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Electron Microscopy Study of Nd doped Misfit Layer Structures in the Pb-Nb-Se System

R. Varadé López[1], A. Gómez- Herrero[2], D. Ávila Brande[1], L. C. Otero-Díaz[1]

[1.]Dpto. QuímicaInorgánica I, F. CC Químicas, Univ. Complutense, E-28040, Madrid, Spain
[2.]Centro Nacional de Microscopía Electrónica (CNME), E-28040, Madrid, Spain.

The so called misfit compounds are a group of compounds that can be formulated as $(AX)_{1+\delta}(BX_2)_n$ where A=Sn, Sb, Bi, Pb; Rare earth; B= Ti, V, Nb, Ta, Cr and X=S,Se. The crystal structure of this kind of compounds can be described as two sublattices interpenetrated. The first one, (AX), with pseudo-tetragonal symmetry (Q),can be described as two atoms thick layers along the [100] of the rock salt type. The second one, (BX_2), is a three atoms thick layer with pseudo ortohexagonal (H) symmetry and it retains the structure of the parent chalcogenide. Both sublattices have at least one direction of non-commensurability [1].Being this fact of great basic interest because of the crystallography involved in their modulated structures which is often known as crystallography of the second generation. In addition some of these compounds exhibit interesting electric (charge transfer between the layers), magnetic and thermoelectric properties. The structures and physical propertiesof the compounds with general $(PbSe)_{1+\delta}(NbSe_2)_n$ n=1,2,3 have already been reported [2,3] showing superconductivity below 5K.

We present here the structural characterization of the misfit layer compound $(Pb,Nd)_{\sim 1.14}(NbSe_2)_2$ using mainly electron microscopy and X-Ray powder data. Our aim in this study is the replacement of some lead for neodymium in the PbSe layers. The sample,with nominal composition $Pb_{0.5}Nd_{0.5}Nb_2Se_5$, has been synthesized from the elements in an evacuated silica ampoule. The treatment was performed at 773K for twohours and thenannealed 28 days at 1273K. SEM study shows that two types of particles are present. The platelet shaped ones correspond to the quaternary misfit compound and to $NbSe_2$. The needle shape particles are niobium selenide ($NbSe_3$) (fig. 1a). The XRPDshows strongestreflections that can be associated to the (00l) planes of the layer-type of crystal (fig. 1b). The average composition from XEDS data from eleven crystal is $Pb_{0.53(3)}Nd_{0.54(2)}Nb_{2,13(6)}Se_{5,14(1)}$. The SAED patterns from lamellae crystals taken along the stacking direction, [001], show two types of reflections (figure 2a). The more intense are associated with the two basic sublattices (Q,H)and the weakest to the modulation. Along the misfit direction [100], the coincidence between sublattices correspond to 4 (Q) ~ 7(H) (fig. 2b).Aberration corrected HRTEM was applied to explore the possible order/disorder between Pb and Nd. No order has been found. STEM ABFmicrographin [100] zone axis (fig 3a) show an alternate stacking of 1x(Pb,Nd)Se (Q) and 2x($NbSe_2$) (H) layers along the stacking direction. ADF micrographs along $[110]_Q$ shows stacking faults in the Q sublattice. From the SAED patternsand the data from XRPD, the unit cells parameters have been calculated,a_Q =0.585(8)nm a_H=0.337(3) nm $b_{Q,,H}$=0.58(1)nm $c_{Q,H}$=1.85(5)nm α=90º β=90º γ=90.82(5)º(1+δ)= 1,14(1) An ideal polyhedral structural model for this new bilayer phase ≈ $[(Pb_{0.46}Nd_{0.47})Se]_{1.14}(Nb_{1,07}Se_2)_2$ is presented in fig 3c, it is built by layers of edge sharing polyhedra, {$NbSe_6$} trigonal prisms(green) and {(Pb,Nd)Se_5} square pyramids (blue)[4].

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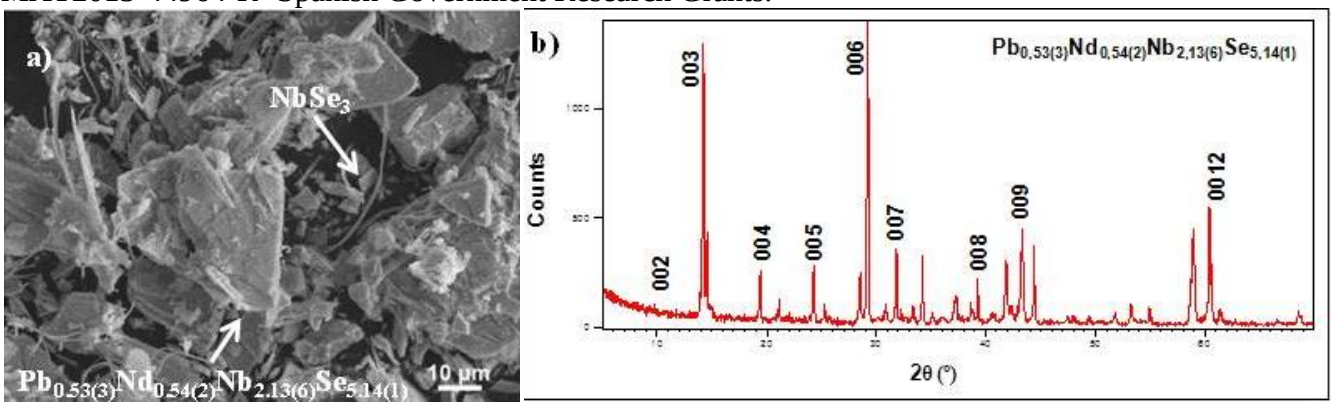

Figure 1. a) SEM micrograph.b) Experimental powder diffraction pattern from the sample. Only(00l) reflections are indexed.

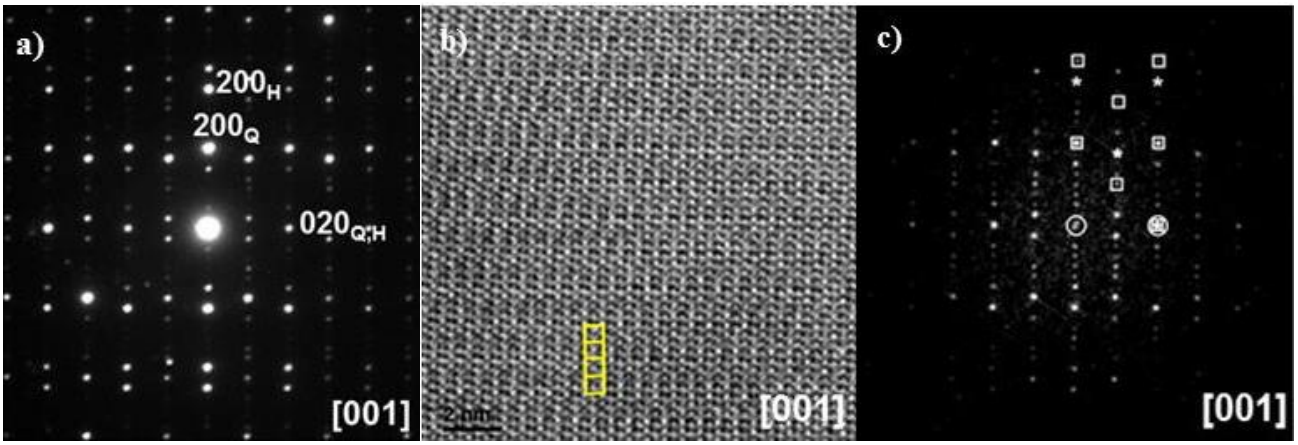

Figure2. a)SAED pattern taken along the stacking direction [001]. b) Corresponding HRTEM micrograph with the supercell 4Q marked in yellow, see modulation at glazing incidence c) FFT from the micrograph,Q reflections are marked with a square, H reflections are marked with a star and common reflections are marked with a circle.

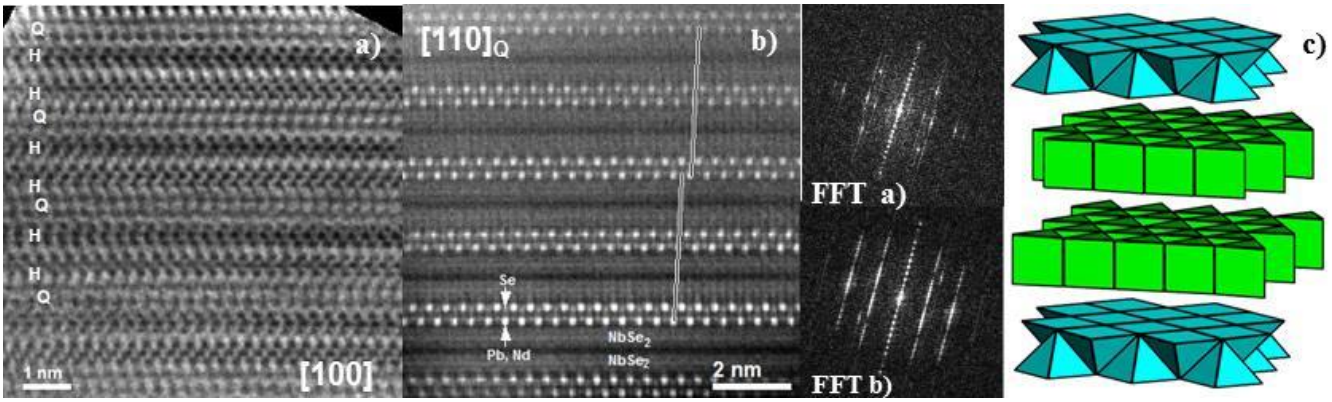

Figure3. a)STEM ABF micrograph along [100] where the sequence QHH,QHH layersare clearly resolved. b) ADF micrograph, sublattice Q oriented in [110] direction. No cationic order can be appreciated; however stacking faults are observed and indicated by the shift between bars. Heavy bright dots are Pb-Nd atoms. a) and b) FFT's. c) Structural model for the new bilayer ≈ $[(Pb_{0.46}Nd_{0.47})Se]_{1.14}(Nb_{1,07}Se_2)_2$ phase.

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