**MS88.P06**


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

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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)$_n$Tt, where X is Rare Earth, Sn, Pb, Sb, Bi; T is 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 (MCL) = [(Bi$_2$Ce$_2$Nd$_3$O)S]$_n$[(Ta$_2$V$_2$O$_6$)C$_2$]$_n$.

SAED patterns (JEOL 2000FX) were taken along the three major zone-axes of the MCL. 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 reveal the incommensurate 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 = 0.6 mm) taken along [001]$_h$ 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 EDS (LINK ISIS 300) yield a composition M$_1$T$_{2n}$, in good agreement with the composition (MS)$_n$T$_n$, that is it is calculated from the misfit ratio measured in the SAED patterns; both data can be combined into a stoichiometry [Bi$_2$Ce$_2$Nd$_3$OS]$_n$[(Ta$_2$V$_2$O$_6$)C$_2$]$_n$.

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.


Keywords: sulphide, misfit, TEM

**MS88.P07**


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

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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$_2$(Mo$_{2(n+2)}$O$_{6(n+1)}$) phases, with n = 3, 4, 5 and 6, (Bi$_{2n}$O$_3$; Mo$_3$O$_7$; 1<$\omega$<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$_2$O$_3$;Mo$_3$O$_7$, 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$_2$Mo$_3$O$_{7n}$ [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.


Keywords: incommensurate modulation, electron diffraction, oxides ionic conductors