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FERROELECTRIC-MAGNETIC MATERIALS IN THE SYSTEM $PbFe_{2/3}W_{1/3}O_3$--Pb_2YbNbO_6

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New ferroelectric-magnetic solid solutions with the perovskite structure were prepared and investigated; at certain compositions, they combined ferroelectric or antiferroelectric properties with ferrimagnetic ones. Some results were obtained which indicated a coupling between the electric and magnetic dipole structures in the investigated compositions.

INTRODUCTION

ALTHOUGH at present over 10 ferroelectric-magnetic compounds are known,[1] the properties of these substances have not yet been fully investigated. There is still a need to increase the number of ferroelectric-magnetic materials for the purpose of further investigations and in order to determine the range of their possible applications. Experiments show that the formation of solid solutions is an effective way of determining some of the relationships between the properties of substances and of preparing materials with desired properties.

In the present study we investigated solid solutions in the system $PbFe_{2/3}W_{1/3}O_3$—Pb_2YbNbO_6. In this system, $PbFe_{2/3}W_{1/3}O_3$ is a ferroelectric antiferromagnet with its Curie (T_C) and Neél (T_N) points at −90 and +100°C, respectively,[2] and Pb_2YbNbO_6 is an antiferroelectric with its Curie point at +310°C.[3,4] Both compounds have the perovskite-type structure: in Pb_2YbNbO_6, the Yb and Nb ions are ordered,[4] while in $PbFe_{2/3}W_{1/3}O_3$, the Fe and W ions are distributed at random in octahedral sites. It is postulated that, in the formation of solid solutions between these two compounds, the degree of ordering in the distribution of the Fe, W, Yb, and Nb ions is partly conserved and, owing to the different occupancies of the oxygen octahedra by the Fe and Yb ions, a resultant magnetic moment should appear in addition to the general antiferromagnetic configuration.

Also worthy of investigation was the appearance of a coupling between the electric and magnetic dipole structures in ferroelectric-magnetic compositions when the magnetic structure was formed.

SYNTHESIS OF SAMPLES AND INVESTIGATION METHOD

The investigations were carried out on polycrystalline samples prepared by firing the appropriate oxides: WO_3 (spectroscopically pure), Fe_2O_3, Nb_2O_5 (of analytic purity), Yb_2O_3 (99.96%), and the carbonate $PbCO_3$ (of analytic purity) at temperatures of 700—1000°C (double firing) applied for 1—7 hours. A small amount of mineralizer (up to 1 mol.%) was added to some compositions to improve their sintering and equilibrium properties.

A URS-50-IM diffractometer and Cu K_α—radiation were used in a preliminary phase analysis. To determine the nature of distortions of the unit cells and their parameters, we employed our usual method.[5] The samples were exposed, in RKU-114 cameras, to Cu- or Cr-radiation, depending on the composition of the sample. The cell parameters were determined from the lines with $\Sigma_i h_i^2 = 10, 12, 26$, lying in the accurately measurable range of angles $\theta = 60—80°$. The accuracy of determination of the periods was (± 0.001—0.003) Å and that of the angles (± 2—3)′. To investigate the structure of some of the compositions at high temperatures, we used the high-temperature x-ray method, employed by us earlier.[4]

The dielectric measurements were carried out on ceramic tablets, provided with silver electrodes, using the standard bridge circuit (an MPP-300 bridge, a GZ-7A oscillator, a 2G-I oscillograph) at 200 kc frequency in a weak field (several V/cm). The investigated range of temperatures was from −160 to +300°C. The accuracy of the determination of the permittivity was of the order of 5%; the temperature was determined to

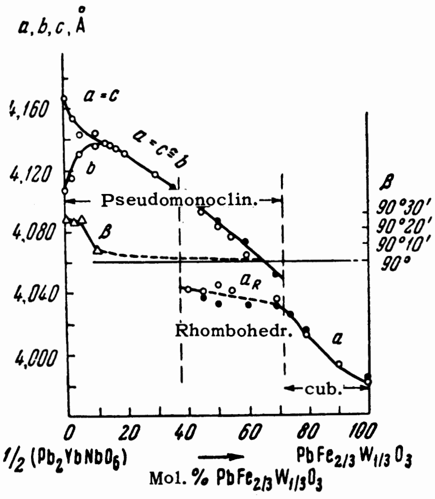

FIG. 1 Variation of the unit cell parameters (periods a, b, c, and the monoclinic angle β) in the solid solutions of the system $PbFe_{2/3}W_{1/3}O_3 - Pb_2YbNbO_6$ at room temperature: ○ samples without mineralizer; ● samples with mineralizer.

within ±3 deg C.

The magnetic measurements were carried out by the Faraday method on ceramic samples of nearly spherical shape (1–3 mm diameter) in the temperature range from −160 to +400°C. The method was described in detail in[6]. The accuracy of the determination of the magnetic susceptibility was ≈ 2%, and of the spontaneous magnetic moment ≈ 4%.

EXPERIMENTAL RESULTS

From the x-ray diffraction data (Fig. 1), it follows that several solid solutions are formed in the system $PbFe_{2/3}W_{1/3}O_3$–Pb_2YbNbO_6; in the concentration range ≈ 37–72 mol.% samples of $PbFe_{2/3}W_{1/3}O_3$ could not be obtained in the single-phase form, in spite of a considerable amount of work on the optimum selection of the conditions of preparation. These samples contained, in addition to the main perovskite phase, a small amount (≈ 10%) of a second perovskite phase with a unit cell period varying weakly with composition. The scatter of the values of the period was obviously due to the difficulty, owing to their weakness, in measuring the lines in the diffractograms. It was noticed that the content of the second phase depended on the conditions of preparation but it was not possible to eliminate it altogether. High-temperature x-ray patterns showed that both phases were retained in the range of temperatures much higher than the T_C of these compositions (up to 300°C). Weak superstructure lines, due to the B-ion ordering, were observed in the diffractograms only on the Pb_2YbNbO_6 side, which may have been partly due to a change in the type and degree of ordering on approach to the composition $PbFe_{2/3}W_{1/3}O_3$. Figure 1 shows that the monoclinic distortion of the perovskite subcell is observed near room temperature in the 0–12 mol.% $PbFe_{2/3}W_{1/3}O_3$ region; this decreases with the addition of $PbFe_{2/3}W_{1/3}O_3$. In the range of concentrations ≈ 70–100% this subcell is cubic. In the 12–70% composition range, it was not possible to observe any splitting of the lines due to the main and secondary phases but the observed broadening may have been due to the presence of a dielectric phase transition near room temperature. We can assume that in the two-phase region the main-phase cell is pseudomonoclinic and the secondary-phase cell is probably rhombohedral (at room temperature).

The characteristic feature of the curves repre-

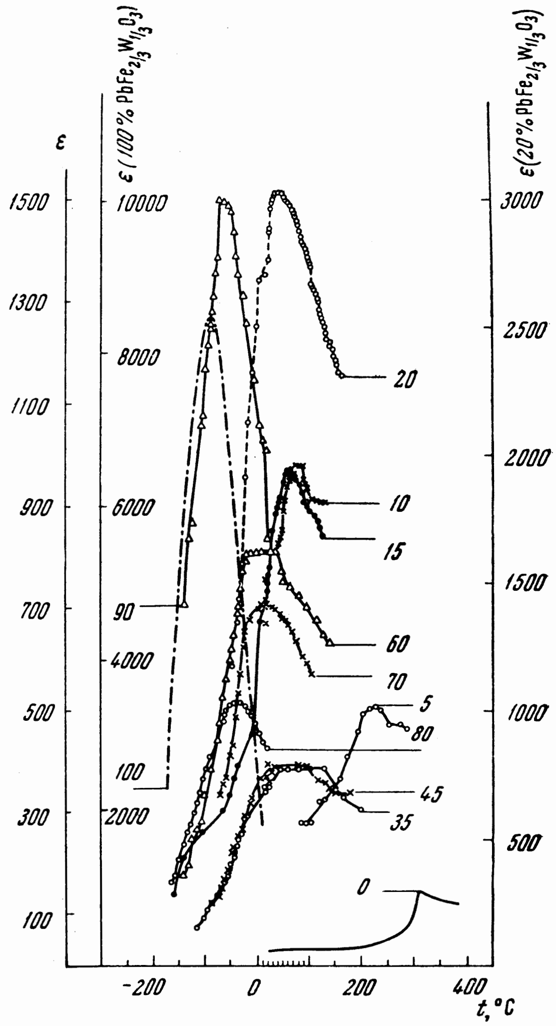

FIG. 2. Temperature dependence of the permittivity ε for samples of various compositions in the system $PbFe_{2/3}W_{1/3}O_3$ – Pb_2YbNbO_6. The curves for $PbFe_{2/3}W_{1/3}O_3$ and Pb_2YbNbO_6 are taken from[2, 4]. The numbers by the curves indicate the $PbFe_{2/3}W_{1/3}O_3$ content in mol. %.

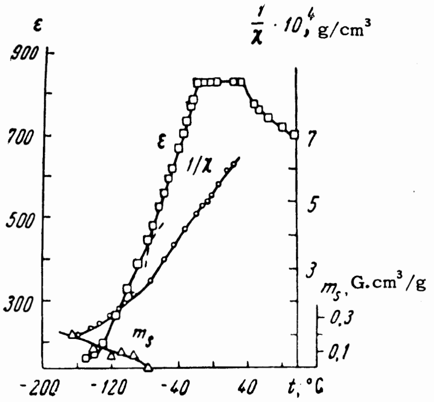

FIG. 3. Temperature dependences of the permittivity ϵ, the spontaneous magnetic moment m_s, and the reciprocal magnetic susceptibility $1/\chi$ for a sample with the composition 60 mol.% $PbFe_{2/3}W_{1/3}O_3$ – 40 mol.% ½ (Pb_2YbNbO_6).

senting the lattice parameters is the presence of discontinuities at 30 and 70 mol.%.

Finally, it is evident from Fig. 1 that the small amounts of mineralizer have practically no influence on the parameters of the solid-solution subcells. The temperature dependence of the permittivity (Fig. 2) shows clear ϵ(t) maxima, whose positions vary with composition. It is evident from Fig. 2 that the compositions in the middle of the system (≈ 35–60 mol.% $PbFe_{2/3}W_{1/3}O_3$) have broader peaks than the compositions close to the two initial components. We also note that the addition of the mineralizer sharpens the maxima. Some results of the magnetic measurements are given in Figs. 3-5, together with the results of the dielectric measurements. The form of the $1/\chi(t)$ curve (where χ is the magnetic susceptibility) for the compositions having 60, 80, and 90 mol.% $PbFe_{2/3}W_{1/3}O_3$, and the appearance of the spontaneous magnetic moment m_s (which was found by linear extrapolation of the magnetization isotherms to zero field H), indicate the presence of ferrimagnetic properties in these and in the intermediate compositions. As is known, the magnetic ordering occurs over a certain range of temperatures. Therefore, we arbitrarily took the transition point to be the temperature at which the spontaneous magnetic moment m_s first appeared; in the same region, an inflection was observed in the $1/\chi$ curves. The temperature of the ferrimagnetic transition decreased continuously with the addition of Pb_2YbNbO_6. For a sample with 45 mol.% $PbFe_{2/3}W_{1/3}O_3$, the transition occurred below −160°C.

We note that the compositions close to $PbFe_{2/3}W_{1/3}O_3$ and free of the mineralizer contained a small amount (not detected by x-ray diffraction) of ferrite garnet $5Fe_2O_3 \cdot 3Yb_2O_3$, which was identified from the results of the magnetic measurements. In such samples, irrespective of their composition, the magnetic moment appeared at t = 270°C (for this ferrite T_C is 275°C, according to [7]) and on further cooling a new discontinuity is found in the $m_s(t)$ curves, corresponding to the temperature of the ferrimagnetic transition in an intrinsic perovskite structure (dashed curve in Fig. 5). The addition of the mineralizer made it much easier to determine the temperature of this transition, by destroying the stray ferrimagnetism. Figures 3–5 present the data for samples containing an admixture of the mineralizer.

PHASE DIAGRAM AND DISCUSSION OF RESULTS

We can plot the phase diagram (Fig. 6) from the x-ray diffraction, dielectric, and magnetic data. It shows clearly three regions of different composition dependence of the dielectric phase transition temperature. In region I (from 0 to 30 mol.% $PbFe_{2/3}W_{1/3}O_3$), T_C falls sharply from

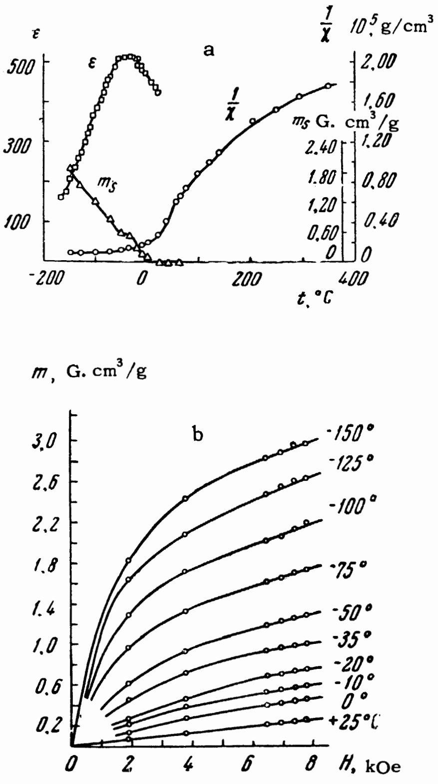

FIG. 4. a) Temperature dependences of ϵ, m_s, and $1/\chi$ for a sample with the composition 80 mol.% $PbFe_{2/3}W_{1/3}O_3$ – 20 mol.% ½(Pb_2YbNbO_6); b) dependence of the magnetization of the solid solution 80 mol.% $PbFe_{2/3}W_{1/3}O_3$ – 20 mol.% ½(Pb_2YbNbO_6) on the magnetic field intensity H at various temperatures.

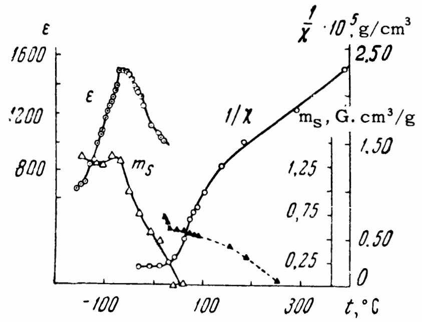

FIG. 5. Temperature dependences of ϵ, m_s, and $1/\chi$ for a sample with the composition 90 mol.% $PbFe^2/_3W^1/_3O_3$ – 10 mol.% ½(Pb_2YbNbO_6). The dashed curve gives the dependence $m_s(t)$ for a sample containing a ferrite garnet as an impurity (this sample was free of the mineralizer).

+310°K to ≈ t_{room}; in region III (from 65 to 100 mol.% $PbFe_{2/3}W_{1/3}O_3$) a similar further decrease of T_C is observed down to −90°C, and in both regions, I and III, the transition point is quite sharp. In region II (30–65 mol.% $PbFe_{2/3}W_{1/3}O_3$), the transition occurs over a relatively wide range of temperatures, and the slope of the T_C curve is considerably less in regions I and III. The three regions have different types of superstructure due to the ordering (by analogy with the system Pb_2CoWO_6–Pb_2YbNbO_6 [4]) and to the occurrence, in regions I and II, of antiferroelectric (antiparallel) ion shifts, indicated by the discontinuities, at t_{room} (Fig. 1), in the curves representing the cell parameters. We may assume that region II is intermediate between the ferroelectric and antiferroelectric phases and that in this region, as indicated by the x-ray diffraction data, the antiferroelectric phase is dominant, which is confirmed by the absence of dielectric hysteresis loops—which were investigated at t_{room} for compositions with $T_C > t_{room}$. The presence of such a two-phase region was mentioned by Fedulov and Venevtsev.[8] In the present case, the existence of a wide intermediate region (≈ 40 mol.%) may be explained by the presence of four types of ion (Fe, W, Yb, Nb) at octahedral sites and the slight ordering of these ions.

The magnetic transition point decreases from +100°C for $PbFe_{2/3}W_{1/3}O_3$ to $t < -160$°C for a sample with the composition 45 mol.% $PbFe_{2/3}W_{1/3}O_3$, and it follows from the magnetic measurements that even the addition of 5 mol.% of ½ (Pb_2YbNbO_6) to these compositions produces partial ordering and a resultant spontaneous magnetic moment, whose value (taken at some fixed temperature, for example, −150°C) increases in the region of 80 mol.% $PbFe_{2/3}W_{1/3}O_3$ and then decreases due to a reduction in the concentration of the iron ions. The ferrimagnetic region at T = 0°K lies in the range ≈ 35–95 mol.% $PbFe_{2/3}W_{1/3}O_3$ and the ferroelectric or antiferroelectric properties are also observed in this region. Consequently, in the investigated system we are able to obtain solid solutions exhibiting simultaneously ferroelectric and magnetic properties over a relatively wide range of concentrations and temperatures.

Examination of the $m_s(t)$ curves for a number of ferroelectric and magnetic compositions (Figs. 3–5) shows that at the ferroelectric transition point these curves exhibit certain anomalies (increase in the magnetic moment) which may be treated as the appearance of a coupling between the dielectric and magnetic structures. At the same time, the $\epsilon(t)$ curves exhibit inflections at the magnetic phase transition points (cf. Fig. 3), indicating the influence of the magnetic ordering on the structure of the electric dipoles. Such coupling effects in ferroelectric-magnetic materials were observed earlier.[9,10]

Thus, we were able to prepare and investigate solid solutions exhibiting simultaneously ferrimagnetic and ferroelectric or antiferroelectric properties. The latter seem to us of greater practical interest than antiferromagnets. Some of the solid solutions on the $PbFe_{2/3}W_{1/3}O_3$ side have, in principle, properties which are very promising for applications in microwave technology because they combine ferrimagnetic and ferroelectric properties, and the ferroelectric Curie points of these compositions lie below t_{room}, while the ferrimagnetic transition points

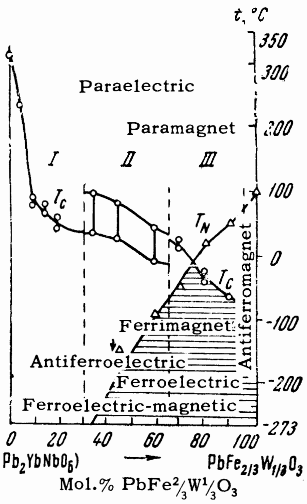

FIG. 6. Phase diagram of the system $PbFe^2/_3W^1/_3O_3$ – Pb_2YbNbO_6. The values of T_N and T_C for $PbFe^2/_3W^1/_3O_3$ and Pb_2YbNbO_6 are taken, respectively, from(2, 4).

lie above t_{room} (the microwave-frequency dielectric losses of ferroelectrics in the paraelectric state are small[11]). However, the spontaneous magnetic moment of these compositions is relatively small (several G.cm³/g). This poses the problem of preparing similar materials with stronger ferromagnetic or ferrimagnetic properties for the purpose of investigating them and determining their possible applications.

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