JOURNAL OF SOLID STATE CHEMISTRY **118**, 74–77 (1995)

Powder X-Ray and IR Studies of the New Oxyselenides *M*OCuSe (*M* = Bi, Gd, Dy)

P. S. Berdonosov, A. M. Kusainova, L. N. Kholodkovskaya, V. A. Dolgikh,[1,2] L. G. Akselrud,*[,3] and B. A. Popovkin

*Department of Chemistry, Moscow State University, Leninskie Gory, 119899, Moscow V-234, Russia; and *Department of Chemistry, L'viv State University, Lomonosov Street, 6, 290005, L'viv, Ukraine*

Received May 16, 1994; in revised form January 11, 1995; accepted January 12, 1995

The group of oxyselenides with the formula (*M*O)(CuSe) (*M* = Gd, Dy, and Ho) has been prepared by reacting M_2O_3, Cu, *M*, and Se at 750°C for 240 hr. All compounds were characterized by IR-spectra analysis. Powder diffraction structure analysis was made for GdOCuSe and DyOCuSe (Rietveld profile analysis) in *P*4/*nmm* symmetry. Crystal data are as follows: GdOCuSe, a = 3.9186(2), c = 8.723(5) Å; DyOCuSe, a = 3.8854(2), c = 8.701(4) Å; HoOCuSe, a = 3.866(2), c = 8.685(7) Å. Crystal structures are built up of $[M_2O_2]$ fluorite-like layers (*M* = Gd, Dy), normal to the *Z*-axis, alternating with $[Cu_2Se_2]$ layers formed by slightly distorted edge-sharing $CuSe_4$ tetrahedra. The structures were compared with those of other similar layered compounds. © 1995 Academic Press, Inc.

INTRODUCTION

In a previous paper (1), we reported the synthesis of a new group of copper oxychalcogenides with the general formula (*M*O)(CuSe), where *M* = Bi, Nd, Gd, Dy, the group also includes BiOCuS. On the basis of the structure analysis of a BiOCuSe powder sample and of X-ray powder diffraction data of other members of this group, the crystals of (*M*O)(CuSe) were attributed to the LaOAgS structure type (2).

The crystal structure of (*M*O)(CuSe) is built up by the alternation of double metal–oxygen layers (La_2O_2, Bi_2O_2) with Cu_2Se_2 layers that are constructed from $CuSe_4$ tetrahedra sharing Se–Se edges. No other information about these compounds could be found in the literature.

Now we first intended to synthesize similar (*M*O)(CuSe) compounds containing the heavier rare earth elements, namely Er and Yb, and second to establish the relation of the radii of rare earth elements and bismuth with the distortion of polyhedra and interatomic distances in layers. It was for this purpose that we investigated the IR- spectra and determined the crystal structures of different members of this group. Of the known compounds, BiOCuSe, GdOCuSe, and DyOCuSe were chosen.

EXPERIMENTAL

Sample Preparation and Characterization

Synthesis. Powder samples were obtained by the method described in (1), using stoichiometric mixtures of the initial components in accordance with the equation

$$M + M_2O_3 + 3Cu + 3Se = 3MOCuSe.$$

The mixtures were heated in evacuated sealed quartz ampoules (10^{-2} Torr, 750°C, 240 hr). M_2O_3, elementary Se, Cu, and *M* (*M* = Bi, Gd, Dy, Ho, Er, Yb) were used. All reagents were of high purity. M_2O_3 (*M* = RE) were preliminarily heated at 950°C for a 24-hr period to eliminate trace amounts of water and CO_2.

X-ray powder diffraction. X-ray powder diffraction (Enraf–Nonius, FR-552, Cu$K\alpha_1$, with Ge as an internal standard) was used for identification of the products of the reaction. X-ray diffraction powder patterns of gray-yellow GdOCuSe, dark green DyOCuSe, and black BiOCuSe were completely similar to the X-ray diffraction patterns described in (1). In the case of Ho we always had mixture of Ho_2O_2Se, $Cu_{2-x}Se$[4] and probably HoOCuSe, with tetragonal cell parameters a = 3.866(2) Å and c = 8.685(7) Å. Decreasing the temperature of synthesis to 590°C did not give better results. In the case of Er and Yb, the main reflections in the X-ray powder diffraction patterns belong to Er_2O_2Se or Yb_2O_2Se and $Cu_{2-x}Se$, while others could not be attributed to any other known compounds.

---

[1] To whom correspondence should be addressed.

[2] E-mail: DOLG@nns.admin.chem.msu.su.

[3] E-mail: levga@vitkp.cscd.lviv.ua.

[4] JC PDS 6-0680 data file.

0022-4596/95 $12.00

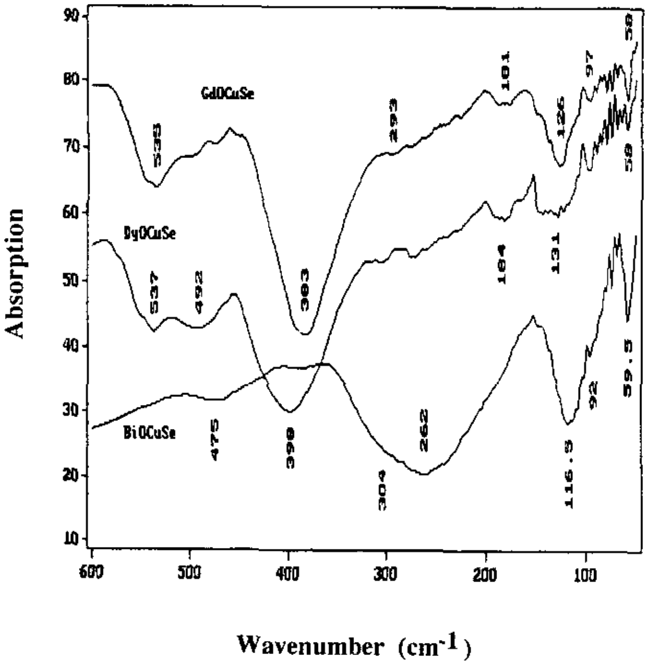

FIG. 1. IR reflection spectra of *Ln*OCuSe (*Ln* = Gd, Dy, and Bi) pressed pellets.

IR-spectra analysis. IR spectra were recorded on a Perkin–Elmer FT-IR 1700x spectrometer. The samples of BiOCuSe, GdOCuSe, and DyOCuSe were pressed in pellets with polyethylene, or were suspended in Vaseline oil for obtaining the IR spectra. IR spectra are presented in Fig. 1.

Powder diffraction X-ray intensity. Data for the GdOCuSe structure determination were collected with a DRON-3M diffractometer (Cu$K\alpha$ radiation, reflection geometry, with a step 0.05° 2θ). X-Ray intensity data for DyOCuSe structure determination were taken with a STOE STADI/P diffractometer using a rotating sample mounted in a symmetric transmission mode. Strictly monochromatic Cu$K\alpha_1$ radiation was used (a germanium crystal with a 220-mm radius of curvature) with a step of 0.02° 2θ.

The integrated intensities obtained by profile analysis were used for the structure determination. Seventy-six peaks with $I > 3\sigma$ were collected as experimental data for GdOCuSe in the $20 < 2\theta < 114°$ region, and for DyOCuSe 77 peaks were collected in the $9.6 < 2\theta < 118.57°$ region.

Data collection conditions, crystallographic data, and final reliability factors are presented in Table 1. Intensities were corrected for multiplicity, Lorentz–polarization, and absorption effects, and converted into structure factors. All calculations were carried out with the CSD structure package on an IBM PC/AT computer.

TABLE 1
Crystal Data For GdOCuSe and DyOCuSe

	GdOCuSe	DyOCuSe
Molecular weight	631.50	642.00
Color	Gray-yellow	Dark green
Crystal system	Tetragonal	Tetragonal
Space group	*P*4/*nmm* (No. 129)	*P*4/*nmm* (No. 129)
Cell constants (Å)[a]	a = 3.9186(2) c = 8.723(5)	a = 3.8854(2) c = 8.701(4)
Volume (Å^3)	133.89(1)	131.38(3)
Z	2	2
Calculated density (g/cm^3)	7.8313(7)	8.114(2)
Diffractometer	DRON-3M	STADI/P
T (K) of data collection	298	298
Radiation	Cu$K\alpha$	Cu$K\alpha_1$
2θ (max)	114	118.57
Calculated reflections	76	77
R_1	0.0419	0.0459
R_{Pr}[b]	0.1608	0.1525
R_{WP}[c]	0.0443	0.0733

[a] Enraf–Nonius, Fr-552, Cu$K\alpha_1$, Ge as an internal standard.
[b] $R_{\mathrm{Pr}} = (\Sigma\,|Y_{oi} - (1/C)\,\Sigma\, Y_{ci}|/\Sigma\, Y_{oi}$.
[c] $R_{\mathrm{WP}} = (\Sigma\, w_i|Y_{oi} - (1/C)\,\Sigma\, Y_{ci}|/\Sigma\, w_i Y_{oi}$.

The structure was solved using the model of BiOCuSe. The model was refined in space group *P*4/*nmm* (No. 129). The final positional and thermal parameters were obtained using a full-profile Rietveld method. The experimental and calculated profiles for GdOCuSe and DyOCuSe are shown in Figs. 2a and 2b. The final position and isotropic thermal parameters are given in Tables 2 and 3. The interatomic distances are given in Table 4. The crystal structure of investigated substances is shown in Fig. 3 (DyOCuSe).

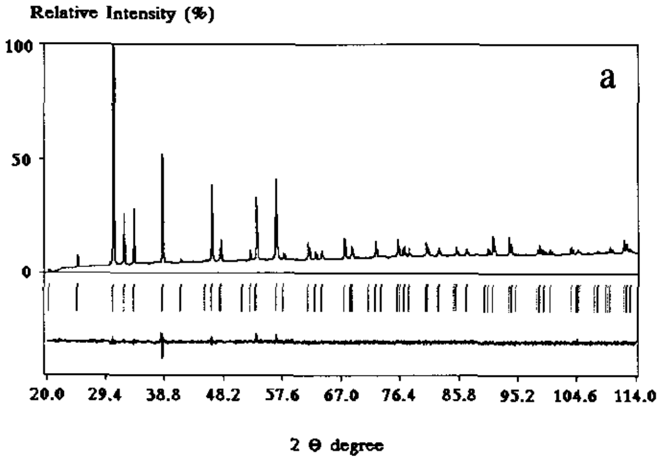

FIG. 2a. Observed and difference X-ray powder diffraction profiles for GdOCuSe.

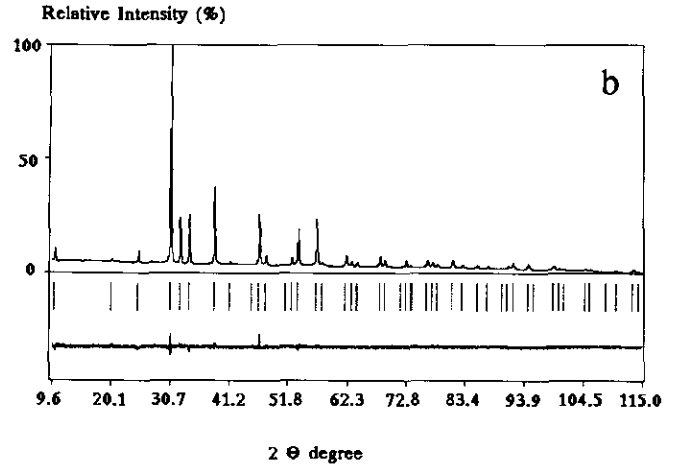

FIG. 2b. Observed and difference X-ray powder diffraction profiles for DyOCuSe.

DISCUSSION

In our experiments we did not find *M*OCuSe for *M* = Er and Yb. The oxyselenide group with the structure described above may end at holmium.

As determined from our structure experiments, GdOCuSe and DyOCuSe are isostructural to BiOCuSe.

Both crystal structures described are built up of [M_2O_2] fluorite-like layers (*M* = Gd, Dy) normal to the *Z*-axis alternating with [Cu_2Se_2] layers formed by slightly distorted $CuSe_4$ tetrahedra that share Se–Se edges. (Fig. 4).

The coordination polyhedra of *M* and Se atoms in the described structures are the distorted square antiprisms with four O atoms in one base and four Se atoms in another base for each *M* atom, and with four Cu atoms in one base, and four *M* atoms in another base for Se.

In accordance with structural peculiarities of substances under investigation, bands of the IR spectra in the range 450–150 cm^{-1} were attributed to the *Ln*–O bond vibration in the [M_2O_2] layer. They are similar for GdOCuSe and DyOCuSe IR spectra. In the case of BiOCuSe the corresponding bands are displaced toward a low-energy region. This fact is in good agreement with the analogous displacement in the well-known Sillen phases *Ln*OCl and BiOCl (*Ln* = Y, La, Sm, Eu, Gd, Dy, Ho) (3).

TABLE 2
Positional and Thermal Parameters for GdOCuSe

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	$B_{(iso)}$
Gd	2(*c*)	1/4	1/4	0.1321(3)	0.39(7)
Se	2(*c*)	1/4	1/4	0.6821(6)	0.68(5)
Cu	2(*b*)	3/4	1/4	1/2	1.7(2)
O	2(*a*)	3/4	1/4	0	0.500

TABLE 3
Positional and Thermal Parameters for DyOCuSe

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	$B_{(iso)}$
Dy	2(*c*)	1/4	1/4	0.1295(2)	1.98(4)
Se	2(*c*)	1/4	1/4	0.6833(3)	0.54(8)
Cu	2(*b*)	3/4	1/4	1/2	1.34(11)
O	2(*a*)	3/4	1/4	0	0.6(4)

The bands in GdOCuSe, DyOCuSe, and BiOCuSe IR spectra in the range 70–50 cm^{-1}, which is characteristic for all obtained IR spectra, were attributed to the Cu–Se bond vibration.

Table 4 shows that there is no difference between Cu–Se distances in these two crystal structures. These distances are practically the same as those in the crystal structure of BiOCuSe. This fact corresponds with IR-spectra data. Thus, Cu–Se distances in BiOCuSe and *Ln*OCuSe are practically independent of the type of cation in separating fluorite-like layers (Table 4).

TABLE 4
Interatomic Distances (Å) and angles (°) in GdOCuSe and DyOCuSe

Bond		Distance	Angle
Bi–O	(×4)	2.330(3)	
Bi–Se	(×4)	3.201(8)	
Cu–Se	(×4)	2.531(9)	
Bi–O–Bi	(×4)		106.9(2)
	(×2)		114.6(2)
Se–Cu–Se	(×2)		101.4(2)
	(×4)		113.6(2)
Gd–O	(×4)	2.274(2)	
Gd–Se	(×4)	3.207(3)	
Cu–Se	(×4)	2.522(3)	
Gd–O–Gd	(×4)		104.96(7)
	(×2)		118.94(7)
Se–Cu–Se	(×2)		101.8(2)
	(×4)		113.4(1)
Dy–O	(×4)	2.246(1)	
Dy–Se	(×4)	3.193(2)	
Cu–Se	(×4)	2.515(2)	
Dy–O–Dy	(×4)		104.38(5)
	(×2)		120.23(5)
Se–Cu–Se	(×2)		101.16(5)
	(×4)		113.78(5)

Note. Compare with interatomic distances and angles (°) in BiOCuSe (1).

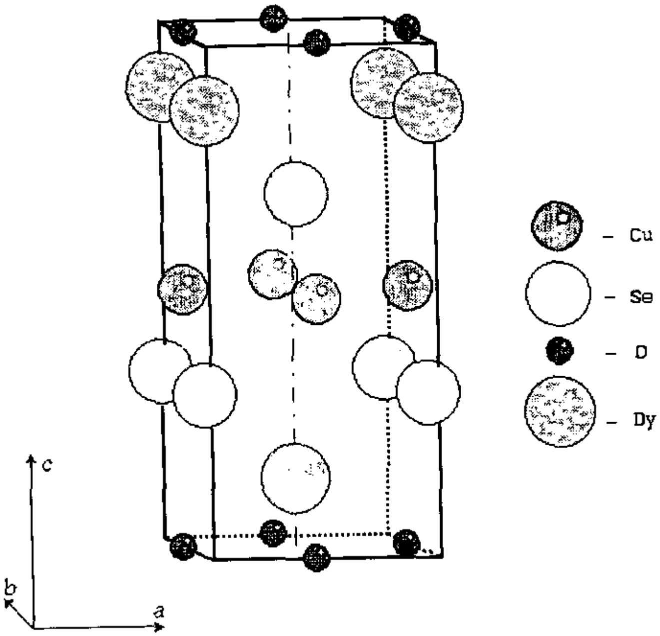

FIG. 3. The crystal cell of DyOCuSe.

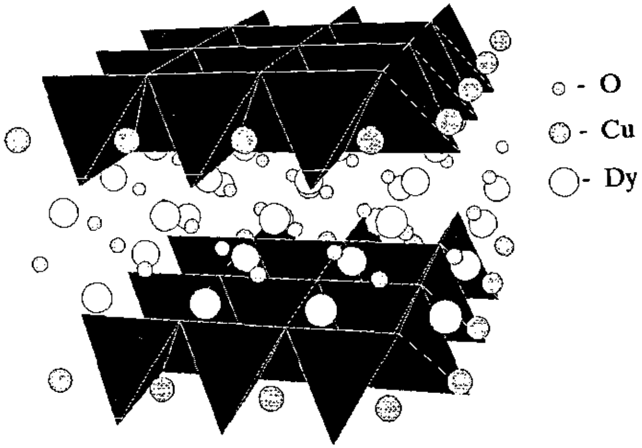

FIG. 4. *Polyhedral representation of the layers* [Cu_2Se_2] *in the* DyOCuSe structure.

Nevertheless, M–O interatomic distance decreases in [M_2O_2] layers in accordance with the ionic radii of the cations. The (MO)(CuSe) layered structures with the "small" ions Er^{3+} and Yb^{3+} were not found under the experimental conditions mentioned above.

[Cu_2Se_2] layers formed by edge-sharing CuX_4 tetrahedra may be considered stable structure fragments. The stability of this structure element could be demonstrated by the existence of a wide range of compounds with common formulas MCu_4X_3 (4, 5), $TlCu_2Se_2$ (X = S, Se), and $BaCu_2S_2$ ($ThCr_2S_2$-type) (6–8), besides those mentioned above.

ACKNOWLEDGMENTS

This study was supported by Russian Fundamental Research Foundation. This work is a part of project 93-03-5724.

REFERENCES

1. A. M. Kusainova, P. S. Berdonosov, L. N. Kholodkovskaya, L. G. Akselrud, V. A. Dolgikh, and B. A. Popovkin, *J. Solid State Chem.* **116,** 406 (1995).
2. M. Palazzi, *C.R. Acad. Sci. Ser. 2* **292,** 789 (1982).
3. H. Haeuseler, "Proceedings, 2nd European Conference on Solid State Chemistry, Veldhoven, June 7–9, 1982" p. 513.
4. W. Rudorff, H. G. Schwarz, and M. Waiter, *Z. Anorg. Allg. Chem.* **269,** 141 (1952).
5. K. Klepp, H. Boller, and H. Vollenkle, *Monatsh. Chem.* **111,** 727 (1980).
6. K. Klepp and H. Boller, *Monatsh. Chem.* **109,** 1049 (1978).
7. M. Saiki, M. Onoda, and H. Nozaki, *Mater. Res. Bull.* **23**(4), 603 (1988).
8. M. Saiki and M. Onoda, *Mater. Res. Bull.* **24**(11), 1337 (1989).