

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

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

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.

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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 $(MX)_{1+8}(T_{1+e}X_2)_n$ ($M = \text{Rare Earth, Sn, Pb, Sb, Bi; T = Ti, V, Cr, Nb, Ta; X = S, Se}$).

Here we report the structural determination by electron microscopy/diffraction and associated techniques of a new misfit layer compound (MLC) $\sim [(\text{Bi}_{0.04}\text{Ce}_{0.66}\text{Nd}_{0.30})\text{S}]_{1.21}[(\text{Ta}_{0.08}\text{V}_{0.52}\text{Cr}_{0.39})\text{S}_2]$.

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, $C_s = 0.6 \text{ mm}$) 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 $M_{1.1}\text{TS}_{3.2}$, in good agreement with the composition $(\text{MS})_{1.21}\text{TS}_2$ that it is calculated from the misfit ratio measured in the SAED patterns; both data can be combined into a stoichiometry $[(\text{Bi}_{0.04}\text{Ce}_{0.55}\text{Nd}_{0.25})\text{S}]_{1.21}[(\text{Ta}_{0.08}\text{V}_{0.52}\text{Cr}_{0.39})\text{S}_2]$. The unit cell parameters of the two sublattices (measured by SAED) are: $a = 3.5 \text{ \AA}; b = 5.9 \text{ \AA}; c = 11.3 \text{ \AA}; \alpha = 95.4^\circ; \beta = 95.5^\circ; \gamma = 89.7^\circ$ for the H Subcell and $a = 5.8 \text{ \AA}; b = 5.9 \text{ \AA}; c = 11.3 \text{ \AA}; \alpha = 95.4^\circ; \beta = 90.7^\circ; \gamma = 90.1^\circ$ for the Q Subcell. No intralayer cation ordering has been observed.

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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 $\text{Bi}_{2(n+2)}\text{Mo}_n\text{O}_{6(n+1)}$ phases, with $n = 3, 4, 5$ and 6 , $(x\text{Bi}_2\text{O}_3 : \text{MoO}_3, 1 < x < 2)$ 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 ($x\text{Bi}_2\text{O}_3 : \text{MoO}_3, x = 3, 3.5$). 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 $\text{Bi}_{38}\text{Mo}_7\text{O}_{78}$ [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.

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