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PEROVSKITES WITH FERROELECTRIC-MAGNETIC PROPERTIES

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By varying the preparation conditions, we were able to obtain single-phase perovskites whose composition was close to $Pb(Fe_{1/2}Ta_{1/2})O_3$ (I), as well as the following compositions (charge compositions): $Pb(Co_{1/2}Ta_{1/2})O_3$ + 1 mol.% La_2O_3 (II), $(Pb_{0.95}Ba_{0.05})(Ni_{1/2}Nb_{1/2})O_3$ (III), and $(Pb_{0.95}Sr_{0.05})(Mn_{1/2}Ta_{1/2})O_3$ (IV). Dielectric and magnetic measurements established that: 1) I and III are ferrimagnetic-ferroelectrics with magnetic and ferroelectric transition points at $T_{Cm} = -140°C$, $T_{Ce} = -40°C$ (for I) and $T_{Cm} = -10°C$, $T_{Ce} = -100°C$ (for III); 2) II is an antiferromagnetic-ferroelectric, with the transition points $T_{Cm} = -120°C$ and $T_{Ce} = -70°C$; 3) IV is a ferromagnetic-ferroelectric with $T_{Cm} < -170°C$, $T_{Ce} \approx +140°C$.

In spite of the fact that quite a few ferroelectric-magnetic compounds are known already (cf., for example,[1]), the preparation of new materials of this type is now very appropriate because it satisfies the need for more detailed investigations of this new class of materials and the need to have ferroelectric-magnetic materials of practical importance. Among the known ferroelectric-magnetic materials, there are some compounds whose compositions can be written in the form $Pb(B'_{1/2}B''_{1/2})O_3$, where B′ represents trivalent ions of some transition metals, and B″ represents Nb^{5+} or Ta^{5+}. However, single-phase perovskites cannot be obtained for all combinations of B′ and B″ ions. Thus samples of the composition $Pb(Fe_{1/2}Ta_{1/2})O_3$ prepared by Agranovskaya,[2] contained, apart from the perovskite phase, a certain amount of the pyrochlore phase. Sample with the composition $Pb(Mn_{1/2}Ta_{1/2})O_3$ could not be obtained with the perovskite structure at all.

In the present investigation, we prepared single-phase samples having the perovskite structure and compositions close to $Pb(Fe_{1/2}Ta_{1/2})O_3$ and $Pb(Mn_{1/2}Ta_{1/2})O_3$. We investigated their magnetic and dielectric properties. In addition to them, we also studied the properties of two other perovskites which were close in composition to $Pb(Co_{1/2}Ta_{1/2})O_3$ and $Pb(Ni_{1/2}Nb_{1/2})O_3$, whose preparation (without admixtures) and dielectric properties were briefly reported earlier.[3]

In the synthesis of the investigated compositions, the initial materials were: Fe_2O_3, $PbCO_3$, Nb_2O_5 (analytic purity grade), Ni_2O_3, Ta_2O_5 (pure grade), and Mn_2O_3 (analytic purity grade). All the samples were synthesized by the standard ceramic techniques using double firing. The firing conditions are given in the table. We obtained single-phase perovskites of the following (charge) compositions:

I. $Pb(Fe_{1/2}Ta_{1/2})O_3$ (ignoring a small amount of an admixture introduced into the charge);

II. $Pb(Co_{1/2}Ta_{1/2})O_3$ + 1 mol.% La_2O_3;

III. $(Pb_{0.95}Ba_{0.05})(Ni_{1/2}Nb_{1/2})O_3$;

IV. $(Pb_{0.95}Sr_{0.05})(Mn_{1/2}Ta_{1/2})O_3$.

It should be mentioned that single-phase samples having the perovskite structure and the compositions given in the table were obtained by using specially selected admixtures to stabilize the perovskite phase and by employing a suitable firing atmosphere (cf. table). Thus, sample III was prepared by the addition of 5 mol.% BaO, and sample IV by the introduction of 5 mol.% SrO. In contrast to Kupriyanov and Fesenko,[3] we were unable to prepare a single-phase perovskite of the composition $Pb(Co_{1/2}Ta_{1/2})O_3$ and only the introduction of 1 mol.% La_2O_3 stabilized the perovskite phase.

The permittivity measurements were carried out using a standard bridge (type MPP-300) at 200 cps in weak fields. The measurement of the temperature dependence of $1/\chi$ was made using the Faraday method, as described in[4]. Standard x-ray apparatus and methods were used in the x-ray diffraction phase analysis and in the determination of the unit cell parameters.

Perovskites I—III had cubic cells at room temperature and the back-reflection lines in the x-ray diffraction patterns of sample IV were slightly broadened, indicating weak distortion of the cell, whose nature could not be determined because of its smallness. The unit cell parameters are listed in the table.

Some data on investigated properties

Sample No.	Heat treatment	Atmosphere used	Geometrical factor	Unit cell parameter, a, Å	T_{Cm}, °C	T_{Ce}, °C	σ_{20}, $\Omega^{-1}\cdot cm^{-1}$	Classification in accordance with properties*
I	900° C, 1.5 hours 980° C, 1 hour	O_2	0.97	3.992_5	—140	—40	$5\cdot10^{-9}$	FE-FIM
II	750° C, 1.5 hours 800° C, 1 hour	O_2	0.98	4.0340	—120	—70	$4\cdot10^{-6}$	FE-AFM
III	800° C, 1 hour 850° C, 1 hour	O_2		4.032	—10	—100	$8\cdot10^{-6}$	FE-FIM
IV	800° C, 1.5 hours 850° C, 1		0.96	4.011	<—170	+40	$1\cdot10^{-4}$	FE-FOM

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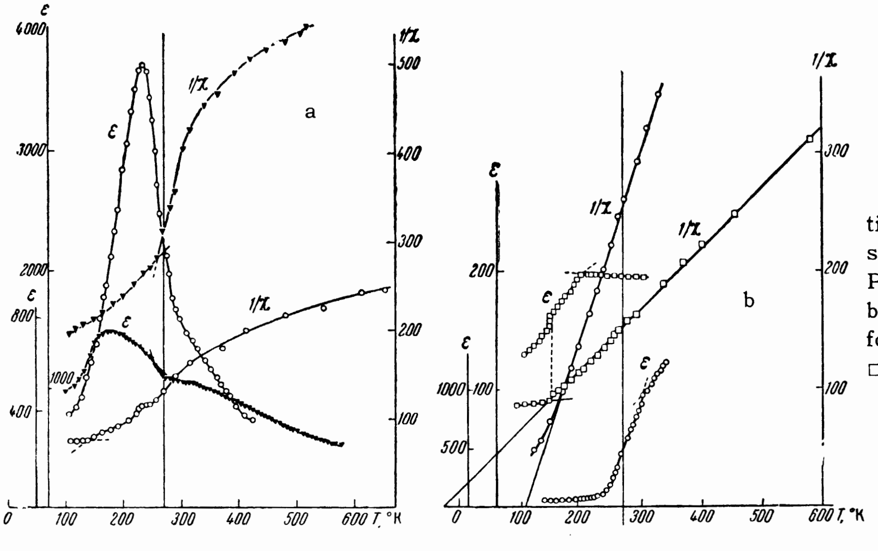
*Notation convention: FE — ferroelectric, FIM — ferrimagnet, AFM — antiferromagnet, FOM — ferromagnet; σ_{20} is the sample conductivity at room temperature; T_{Cm} and T_{Ce} are the temperatures of the magnetic and electrical transitions.

It should be mentioned that the investigated perovskites had conductivities differing by several orders of magnitude (cf. table). The conductivity was measured at room temperature using samples heated first to 100°C to drive off moisture. Perovskite I had a relatively low conductivity of the order of $10^{-9}\ \Omega^{-1}\cdot cm^{-1}$, while the conductivity of perovskite IV was so high ($\sigma_{20} \approx 10^{-4}\ \Omega^{-1}\cdot cm^{-1}$) that we were unable to record a reliable dependence $\epsilon(t)$ for this composition.

The results of the investigation of the temperature dependences of the permittivity ϵ and the reciprocal of the magnetic susceptibility $1/\chi$ are given in the figure. The $\epsilon(T)$ curve for composition I has a sharp peak at $T_{Ce} = -40°C$ and the peak value of ϵ is higher than that reported in[5] for a sample of composition $Pb(Fe_{1/2}Ta_{1/2})O_3$, which, according to[1], was evidently not single-phase. The curves $\epsilon(T)$ of other perovskites have no clear maxima, but from kinks in these curves we may conclude that they have special dielectric properties and we can find the positions of their Curie points (cf. table). All the investigated perovskites contain lead ions and for this reason alone one would expect the presence of special dielectric properties (ferroelectricity, ferrielectricity, or antiferroelectricity). The peaks and kinks in the $\epsilon(T)$ curves may indeed, to a greater or lesser extent, indicate the presence of such properties. Using the geometrical factor t, which varies for these perovskites within the limits 0.96—0.98, we may conclude, on the basis of the work of Zhdanov and one of the present authors,[6] that all these perovskites have ferroelectric properties.

The temperature dependences of $1/\chi$ exhibit characteristic kinks in the region of magnetic ordering, from which we can deduce the magnetic Curie points (cf. the figure). Thus, perovskite I exhibits a kink in the $1/\chi$ curve in the region of −140°C. The temperature of the magnetic transition T_{Cm} of this perovskite is identical, within the limits of the experimental error, with the magnetic Curie point of $Pb(Fe_{1/2}Nb_{1/2})O_3$,[7] which allows us to draw the conclusion that the replacement of the



a) Temperature dependences of the permittivity and of the reciprocal of the magnetic susceptibility for perovskites: ○ – $Pb(Fe_{1/2}Ta_{1/2})O_3$, ▼ – $(Pb_{0.95}Ba_{0.05})(Ni_{1/2}Nb_{1/2})O_3$; b) temperature dependences of the permittivity for perovskites: ○ – $(Pb_{0.95}Sr_{0.05})(Mn_{1/2}Ta_{1/2})O_3$, □ – $Pb(Co_{1/2}Ta_{1/2})O_3$ + 1 mol.% La_2O_3.

Nb atom with Ta does not greatly affect the position of the point T_{Cm}, although the nature of the ordering is somewhat different: $Pb(Fe_{1/2}Nb_{1/2})O_3$ is antiferromagnetic, while perovskite I is, according to our data, ferrimagnetic. Similar kinks in the temperature dependences of $1/\chi$ are observed also for perovskites III and II: they are at – 10 and 120° C, respectively. From the temperature dependences of $1/\chi$ and the presence or absence of the spontaneous moment in the investigated perovskites, we may conclude that perovskites I and III have ferrimagnetic properties, perovskite II has antiferromagnetic properties, and perovskite IV has ferromagnetic properties. The ferrimagnetism of perovskites I and III is also supported, apart from the form of the curve characteristic of ferrimagnets and deviations in the dependence of $1/\chi$ from the Curie—Weiss law above T_{Cm}, by the appearance of a very weak magnetic moment m_S below – 140 and – 10° C, respectively. Unfortunately, using our apparatus, we were unable to obtain the exact values of this moment m_S. The ferrimagnetism in these compositions can be explained by the presence of weak ordering, in the perovskite crystal lattices, of Fe and Ta ions in the former case, and Ni and Nb ions in the latter case.

No spontaneous moment was found in sample IV, but from the positive value of Θ_p (in the Curie—Weiss law, which $1/\chi$ obeys in the investigated range of temperatures) and from some analogy with $Pb(Mn_{1/2}Nb_{1/2})O_3$[1], we could conclude that ferromagnetic properties existed in this perovskite at $T < -180°C$. The ferromagnetism of sample IV is due to the positive exchange interaction between Mn^{3+} and Mn^{3+} ions,[8] but it is possible that this perovskite contains a small amount of Mn^{4+} ions which, together with Mn^{3+}, have an even stronger positive exchange interaction.[8] The rectilinear part of the temperature dependence of $1/\chi$ of perovskite II extrapolates to the negative region ($\Theta_p = -20°K$), which indicates the presence in it of antiferromagnetic properties. The antiferromagnetism of perovskite II is explained by the random distribution of Co and Ta ions in the crystal lattice.

We must mention also that in some cases there are anomalies in the temperature dependences of $1/\chi$ at the points at which the electrical ordering (perovskite I) appears, and some anomalies in the $\epsilon(T)$ curves at the magnetic ordering points (perovskites III, II), which, obviously, indicate a coupling between the electrical and magnetic dipole structures in the ferroelectric-magnetic materials. Thus, from the investigations carried out, we may conclude that four more perovskites (cf. table) exhibit ferroelectric-magnetic properties.

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