JOURNAL OF SOLID STATE CHEMISTRY **113**, 132–137 (1994)

Synthesis, Crystal Structure, and Magnetic Properties of Complex Oxides Cu_2BSbO_6 (B = Mn, Fe, Ga) with a Bixbyite Structure

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Received August 13, 1993; in revised form January 21, 1994; accepted January 24, 1994

New complex oxides Cu_2BSbO_6 ($B = Mn^{3+}, Fe^{3+}, Ga^{3+}$) with a body-centered cubic elementary cell (the bixbyite type structure) and parameters 9.5667(3), 9.5622(3), and 9.5237(3) Å, respectively, have been synthesized in air at 950°C from simple Cu, Sb, Mn, Fe, and Ga oxides. Rietveld's method of full-profile analysis was employed to refine the structure parameters of one of the obtained compounds, Cu_2FeSbO_6. Sb occupies 8b sites and Cu and Fe are in 24d sites. From cation–oxygen and oxygen–oxygen interatomic distances, it was shown that Sb occurs within an almost regular SbO_6 octahedron (R_{Sb-O} = 2.00 Å), while Fe and Cu are located inside strongly distorted octahedra (R_{M-O} (Å) = 1.938, 2.020, and 2.311). Magnetic susceptibility χ of the compounds was measured. For Cu_2GaSbO_6, $\chi(T)$ obeys the Curie-Weiss law in the temperature range 77–300 K. For Cu^{2+}, the values of Weiss's constant and the magnetic moment ($c = 0.42$, $\mu = 1.81\mu_B$) are close to the theoretical ones. A transition to the antiferromagnetic state was observed at 15.6 K for Cu_2FeSbO_6 and at 5.9 K for Cu_2MnSbO_6. © 1994 Academic Press, Inc.

I. INTRODUCTION

The majority of complex oxides $A_2BB'O_6$, where A, B, and B' are bivalent, trivalent, and pentavalent cations, respectively, have a perovskite type structure with ordered and disordered distribution of B^{3+} and B^{5+} cations. Cd, Ca, Sr and Ba have been described in these compounds as A elements, Mn, Fe, Al, Sc, etc. as B elements, and Nb, Ta and Sb as B' elements (1, 2). The compounds under consideration attract attention due to the variety of their physical and physicochemical properties (ferroelectric, magnetic, catalytic, etc.).

It is known (3) for ABO_3 that compounds of the perovskite type structure occur when a certain relationship of ionic radii of A and B elements is achieved. This relationship is determined by the tolerance factor t,

$$t = \frac{R_A + R_O}{(R_B + R_O)\sqrt{2}},$$

where R_A, R_B, and R_O are radii of the A and B cations and the oxygen anion. The range of values of the tolerance factor depends on the valence of the cations; for example it is $0.77 \le t \le 0.99$ for perovskites of the (A^{2+}–B^{4+}) type. From this geometric condition it follows that the A cation should be larger than the B cation. Therefore, with a decrease of the A cation radius below the critical value, a transition from the perovskite structure to another structure type (ilmenite, corundum, C-type, etc. (4)) occurs in the series of ABO_3 compounds. Thus, the compound Mn_2FeSbO_6 considered in (5) is related to the ilmenite structural type since the Mn^{2+} radius (0.83 Å (6)) is not sufficiently large to stabilize the perovskite structure.

We have found no literature devoted to synthesis and investigation of $A_2BB'O_6$ compounds in which A sites are occupied by bivalent cations with radii smaller than those of Cd^{2+} (0.95 Å) and Mn^{2+}. Nevertheless, perovskite-like compounds with other compositions are known; in particular, $CuTa_2O_6$ (7–9), $Cu_{1.5}Cd_{0.5}Ti_2O_6$ (8), and $CaCu_3Mn_4O_{12}$ (10), in which A sites are occupied by Cu^{2+} cations (0.73 Å). In this connection it is worthwhile to investigate the possibility of synthesis of complex oxides $A_2BB'O_6$ with Cu^{2+} cations located in A sites. The present paper reports synthesis conditions, x-ray and structural characteristics, and magnetic properties of Cu_2BSbO_6 compounds, where B is Mn^{3+}, Fe^{3+}, or Ga^{3+}.

II. EXPERIMENTAL

The oxides CuO, Sb_2O_3, Fe_2O_3, MnO_2, and Ga_2O_3, 99.9% pure, were used as initial reagents. Interactions between the oxides were studied and the synthesis was carried out in air in the temperature range 900–1100°C. The temperature was measured by means of a calibrated Pt thermocouple. The samples were examined by X-ray powder diffraction analysis using Cu$K\alpha$ radiation with a DRON-2 diffractometer.

X-ray diffraction data necessary for refinement of structural parameters were obtained with STADI-P (STOE, Germany) by stepwise scanning ($2\theta_H = 15°$, $2\theta_K = 115°$, $\Delta 2\theta = 5°$, $\tau = 30$ min, Cu$K\alpha_1$ radiation) in standard transmission mode using a position-sensitive detector (PSD)

0022-4596/94 $6.00

with effective angle of range $2\theta \simeq 43.5°$ at angular increment 0.015°. A Ge monocrystal, bent according to Iogansson and having a reflecting surface (111), was used as a focusing monochromator. A large PSD has a noticeable nonlinearity of sensitivity at the edges depending upon the number of channels (and consequently upon 2θ), but in the central part of the detector there is a region (~12°) with nonlinear sensitivity that is not less than 1%. Taking these peculiarities of the PSD into account, the following scheme for the formation of an experimental diffraction file was chosen. X-ray diffraction patterns taken with step $\Delta 2\theta = 5°$ were cut to retain only the central part with width $2\theta = 5°$. Separate 5° diffractograms recorded in this way were combined to form a total diffractogram. In order to refine positional parameters, the diffraction data were processed using a full-profile analysis program (11) adapted to work together with a STOE application package. Since the geometry of the survey was changed, additional subroutines allowing for the dependence of absorption μt on the angle 2θ and the function of the monochromator were introduced into the DBW4.1 program. The absorption coefficient was measured from the primary beam decay occurring due to a sample placed between lavsan films ($-\mu t = \ln J/J_0$). Ground monocrystaline silicon was used as an external calibration standard ($a = 5.43075(5)$ Å).

Magnetic susceptibility χ was measured in the temperature range 4.2–300 K in a magnetic field with intensity 0.15 T according to Faraday's method. The error in determining χ was not more than ±3%.

III. RESULTS AND DISCUSSION

When a mixture of oxides CuO, Sb_2O_3 and B_2O_3 (B = Fe, Ga, Mn) taken in the quantities corresponding to the stoichiometry Cu_2BSbO_5 and pressed in tablets was sintered in air at 950°C, products which did not contain the initial components were formed. Allowing for the fact that under experimental conditions Sb^{3+} is oxidized to Sb^{5+}, the resulting chemical reaction can be expressed in the following way:

$$2CuO + 0.5B_2O_3 + 0.5Sb_2O_3 + 0.5O_2 \\ \text{(from air)} \rightarrow Cu_2BSbO_6.$$

X-ray patterns of all the compounds were identical and contained a set of reflections (Fig. 1) indexed in a body-centered cubic unit cell. Table 1 presents lattice parameters, pycnometer and X-ray densities, and colors of the obtained compounds. The variation of the cell parameters is in good agreement with the ionic radii of the trivalent cations Fe (0.645 Å), Mn (0.645 Å), and Ga (0.62 Å) for the coordination number 6 (11). A solid solution based on an Fe-containing compound was found. It has a small region of homogeneity and is described by the formula $Cu_{2-2x}Fe_{1+3x}Sb_{1-x}O_6$ ($0 \leq x \leq 0.07$) within which the a parameter decreases to 9.5515 ∓ 0.0007 Å.

Absence of the systematic extinctions (hkl): $h + k + l = 2n + 1$ and ($0kl$): $k = 2n + 1$ points to the space group $Ia3$, which is characteristic of cubic oxides with the bixbyite type structure (12). In accordance with (13), the ratio of the mean distance Me^{3+}–O to the elementary cell parameter a for such oxides is 0.215, the value which is, apparently, ideal for this structure. Proceeding from the mean values of the interatomic distances Mn^{3+}–O, Fe^{3+}–O, Ga^{3+}–O, Cu^{2+}–O, and Sb^{5+}–O for the coordination number 6, it was found that these ratios in the compounds Cu_2BSbO_6 (one) 0.2164 (Fe), 0.2171 (Mn), and 0.2165 (Ga); i.e., they are close to 0.215.

The papers (14, 15) report the synthesis of the compound $Cu_9Sb_4O_{19}$ with a body-centered cubic cell and $a = 9.620$ Å. X-ray patterns of the compounds Cu_2BSbO_6 obtained by the authors of this paper and those of $Cu_9Sb_4O_{19}$ (14) are identical. The complex oxide $Cu_9Sb_4O_{19}$ was first (14) synthesized under pressure 10 kbar and temperature 1000–1100°C from $CuSb_2O_6$ and CuO taken in the mole ratio 1 : 3.5. More recently (15), it was established that this compound can be obtained in oxygen under $P_{O_2} = 10$ bar and $T = 1000°C$. $Cu_9Sb_4O_{19}$ is not stable in air and at $T > 945°C$ it decomposes into $CuSb_2O_6$ and $Cu_4SbO_{4.5}$, losing oxygen.

Comparing the results of this work with those considered in (14), one can conclude that Mn^{3+}, Fe^{3+}, and Ga^{3+} cations exert a stabilizing effect on the phase with the bixbyite structure making it stable in air at $T < 1000°C$. The annealing of Cu_2FeSbO_6 at 1100°C led to a partial decomposition of this compound with an isolation of the impurity phase $Cu_4SbO_{4.5}$. Another characteristic feature is that no cubic phase was formed when Cu_2GaSbO_6 was synthesized at $T > 1000°C$. The product contained $CuSb_2O_6$, $CuGaO_2$, and $Cu_4SbO_{4.5}$. After additional annealing of this sample in air at 950°C the compound Cu_2GaSbO_6 was formed.

Attempts were made to synthesize other compounds with the composition Cu_2BSbO_6, in particular those where Al^{3+}, Cr^{3+}, Ni^{3+}, and Co^{3+} cations were located in B-positions. However, this phase was not found in the products of sintering in air at 900–1100°C.

A phase with the bixbyite structure was also obtained in the system $CuO–TiO_2–Fe_2O_3–Sb_2O_5$ (16). It has the formula $Cu_{2+x}Ti_{2-x}–Fe_{2-x}Sb_xO_9$ and exists in the range $0 \leq x \leq 1.4$. The mentioned solid solutions were obtained according to the principle of double substitution

$$Fe^{3+} + Ti^{4+} \rightarrow Cu^{2+} + Sb^{5+}$$

in the compound $Cu_2Ti_2Fe_2O_9$ with the bixbyite structure. It is interesting to note that the composition with the

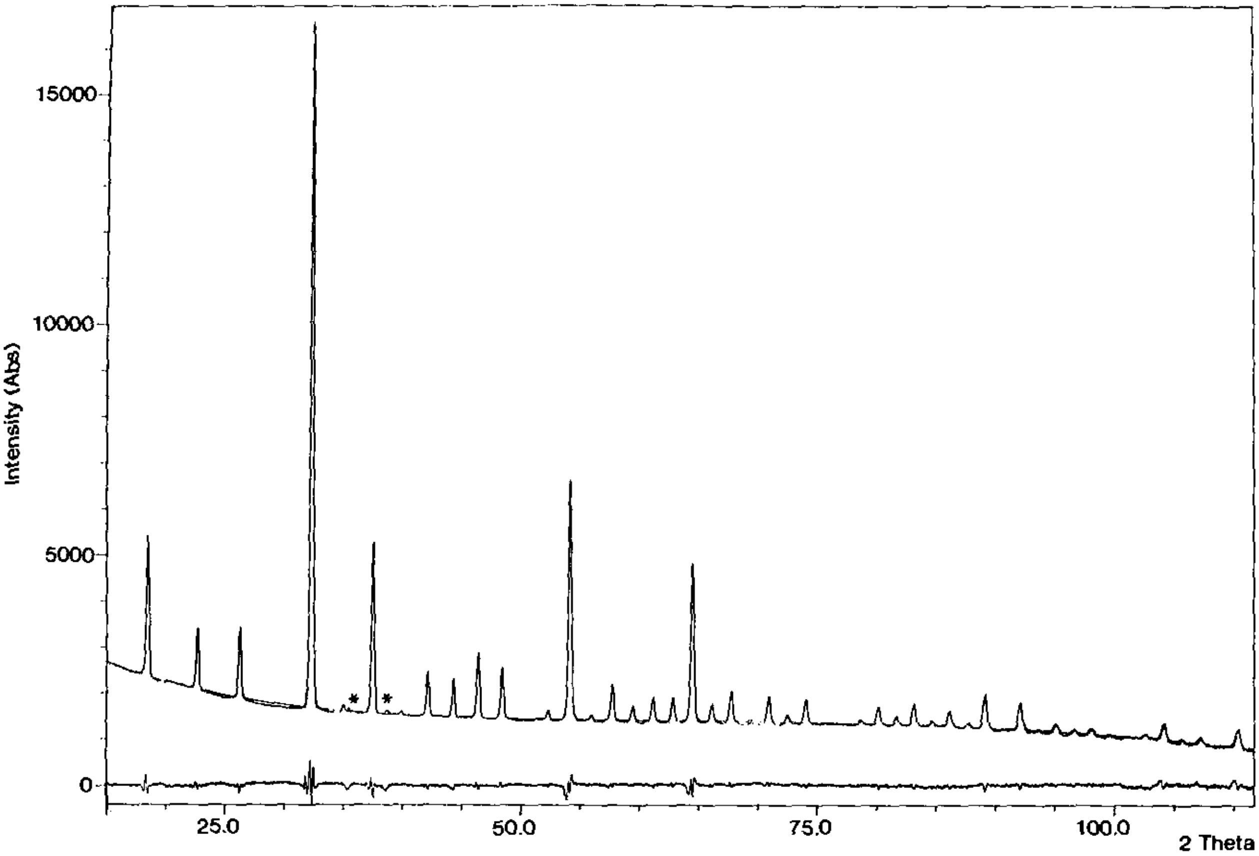

FIG. 1. X-ray Rietveld refinement pattern for Cu_2FeSbO_6 (x—traces of CuO).

limiting value of x, 1.4, has the parameter a (9.5560 Å) close to the parameters of the compounds synthesized by us (see Table 1).

The structural parameters of one of the obtained compounds, namely Cu_2FeSbO_6, were refined on the basis of X-ray diffraction data. Taking into account the measured density (Table 1), it was established that the crystallochemical formula of this compound was $Cu_{16}Fe_8Sb_8O_{48}$ ($z = 8$). This brings up the problem of placing the ions in the sites of the regular system of the $Ia3$ space group.

At the first stage we carried out theoretical modeling basing on the location of ions in the following two models:

Model I: Cu + Fe → 24d, Sb → 8b, 0 → 48e;

Model II: Cu + Sb → 24d, Fe → 8b, 0 → 48e.

The values determined for the cubic phase $(Mn_{0.983}Fe_{0.017})_2O_3$ (12) were used as starting coordinates. It was found that the best agreement between the number of the observed lines and their intensity was achieved with the first model. This model was employed in further calculations performed according to Rietveld's method basing on the full-profile analysis program described above. The results of refinements are given in Table 2. Using these data as the base, the interatomic cation–oxygen and oxygen–oxygen distances (Fig. 2 and Table 3) were calculated. The values obtained show that Sb is located inside an almost undistorted octahedron. At the same time, Fe and Cu ions occupy sites inside a polyhedron with the coordination number 4 + 2. In fact, the first coordination sphere represents a slightly distorted square planar configuration ($R_{M\text{-}O} = 1.938$ Å × 2). The remaining two oxygen atoms ($R_{M\text{-}O} = 2.311$ Å) are located in the second coordination sphere and form, together with oxygen atoms of the first coordination sphere, a distorted octahedron. A fragment of this structure is shown in Fig. 2.

TABLE 1

Characteristics of the Compounds Cu_2BSbO_6, Where B Is Mn, Fe, or Ga

B	a (±0.0003 Å)	$d_{\text{X-ray}}$ (g/cm³)	d_{exp} (g/cm³)	Color
Mn	9.5667	6.06	6.05	Black
Fe	9.5622	6.09	5.95	Dark brown
Ga[a]	9.5237	6.37	—	Green

[a] The sample Cu_2GaSbO_6 contained traces of impurities (see the text).

TABLE 2

Site and profile Parameters for Cu_2FeSbO_6 (Standard Deviations in Parentheses)

Atom	x	y	z	B_i/A^2	N_i
Cu + Fe : 24 d	−0.0328(1)	0	$\frac{1}{4}$	0.49(2)	0.3333 + 0.1667[a]
Sb : 8b	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.10(5)	0.1667[a]
0 : 48e	0.3746(4)	0.1682(2)	0.3965(3)	1[a]	1[a]

R-factor, %: $R_{pf} = 2.52$, $R_{wp} = 2.47$ (expected $R_{wp} = 2.53$), $R_I = 6.02$ Absorption coefficient: $\mu t = 0.13$

Approximating function: pseudo-Voight with angular dependence ETA = 0.1494(164), $m1$ = 0.0016(4)

FWHM parameters: U = 0.1586(64), V = −0.0653(10), W = 0.0745(13)

Assymetry parameter: 1.53(4)

Space group: $Ia3$, $I/I_c = 3.85(3)$

[a] The individual isotropic atomic temperature parameters (B_i) and occupation numbers (N_i) are fixed.

The valence sums $\Sigma_{i=1}^{6} S_i$ for the cations located inside the octahedral were calculated on the basis of the computed cation–anion distances making use of the empirical bond length (r)–bond valence (S) relationship $S_i = \exp[r_0 - r_i)/B_0]$ (17). Here, r_0 and B_0 are empirical values (17). The valence sum was found to be (5.15+) for the Sb site and (2.33+) for the $Cu_{2/3}Fe_{1/3}$ site. This result indicates that Sb, Cu and Fe atoms have oxidation degrees +5, +2, and +3, respectively. The observed distortion of the Cu,Fe-octahedron is caused, first of all, by Jahn–Teller behavior of Cu^{2+} cations. This behavior can be described either as a ratio of axes in the octahedron $\Delta = 2 \times 2.311/(1.938 + 2.020) = 1.16$ or as a mean squared deviation from the M–O bond length: $\Delta = \frac{1}{6} \Sigma_{i=1}^{6} [(R_i - \overline{R})/\overline{R}]^2 = 0.0072$, where $\overline{R} = \frac{1}{6} \Sigma_{i=1}^{6} R_i$. Both values coincide very closely with the results obtained for $Cu_3TiFeSbO_9$ (16). This is quite natural because the occupancy of the polyhedron with Cu^{2+} ions in Cu_2FeSbO_6 and $Cu_3FeTiSbO_9$ is the same.

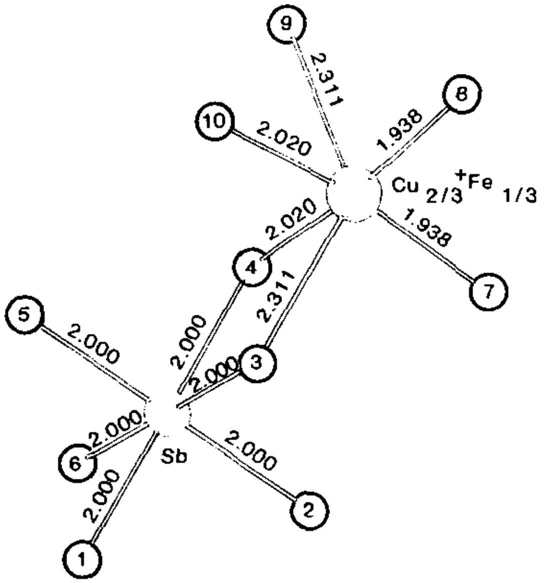

FIG. 2. A fragment of the crystal structure of Cu_2FeSbO_6. Figures in circles denote the number of oxygen atoms in accordance with Table 3. *Cation–anion bond lengths (Å) are shown.*

Figure 3 shows the results of magnetic susceptibility measurements for Cu_2BSbO_6 (B = Mn, Fe, Ga) at 4.2–300 K (B = Mn and Fe) and 77–300 K (B = Ga). It is seen that in the measured temperature range the dependence $1/\chi = f(T)$ for Cu_2GaSbO_6 follows the Curie–Weiss law $\chi = C/(T - \theta)$, where C is Curie's constant, T is temperature, and θ is Weiss's constant. A small anomaly (Fig. 3), the cause of which was not established, is observed in the dependence $\chi = f(T)$ at 220 K for the investigated sample Cu_2GaSbO_6. Experimental values of Curie's constant C (0.42) and the paramagnetic moment μ for the Cu atom in Cu_2GaSbO_6 (1.81 μ_B) are close to the theoretical ones for the d^1 electronic configuration of Cu^{2+} (0.375 and 1.73 μ_B, respectively).

TABLE 3

Anion–Anion Bond Lengths (Å) in Cu_2FeSbO_6 (Standard Deviations Are Given in Parentheses)

O_1–O_2 = 2.953 (3)	O_2–O_7 = 3.100 (3)
O_1–O_3 = 2.953 (3)	O_2–O_8 = 2.866 (3)
O_1–O_6 = 2.999 (3)	O_7–O_9 = 3.616 (3)
O_1–O_5 = 2.699 (3)	O_7–O_4 = 2.644 (3)
O_2–O_3 = 2.953 (3)	O_7–O_3 = 3.121 (3)
O_2–O_4 = 2.699 (3)	O_8–O_9 = 3.121 (3)
O_2–O_6 = 2.699 (3)	O_8–O_{10} = 2.641 (3)
O_3–O_4 = 2.699 (3)	O_8–O_3 = 3.616 (3)
O_3–O_5 = 2.699 (3)	O_9–O_{10} = 2.699 (3)
O_4–O_5 = 2.953 (3)	O_4–O_4 = 2.641 (3)
O_4–O_6 = 2.953 (3)	O_{10}–O_4 = 3.100 (3)
O_5–O_6 = 2.953 (3)	O_{10}–O_3 = 2.641 (3)

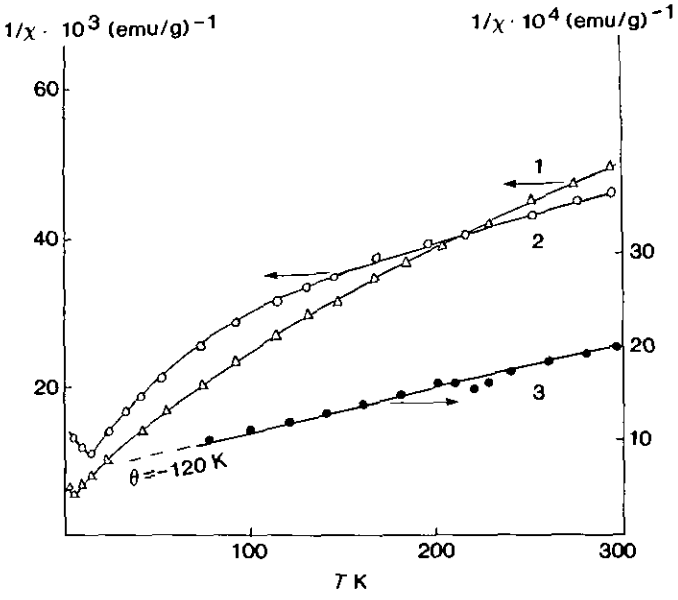

FIG. 3. Inverse magnetic susceptibility as a function of temperature for Cu_2MnSbO_6 (1), Cu_2FeSbO_6 (2), and Cu_2GaSbO_6 (3).

The dependences $\chi = f(T)$ are characterized by maxima at 15.6 K for Cu_2FeSbO_6 and at 5.9 K for Cu_2MnSbO_6 which are due to the transition into the antiferromagnetic state. Thus, the temperatures 15.6 K and 5.9 K are Neel points (T_N) for the compounds Cu_2FeSbO_6 and $CuMnSbO_6$, respectively.

Above T_N, the dependence $1/\chi = f(T)$ for these compounds does not obey the Curie–Weiss law. The nonlinear character of the $1/\chi = f(T)$ dependence points to the presence of a large temperature-independent component. The parameters of the modified Curie–Weiss law

$$\chi = \chi_0 + C/(T - \theta),$$

where χ_0 is temperature-independent susceptibility, were found by statistically processing measured results. The data obtained are given in Table 4. This table presents also the magnetic moments calculated with allowance for the established constants χ_0.

It is seen from Table 4 that the Curie–Weiss parameters and magnetic moments change depending on the temperature interval used in the calculations. These differences were most conspicuous in Cu_2FeSbO_6. The smallest correlation coefficients for the remainders of the equation $\chi = \chi_0 + C/(T - \theta)$ were obtained in the temperature ranges 120–300 K for Cu_2FeSbO_6 and 50–300 K for Cu_2MnSbO_6. The obtained values of C and μ for both compounds were much lower than the additive values calculated for the cations $2Cu^{2+} + Fe^{3+}$ and $2Cu^{2+} + Mn^{3+}$.

In accordance with (12), magnetic ordering in bixbyite type compounds and related phases is caused by paramagnetic ions located exclusively in 24d sites. Since these sites are occupied either by Cu^{2+} and Fe^{3+} or by Cu^{2+} and Mn^{3+} cations, as evidenced by the structural investigation data, established values of T_N should be associated with the ordering of the magnetic moments of these cations.

In summary, as a result of attempts to obtain perovskites with the general composition $A_2BB'O_6$, new complex oxides Cu_2BSbO_6 (where B = Mn, Fe, Ga) with a cubic body-centered cell (the bixbyite type structure) were formed. These compounds are stable in air at $T \leq 1000°C$ (B = Ga) and $T \leq 1100°C$ (B = Mn, Fe); they decompose above these temperatures. Refinement of structural parameters of Cu_2FeSbO_6 allowed us to establish that Sb is located inside an almost undistorted octahedron composed of oxygen anions (8b sites), while Cu and Fe occupy 24d sites with coordination number 4 + 2. Cu_2MnSbO_6 and Cu_2FeSbO_6 were found to be antiferromagnetic with $T \sim 5.9$ K and 15.6 K, respectively. The paramagnetic moment of Cu^{2+} (1.81 μ_B), calculated on the basis of magnetic susceptibility measurements for Cu_2GaSbO_6 in the range 77–300 K, was close to the theoretical value for the d^1 electronic configuration (1.73 μ_B).

TABLE 4

Parameters of the Modified Curie–Weiss Law $\chi = \chi_0 + C/(T - \theta)$ for Cu_2MnSbO_6 and Cu_2FeSbO_6

Compound	Temperature range (K)	χ_0(cm/mol)	θ (K)	μ^a (μ_B)	C^a mol^{-1}
Cu_2MnSbO_6	6.1–300	3.64×10^{-3}	−19	3.49	1.52
	33–300	3.08×10^{-3}	−22	3.625	1.64
	50–300	3.00×10^{-3}	−22	3.644	1.66
Cu_2FeSbO_6	25–300	6.70×10^{-3}	−10.8	2.46	0.76
	53–300	4.99×10^{-3}	−50.2	3.26	1.33
	93–300	3.44×10^{-3}	−105.7	4.12	2.12
	120–300	3.59×10^{-3}	−101.6	4.04	2.04

[a] The calculated values of μ and C are 5.48 μ_B and 3.75 mol^{-1} for Cu_2MnSbO_6 and 6.40 μ_B and 5.125 mol^{-1} for Cu_2FeSbO_6.

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