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Report

Introduction:

Nitromethane is the simplest nitroalkane and a basic energetic material, that decomposes with energy release under shock compression (p> 8 GPa) or thermal initiation. Under static compression, crystalline nitromethane chemically transforms into a dark solid or a transparent liquid, depending on the P and T conditions [1,2] . At room temperature, a chemical reaction initiates above 27 GPa, the (or one of the) product formed may be recovered, it is an amorphous compound chemically close to ammonium oxalate [3] . Raman and IR analyses performed in our labs show that, when pressure is raised along an isotherm, a sluggish change of the spectrum occurs before the onset of the chemical reaction, between 10 and 15 GPa. The spectral changes consist of continuous modifications in the relative intensities, in the appearance or disappearance of components and in slope discontinuities of the frequency vs pressure dependence of the components of most vibrons and phonons. These modification suggest a phase change, but no phase change was detected in our previous X-ray diffraction measurements performed on CH_3NO_2 and CD_3NO_2 powder at ESRF (experiment n. 2157). In that case, no structure refinement could be performed due to the poor quality of the powder (nitromethane spontaneously re-crystallizes). We thus performed this new experiment on nitromethane single crystals, in order to have more accuracy in the determination of the cell parameters and of possible phase changes, and to obtain more accurate intensity data for structure refinement in order to understand what kind of structural change precedes the chemical reaction.

Experimental method:

A diamond anvil cell (DAC) with a large aperture (60°) was used. Stainless-steel gaskets were used. The edge of the gasket hole was covered with a gold ring, in order to have a slower and more hydrostatic pressurization. The pressure was measured with the ruby fluorescence technique. For each run, a liquid nitromethane sample was loaded and pressurized until crystallization occurred, then pressure was slowly decreased and increased until a single crystal with no defects was obtained (at about 1.5 GPa). The X-ray diffraction images were measured at increasing pressures up to 20 GPa, in steps of 1-2 GPa. During the measurements, the DAC was rotated by 60 degrees about the beam axis, with exposure times ranging from 10 to 30s. Panoramic images were detected at each pressure value, while angle-resolved series of images were recorded at about 5-6 GPa intervals. Two different orientations of the nitromethane crystal with respect to the DAC axis were obtained in the different runs.

Results

Nitromethane crystallizes in the orthorhombic system P212121 with Z=4, and the atoms positions up to 6 GPa are known 4. The orientation of the single crystal was obtained from angle-resolved images at 1.5 GPa, using the angular position of two indexed peaks (by Powdercell) of the known structure. The indexing of all the detected diffraction peaks was then possible. At each pressure, each small portion of the panoramic image containing one (or more than one if superposed) peak was integrated with fit2d and fitted with Datlab to obtain the exact value of 2theta and intensity. The lists of the hkl with relative 2theta positions were used to calculate a,b,c with Unitcell, assuming an orthorhombic structure. At the lowest pressures (up to 6-7 GPa) more than 200 indexed peaks with relative 2theta values are available from each image, but only 100 of them were used, corresponding to a fixed region of the image (almost one half) . The number of detectable peaks decreases on increasing pressure above 7-8 GPa, due to an intensity decrease, and is reduced to 20 above 16 GPa, if the same region of the image is considered. Starting at about 8 GPa, many new peaks appear (many of them rather superimposed to the old ones). Most of the new peaks can be indexed assuming the same orthorhombic structure $P2_12_12_1$, but some of them are not yet assigned in this preliminary analysis. Moreover, above 10 GPa the appearance of the image changes quite rapidly from that typical of a single crystal to that of a polycrystalline sample. The pressure dependence of the cell parameters indicates no phase change but the overall behaviour of the diffraction pattern indicate that the single crystal is destroyed above 10 GPa, and this could be due to a new crystalline phase or to some change in the positions of atoms inside the unit cell. Refinement was not yet done due to a lack of information on absolute intensities of the diffraction peaks in the panoramic images detected by the MAR3450; this problem is to date under investigation.

The values of a, b, c are in perfect agreement with the data obtained in the previous experiment 2157. In this case, we are able to detect fine changes (under study) occurring in the same pressure range where the modifications of the vibrational spectra were detected.

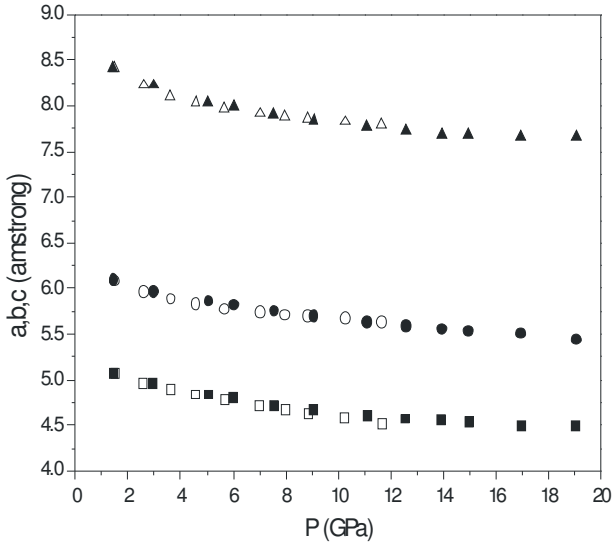

Fig1. Pressure evolution of the cell parameters. squares: a, circles: b, triangles: c
Empty symbols: orientation 1 (up to now we did not analyse data above 12 Gpa due to destruction of the crystal). Full symbols: orientation 2

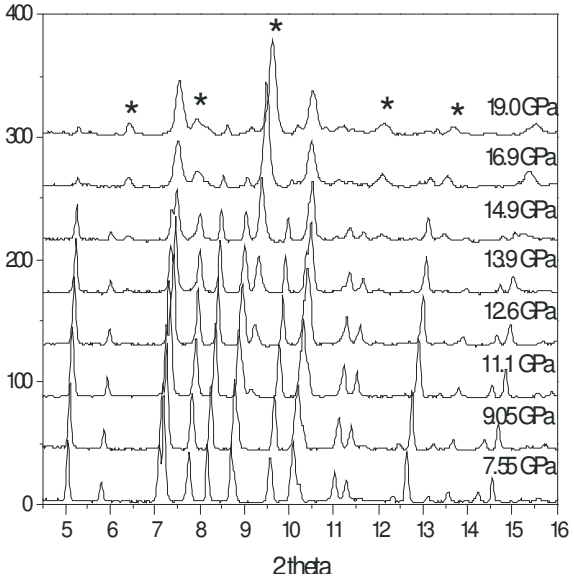

Fig 2. Integration with fit2d of the images on increasing pressures above 7 Gpa (only the right half of each image was intgrated). The stars indicate the strongest new diffraction peaks

References

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