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Figure 1

Figure 1: Figure 1

Abstract

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NEW FERROELECTRICS WITH THE PEROVSKITE AND PYROCHLORE STRUCTURES

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In the present work the task was set of obtaining and studying a series of compounds with the perovskite structure of general composition $A(Bi_{1/2}B^{5+}_{1/2})O_3$ and $A(Bi_{1/3}B^{6+}_{1/3})O_3$, where A = Ba and Pb; $B^{5+} = Nb, Ta$, and V; $B^{6+} = W$ and Mo. Since their composition includes such highly polarizable ions as Pb^{2+}, Bi^{3+}, Ba^{2+}, Nb^{5+}, etc., in the event of the formation of these compounds one could expect special dielectric properties—ferroelectric, ferrielectric, or antiferroelectric.

The samples of the indicated compositions were prepared by the usual ceramic technology by means of double firing. The starting materials used were $PbCO_3$, Bi_2O_3, WO_3, Nb_2O_5, Ta_2O_5 of analytical grade; V_2O_5 of chemically pure grade, and spectrally pure $BaCO_3$. For each of the compositions, optimal conditions for the first and second firings were selected, providing the highest equilibrium and the best ceramic properties of the samples.

Fig. 1. Temperature dependences of the dielectric permittivity of new pyrochlores, measured at a frequency of 200 kHz:
1 –Pb_2BiNbO_6;
2 –Pb_2BiTaO_6;
3 –$Pb_2Bi_{4/3}W_{2/3}O_6$;
4 –$Pb_2Bi_{4/3}Mo_{2/3}O_6$.

X-ray analysis showed that the samples with barium, as expected, were obtained with the perovskite structure, whereas the majority of the samples with lead had the pyrochlore structure, and only in the case of $B^{5+} = V$ was the sample not single-phase, although the principal phase was perovskite. It was not possible to identify the second phase.

Table 1 gives a list of the synthesized compounds, the conditions for their preparation, X-ray data, and also some data from electrical measurements, which will be discussed below.

In the X-ray diffraction patterns of most of the perovskites, in addition to the main lines corresponding to a cell with a period of ~ 4 Å, there is also a series of weak lines evidently due to an ordered arrangement of Bi and B^{5+} ions or of Bi and B^{6+} ions. Such superstructure lines are not observed only in the X-ray diffraction pattern of the perovskite Ba_2BiTaO_6, which may be explained by the closeness of the atomic numbers of Bi (83) and Ta (73), the square of whose difference is proportional to the intensities of the superstructure lines. At the same time,

in this case, in the X-ray diffraction patterns of perovskites of the initial composition $Ba(Bi_{1/2}Mo_{1/2})O_3$ and $Ba(Bi_{1/2}V_{1/2})O_3$, in addition to superstructure lines due to ordering, characteristic superstructure lines due to antiparallel displacements of ions are present. In the case of the compounds $Ba_2BiB^{5+}O_6$, where B^{5+} = Nb, Ta, and V, and also, apparently, in the case of the compound Pb_2BiVO_6, the periods of the superstructural

Table 1

Some data on new perovskites and pyrochlores

Formula	Heat treatment	X-ray data*	Curie temp., °C	$\rho_{20°}$, ohm^{-1} · cm^{-1}
Perovskites	**Perovskites**	**Perovskites**	**Perovskites**	**Perovskites**
Ba_2BiNbO_6	$T_1 =$ 720°, 2 h $T_2 =$ 800°, 5 h	Rhombohedral distort. $a =$ 8.630 Å $\alpha =$ 90°18′	420	$1 \cdot 10^{-9}$
Ba_2BiTaO_6	$T_1 =$ 800°, 4 h $T_2 =$ 880°, 1 h	Rhombohedral distort. $a =$ 8.568 Å $\alpha =$ 90°13′	410	$1 \cdot 10^{-9}$
Ba_2BiVO_6	$T_1 =$ 700°, 2 h $T_2 =$ 900°, 1 h	Monoclinic distort. $a = c =$ 8.700 Å $b =$ 8.622 Å $\beta =$ 90°32′	320	$5 \cdot 10^{-8}$
$Ba_3Bi_2WO_9^{**}$	$T_1 =$ 700°, 1 h $T_2 =$ 1050°, 1 h	Rhombohedral distort. $a =$ 4.348 Å $\alpha =$ 90°20′	> 400	$6 \cdot 10^{-8}$

Formula	Heat treatment	X-ray data*	Curie temp., °C	ρ_{20°, ohm$^{-1}\cdot$ cm^{-1}
$Ba_3BiMoO_9^{**}$	$T_1 =$ 600°, 4 h$T_2 =$ 950°, 1 h	Monoclinic distort.$a = c =$ 4.360 Å$b =$ 4.324 Å$\beta =$ 90°30′	260	$6 \cdot 10^{-8}$
Pyrochlores*	**Pyrochlores***	**Pyrochlores***	**Pyrochlores***	**Pyrochlores***
Pb_2BiNbO_6	$T_1 =$ 650°, 2 h$T_2 =$ 750°, 1 h	Monoclinic distort.$a = c =$ 10.777 Å$b =$ 10.643 Å$\beta =$ 90°29′	475	$3 \cdot 10^{-13}$
Pb_2BiTaO_6	$T_1 =$ 700°, 2 h$T_2 =$ 780°, 1 h	Tetragonal distort.$a =$ 10.686 Å$c =$ 10.816 Å	420	$4 \cdot 10^{-13}$
$Pb_2Bi_{4/3}W_{2/3}O_6$	$T_1 =$ 700°, 2 h$T_2 =$ 750°, 1 h	Tetragonal distort.$a =$ 10.637 Å$c =$ 10.799 Å	400	$2 \cdot 10^{-13}$
$Pb_2Bi_{4/3}Mo_{2/3}O_6$	$T_1 =$ 600°, 3 h$T_2 =$ 740°, 1 h	Tetragonal distort.$a =$ 11.262 Å$c =$ 11.452 Å	500	$2 \cdot 10^{-13}$

* X-ray diffraction patterns were obtained from carefully ground ceramic.

** For data on the composition, see the text.

*** The Curie points for the pyrochlores were determined as the temperatures corresponding to the centers of the transition regions (plateaus) on the $\varepsilon(t)$ curves (Fig. 1).

cell due to ordering are doubled in comparison with the periods of the subcells (which is reflected only conventionally in the writing of the formulas of these compounds). In other words, in the indicated compounds this superstructure is the same as in the compound Ba_2MgWO_6 (1). In the case of compounds of initial composition $Ba(Bi_{2/3}W_{1/3})O_3$ and $Ba(Bi_{2/3}Mo_{1/3})O_3$, the periods of the superstructural cell due to ordering are most likely tripled in comparison with the periods of the subcells. In this connection, we shall conventionally write the formulas of these compounds as $Ba_3Bi_2B^{6+}O_9$, where $B^{6+} =$ W and Mo.

The unit cells of all the perovskites and pyrochlores are slightly distorted at

Fig. 2. Temperature dependences of the dielectric permittivity of new perovskites, measured at a frequency of 200 kHz: 1 –Ba2BiNbO6; 2 –Ba3Bi2MoO9; 3 –Ba2BiVO6; 4 –Ba2BiTaO6; 5 –Ba3Bi2WO9

Figure 2: Fig. 2. Temperature dependences of the dielectric permittivity of new perovskites, measured at a frequency of 200 kHz: 1 –Ba2BiNbO6; 2 –Ba3Bi2MoO9; 3 –Ba2BiVO6; 4 –Ba2BiTaO6; 5 –Ba3Bi2WO9

room temperature (see Table 1).

In the investigated temperature dependences of the dielectric permittivity $\varepsilon(t)$ of all synthesized pyrochlores (Fig. 1), distinct maxima are present at comparatively high temperatures. On analogous curves for perovskites, for Ba_2BiNbO_6, Ba_2BiTaO_6, $Ba_3Bi_2MoO_9$, and Ba_2BiVO_6, maxima are also observed, expressed to a greater or lesser degree, and they are not due solely to the increased conductivity of these specimens at high temperatures. The Curie point of the compound $Ba_3Bi_2WO_9$ was not determined because of its increased conductivity. Its T_k is evidently above 400°.

The discovery, in the cells of the synthesized perovskites and pyrochlores, of distortions, elevated values of dielectric permittivity, and the existence of maxima on the $\varepsilon(t)$ curves makes it possible to conclude that these new substances possess special dielectric properties. At the same time, proceeding from the fact that Ba_2BiNbO_6, Ba_2BiTaO_6, and $Ba_3Bi_2WO_9$ have rhombohedrally distorted cells and lack a superstructure caused by antiparallel displacements of ions, whereas in the case of Ba_2BiVO_6 and $Ba_3Bi_2MoO_9$ a monoclinic distortion of the original cells is observed and such a superstructure exists, the former are most likely, according to (5), ferroelectrics, and the latter antiferroelectrics. All the new pyrochlores, like the already known $Cd_2Nb_2O_7$ (2,3) and $Sr_2Ta_2O_7$ (4), are apparently ferroelectrics.

Fig. 2. Temperature dependences of the dielectric permittivity of new perovskites, measured at a frequency of 200 kHz:
1 –Ba_2BiNbO_6; 2 –$Ba_3Bi_2MoO_9$; 3 –Ba_2BiVO_6; 4 –Ba_2BiTaO_6; 5 –$Ba_3Bi_2WO_9$.

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CITED LITERATURE

1. E. G. Steward, H. P. Rooksby, *Acta crystallogr.*, **4**, 503 (1951).
2. W. R. Cook jr., H. Jaffe, *Phys. Rev.*, **89**, No. 6, 1297 (1953).
3. W. R. Cook jr., H. Jaffe, *Phys. Rev.*, **88**, 1426 (1952).
4. V. A. Isupov, Candidate dissertation, Phys. Inst. named after P. N. Lebedev, Academy of Sciences of the USSR, 1958.
5. Yu. N. Venevtsev, G. S. Zhdanov, *Izv. AN SSSR, ser. fiz.*, **21**, No. 2, 275 (1957).

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