

$$\tilde{V}^{vw}(\mathbf{k}_{\parallel\Gamma} \rightarrow \mathbf{0}) < \tilde{V}^{vw}(\mathbf{k}_{\parallel\Gamma} \rightarrow \mathbf{0}) < \tilde{V}^{vw}(\mathbf{k}_{\parallel\Gamma} \rightarrow \mathbf{0}) < \tilde{V}^{vw}(\mathbf{k}_{\parallel\Gamma} \rightarrow \mathbf{0}).$$

$$\text{If } (A[100] + Q + \tilde{\varphi}_{\text{el.chem}}(\mathbf{0}) + k_B T / [c(1-c)]) / [2(B[100] + \gamma)] < 0,$$

where, e.g., within the scope of the Debye approximation,

$$Q \cong 9K^2(L')^2(a_0^3/4) \left\langle (1 + 2\xi X + 3\xi^2 Y) / D(\mathbf{n}) \right\rangle_{\mathbf{n}},$$

$$D(\mathbf{n}) = C_{11} + \xi(C_{11} + C_{12})X + \xi^2(C_{11} + 2C_{12} + C_{44})Y,$$

$X = n_x^2 n_y^2 + n_x^2 n_z^2 + n_y^2 n_z^2$ ,  $Y = n_x^2 n_y^2 n_z^2$ , the modulated structure can appear along the [100] direction.

Dependence of the modulated-structure period on  $T$  is plotted.

[1] C. Abromeit, *Int. J. Mod. Phys. B* **1989**, 3, 1303-1314. [2] A.G. Khachatryan, *Theory of Structural Transformations in Solids* (New York: John Wiley & Sons), **1983**. [3] A.A. Katsnelson, A.I. Olemskoi, *Microscopic Theory of Inhomogeneous Structures* (Moscow: MGU Publ.), **1987** (in Russian).

**Keywords: modulated structures, strain-induced interaction**

## MS88.P06

*Acta Cryst.* (2011) **A67**, C757

### Misfit structure determination of a multication Ce, Nd, (Bi) Cr, V, (Ta) Sulphide

L.C. Otero-Díaz,<sup>b</sup> A.Gómez-Herrero,<sup>a</sup> *Centro de Microscopia, Univ. Complutense de Madrid, Av. Complutense s/n, E-28040 Madrid, (Spain).* <sup>b</sup>Dpto. Química Inorgánica, Fac. CC. Químicas, Univ. Complutense de Madrid, E-28040 Madrid, (Spain). E-mail: carlos1@quim.ucm.es.

In the last 30 years, the synthesis and structure determination of over a hundred synthetic metal chalcogenides presenting misfit layer structure (a subclass of composite modulated structure) has been reported [1], [2], [3], [4]. Their complex stoichiometries are represented by  $(MX)_{1+8}(T_{1+e}X_2)_n$  (M = Rare Earth, Sn, Pb, Sb, Bi; T = Ti, V, Cr, Nb, Ta; X = S, Se).

Here we report the structural determination by electron microscopy/diffraction and associated techniques of a new misfit layer compound (MLC)  $\sim [(Bi_{0.04}Ce_{0.66}Nd_{0.30})S]_{1.21}[(Ta_{0.08}V_{0.52}Cr_{0.39})S_2]$ .

SAED patterns (JEOL 2000FX) were taken along the three major zone-axes of the MLC. The SAED patterns taken along the [001] axis consist of two basic sublattices of reflections (Q and H). In addition, the splitting of the misfit satellite reflections reveals the incommensurate mutual modulation of the two sublattices. The [010] zone axis SAED patterns provide evidence of the divergence of the  $a^*$  axes of the two sublattices. HRTEM images (JEOL JEM 3000F,  $C_s = 0.6$  mm) taken along  $[001]_Q$  show the basic Q substructure with superimposed modulation fringes. The HAADF STEM images (JEOL JEM 3000F) taken along the [100] zone axis show the alternating stacking of the two substructures. In addition, the line-scan profiles (JEOL JEM 3000F, Gatan Enfina), confirm the presence of Ce and Nd in the Q sublattice and V and Cr in the H sublattice. The microanalyses of the crystals by XEDS (LINK ISIS 300) yield a composition  $M_{1.1}TS_{3.2}$ , in good agreement with the composition  $(MS)_{1.21}TS_2$  that it is calculated from the misfit ratio measured in the SAED patterns; both data can be combined into a stoichiometry  $[(Bi_{0.04}Ce_{0.55}Nd_{0.25})S]_{1.21}[(Ta_{0.08}V_{0.52}Cr_{0.39})S_2]$ . The unit cell parameters of the two sublattices (measured by SAED) are:  $a = 3.5$  Å;  $b = 5.9$  Å;  $c = 11.3$  Å;  $\alpha = 95.4^\circ$ ;  $\beta = 95.5^\circ$ ;  $\gamma = 89.7^\circ$  for the H Subcell and  $a = 5.8$  Å;  $b = 5.9$  Å;  $c = 11.3$  Å;  $\alpha = 95.4^\circ$ ;  $\beta = 90.7^\circ$ ;  $\gamma = 90.1^\circ$  for the Q Subcell. No intralayer cation ordering has been observed.

This research was supported by the project MAT2010-19460.

[1] E. Makovicky, B.G. Hyde, *Materials Science Forum* **1992**, 100/101, 1-100. [2] S. Kuyppers, J. van Landuyt, *Materials Science Forum* **1992**, 100/101, 223-271. [3] G.A. Wiegers, *Prog. Solid State Chem.* **1996**, 24, 1-139. [4] A.R. Landa-

Cánovas, A. Gómez-Herrero, L.C. Otero-Díaz, *Micron* **2001**, 32, 481-485.

**Keywords: sulphide, misfit, TEM**

## MS88.P07

*Acta Cryst.* (2011) **A67**, C757

### Transmission electron microscopy study of low Mo-content Bi-Mo-O phases

A. R. Landa-Cánovas,<sup>a</sup> E. Vila,<sup>a</sup> Jorge Hernández-Velasco,<sup>a</sup> J. Galy,<sup>b</sup> A. Castro,<sup>a</sup> *Departament of Energy, Environment and Sustainable Technologies, Instituto Ciencia de Materiales de Madrid-ICMM, CSIC, 28049 Madrid, (Spain).* <sup>b</sup>Centre d'Elaboration de Matériaux et d'Etudes Structurales (CEMES-CNRS), 29, rue Jeanne Marvig, BP 94347,31055 Toulouse (France). E-mail: landa@icmm.csic.es

The Bi-Mo-O system presents a wide variety of crystalline phases which have great interest because of their catalytic and ionic conductivity properties. Transmission electron microscopy has probed to be a paramount technique for the crystallographic characterization of many phases in this system and even for the elucidation of their atomic structure [1-3]. In this system we have characterized a whole new homologous series of  $Bi_2(n+2)Mo_nO_{6(n+1)}$  phases, with  $n = 3, 4, 5$  and  $6$ ,  $(xBi_2O_3 : MoO_3, 1 < x < 2)$  which were isolated at low temperature by the n-butylamine wet synthesis method.

Using the same low temperature methods we have isolated additional low temperature phases at higher values of  $x$  ( $xBi_2O_3 : MoO_3, x = 3, 3.5$ ). The powder nature of the new obtained phases hinders a deep characterization of the structure by traditional crystallographic methods like X-ray diffraction. Therefore, we have studied their structure mainly by means of transmission electron microscopy.

Selected area electron diffraction patterns are very complex but can be interpreted as a basic lattice of fluorite-type structure which gives rise to the basic lattice reflections, plus weaker satellite reflections produced by a structural modulation. Although in general, modulation satellites are very weak, in the present case they exhibit a very high intensity and at least nine harmonics. This modulation is incommensurate with the basic fluorite-type lattice and it is related to the fluorite commensurate superstructure observed in  $Bi_{38}Mo_7O_{78}$  [4], [5].

The modulation vector differs clearly from the commensurate one reported in [4], [5] changing in amplitude and direction. The HRTEM micrographs reveal the wave-like nature of the modulation superimposed on the basic fluorite lattice and allows its comparison with the commensurate fluorite superstructures found at the high-temperature phase.

These incommensurate modulations suggest the presence of non-stoichiometry ranges at low temperature phases which can vary the structure and in a very subtle way depending on the synthesis conditions.

[1] E. Vila, A.R. Landa-Cánovas, J. Galy, J.E. Iglesias, A. Castro, *J. Solid State Chem.* **2007**, 180, 661-669. [2] J. Galy, J. Hernández-Velasco, A.R. Landa-Cánovas, E. Vila, A. Castro, *J. Solid State Chem.* **2009**, 182, 1177-1187. [3] A.R. Landa-Cánovas, E. Vila, J. Hernández-Velasco, J. Galy, A. Castro, *Acta Crystallogr. B* **2009**, 65, 458-466. [4] D.J. Buttrey, D.A. Jefferson, J.M. Thomas, *Mater. Res. Bull.* **1986**, 21, 739. [5] X. Kuang, Y. Li, C.D. Ling, R.L. Withers, I. Radosavljevic Evans *Chem. Mater.* **2010**, 22, 4484-4494.

**Keywords: incommensurate modulation, electron diffraction, oxides ionic conductors**