THE ULTRASOFT X-RAY EMISSION BANDS NAROWING EFFECT AND ITS DEPENDENCE ON CHEMICAL BONDS TYPE IN CRYSTALL POWDERS AND CARBON NANOMATERIALS

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Introduction

The crystal powders electronic structure changing under transition from bulk to nanosize state and carbon nanomaterials electronic structure were studied by means of the ultrasoft X-ray spectroscopy.

Results and discussion

The effect of ultrasoft x-ray emission bands (UXREB) shape changing and narrowing was revealed under nanopowders dispergation. The C*Kα*-spectra of nanodiamonds with coherent scattering region 2, 3 and 5 nm showed the bands narrowing from 0,3 to 0,9 eV at $I=2/3I_{max}$. The B*Kα*- and N*Kα*-bands of isostructural nanopowder of blende-like BN (fig. 1) study showed that NKα-bands narrowing is noticeably greater than that in BKα.

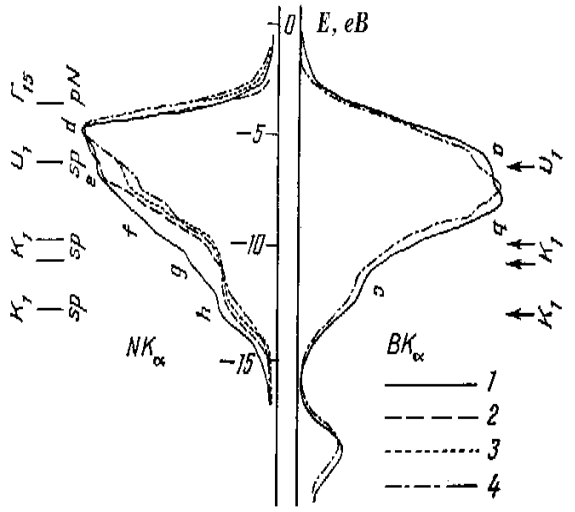

Fig1. Comparison of the BKα– and NKα–bands in ultradispersed powder of cubic BN with different dispersion degree (r=0.1 (4), 0.3 (3), 0.5 (2) and more than 2μm (1)).

Study of CKα-, NKα- and TiLα-bands of nanopowders with different dispersibility also showed that narrowing of the bands reflecting X*p* and Ti*d*-states distribution essentially differed owing to different width in initial bulk materials.

Therefore it was coined the relative narrowing $\eta=(\Delta E^0_{1/2}-\Delta E^u_{1/2})/\Delta E^0_{1/2}$, where the energy width of the band at $I=1/2I_{max}$ $\Delta E^0_{1/2}$ – for coarse powders and $\Delta E^u_{1/2}$ – for nanopowders.

The relative narrowing analysis showed that $\eta_{XK\alpha}>\eta_{MeL\alpha}$ (fig. 2) and they increase when nanoparticles size decrease.

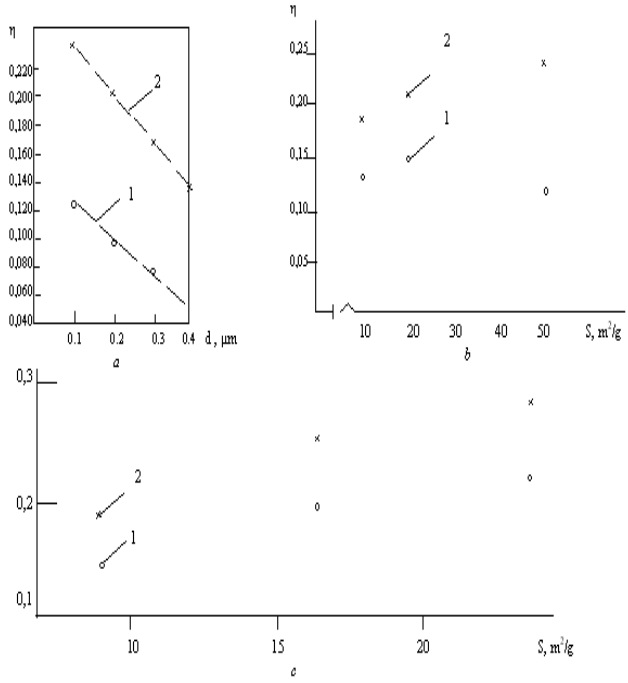

Fig. 2. The relative narrowing dependence of 1) BKα- and TiLα-bands 2) CKα- and NKα-bands on average size of blende-like BN nanoparticles (*a*), TiC (*b*) и TiN (*c*).

It was established that bands relative narrowing depends on chemical bonds type in these materials [1-3].

Since the ultrasoft x-ray spectra reflect the energy distribution of valence electrons of atoms that located on less than ten nearsurface layers it was shown that this effect appears owing to valence electron states energy levels degeneration as a

result of surface atoms bonds breaking and parameters changing of interatomic interaction in nearsurface layers of nanoparticles when their number are commensurable with atoms quantity in volume.

As the emission spectra is a result of valence electrons transition to the inner atoms levels than the greater occupation of degenerated electronic levels corresponding to broken chemical bonds the grater influence on emission bands narrowing. Hence it was determined that $\eta_{NK\alpha}/\eta_{BK\alpha}=Q^{v}_{Np}/Q_{Bp}$ for *BNкуб* and $\eta_{XK\alpha}/\eta_{TiL\alpha}=Q^{v}_{Xp}/Q_{Tisd}$ (X=*N*, *C*) for *TiN* and *TiC* – are values that don't depends on nanoparticles size.

The UXREB and *BN, TiC, TiN* electronic structure theoretical calculation data comparing showed that the UXREB greatest narrowing appears in energy range corresponding to hybrid X*p*+Me*sd* – states in consequence of their dispersion.

The $BaTiO_3$ coarse and nanopowders electronic structure study by means of x-ray photoelectronic and emission spectroscopy showed that valance band narrowing of the powder under dispersion entailed by the nanopowders surface atoms charge state change. It's a consequence of undivided transition of charge from barium to oxygen under ionic Ba-O–bonds break whereas Ti-O-bonds break doesn't change the titanium charge state.

The narrowing effect of UXREB CKα observed also in bulk and nanocarbon materials (fullerenes, onions, nanotubes, nanofibers) study. The CKα-bands of this materials narrowed due to the number of Cp_z-orbitals that didn't involve in π-bonds commensurable with sp^2-hybryd states quantity.

It was shown that fullerene molecule stabilized in unstable conditions as a result of mixed σ+π-bonds inside of molecule and π-bonds weakening above its surface. The fullerene, pyrolitic, thermally exfoliated graphite, nanodiamond and onion comparative analysis (fig. 3) showed that the electrons distribution in lowenergy part of the valence band is practically identical owing to the hybridisation of the sp^2-states involving to σ-bonds.

The *CKα*-bands nanosize narrowing in highenergy range appears owing to π- and σ+π-states energy decreasing under the large overlapping in twisted and bended graphene layers which number substantially increased with carbon fibers thinning.

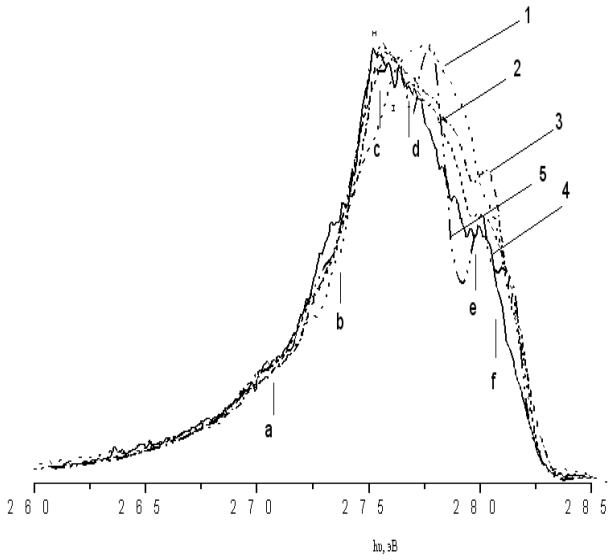

Fig. 3. Comparison CKα– emission bands of nanodiamond (1), pyrolitic graphite (2), thermally exfoliated graphite (3), onion (4), fullerene (5).

Conclusions

The value of X-ray emission bands narrowing in nanomaterials significantly depends on chemical bonds type and electronic states hybridization. The nanopowders consolidation under high pressures and room temperatures leads to reverse spectra widening owing to recombination of broken bonds under dispersion.

References

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