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Synthesis and characterisation of the new oxyselenide $Bi_2YO_4Cu_2Se_2$†

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In this communication we report the synthesis, structure and preliminary characterisation of $Bi_2LnO_4Cu_2Se_2$ (Ln = Y, Gd, Sm, Nd, La) phases; these materials are members of a new family of layered oxychalcogenides.

The range of technologically important applications of mixed metal oxides and mixed metal chalcogenides is vast. They have been exploited (*inter alia*) for their conductivity, magnetic, catalytic, optical, energy storage and structural properties. In contrast, the amount of work on oxychalcogenides, materials that contain both oxide and chalcogenide anions, is relatively sparse. This is, of course, partially due to the propensity of such materials to decompose to species containing oxyanions (SO_4^{2-}, SO_3^{2-}, *etc.*) in which the chalcogen has been oxidised. There are, however, a number of such phases known ranging from simple species such as ZrOS[1] and natural minerals such as kermesite and sarabauite (Sb_2OS_2 and $CaSb_{10}S_6O_{10}$);[2,3] three-dimensional phases such as $La_2Ta_2S_2O_8$[4] and $LaCrOS_2$;[5] layered materials such as $Na_2Cu_4OSe_2$,[6] $(LaO)_4Sn_2S_6$[7] and $Sr_2Cu_2CoO_2S_2$[8] and very recently Ruddlesden–Popper phases such as $Ln_2Ti_2O_5S_2$ (Ln = Pr, Nd, Sm–Er, Y) and their alkali metal intercalates.[9–11] Such phases are of interest in that they offer potential control of material properties *via* the anion rather than the cation sublattice.

In this communication we report the synthesis and structural characterisation of a new family of layered oxyselenides of general formula $Bi_2LnO_4Cu_2Se_2$. These phases were targeted using a simple 'building block' strategy[12,13] and were anticipated to contain the stable $[Cu_2Se_2]^{n-}$ building block and oxide layers related to those in other oxide/mixed anion phases.

$Bi_2LnO_4Cu_2Se_2$ phases were prepared by heating a stoichiometric mixture of Ln_2O_3, Bi_2O_3, Cu, Bi and Se in an evacuated sealed silica ampoule to a temperature of 850 °C for 24 h. Lower temperatures resulted in the predominance of the stable BiOCuSe,[14,15] whilst higher temperatures or longer reaction times led to higher impurity levels (presumably due to side reactions with the silica ampoule) and sample decomposition.

Initial inspection of laboratory powder X-ray diffraction data of $Bi_2YO_4Cu_2Se_2$ suggested that the material had the structure type anticipated. This was confirmed by Rietveld refinement of laboratory X-ray powder data and time of flight neutron diffraction data collected on the SEPD diffractometer at the Intense Pulsed Neutron Source (IPNS) at the Argonne National Laboratory, USA. Refinement results are shown in Fig. 1 and Table 1.‡ The structure of $Bi_2YO_4Cu_2Se_2$ is shown in Fig. 2. It has space group *I*4/*mmm* with $a = b = 3.864$ Å, $c = 24.428$ Å and can be described as formally containing layers of $[Cu_2Se_2]^-$ Cu centred edge sharing tetrahedra interspersed with $[Bi_2YO_4]^+$ oxide layers. Similar $[Cu_2Se_2]^{n-}$ blocks are found in materials such as $TlCu_2Se_2$, BiOCuSe[14,15] and others. We note that if one assumes formal oxidation states of Cu^{1+} and Se^{2-} there must be holes present in the valence band.[16] The oxide slabs contain Y in a pseudo-cubic coordination environment (8 × O at 2.378 Å) with a *c*/*a* ratio of the YO_8 unit of 1.015. Bi adopts a coordination environmnent typical of a lone pair cation with four short bonds to oxygen (4 × 2.232 Å) and four longer bonds to Se (4 × 3.431 Å) of the Cu_2Se_2 layers. A similar oxide building block can be found in Bi_2LaO_4Cl.[17]

Other members of this family with Ln = Y, Gd, Sm, Nd and La have been prepared and characterised. Their unit cell

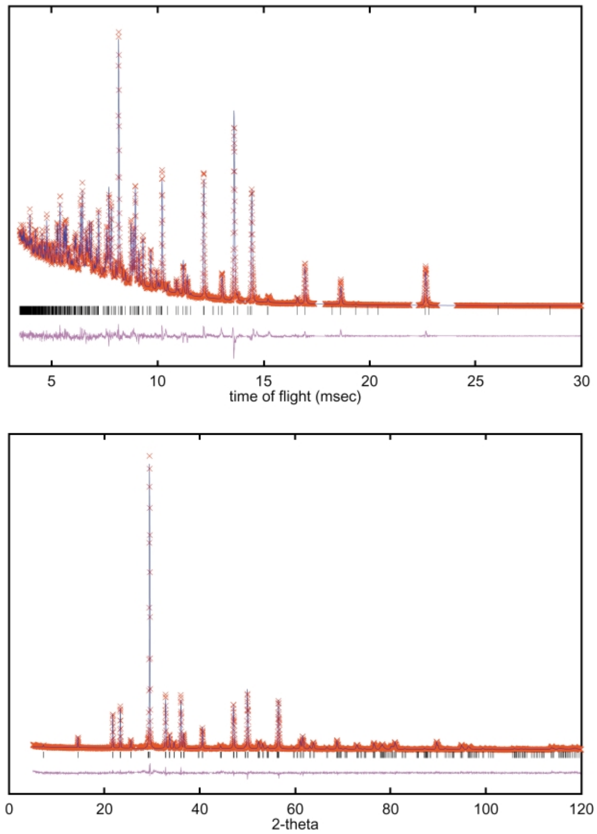

Fig. 1 Results of (a) neutron and (b) X-ray Rietveld refinements. Red points show the observed data, blue line the calculated pattern and the lower pink line the difference curve. Vertical tick marks show positions of allowed reflections. Minor impurity regions have been excluded from neutron data.

Table 1 Fractional atomic coordinates determined by combined refinement of X-ray and neutron diffraction data[a]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$100U_{iso}$/Å^2
Bi	0.5	0.5	0.89748(6)	0.87(3)
Y	0.5	0.5	0.5	0.45(5)
O	0.0	0.5	0.94322(8)	0.94(5)
Cu	0.0	0.5	0.25	1.39(4)
Se	0.5	0.5	0.31254(7)	1.24(4)

[a] Space group *I*4/*mmm*, 293 K, $a = b = 3.86463(3)$, $c = 24.428(4)$ Å.

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† Electronic supplementary information (ESI) available: fractional atomic coordinates from Rietveld refinement of $Bi_2Ln_4O_4Cu_4Se_2$ phases. See http://www.rsc.org/suppdata/cc/b2/b200892k/

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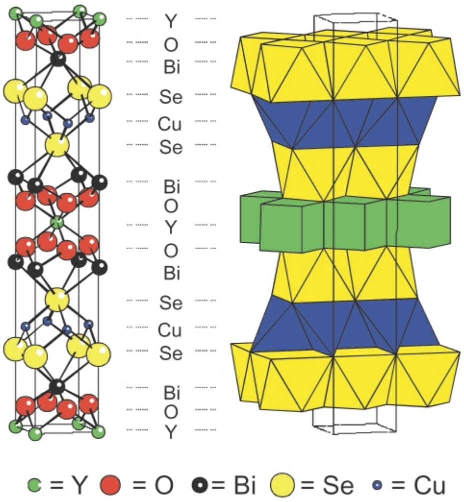

Fig. 2 Structure of $Bi_2YO_4Cu_2Se_2$ in ball and stick and polyhedral representations.

Table 2 Cell parameters of $Bi_2LnO_4Cu_2Se_2$ phases determined by X-ray diffraction data

Atom	*a*	*c*	$V/Å^3$
Y	3.8631(5)	24.4227(5)	364.47(1)
Gd	3.88631(8)	24.4535(6)	369.33(1)
Sm	3.89976(7)	24.4620(6)	372.02(1)
Nd	3.91795(10)	24.5001(8)	376.09(2)
La	3.95319(29)	24.6314(23)	384.93(5)

parameters are included in Table 2§ and show the expected trends with Ln radius.

Preliminary measurements of electrical resistivity were carried out on pellets of $Bi_2YO_4Cu_2Se_2$ using evaporated In contacts in a conventional four-probe arrangement. Current-voltage measurements confirmed that the contacts were ohmic. Resistivity (ρ)–temperature (T) characteristics were measured under constant current conditions over the temperature range 77–300 K using an Oxford Instruments DN107 liquid nitrogen crysostat controlled by an Oxford Instruments ITC4 controller. Room temperature values of resistivitiy were $\sim 2 \times 10^{-2}\ \Omega$ cm and were found to vary linearly with temperature, implying that conduction was essentially metallic in character. The temperature coefficient was $\sim 4 \times 10^{-5}\ \Omega\ \text{cm K}^{-1}$.

Further studies on the properties and chemistry of this family of materials are in progress.

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Notes and references

‡ Neutron diffraction data were recorded on a 4.9 g sample on the SEPD diffractometer of the Intense Pulsed Neutron Source at Argonne National Laboratory. Data were collected and analysed over a time of flight range of 3–30 ms (d = 0.47–4.01 Å). This sample contained small impurities (not present in smaller scale syntheses) which were excluded from the refinement. X-Ray diffraction data were collected from 10–120° 2θ on a Siemens d5000 diffractometer equipped with a graphite diffracted beam monochromator. A step size of 0.02° and a time per step of 10 s were used. To obtain high precision fractional coordinates a combined refinement of neutron and X-ray data was performed in the GSAS software suite.[18] A total of 33 variables were refined (2 scale factors, 2 cell parameters, 3 fractional coordinates, 5 temperature factors, 8 profile coefficients, 6 background terms per phase). Final agreement factors were $\chi^2 = 3.0$, $R(F^2) = 9.78/7.74\%$, $wR_p = 11.09/8.23\%$ (X-ray/neutron). Fig. 1 contains X-ray data of a higher purity sample refined on the same structural model that gave $\chi^2 = 2.0$, $R(F^2) = 8.69\%$, $wR_p = 9.85\%$.

§ Cell parameters were determined by Rietveld refinement of data collected from 5–120° 2θ with a step size of 0.02° and a collection time per step of 9 s. Fractional coordinates derived from these refinements have been deposited as ESI.†

1 G. A. Eisman, J. S. Swinnea and H. Steinfink, *J. Solid State Chem.*, 1985, **56**, 397.
2 P. Bonazzi, S. Menchetti and C. Sabelli, *Neues Jahrb. Mineral.-Monatsh.*, 1987, 557.
3 I. Nakai, K. Nagashima, K. Koto and N. Morimoto, *Acta Crystallogr., Sect. B*, 1978, **34**, 3569.
4 T. D. Brennan and J. A. Ibers, *J. Solid State Chem.*, 1992, **98**, 82.
5 J. Dugue, T. Vovan and J. Villers, *Acta Crystallogr., Sect. B*, 1980, **36**, 1291.
6 Y. B. Park, D. C. Degroot, J. L. Schindler, C. R. Kannewurf and M. G. Kanatzidis, *Chem. Mater.*, 1993, **5**, 8.
7 M. Guittard, S. Benazeth, J. Dugue, S. Jaulmes, M. Palazzi, P. Laruelle and J. Flahaut, *J. Solid State Chem.*, 1984, **51**, 227.
8 W. J. Zhu, P. H. Hor, A. J. Jacobson, G. Crisci, T. A. Albright, S. H. Wang and T. Vogt, *J. Am. Chem. Soc.*, 1997, **119**, 12398.
9 C. Boyer, C. Deudon and A. Meerschaut, *C. R. Acad. Sci. Ser. IIC*, 1999, **2**, 93.
10 M. Goga, R. Seshadri, V. Ksenofontov, P. Gutlich and W. Tremel, *Chem. Commun.*, 1999, 979.
11 S. G. Denis and S. J. Clarke, *Chem. Commun.*, 2001, 2356.
12 Y. Tokura and T. Arima, *Jpn. J. Appl. Phys.*, 1990, **29**, 2388.
13 M. T. Weller and C. S. Knee, *J. Mater. Chem.*, 2001, **11**, 701.
14 P. S. Berdonosov, A. M. Kusainova, L. N. Kholodkovskaya, V. A. Dolgikh, L. G. Akselrud and B. A. Popovkin, *J. Solid State Chem.*, 1995, **118**, 74.
15 A. M. Kusainova, P. S. Berdonosov, L. G. Akselrud, L. N. Kholodkovskaya, V. A. Dolgikh and B. A. Popovkin, *J. Solid State Chem.*, 1994, **112**, 189.
16 G. V. Vajenine and R. Hoffmann, *Inorg. Chem.*, 1996, **35**, 451.
17 C. J. Milne, P. Lightfoot, J. D. Jorgensen and S. Short, *J. Mater. Chem.*, 1995, **5**, 1419.
18 A. C. Larson and V. Dreele, *Los Alamos Internal Report No. 86-748*, 1994.