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High Pressure Synthesis and Polymorphism of Complex Oxides Mn_2BSbO_6(B = Fe, V, Cr, Ga, Al)

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Conditions for formation of a synthetic analog of the natural mineral melanostibite with the composition Mn_2FeSbO_6 which crystallizes in the structural type of ilmenite and of some other compounds belonging to the series Mn_2BSbO_6, B = Cr, V, Ga, Al, have been found. It has been established that none of these compounds is formed from simple oxides when their mixtures are sintered in air at 900–1320°C. The products of synthesis under these conditions were binary oxides $MnSb_2O_6$, $Mn_2Sb_2O_7$, and spinel phases of the MnB_2O_4 composition. The compound Mn_2FeSbO_6 with the structure of ilmenite has been synthesized under a pressure of 3 GPa and temperature 900°C. The lattice parameters of this phase (a = 5,238(1), c = 14,344(3) Å, hexagonal unit cell) approximate those determined for the natural mineral. A phase transition from the ilmenite to the perovskite modification was registered for Mn_2FeSbO_6 at 5 GPa and 900°C. The perovskite phase in the pure form has been obtained at 6 GPa and 900°C. The orthorhombic unit cell with a = 5.394(2), b = 5,246(1), c = 7,652(3) Å and ordered distribution of Fe^{3+} and Sb^{5+} cations in octahedral sites of the perovskite structure was established for this phase. The other compounds from this series also form ilmenite and perovskite structures under high pressures. In the process of high pressure synthesis it was also found that all the investigated systems contain phases with the cubic pyrochlore structure, the composition of which was not identified.

I. INTRODUCTION

Compounds of the general composition ABO_3, where A and B are atoms of different elements, form several types of crystal structures—perovskite, ilmenite, pyroxene, etc., depending upon relative sizes of the constituent cations. It follows from the geometric conditions necessary for these compounds to form the perovskite structure that there is a lower limit to the size of cation A (at a given value of B), beyond which a transition to other structural types occurs, in particular, to ilmenite, corundum, C-type (1). Similar changes in structure take place also in the series of compounds with the more complex composition $A_2BB'O_6$, in which A- sites are occupied by divalent cations and B- and B'-sites by trivalent and pentavalent cations, respectively. So, A_2FeSbO_6, where A is Sr, Ca, are perovskites (2), Mn_2FeSbO_6 is ilmenite (3), and Cu_2FeSbO_6 is bixbyite (C-type) (4). The reason for morphotropism in this series of the same type compounds is a decrease in ionic radii of bivalent cations (1.18 and 1.00 Å for Sr^{2+} and Ca^{2+}, respectively, 0.83 Å for Mn^{2+}, and 0.73 Å for Cu^{2+} for the coordination number 6 (5)).

The region of existence of the perovskite structure on the stability fields diagram of the ABO_3 type compounds can be extended by using high pressures and high temperatures in the process of synthesis. The compound $MnVO_3$ provides an example of the ilmenite–perovskite transformation at 45 kbar. Some information concerning polymorphous transitions to the perovskite modification occurring under high pressure and high temperature conditions in compounds, which in usual conditions form ilmenite, corundum, or pyroxene structures, is generalized in (7). The reason the perovskite structure is formed under high pressures has to do with a closer packing of atoms resulting from an increased coordination of anions around cations. On the other hand, the fact that some compounds, which are not formed under usual conditions, can be synthesized under high pressures is of considerable significance.

The conditions of high pressure and high temperature synthesis and polymorphism of Mn_2BSbO_6 compounds, where B is Fe, Cr, V, Ga, and Al, have been studied in the present work. Only one compound from this series, namely Mn_2FeSbO_6, has been described in the earlier literature (3). This compound was identified owing to investigations of samples of the natural mineral melanostibite. According to chemical analysis data the composition of this mineral was determined as Mn and Fe antimonate. X-ray diffraction studies showed that Mn_2FeSbO_6 crystallizes in the rhombohedral unit cell (space group $R3$, ilmenite type structure) with parameters (for the hexagonal unit cell) a_h = 5.226 Å and c_h = 14.325 Å.

II. EXPERIMENTAL

The oxides MnO_2, Sb_2O_3, Fe_2O_3, V_2O_5, Cr_2O_3, Ga_2O_3, and Al_2O_3 containing minimum 99.9% of the basic sub-

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stance were used in this work as initial reagents. The oxide mixture was prepared for high pressure synthesis according to the reaction

$$2Mn_2O_3 + B_2O_3 + Sb_2O_3 = 2\,Mn_2BSbO_6, \qquad [1]$$

where B = Fe, V, Cr, Ga, Al.

The oxide Mn_2O_3 was preliminarily obtained from MnO_2 by sintering in air at 600°C during 18 h. The V_2O_3 oxide was prepared from V_2O_5 by reduction in a H_2 flow at 900°C during 8 h.

To produce high pressures (3–9 GPa) and temperatures (700–900°C), a press was used with a force of 784 kN. A sample in the powder form was placed in a graphite heater lined with Pt-foil to prevent interaction of the powder with the material of the heater. The press was calibrated for pressure based on the transitions in bismuth, and the temperature was measured by means of a thermocouple. In each experiment the pressure was first set to the rated value, then the temperature was increased. The time of high pressure treatment of samples was, as a rule, 15 min. On completion of the experiment, the temperature of a sample was reduced to room temperature; after that the pressure was decreased to the normal one. The phase composition of the reaction products was studied by powder X-ray diffraction (XRD) method using CuK_α radiation with a DRON-2 diffractometer. Silicon was used as a standard to establish the interplanar distances.

Magnetic susceptibility χ was measured in the temperature range 4.2–300 K by magnetic scales with electromagnetic compensation according to Faraday's method. The error in determining χ was not more than ±2%.

III. RESULTS AND DISCUSSION

Investigation of the products of reaction [1], carried out under atmosphere pressure in air at 950–1320°C, revealed that none of the compounds with the composition Mn_2BSbO_6, where B = Fe, Cr, Ga, and Al, are formed under these conditions (we did not try to synthesize the V-containing compound since the trivalent state of this element is not stable in air at high temperatures). The phase composition of the samples obtained at 900 and 1200°C is given in Table 1. The binary oxides $MnSb_2O_6$, $Mn_2Sb_2O_7$, and phases with the spinel structure composition approximating that of MnB_2O_4 have been identified among the synthesized compounds. These findings indicate that the ternary oxides Mn_2BSbO_6 cannot be obtained by the solid phase reaction method in air under atmosphere pressure. It should be also inferred that the conditions for formation of melanostibite mineral in the earth-crust considerably from the usual ones.

TABLE 1

The Phase Composition of the Products of Synthesis of Mn_2BSbO_6 (B = Fe, Ga, Cr, Al) in Air

B	950°C	1200°C
Fe	$MnSb_2O_6$, $Mn_2Sb_2O_7$, Mn_2O_3	$Mn_2Sb_2O_7$, spinel
Ga	$MnSb_2O_6$, $Mn_2Sb_2O_7$, X-phase[a]	$Mn_2Sb_2O_7$, spinel
Cr	$MnSb_2O_6$, spinel, X-phase	$Mn_2Sb_2O_7$, spinel
Al	$MnSb_2O_6$, $Mn_2Sb_2O_7$, spinel	$Mn_2Sb_2O_7$, spinel

[a] X-phase = unidentified phase.

Table 2 presents the data on the composition of products obtained by thermobaric treatment of oxide mixtures taken in the quantities corresponding to reaction [1]. As follows from this table, Mn and Fe antimonate of the composition Mn_2FeSbO_6 with the ilmenite structure is formed under a pressure of 3 GPa and temperature 900°C. It should be pointed out that treatment at 3 or 6 GPa and 900°C of a sample with the same composition which had been preliminarily annealed in air at 950°C did not lead to formation of the desired compound. This result stems from the change in the initial composition of the mixture in oxygen occurring during annealing in air. This conclusion was made on the basis of data presented in Table 1, from which it follows that the product of treatment in air at 950°C contains a phase with the Mn_2O_3 type structure.

Powder XRD pattern of the synthetic ilmenite Mn_2FeSbO_6 (Fig. 1) is close to that published in (3) for the natural mineral melanostibite. The lattice parameters (Table 3) are also similar to those found in (3). High intensity of reflections with indices 003, 006, and 009 on the XRD pattern of the compound obtained by us (Fig. 1) is due to the presence of preferred orientation in the powder sample under study. The synthesized compound has a dark-

TABLE 2

Conditions of Synthesis and Phase Composition of the Products, Obtained from High Pressure and High Temperature Treatment of Mn_2BSbO_6 (B = Fe, V, Cr, Ga, Al)

	Conditions of treatment							
	3 GPa		4 GPa	5 GPa		6 GPa		9 GPa
B	700°C	900°C	900°C	700°C	900°C	700°C	900°C	900°C
Fe		I, P	I, P	P, I	Pv, P		Pv	
V		P, X_1, X_2					Pv, X_2	Pv, P, X_2
Cr		P, X_1					P, Pv	Pv, P, X_2
Ga	P, I	I, P				I, P	I	Pv, P, I
Al		P, I	P, I				I, P	P, Pv

Note. Designations: I, ilmenite; P, pyrochlore; Pv, perovskite; X_1, spinel; X_2, unidentificated phases.

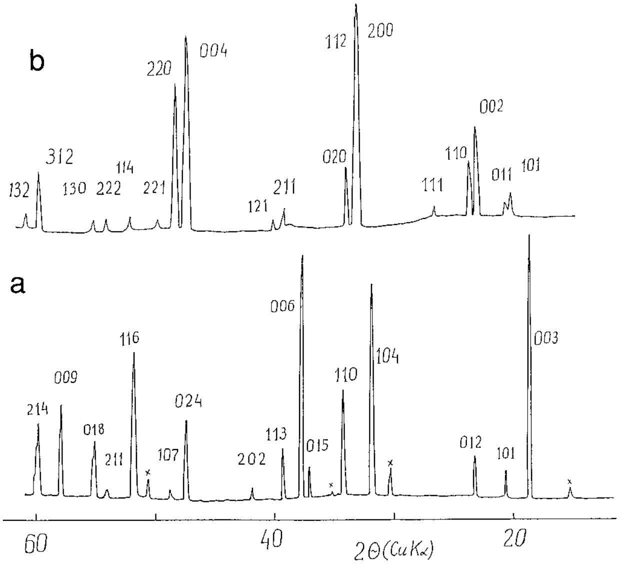

FIG. 1. X-ray diffraction patterns of Mn_2FeSbO_6 with ilmenite (a) and perovskite (b) structures (x, traces of the pyrochlore phase).

brown color. The density of Mn_2FeSbO_6 calculated from the unit cell parameters is 5.60 g/cm^3. The absence of superstructural reflections on the diffractogram pattern of Mn_2FeSbO_6 is indicative of a disordered location of Fe^{3+} and Sb^{5+} cations in the lattice. This inference coincides with the conclusion made in (3) for the natural mineral melanostibite.

According to the powder XRD pattern (Fig. 1), a sample of Mn_2FeSbO_6 obtained at 3 GPa contains a small amount of an impurity, which has a cubic pyrochlore-type structure ($a = 10.178 \pm 0.002$ Å). The greatest quantity of the impurity phase was found in a sample synthesized at 5 GPa and 700°C. The cubic structure of the pyrochlore type with $a = 10.17$ Å, as evidenced by the data of (8), is characteristic of the manganese antimonate $Mn_2Sb_2O_7$. However, it was shown in (9, 10) that this compound has a rhombohedral distorted pyrochlore structure. In (11), a trigonal fluorite-like structure of the mentioned antimonate was postulated on the basis of structural investigations performed. The $Mn_2Sb_2O_7$ compound obtained by us in air at 1200°C had a powder XRD pattern analogous to that given in (11). Upon thermobaric treatment at 3 and 6 GPa and 900°C, the crystal structure of the manganese antimonate $Mn_2Sb_2O_7$ underwent no changes. This result allows us to assert that a new phase with the cubic pyrochlore structure with $a = 10.178$ Å is formed in the Mn–Fe–Sb–O system under high pressure.

In addition to the compound with the pyrochlore structure, a phase with the perovskite structure has been found in the product of treatment at 5 GPa and 900°C. This finding is attributed to the change in the structure of Mn and Fe antimonate occurring at 5 GPa. As a consequence, this complex oxide undergoes a phase transition from ilmenite to perovskite. The pure perovskite phase was obtained at 6 GPa and 900°C (Fig. 1). The powder XRD pattern of the perovskite-like modification of the compound Mn_2FeSbO_6 was indexed in the orthorhombic symmetry (possible space group *Pbnm*) with the parameters that are related with parameter a_o of the perovskite's ideal cubic lattice by relationships $a \cong \sqrt{2}a_o, b \cong \sqrt{2}a_o$, $c \cong 2a_o$. The presence of low intensity reflections with indices 011 and 101 (Fig. 1) points to the order in the location of cations occupying octahedral sites of the perovskite structure (in this case Fe^{3+} and Sb^{5+}). In this regard the perovskite Mn_2FeSbO_6 is analogous to Ca_2FeSbO_6 (2). The density of the perovskite modification of manganese and iron antimonate calculated from the unit cell parameters (Table 3) is 5% greater than that of ilmenite. This fact accounts

TABLE 3
Unit Cell Parameters and Density of Polymorphous Modifications of Mn_2BSbO_6 (B = Fe, V, Cr, Ga, Al)

			Parameters (Å)				
B	R_B^{3+}(A)	Crystal structure	*a*	*b*	*c*	V(Å^3)	ρ (g/cm^3)
		Ilmenite[a]	5,238(1)	—	14,344(3)	340,8	5,60
Fe	0,645	Pyrochlore[b]	10,178(2)				
		Perovskite	5,394(2)	5,246(1)	7,652(3)	216.5	5.88
V	0.640	Pyrochlore[b]	10,161(1)				
Ga	0.620	Ilmenite	5.210(1)	—	14.417(7)	338.9	5.84
		Pyrochlore[b]	10.168(1)				
Cr	0,615	Pyrochlore[b]	10,169(1)				
Al	0.53	Ilmenite	5.153(2)	—	14.413(3)	331.5	5,33
		Pyrochlore[b]	10.138				

[a] Parameters of all the compounds with ilmenite structure are given in the hexagonal system.

[b] The pyrochlore phase composition has not been identified.

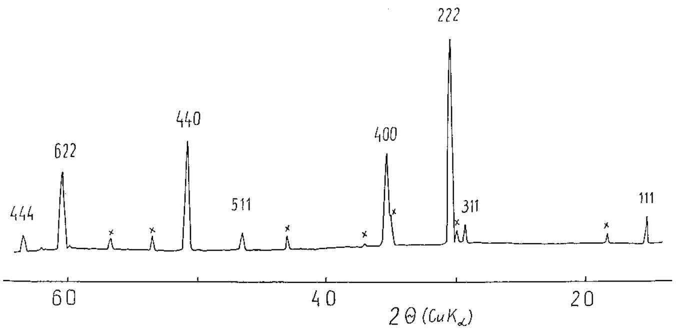

FIG. 2. X-ray diffraction patterns of the sample Mn_2CrSbO_6 synthesized at 3 GPa and 900°C (x, traces of the spinel phase).

for the cause of the phase transition ilmenite–perovskite observed in Mn_2FeSbO_6 at increased pressure.

High pressure and high temperature synthesis of Mn_2BSbO_6 compounds with V, Cr, Ga, and Al atoms occupying B-sites has led to the following results. It is evident from Table 2 that all the products of treatment of samples with the same composition also contain a phase with the cubic pyrochlore structure. As a rule, the pyrochlore phase is formed when pressure and temperature parameters have the lowest values. This testifies that the pyrochlore phase is formed as the initial product in the synthesis of complex oxides with the composition Mn_2BSbO_6. The lattice parameters a of the pyrochlore phases correlate with the radii of cations B^{3+} (Table 3). Only the value of a for the V-containing compound does not come within the general dependence, a fact which can be attributed to the variable degree of oxidation of this element. Figure 2 presents a powder XRD pattern of a sample with the composition Mn_2CrSbO_6 treated at 3 GPa and 900°C. The pyrochlore phase is seen to prevail in the product of high pressure synthesis. Along with pyrochlore, a complex oxide with the spinel structure is identified. Similar findings have been obtained for the V-containing sample. Al- and especially Ga-containing compositions contain at 3 GPa and 900°C the ilmenite modification of Mn_2BSbO_6 compounds in addition to pyrochlore.

The results obtained indicate that the cubic phases formed as initial products of synthesis contain B^{3+} cations. Three versions of the composition of the phase with the pyrochlore structure have been analyzed:

1. Mn_2BSbO_7. Treatment at 3 and 6 GPa and 900°C of mixtures of oxides (B = Ga) taken in the quantities corresponding to the above stoichiometry did not give rise to ternary oxides. The products contained rutile (apparently, $GaSbO_4$) and Mn_2O_3 phases.

2. $Mn_2B_{0.5}Sb_{1.5}O_{6.5}$. Examination of the sample with B = Ga synthesized at 3 GPa and 900°C showed that its phase composition is close to that of Mn_2GaSbO_6 (Table 2) obtained under the same conditions, the difference being that instead of the cubic pyrochlore phase the former contains $Mn_2Sb_2O_7$ with a fluorite-like structure: 2 $Mn_2Ga_{0.5}Sb_{1.5}O_{6.5} = Mn_2GaSbO_6$ (ilmenite) + $Mn_2Sb_2O_7$.

3. The cubic pyrochlore structure is characteristic of Mn_2BSbO_6 compounds at the certain temperatures and pressures. Such complex oxides with the structure of defective pyrochlore have already been described in the literature, for example, $Cd_2B^{3+}M^{5+}O_6$, where B = Cr, Mn, Fe, Sc; M = Nb, Ta (12). However, the circumstance that samples treated in a wide pressure and temperature range contain impurity phases with another ratio of cations, in particular, spinel phases (Table 2), does not permit us to accept this viewpoint as final.

The ilmenite modification in the pure form was obtained at 6 GPa and 900°C for Mn_2GaSbO_6. The maximum content of this modification in the Al-containing sample is 50%, which is achieved upon treatment at 6 GPa and 900°C during 15 min. Thus, the ilmenite modification is formed only in the three investigated compounds—Mn_2FeSbO_6, Mn_2GaSbO_6, and Mn_2AlSbO_6. The volume of the ilmenite unit cell increases with an increase in the ionic radius of B^{3+}-cations (Table 3). In order to discover the ilmenite–perovskite transition in Al- and Ga-containing Mn_2BSbO_6 compounds, we carried out their synthesis for 2 min at 9 GPa and 900°C. The X-ray diffraction studies performed showed that after this treatment both samples were not single phase. They both contained a perovskite-like phase, a fact which bears witness to the presence in these compounds of a phase transition similar to that observed in Mn_2FeSbO_6.

At 6 GPa, Mn_2BSbO_6 compounds, where B = V and Cr, form a perovskite-like modification along with the cubic pyrochlore phase. However, the perovskite phase could not be obtained in the pure form even at 9 GPa. The ilmenite modification has not been found for these compounds.

Magnetic susceptibility of the Mn_2GaSbO_6 sample with the ilmenite structure and of the Mn_2FeSbO_6 samples having ilmenite and perovskite structures has been measured. Figure 3 displays the results of measurements for the Ga-containing sample. It is seen that in the temperature range 50–300 K magnetic susceptibility χ obeys the Curie–Weiss law $\chi = c/(T - \theta)$. The values of the Curie–Weiss equation constants c and θ are 4.19 and -157 K, respectively. The calculated effective magnetic moment equals 5.79 μ_B, a value which is close to the theoretical one for the Mn^{2+} ion (5.92 μ_B) for the external electronic configuration d^5. Below 50 K, magnetic susceptibility of Mn_2GaSbO_6 with the ilmenite structure deviates from the Curie–Weiss law. Apparently, this is connected with a transition to the magnetically ordered state.

At 300 K, both modifications of the compound Mn_2FeSbO_6 exhibit a relationship between magnetic susceptibility and the magnetic field applied. The reason for

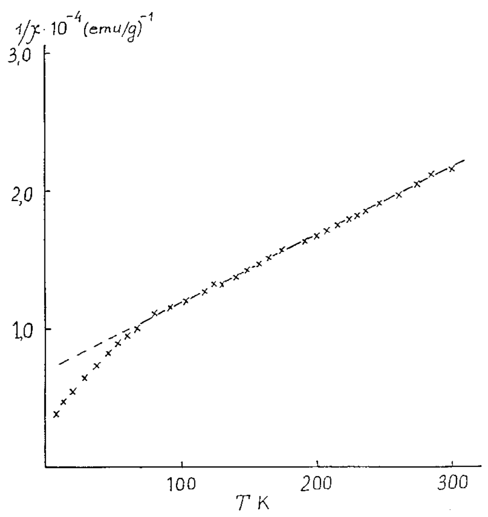

FIG. 3. Inverse magnetic susceptibility as a function of temperature for Mn_2GaSbO_6 with the ilmenite structure.

this relationship may be either the ferromagnetic properties of the compound or the presence of an uncontrollable impurity—a phase with the spinel structure.

In summary, it was established in this work that the synthetic analog of the natural mineral melanostibite Mn_2FeSbO_6, like other complex oxides from the Mn_2BSbO_6 series, where B = Cr, V, Ga, Al, can be obtained under high pressure and high temperature conditions. Depending upon the parameters of treatment, the compounds in question form ilmenite (B = Fe, Ga, Al) and perovskite (B = Fe, Cr, V, Ga, Al) structures. With an increase in pressure, all the compounds forming the ilmenite structure undergo a transition to the perovskite structure characterized by a closer packing of atoms. Pyrochlore phases were registered in all the systems as a result of high pressure synthesis with the lowest parameters. Based on the magnetic susceptibility measurements performed it was found that Mn in Mn_2GaSbO_6 is in the bivalent state.

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