CRYSTALLOGRAPHY

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Abstract

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NEW LEAD-CONTAINING PEROVSKITE COMPOUNDS OF COMPLEX COMPOSITION

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Among substances with the perovskite structure, a number of compounds and solid solutions are known that possess special dielectric properties (ferro-, ferri-, and antiferroelectrics), or special magnetic properties (ferro-, ferri-, and antiferromagnets), or a combination of special dielectric and special magnetic properties (ferromagnetics). However, only a few of them have found application. Therefore, the synthesis of new perovskite compounds with the aim of studying their properties, creating a theory explaining these properties, and elucidating the possibilities for their use is an urgent task. In formulating the problem of synthesizing new lead-containing perovskites of complex composition, $Pb(B', B'')O_3$ and $Pb(B', B'', B''')O_3$, we were encouraged by the fact that all lead-containing perovskites known at present, both of simple composition $PbBO_3$ and of more complex composition, possess special dielectric properties. In selecting the constituent ions of type B, we took into account the results of previous works ([1–6]) and proceeded from the crystal-chemical possibility of formation by these ions of BO_6 octahedra, as well as from the necessity of preserving the overall stoichiometry and electroneutrality of the crystal as a whole. In addition, the requirement was taken into account that the geometric criterion t should be close to unity. As experience shows, proceeding only from these premises, in a number of cases one can predict the formation of new perovskites. However, such prediction always requires experimental verification and investigation.

In the present work, the synthesis of a large number of samples was carried out; their compositions included, in various ratios, both two and three ions of type B with different valences. All synthesized samples were obtained in the form of ceramics. In order to avoid changes in the valence of the constituent ions, firing of some samples was carried out not in air, but in a neutral (nitrogen) or oxidizing (oxygen) atmosphere. For each composition, optimal firing conditions were selected (in terms of single-phase character and ceramic density). The phase composition of the samples was monitored radiographically after each firing. Experience showed that only a small fraction of the synthesized and studied samples could be obtained with the perovskite structure, whereas the greater part had a pyrochlore structure stable at various temperatures, or the samples proved to be non-single-phase and consisted of perovskite and pyrochlore phases, or of other phases.

Table 1 presents the new perovskite compounds synthesized by us. In all, 45 new compounds with the perovskite structure were successfully synthesized. In a considerable portion of the synthesized compounds, a superstructure was established, caused by complete or partial ordering of the arrangement in the crystal lattice of ions B', B'', and B''' of different kinds. In the remaining compounds the superstructure is absent, which indicates a statistical arrangement of these ions. X-ray analysis also showed that some of the compounds (3, 5, 22, 23, 26, 27, 29–34) have, at room temperature, weakly distorted cells, which is characteristic of ferro- and

Table 1

New lead-containing perovskites of complex composition

Nos.	Composition	Nos.	Composition
	Without superstructure*		**Without superstructure***
1, 2	$Pb\,(B^{3+}_{1/2},\ Nb^{5+}_{1/2})O_3$, B^{3+} = Co, Mn**	14	$Pb\,(Co^{3+}_{1/3},\ Fe^{3+}_{1/3},\ W^{6+}_{1/3})O_3$
3	$Pb\,(Mn^{3+}_{2/3},\ W^{6+}_{1/3})O_3$	15, 16	$Pb\,(Mn^{3+}_{1/3},\ B^{3+}_{1/3},\ W^{6+}_{1/3})O_3$
4	$Pb\,(Cd^{2+}_{1/3},\ Nb^{5+}_{2/3})O_3$	15, 16	B^{3+} = Fe, Cr
5	$Pb\,(Cd^{2+}_{1/3},\ Mn^{4+}_{1/3},\ W^{6+}_{1/3})O_3$	17	$Pb\,(Li_{1/6},\ Ti^{4+}_{1/3},\ V^{5+}_{1/2})O_3$
6-10	$Pb\,(B^{2+}_{1/4},\ Mn^{4+}_{1/4},\ Nb^{5+}_{1/2})O_3$	18	$Pb\,(Li_{1/6},\ Mn^{4+}_{1/3},\ Nb^{5+}_{1/2})O_3$
6-10	B^{2+} = Ni, Co, Cd, Mg, Zn	19	$Pb\,(Fe^{3+}_{1/2},\ Mn^{4+}_{1/4},\ W^{6+}_{1/4})O_3$
11-13	$Pb\,(B^{2+}_{1/4},\ Mn^{4+}_{1/4},\ Ta^{5+}_{1/2})O_3$	20	$Pb\,(Ti^{4+}_{1/2},\ Ni^{2+}_{1/4},\ W^{6+}_{1/4})O_3$
11-13	B^{2+} = Mg, Ni, Co	21	$Pb\,(Yb_{1/2},\ Ti^{4+}_{1/4},\ W^{6+}_{1/4})O_3$
	With superstructure***		**With superstructure*****
22	$Pb\,(Sc_{1/4},\ Cr^{3+}_{1/4},\ Nb^{5+}_{1/2})O_3$	35	$Pb\,(Li_{1/6},\ Mn^{4+}_{1/3},\ W^{6+}_{1/2})O_3$
23	$Pb\,(Cd_{1/9},\ Nb^{5+}_{5/9},\ W^{6+}_{1/3})O_3$	36	$Pb\,(Sc_{1/3},\ Mn^{3+}_{1/3},\ W^{6+}_{1/3})O_3$
24	$Pb\,(Sc_{5/9},\ Nb^{5+}_{1/3},\ W^{6+}_{1/9})O_3$	37-39	$Pb\,(Li_{1/4},\ B^{3+}_{1/4},\ W^{6+}_{1/2})O_3$
25	$Pb(Sc_{2/3},\ W_{1/3})O_3$	37-39	B^{3+} = Fe, Yb, La

Nos.	Composition	Nos.	Composition
26, 27	Pb $(Mn^{2+}_{1/2}, B^{6+}_{1/2})O_3$, B^{6+} = W, Re	40–42	Pb $(Na_{1/4}, B^{3+}_{1/4}, W^{6+}_{1/2})O_3$
28, 29	Pb $(B^{3+}_{1/2}, W^{5+}_{1/2})O_3$, B^{3+} = Fe, Mn	40–42	B^{3+} = Fe, Yb, Sc
30	Pb $(Mn^{3+}_{1/2}, Re^{5+}_{1/2})O_3$	43	Pb $(Li_{1/3}, Nb^{5+}_{1/3}, W^{6+}_{1/3})O_3$
31–34	Pb $(B^{2+}_{1/4}, Mn^{4+}_{1/4}, W^{5+}_{1/2})O_3$	44, 45	Pb $(Li_{1/3}, B^{4+}_{1/6}, W_{1/2})O_3$
31–34	B^{2+} = Mg, Co, Ni, Cd	44, 45	B^{4+} = Zr, Hf

* Due to ordering of ions of type B.
** In works (4, 7) it was not possible to obtain single-phase samples of composition $Pb(Mn^{3+}_{1/2}, Nb^{5+}_{1/2})O_3$ with the perovskite structure.
*** The compositions of the compounds are given without taking the superstructure into account.

antiferroelectrics with a Curie temperature $T_K > 20°$. In many of the compounds obtained, the cells are cubic at room temperature, but this only means that the Curie temperatures of these compounds lie in the temperature region below room temperature. Indeed, selective monitoring of the character of the temperature dependences of the dielectric permittivity ε of samples Nos. 3, 23, 26, 29 with distorted cells and of samples Nos. 19, 25 with cubic cells showed the presence, respectively in the high- and low-temperature regions, of maxima on the $\varepsilon(t)$ curves, which are characteristic of perovskites with special dielectric properties. All these facts may be regarded as well-known confirmation of the empirical rule mentioned above: that all lead-containing perovskite compounds exhibit special dielectric properties.

In view of the fact that paramagnetic ions enter into the composition of many of the synthesized compounds, these compounds should be expected to possess special magnetic properties. Our preliminary analysis showed that, at room temperature, no appreciable magnetic properties are observed in these compounds. At the same time, measurements at liquid-nitrogen temperature show that the magnetic properties in a number of compounds are already expressed to a greater or lesser degree. On the basis of this fact,

On the basis of the known data on the sign of the indirect exchange interaction of various paramagnetic ions in perovskites (^8), certain experimental data on the "leakage" effect (^9), the data obtained on the ordering of type-B ions in the synthesized compounds, and also other data (^6, ^10), the following conclusion may be drawn concerning the nature of the magnetic properties of our compounds. Six compounds (Nos. 6, 7, 12, 13, 27, 30), in addition to special dielectric properties, also have ferrimagnetic properties, while five compounds (Nos. 3, 14, 15, 16, 19) have antiferromagnetic properties.

Thus, in the present work 45 new lead-containing perovskites have been synthesized, of which 34 are, in our opinion, ferroelectrics, ferroelectrics or antiferroelectrics, and 11 are ferroelectric magnets.

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CITED LITERATURE

1. E. G. Steward, H. P. Rooksby, *Acta Cryst.*, **4**, 503 (1951).
2. R. Roy, *J. Am. Chem. Soc.*, **37** (12), 581 (1954).
3. G. A. Smolenskii, A. I. Agranovskaya, *ZhTF*, **28**, No. 7, 1491 (1958).
4. V. S. Filip' ev, N. P. Smolyaninov et al., *Kristallografiya*, **8**, issue 5, 790 (1963).
5. I. N. Belyaev, V. S. Filip' ev, E. G. Fesenko, *Zhurnal strukturnoi khimii*, **4**, No. 4, 719 (1963).
6. J. Longo, R. Ward, *J. Am. Chem. Soc.*, **83**, 2816 (1961).
7. A. I. Agranovskaya, Candidate' s dissertation, Institute of Silicate Chemistry, Academy of Sciences of the USSR, Leningrad, 1962.
8. G. H. Jonker, *Physica*, **22**, 707 (1956).
9. O. N. Venevtsev, G. S. Zhdanov et al., *Izv. AN SSSR, ser. fiz.*, **28**, issue 4 (1964).
10. G. A. Smolenskii, V. A. Isupov et al., *Izv. AN SSSR, ser. fiz.*, **25**, No. 11, 1333 (1961).

Note: Figure translations are in progress. See original paper for figures.