NEW PEROVSKITES

CRYSTALLOGRAPHY

1966

SovietRxiv

Abstract

Full Text

UDC 548:53

CRYSTALLOGRAPHY

A. G. KAPYSHEV, V. V. IVANOVA, Yu. N. VENEVTSEV

NEW PEROVSKITES

(Presented by Academician N. V. Belov on 8 VII 1965)

The synthesis and study of new perovskites is of scientific and practical interest because many of them exhibit various physical properties (ferroelectric, ferromagnetic, and others).

As a rule, in the search for and synthesis of new perovskites of composition ABO_3 and the more complex $(A', A'', ...)(B', B'', ...)O_3$, such factors are taken into account as the size and valence of the ions, their tendency to form particular coordinations, and other factors favoring the formation of substances with the perovskite structure. If the task is to synthesize perovskites with ferroelectric properties, then one usually seeks to introduce highly polarizable ions into the composition of the substances being synthesized; in the synthesis of ferromagnets, paramagnetic ions are also introduced into the perovskites.

In the present work the task was to synthesize a number of new perovskites for the purpose of further studying their properties. The composition of all the synthesized perovskites can be described by the general formulas $A(B', B'')O_3$ and $A(B', B'', B''')O_3$, where A = Ba or Sr, while ions of the B type used were Li, Na, Cu^{2+}, Cd^{2+}, In^{3+}, Sc^{3+}, Ho^{3+}, Dy^{3+}, Nb^{5+}, Ta^{5+}, W^{6+}, Mo^{6+} in various combinations ensuring electroneutrality of the crystal lattice and preservation of the overall stoichiometry.

Samples for investigation were prepared by the usual ceramic technology—by reactions in the solid phase. Carbonates and oxides of metals of reagent, chemically pure, and pure grades were used as starting materials.

The phase composition of the synthesized samples was monitored by X-ray diffraction (from radiographs obtained in RKD-57 cameras with CuK_α radiation). The nature of the distortion and the unit-cell parameters were determined from radiographs obtained in RKD-114 cameras (designed at the L. Ya. Karpov Physicochemical Institute), with the radiation giving the highest resolution used in each particular case.

Table 1 gives the newly synthesized perovskites, the starting materials for the synthesis, the firing temperatures with holding times at these temperatures, and also the unit-cell parameters (without taking into account the atomic superstruc-

ture due to ordering of B-type ions). The unit-cell periods were determined with an accuracy of ±0.001 Å, rhombohedral angles ±2′, and axial ratios ±0.0005.

On the radiographs of compounds Nos. 1 and 4 there are superstructure lines that make it possible to conclude that the ions B′ and B″ are ordered, analogous to what occurs in the compound Ba_2MgWO_6 ([3]). On the radiographs of the other compounds there are also weak lines, which may be associated with the existence of a superstructure in these compounds as a result of ordering of the B ions. However, the question of the character of the superstructure of these compounds was not examined in detail in the present work.

As can be seen from Table 1, at room temperature a number of compounds (Nos. 1-6) have tetragonally distorted cells with $c/a > 1$; compounds Nos. 7-9 have rhombohedrally distorted cells; compounds Nos. 11-14, 17, 18 have cubic cells. Finally, compounds Nos. 19, 20 have weakly distorted cells. Some nonequilibrium character of the samples of the latter compounds (judging from the observed diffuseness of the lines in the X-ray patterns) made it difficult to determine the nature of the distortion

Table 1

Sample No.	Compound obtained	Starting materials	Firing temperature in °C and holding time in hours	Unit-cell parameters (a, c in Å)
1	$Ba(Cu_{1/2}W_{1/2})O_3$	$BaCO_3$, CuO, WO_3	950 (2), 1200 (1)	$a = 3.937$, $c = 4.312$, $c/a = 1.095$
2	$Ba(Cu_{1/3}Nb_{2/3})O_3$	$BaCO_3$, CuO, Nb_2O_5	1150 (2), 1300 (1)	$a = 4.048$, $c = 4.174$, $c/a = 1.031$
3	$Ba(Cu_{1/3}Ta_{2/3})O_3$	$BaCO_3$, CuO, Ta_2O_5	1150 (2), 1350 (1)	$a = 4.066$, $c = 4.216$, $c/a = 1.037$
4	$Sr(Cu_{1/2}W_{1/2})O_3$	$SrCO_3$, CuO, WO_3	1150 (1), 1300 (1)	$a = 3.840$, $c = 4.205$, $c/a = 1.095$
5	$Sr(Cu_{1/3}Nb_{2/3})O_3$	$SrCO_3$, CuO, Nb_2O_5	1250 (1), 1350 (1)	$a = 3.944$, $c = 4.074$, $c/a = 1.033$

Sample No.	Compound obtained	Starting materials	Firing temperature in °C and holding time in hours	Unit-cell parameters (a, c in Å)
6	$Sr(Cu_{1/3}Ta_{2/3})O_3$	$SrCO_3$, CuO, Ta_2O_5	1300 (1), 1380 (1)	$a = 3.930$, $c = 4.124$, $c/a = 1.049$
7	$Ba(Li_{1/3}Nb_{1/3}W_{1/3})O_3$	$BaCO_3$, Li_2CO_3, Nb_2O_5, WO_3	900 (2), 1250 (1.5)	$a = 4.098$, $\alpha = 89°52'$
8	$Ba(Li_{1/3}Ta_{1/3}W_{1/3})O_3$	$BaCO_3$, Li_2CO_3, Ta_2O_5, WO_3	900 (2), 1300 (1.5)	$a = 4.095$, $\alpha = 89°53'$
9	$Ba(Li_{1/3}Nb_{1/3}Mo_{1/3})O_3$	$BaCO_3$, Li_2CO_3, Nb_2O_5, H_2MoO_4	750 (1), 900 (1)	$a = 4.091$, $\alpha = 89°50'$
10	$Ba(Li_{1/3}Ta_{1/3}Mo_{1/3})O_3$	$BaCO_3$, Li_2CO_3, Ta_2O_5, H_2MoO_4	800 (1), 940 (1)	$a = 4.090$
11	$Ba(Na_{2/5}W_{3/5})O_3$	$BaCO_3$, Na_2CO_3, WO_3	850 (1), 940 (1)	$a = 4.158$
12	$Ba(In_{2/3}Mo_{1/3})O_3$	$BaCO_3$, In_2O_3, H_2MoO_4	950 (1), 1350 (1.5)	$a = 4.163$
13	$Ba(In_{2/3}W_{1/3})O_3$	$BaCO_3$, In_2O_3, WO_3	950 (1), 1350 (1.5)	$a = 4.160$
14	$Ba(Sc_{2/3}W_{1/3})O_3$	$BaCO_3$, Sc_2O_3, WO_3	1350 (2)	$a = 4.109$
15	$Ba(Ho_{2/3}W_{1/3})O_3$	$BaCO_3$, Ho_2O_3, WO_3	1200 (1.5), 1350 (2)	$a = 4.252$
16	$Ba(Dy_{2/3}W_{1/3})O_3$	$BaCO_3$, Dy_2O_3, WO_3	1200 (1.5), 1350 (2)	$a = 4.262$
17	$Ba(Li_{1/4}Nb_{3/4})O_3$	$BaCO_3$, Li_2CO_3, Nb_2O_5	1100 (1), 1300 (1)	$a = 4.095$
18	$Ba(Na_{1/4}Nb_{3/4})O_3$	$BaCO_3$, Na_2CO_3, Nb_2O_5	1100 (1), 1300 (1)	$a = 4.107$

of the cells; therefore their periods were calculated under the assumption of cubic symmetry of their cells.

It is surprising that all compounds Nos. 1-6, containing divalent copper ions, exhibit the same type of tetragonal distortion ($c/a > 1$), and that this distortion is comparatively large. In the case of compounds Nos. 1, 4, 6 it is approximately the same as, or greater than, that of the well-known ferroelectric $PbTiO_3$ ($c/a = 1.06$) (4). Moreover, from an analysis of the data for compounds Nos. 1-5 it may be concluded that replacing barium by strontium has a comparatively weak

effect on the degree of tetragonality of the cells (c/a), whereas the values of the periods a and c themselves change, reflecting the replacement of Ba by Sr.

Proceeding from the fact that perovskites Nos. 1-9 exhibit cell distortions characteristic of ferroelectrics ($c/a > 1$ or $\alpha < 90°$) (5), and that their composition includes highly polarizable ions, it may be assumed that they possess ferroelectric properties.

In conclusion, we express our gratitude to Prof. G. S. Zhdanov for his interest in the work and for discussing the results.

Physicochemical Institute
named after L. Ya. Karpov

Received
6 VII 1965

References

1. Yu. N. Venevtsev, Yu. E. Roginskaya et al., DAN, **158**, No. 1 (1964).
2. A. S. Viskov, Yu. N. Venevtsev, G. S. Zhdanov, DAN, **162**, No. 2 (1965).
3. E. G. Steward, H. P. Rooksby, Acta crystallogr., **4**, 503 (1951).
4. J. Naray-Szabo, Muegyetemi közlemenyek, Budapest, No. 1, 30 (1947).
5. Yu. N. Venevtsev, G. S. Zhdanov, Izv. AN SSSR, ser. fiz., **21**, No. 2 (1957).

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