of the spontaneous moment, may indicate the presence of ferromagnetic properties in this compound, which is in agreement with the positive sign of the indirect exchange interaction proposed by Goodenough for Mn^{2+} and Re^{6+} ions.[17] However, as shown by Sleight et al.[4] who measured the spontaneous magnetic moment of the compounds $Ba_2Mn^{2+}Re^{6+}O_6$, $Ba_2Mn^{3+}Re^{5+}O_6$, Ba_2FeReO_6 at 4.2°K, the magnitudes of the theoretical calculated spontaneous moments agree with the experimental values only on the assumption of an antiferromagnetic interaction between ions distributed in an ordered fashion over the octahedral vacancies. In such a case, the difference between the values of the magnetic moments of these ions leads to the ferrimagnetic properties. The small value of the spontaneous moment established by us for $Pb_2Mn^{2+}Re^{6+}O_6$ tends to support the ferrimagnetic rather than the ferromagnetic state. However, the Curie-Weiss law is not in general satisfied by ferrimagnets in the paramagnetic region and the temperature dependence of χ^{-1} is not rectilinear. The presence of a rectilinear part in the $\chi^{-1}(T)$ curve of $Pb_2Mn^{2+}Re^{6+}O_6$ may be explained by the fact that the determination of χ in the paramagnetic region was carried out over a relatively narrow range of temperatures ($\approx$ 200 deg) and the general nature of the temperature dependence of χ^{-1} was not established over this whole range.

Similar investigations were carried out on samples of $Pb_2Mn^{3+}Re^{5+}O_6$, whose subcell is slightly smaller in volume compared with $Pb_2Mn^{2+}Re^{6+}O_6$, but has a larger angle of the monoclinic distortion. The antiferroelectric Curie point of this compound is 95°C and its Néel point is -150°C.

3. $PbFe_{1/2}Mn_{1/4}W_{1/4}O_3$. This compound exhibits a maximum in the temperature dependence of ϵ at -8°C (Fig. 3). We did not investigate the dielectric hysteresis loops but, using the value of the factor t = 0.99 (a factor of this order is characteristic of ferroelectric perovskites[13]), we postulate the presence of ferroelectric properties in $PbFe_{1/2}Mn_{1/4}W_{1/4}O_3$ below -8°C. At -130°C, this compound exhibits weak ferrimagnetic properties and this is reflected in the $\epsilon(T)$ curve by the appearance of a small maximum.

4. Pb_2CoNbO_6 and $PbMn_{1/2}Nb_{1/2}O_3$. The synthesis and the anomalous dielectric properties of the compound Pb_2CoNbO_6 have been reported in an independent paper.[18] Since the authors of that paper prepared the compound in air and used $CoCO_3$ as the initial compound containing cobalt ions, they obtained a large number of Co^{2+} ions, as indicated by the gray-green color of their ceramic. Thus, obviously, Kupriyanov and Filip'ev[18] obtained some solid solution of the compounds $PbCo_{1/3}Nb_{2/3}O_3$ (the synthesis and investigation of the properties of which were reported in[19]) and Pb_2CoNbO_6. We used Co_2O_3 as the initial oxide and fired it in an atmosphere of O_2, to suppress completely the formation of Co^{2+} ions. For the same reasons as in the case of $PbFe_{1/2}Mn_{1/4}W_{1/4}O_3$ [the presence of a maximum in the $\epsilon(T)$ curve at 11°C (Fig. 4) and the value t = 0.98], Pb_2CoNbO_6 may be assumed to be a ferroelectric.

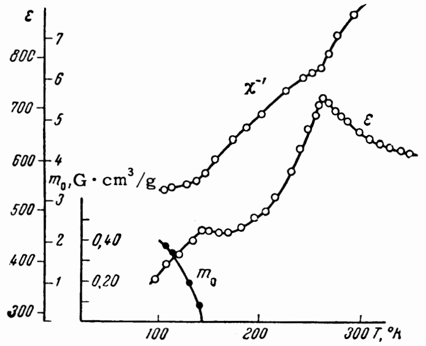

FIG. 3. Temperature dependences of the permittivity ϵ, of the reciprocal magnetic susceptibility χ^{-1}, and the spontaneous magnetic moment m_0 of the compound $PbFe_{1/2}Mn_{1/4}W_{1/4}O_3$.

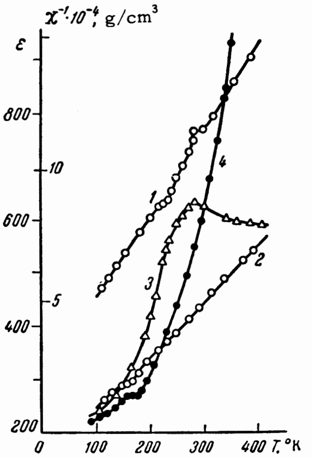

FIG. 4. Temperature dependences of the reciprocal magnetic susceptibility χ^{-1} (curves 1 and 2) and of the permittivity ϵ (curves 3 and 4) of the compounds $PbCoNbO_6$ and $PbMn_{1/2}Nb_{1/2}O_3$, respectively.

The magnetic properties of this compound (Fig. 4) are similar to those of $PbMn_{1/3}W_{1/3}O_3$. Therefore, Pb_2CoNbO_6 may be classified as an antiferromagnet with the Néel point at -60°C and $\Theta_p = -60$°K.

The χ^{-1} curve of the compound $PbMn_{1/2}Nb_{1/2}O_3$ (Fig. 4) exhibits a kink at -108°C, above which the Curie-Weiss law with a positive value of Θ_p = 65°K is satisfied. The spontaneous magnetic moment is absent below -108°C. The positive value of Θ_p and the linear temperature dependence of χ^{-1} up to -108°C indicate that below the magnetic Curie point, which was not reached by us, this compound has ferromagnetic properties. Measurements of ϵ of $PbMn_{1/2}Nb_{1/2}O_3$ in the range from -175 to $+100$°C showed a small maximum at -108°C (Fig. 4). However, the x-ray diffraction patterns of $PbMn_{1/2}Nb_{1/2}O_3$ obtained at room temperature show a considerable broadening of the lines 310 and 222, indicating the presence of distortions in the cubic perovskite structure even at $\approx$ 20°C. The value of the factor t = 0.97 suggests the presence of ferroelectric properties in the distorted modification. The absence of anomalies in the $\epsilon = f(T)$ curve at temperatures close to 20°C, which might indicate dielectric phase transitions, is explained by the considerable conductivity of samples of this compound. The phase transition at -108°C should obviously be associated with structural changes or with a second ferroelectric transition.

5. **$Pb_2Mn^{2+}W^{6+}O_6$, $Pb_2Mn^{3+}W^{5+}O_6$, and $Pb_2Fe^{3+}W^{5+}O_6$.** The data of the dielectric measurements given in Fig. 5 (the presence of a maximum in the temperature dependence of ϵ), the results of the x-ray diffraction studies (the monoclinic distorted perovskite subcell) and the geometrical factor $t < 1$ indicate that the first two compounds are antiferroelectric with T_C at 150 and 165°C, respectively. The spontaneous magnetization is absent in these compounds in the temperature range where χ was measured (Fig. 5) and the temperature dependences of χ^{-1} have the form characteristic of paramagnets (they extrapolate to 0°K). While in the case of $Pb_2Mn^{2+}W^{6+}O_6$, the paramagnetic properties are easily explained by the ordered distribution of paramagnetic Mn^{2+} ions and diamagnetic W^{6+} ions (which excludes the possibility of indirect exchange), ferrimagnetic properties could be expected in the case of $Pb_2Mn^{3+}W^{5+}O_6$ because of the paramagnetic nature of the W^{5+} ion. However, like Patterson et al.[3] in the case of $Ba_2Mn^{3+}W^{5+}O_6$, we were unable to find ferrimagnetic properties although the presence of W^{5+} ions was proved in[3]. It remains to conclude that not all tungsten is in the W^{5+} state but there are W^{6+} ions which make the conditions more difficult for the indirect exchange interaction to take place.

The compound $Pb_2Fe^{3+}W^{5+}O_6$ does not exhibit any anomalies in its $\epsilon(T)$ curve in the range from -175 to $+25$°C. The magnetic measurements confirmed the presence of the spinel phase in a sample of this composition. A considerable spontaneous magnetic moment appeared below 560° (which is the magnetic T_C of Fe_3O_4).

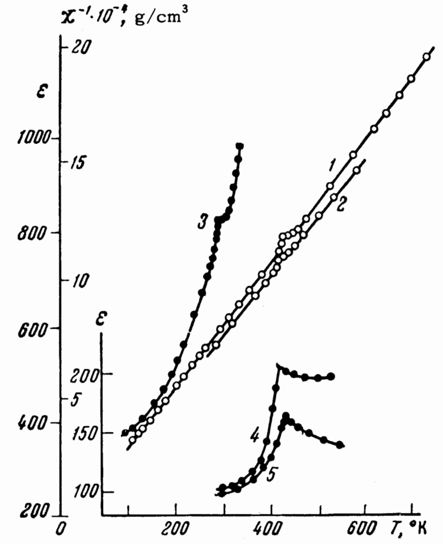

FIG. 5. Temperature dependences of the reciprocal magnetic susceptibility χ^{-1} of the compounds $Pb_2Mn^{3+}W^{5+}O_6$ (curve 1) and $Pb_2Mn^{2+}W^{6+}O_6$ (curve 2) and of the permittivity ϵ of the compounds $PbCd_{1/4}Mn_{1/4}Nb_{1/2}O_3$ (3), $Pb_2Mn^{2+}W^{6+}O_6$ (4), and $Pb_2Mn^{3+}W^{5+}O_6$ (5).

6. **$PbCd_{1/4}Mn_{1/4}Nb_{1/2}O_3$ and $PbCd_{1/3}Mn_{1/3}W_{1/3}O_3$.** The former compound exhibits a small kink in the $\epsilon(T)$ curve at 25°C (Fig. 4) and some diffuse lines in the x-ray diffraction patterns. Since the value of the factor $t = 0.95$ makes it difficult to determine unambiguously the nature of the dielectric properties, we may conclude from the cited observations that $PbCd_{1/4}Mn_{1/4}Nb_{1/2}O_3$ is a ferroelectric or an antiferroelectric with $T_C = 25$°C. The monoclinic modification of $PbCd_{1/3}Mn_{1/3}W_{1/3}O_3$ is transformed into the cubic form at 300°C, as established by means of x-ray diffraction at high temperatures. From the same observations which were used to justify the conclusion about the antiferroelectric properties of Pb_2CdWO_6,[20] we may conclude that the solid solution $PbCd_{1/3}Mn_{1/3}W_{1/3}O_3$, one of whose components is Pb_2CdWO_6, is an antiferroelectric with $T_C = 300$°C. The perovskites $PbCd_{1/4}Mn_{1/4}Nb_{1/2}O_3$ and $PbCd_{1/3}Mn_{1/3}W_{1/3}O_3$ are paramagnets due to the large amounts of diamagnetic randomly distributed B ions which impede the indirect exchange between paramagnetic Mn^{4+} ions.

Thus we synthesized and investigated ten new perovskite compounds, of which six (1—5 and 9) are magnetic ferroelectrics, two (7 and 8) are paramagnetic antiferroelectrics, and one (10) is a paramagnetic ferroelectric (or antiferroelectric). As shown earlier, the six new magnetic ferroelectrics exhibit, over certain temperature intervals, the coexistence of special magnetic (antiferromagnetic, ferromagnetic, and ferrimagnetic) properties with special dielectric (ferroelectric or antiferroelectric) properties. The appearance of certain anomalies (small maxima or inflections) in the $\epsilon(T)$ curves at the points of the appearance of the magnetic ordering in the presence of the electric ordering in the compounds $PbMn_{2/3}W_{1/3}O_3$ and $PbFe_{1/2}Mn_{1/4}W_{1/4}O_3$ indicates an interrelationship of the magnetic and electric dipole structures in these compounds. The existence of such anomalies, which appear as a result of the interrelationship of the magnetic and electric dipole structures, has been predicted in theory.[21,22] In the case of Pb_2CoNbO_6, this interrelationship is less clear (Fig. 4). If we bear in mind that so far only three perovskite magnetic ferroelectrics have been known, $BiFeO_3$,[23-26] $PbFe_{2/3}W_{1/3}O_3$ and $PbFe_{1/2}Nb_{1/2}O_3$,[14] the preparation of six new such compounds represents a considerable extension of the number of magnetic ferroelectrics and suggests a practical basis for the formation of magnetoferroelectric solid solutions with desired properties.

In conclusion, it should be mentioned that in the case of some of the most interesting compounds it would be necessary to grow single crystals and carry out more detailed investigations.

---

[1] Venevtsev, Roginskaya, Viskov, Ivanova, Tomashpol'skiĭ, Svorneva, Kapyshev, Teverovskiĭ, and Zhdanov, DAN SSSR **158**, 86 (1964), Soviet Phys. Doklady **9**, 751 (1965).

[2] H. Nechamkin and C. F. Hiskey, Inorg. Syntheses, No. 3, 186 (1960).

[3] Patterson, Moeller, and Roland, Inorg. Chem. **2**, 196 (1963).

[4] Sleight, Longo, and Ward, Inorg. Chem. **1**, 245 (1962).

[5] Bertaut, Forrat, and Fang, Compt. Rend. **256**, 1958 (1963).

[6] Bertaut, Mercier, and Pauthenet, J. Phys. **25**, 550 (1964).

[7] I. G. Ismailzade and S. A. Kizhaev, Abstracts of Papers presented at the IV All-union Conference on Ferroelectricity, Rostov-on-Don, 12-18 September, 1964, Izd. RGU, p. 24.

[8] Smolenskiĭ, Bokov, and Mitsek, Izv. AN SSSR, ser. fiz. **28**, 614 (1964), Transl. Bull. Acad. Sci. Phys. Ser., p. 521.

[9] Yu. N. Venevtsev and S. P. Solov'ev, Zavodskaya laboratoriya **27**, 1113 (1961).

[10] Roginskaya, Venevtsev, Fedulov, and Zhdanov, Kristallografiya **8**, 610 (1963), Soviet Phys. Crystallography **8**, 508 (1964).

[11] A. I. Agranovskaya, Dissertation for Candidate's Degree, Silicate Chemistry Institute, Academy of Sciences, U.S.S.R., 1962.

[12] Filip'ev, Kupriyanov, and Fesenko, Kristallografiya **8**, 790 (1963), Soviet Phys. Crystallography **8**, 630 (1964).

[13] Yu. N. Venevtsev and G. S. Zhdanov, Izv. AN SSSR, ser. fiz. **21**, 275 (1957), Transl. Bull. Acad. Sci. Phys. Ser., p. 277.

[14] Bokov, Myl'nikova, and Smolenskiĭ, JETP **42**, 643 (1962), Soviet Phys. JETP **15**, 447 (1962).

[15] V. S. Filip'ev and E. G. Fesenko, Kristallografiya **9**, 293 (1964).

[16] Yu. Ya. Tomashpol'skiĭ and Yu. N. Venevtsev, FTT **6**, 2998 (1964), Soviet Phys. Solid State **6**, 2388 (1965).

[17] J. B. Goodenough, Magnetism and the Chemical Bond, New-York-London, 1963.

[18] M. F. Kupriyanov and V. S. Filip'ev, Abstracts of Papers presented at the IV All-Union Conference on Ferroelectricity, Rostov-on-Don, 12—18 September, 1964, Izd. RGU p. 16.

[19] V. A. Bokov and B. I. Myl'nikova, FTT **3**, 841 (1961), Soviet Phys. Solid State **3**, 613 (1961).

[20] Yu. E. Roginskaya and Yu. N. Venevtsev, Kristallografiya **10** (1965) (in press).

[21] A. I. Mitsek and G. A. Smolenskiĭ, FTT **4**, 3581 (1962), Soviet Phys. Solid State **4**, 2620 (1962).

[22] V. N. Lyubimov, Izv. AN SSSR, seriya fiz. **28**, (1964).

[23] Venevtsev, Zhdanov, Solov'ev, Bezus, Ivanova, Fedulov, and Kapyshev, Kristallografiya **5**, 620 (1960).

[24] S. V. Kiselev and R. P. Ozerov, DAN SSSR **145**, 1255 (1962), Soviet Phys. Doklady **7**, 742 (1963).

[25] Smolenskiĭ, Yudin, Sher, and Stolypin, JETP **43**, 877 (1962), Soviet Phys. JETP **16**, 622 (1963).

[26] Roginskaya, Venevtsev, and Zhdanov, JETP **44**, 1418 (1963), Soviet Phys. JETP **17**, 955 (1963).

Translated by A. Tybulewicz
185