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New Layered Compounds with the General Composition (*M*O)(CuSe), Where *M* = Bi, Nd, Gd, Dy, and BiOCuS: Syntheses and Crystal Structure

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The syntheses of four new copper oxyselenides with the general formula (*M*O)(CuSe) (*M* = Bi, Nd, Gd, Dy) and one copper oxysulfide, BiOCuS, are reported. The tetragonal unit cell dimensions of all compounds are given. A new bismuth–copper oxyselenide, BiOCuSe, has been structurally characterized from powder X-ray diffraction data and finally solved by the Rietveld profile method with $R_I = 0.069$. The BiCuSeO crystal structure is formed by alternating $[Bi_2O_2]$ and $[Cu_2Se_2]$ layers. © 1994 Academic Press, Inc.

INTRODUCTION

This paper deals with the preparation and X-ray investigation of a group of new copper oxyselenides with the general formula (*M*O)(CuSe), where *M* = Bi, Nd, Gd, Dy; one copper oxysulfide, BiOCuS; and the crystal structure solution of BiOCuSe.

Among all inorganic compounds with layered structures, there are two well-studied families: Sillen phases (1) and Aurivillius phases (2). Fluorite-like $[Bi_2O_2]$ (or $[Ln_2O_2]$) layers are typical of the crystal structures of both families. However, in the Sillen phases these layers alternate with single, double, or triple halogen or chalcogen layers (Fig. 1a), and in the Aurivillius phases the layers are separated by perovskite-like sheets with the general formula $A_{n-1}B_nO_{3n+1}$ with $1 < n < 5$, where *A* = Ca, Ba, Sr and *B* = Ti, Nb, Ta (Fig. 1b).

In addition, in several structures the described $[Ln_2O_2]$ fluorite-like layers alternate with layers of CuS_4 tetrahedra. The existence of at least two compounds with formulas LaOCuS and LaOAgS has already been noted in the literature (5–7). We found it interesting to search for new compounds with LaOCuS-type structure containing fluorite-like $[M_2O_2]$ layers, where *M* = Bi, *Ln*, and layers of CuX_2-tetrahedra, whereas *X* = Se, S.

EXPERIMENTAL

Powder samples of black BiOCuSe and BiOCuS and dark-green NdOCuSe, GdOCuSe, and DyOCuSe were prepared by direct interaction of compounds in evacuated sealed quartz ampoules. Bi_2O_3 (α-form), Nd_2O_3, Gd_2O_3, Dy_2O_3, and elementary Se, S, Cu, Bi, Nd, Gd, and Dy were weighed in proper stoichiometry to an accuracy of ±0.1 mg and hand-mixed in an agate mortar. All starting materials were of high purity. The mixtures were heated at 400°C for 48 hr and finally annealed at 720°C for 300 hr. In the case of BiOCuS, the time of annealing was 600 hr. This method was used for the syntheses of (*M*O)(Cu*X*) compounds for the first time and it gave good results.

All the reflections on the X-ray diffraction powder pattern of all samples (Enraf–Nonius, FR-552, $CuK\alpha_1$, Ge as an internal standard) were fully indexed in tetragonal unit cells with the parameters given in Table 1. Intensities were estimated visually. X-ray intensity data for BiOCuSe structure determination were measured with a STOE STADI/P diffractometer in the symmetric transmission mode using a rotating sample. Strictly monochromatic $CuK\alpha_1$ radiation was used (a germanium crystal with a 220-mm radius of curvature) with a step size of 0.03°.

STRUCTURE DETERMINATION OF BiOCuSe

The crystallographic data for BiOCuSe are presented in Table 2. Fifty-four unambiguously indexed integrated intensities with $I > 3\sigma$ in the region $13 < 2\theta < 115$ were corrected for multiplicity, Lorentz polarization, and absorption effects and were converted into structure factors. All calculations were carried out with the CSD structure package on an IBM-286 XT computer. The structure was solved using the model of LaOCuS. The model was refined in the space group *P4/nmm* (No. 129). The atom positions were initially refined by conventional least-squares method using integrated intensity data. The resulting posi-

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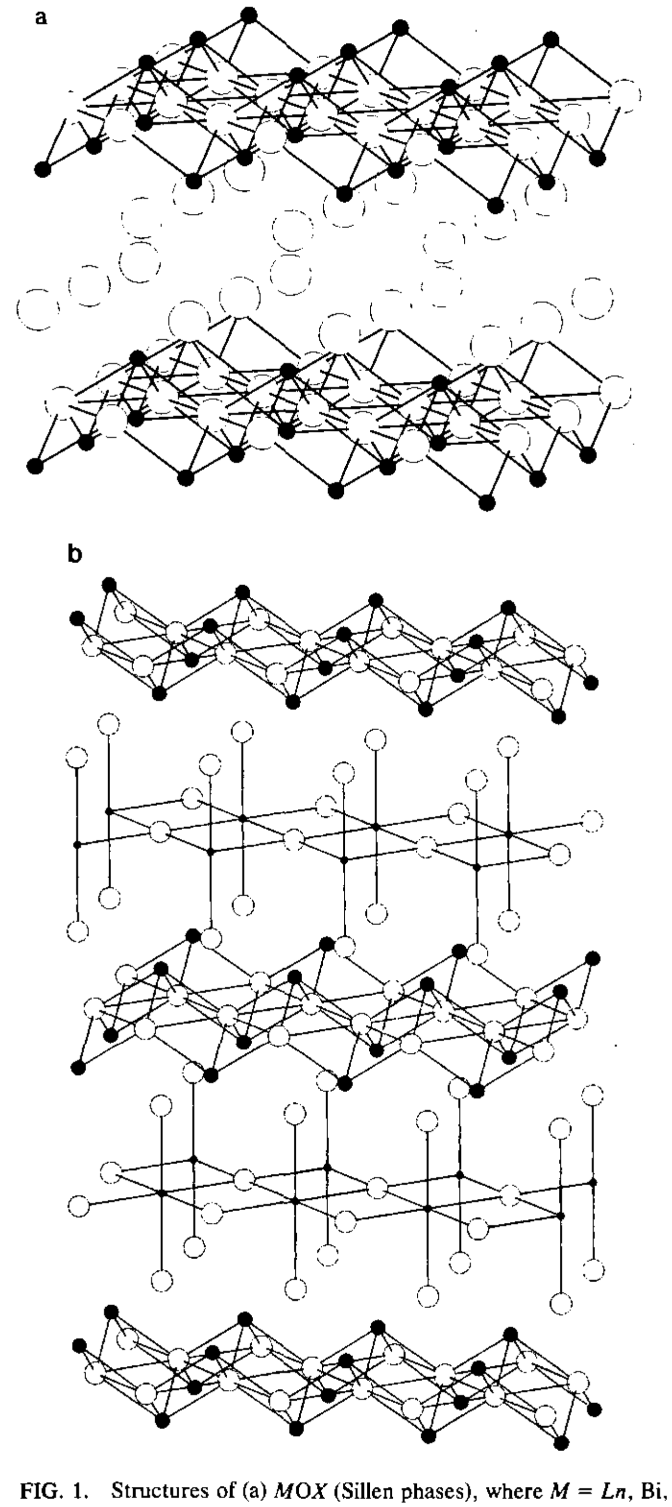

FIG. 1. Structures of (a) MOX (Sillen phases), where $M = Ln$, Bi, and X = F, Cl, Br, I; (b) γ-Bi_2WO_6 (Aurivillius phase).

tional parameters were then used to start a Rietveld profile method. Figure 2 shows the final Rietveld profile obtained between the calculated and the observed STADI/P patterns. The reliability factors are $R_{pr} = 0.081$, $R_f = 0.127$, $R_I = 0.069$, and $R_e = 0.053$.

TABLE 1
Lattice Parameters for (MO)(CuSe), Where M = Bi, Nd, Gd, Dy, and BiOCuS

Compound	a (Å)	c (Å)	V (Å^3)
BiOCuSe	3.9213(1)	8.9133(5)	137.09(3)
NdOCuSe	3.986(1)	8.833(4)	140.34(6)
GdOCuSe	3.9206(8)	8.743(2)	134.39(3)
DyOCuSe	3.8865(6)	8.709(1)	131.55(1)
BiOCuS	3.8705(5)	8.561(1)	128.25(1)

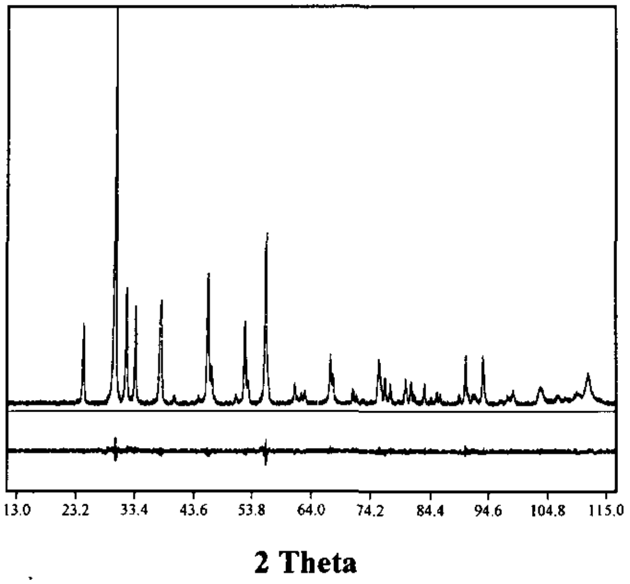

FIG. 2. The final Rietveld profile of BiOCuSe from the STADI/P data set.

TABLE 2
Crystal Data for BiOCuSe

Molecular weight	730.96
Color	Black
Crystal system	Tetragonal
Space group	$P4/nmm$ (No. 129)
Cell constants (Å)	a = 3.9213(1)
	c = 8.9133(5)
Volume (Å^3)	137.09(3)
Z	2
Calculated density (g/cm^3)	8.902(2)
Diffractometer	STOE
T(°K) of data collection	298
Radiation	Cu$K\alpha_1$
$2\theta_{max}$	123.0
Calculated reflections	54
R_{int}	0.081
R_{pr}	0.127
R_f	0.069
R_e	0.053
Weight scheme	Unit

TABLE 3
Positional and Thermal Parameters for BiOCuSe

Atom	Site	x/a	y/b	z/c	B_{eq}(Å^2)
Bi	2(*c*)	1/4	1/4	0.1411(7)	1.080(3)
Se	2(*c*)	1/4	1/4	0.680(2)	1.360(9)
Cu	2(*b*)	3/4	1/4	1/2	2.600(2)
O	2(*a*)	3/4	1/4	0	0.307(4)

DESCRIPTION

The final positional and thermal parameters for BiO CuSe are given in Table 3. The interatomic distances are given in Table 4.

The crystal structure of BiCuSeO is shown in Fig. 3. It is built of [Cu_2Se_2] layers normal to the Z-axis alternating with [Bi_2O_2] fluorite-like layers. The latter are built of slightly distorted Bi_4O tetrahedra that share Bi–Bi edges. The Bi–O–Bi bond angles for the Bi_4O tetrahedra are 106.95(12)° (three angles) and 114.65(12)° (three angles).

Slightly distorted $CuSe_4$ tetrahedra share Se–Se edges forming [Cu_2Se_2] layers. Three Se–Cu–Se bond angles exist, ranging from 106.95(12)° to 114.65(12)° with an average of 107.6°.

The coordination of Bi is a distorted square antiprism with four O in one base and four Se in the other; such coordination is very typical of Sillen phases. The Bi–O bond length is not significantly different from the Bi–O distance found in Bi_2O_2Se (2.32 Å) (4). The Bi–Se distances may also be compared with those in Bi_2O_2Se (3.28 Å).

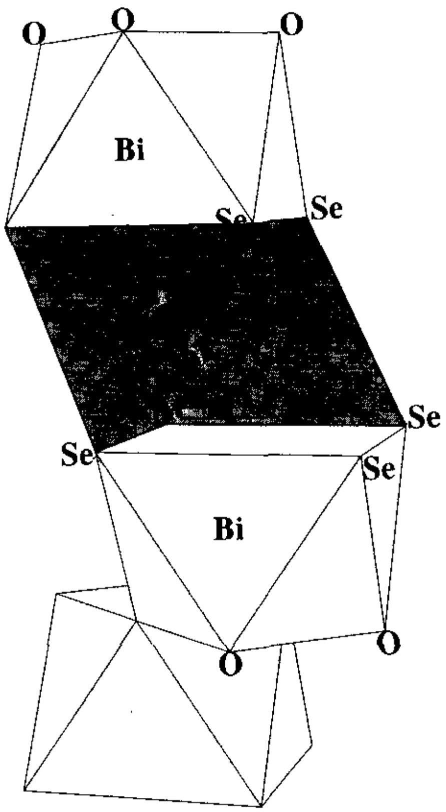

FIG. 3. A view of the crystal structure of BiOCuSe.

DISCUSSION

The good agreement of Miller indices, the observed intensities for the reflections of investigated phases, and the monotonic decrease in parameters a and c with the increase in the RE element number lead us to believe that all new oxyselenides with the general formula *Ln*OCuSe (*Ln* = Nd, Gd, Dy), as well as BiOCuS, crystallize in the same space group $P\ 4/nmm$ and posses the same structures as LaOCuS does. Thus, all the new compounds (*M*O)(CuSe), where M = Bi, Nd, Gd, Dy, and BiOCuS appear to be isostructural with LaOCuS (LaOAgS type).

TABLE 4
Interatomic Distances in BiOCuSe

Bond	Number	Distance (Å)
Bi–O	4	2.330(3)
Bi–Se	4	3.201(8)
Cu–Se	4	2.531(9)

Perhaps it would be possible to synthesize some other representatives of this type of structure or to increase the thickness of a tetrahedral layer as in the well-known Aurivillius phases. Finally, we hope that this new group of substances with the general composition (*M*O)(Cu*X*) may be developed by heterovalent substitution of *M*-labeled atoms.

Some of these studies are now in progress.

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