

## Raman Spectroscopy and Microstructural Study of Natural Graphite Processed by High-Energy Ball Mill

J.M. Mendoza-Duarte, M.H. Bocanegra-Bernal, R. Martínez-Sánchez, I. Estrada-Guel.

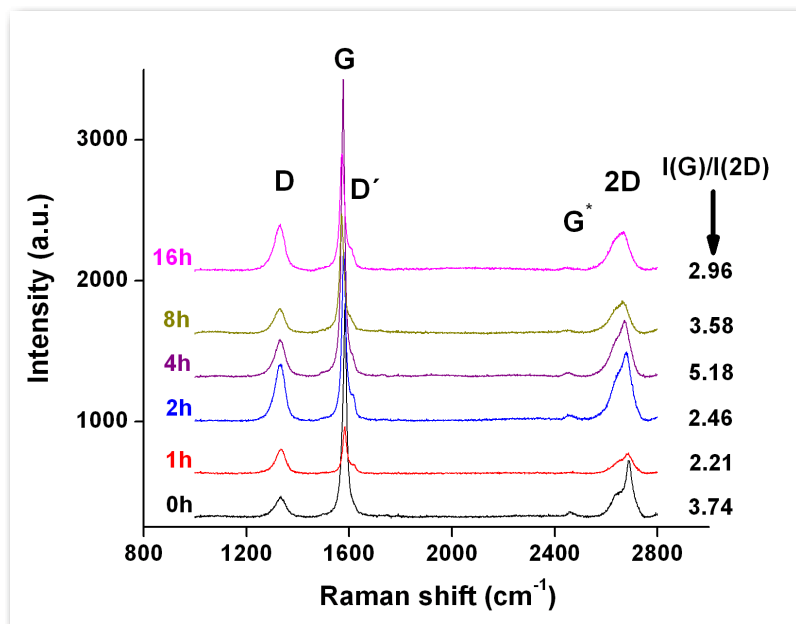
Centro de Investigación en Materiales Avanzados (CIMAV). Laboratorio Nacional de Nanotecnología, Miguel de Cervantes No. 120, 31109, Chihuahua, Mexico.

Graphite is one of the longest-known forms of pure carbon and familiar from everyday life. Also is an excellent lubricant; this characteristic is attributed to its lamellar structure and weak interlayer bonding. During sliding, its interlayer bonding can be easily broken, making the adjacent layers slide relatively to reduce friction. Macroscopic single crystals of graphite do not occur in nature [1]. In order to obtain a reduction of the crystallite thickness in the c-direction of nature graphite, some methods have been tested. The ball-milling process can be used to obtain this effect, but further processing can induce the formation of undesirable agglomerates and clusters formed from single sheets. A good control between the reduction of stockpile structure and agglomeration formation be beneficial in order to improve valuable properties of graphite for specific applications.

The lattice dynamics and vibrational spectroscopy of  $sp^2$  carbon materials has been the subject of numerous investigations with Raman spectroscopy. This technique is one of the most powerful characterization techniques for carbon materials; specially considering the fact that conjugated and double carbon-carbon bonds lead to high Raman intensities. Graphite has three most intense Raman features at  $\sim 1580\text{ cm}^{-1}$  (denominated G band),  $\sim 2700\text{ cm}^{-1}$  (2D band) as well as the (weak) disorder band caused by the graphite edges (D-band) at approximately  $1350\text{ cm}^{-1}$ .

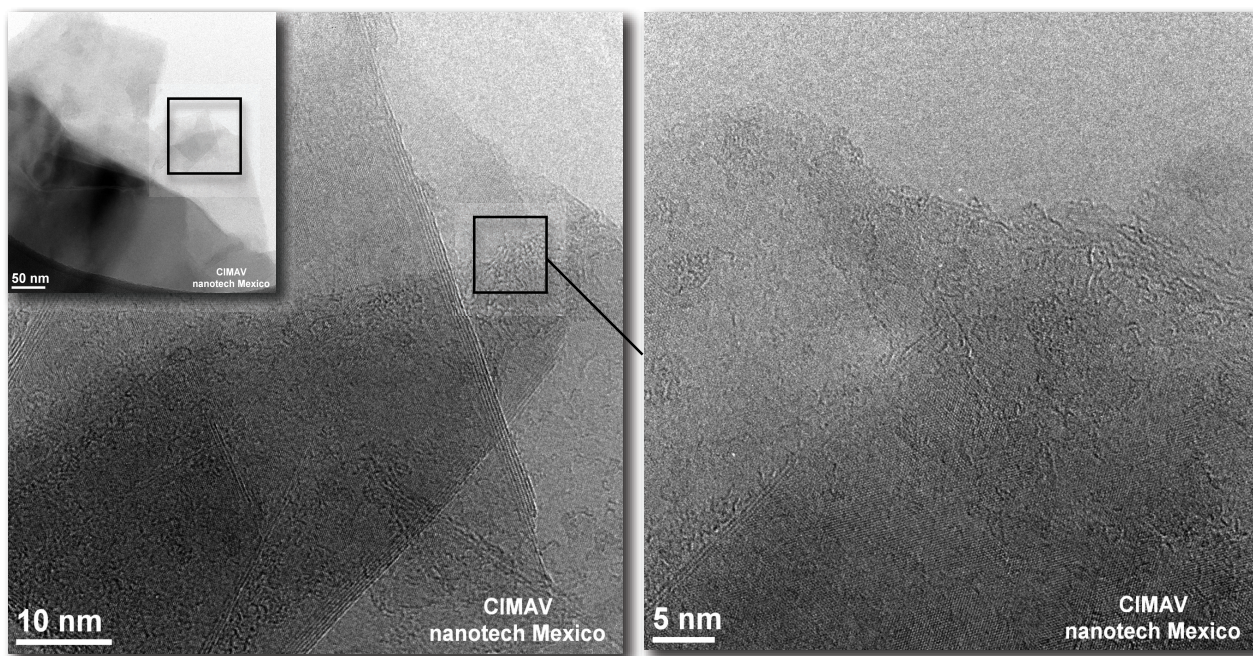
The present work deals with the processing of natural graphite by high-energy ball milling and the evaluation of milling intensity over graphite structure. The used material was: pure graphite flakes (-10 mesh in size and purity of 99.9%). The milling process was conducted in a SPEX 8000M mixer-mill using a hardened steel vial and chromium steel balls under an inert argon atmosphere. During milling, the ball-to-powder weight ratio (BPR) was maintained constant at 5:1 for all experimental runs.  $\sim 8$  grams of graphite was milled at different times (0 to 16h). Milled powders were then microstructural characterized using a Raman spectrometry (Horiba model Lab Ram HR, He-Ne laser 632.8nm) and electronic microscopy: SEM JEOL model JEM-9320FIB and TEM JEOL JEM-2200FS.

The Fig. 1 shows some Raman spectra corresponding to the natural graphite milled for several times in order to reach different exfoliation degrees. From this figure it is clear that this graphite has a sufficient concentration of defects according to the  $D'$  band, located at  $\sim 1620\text{ cm}^{-1}$  which can partially merge with the G band. On the other hand, it is seen that the intensity ratio G and 2D ( $I(G) / I(2D)$ ) modes increases with the number of graphite layers. In this case, it is observed that a milling time of 4 h has led to high degrees of exfoliation. It is also important to stress that the appearance of D band could be indicative of the intense formation of structural defects and dramatic break of the original graphite domains into several smaller ones during graphite milling. In well-ordered graphite and grapheme, this D band is absent. Likewise, the broadened asymmetrical G band and the wide D band illustrated in the spectra are indicative for nanocrystalline graphite and a high concentration of defects in the samples, in agreement with observations by [2, 3].



← **Figure 1.** Raman spectra of milled samples as a function of milling time, location of the main graphite bands are indicated. The numerical ratio between G and 2D bands are also showed.

**Figure 2.** TEM micrograph of milled graphite sample (4h). It is evident the reached defoliation level and the presence of high concentration of defects induced by the milling process.



#### References:

- [1] Reich Stephanie, Thomsen Christian, Phil. Trans. R. Soc. Lond. A **362** (2004) p. 2271-2288.
- [2] Duhee Yoon, Hyerim Moon, Hyeonsik Cheong, Journal of the Korean Physical Society, **55-3** (Sep. 2009) p. 1299-1303.
- [3] Anindya Das, Biswanath Chakraborty, A. K. Sood, Bull. Mater. Sci. **31-3** (Jun. 2008) p. 579-584.
- [4] The Research was supported by CONACYT (Project No. 169262) and Redes Temáticas de Nanociencias y Nanotecnología (124886).