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Compressibility and structural stability of ultra-incompressible bimetallic interstitial carbides and nitrides

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We have investigated by means of high-pressure x-ray diffraction the structural stability of Pd_2Mo_3N, $Ni_2Mo_3C_{0.52}N_{0.48}$, $Co_3Mo_3C_{0.62}N_{0.38}$, and Fe_3Mo_3C. We have found that they remain stable in their ambient-pressure cubic phase at least up to 48 GPa. All of them have a bulk modulus larger than 330 GPa, the least compressible material being Fe_3Mo_3C, $B_0 = 374(3)$ GPa. In addition, apparently a reduction of compressibility is detected as the carbon content is increased. The equation of state for each material is determined. A comparison with other refractory materials indicates that interstitial nitrides and carbides behave as ultra-incompressible materials.

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A great effort is currently focused on the synthesis and characterization of materials exhibiting very low compressibility and large durability.[1] In particular, transition-metal nitrides and carbides have attracted special attention.[2] These refractory materials have numerous industrial applications and a promising future, on top of being of great interest to the scientific community. Many incompressible nitrides have been recently discovered combining the application of high pressure (HP) and high temperature. However, only small amounts of them can be synthesized and their industrial preparation presents several difficulties. In contrast, interstitial bimetallic nitrides can be prepared in large amounts at ambient pressure,[3] they (e.g., Ni_2Mo_3N, Co_3Mo_3N, and Fe_3Mo_3N) having similar mechanical properties to many ultrahard compounds.[4] In particular, their compressibility is smaller than that of cubic Si_3N_4 and comparable to that of cubic BN.[4] Thus, interstitial nitrides could be considered as potential cheap substitutes for nowadays industrial refractory materials. Isomorphic carbides[5] could be probably even better candidates since the substitution of nitrogen by carbon is expected to reduce compressibility.[6]

In this work we extend the study of the compressibility and structural properties of molybdenum bimetallic compounds to Pd_2Mo_3N, Fe_3Mo_3C, $Ni_2Mo_3C_{0.52}N_{0.48}$, and $Co_3Mo_3C_{0.62}N_{0.38}$. They were studied by HP x-ray diffraction (XRD) up to 48 GPa, being found to remain in their ambient-pressure cubic structure. They are also ultra-incompressible materials, with Fe_3Mo_3C challenging the incompressibility of cubic BN.

Pd_2Mo_3N was synthesized by ammonolysis of a crystalline precursor following the procedure described by El-Himri *et al.*[3] $Co_3Mo_3C_{0.62}N_{0.38}$, $Ni_2Mo_3C_{0.52}N_{0.48}$, and Fe_3Mo_3C were synthesized by carburization of the corresponding nitrides.[7–9] The nitrides were heated at 10 K/min up to 923 K under flowing of a carburizing mixture of gases (360 cm^3/min, 4.4% CH_4, 1.1%, 94.5% Ar). The temperature was held for 2 h (Fe and Co compounds) and 4 h (Ni compound). Then, the solids were quenched to room temperature (RT). The compositions of the compounds were determined by energy-dispersive x-ray analysis on a scanning electron microscope (Phillips XL-30) operating at 20 kV, and equipped with a super-ultrathin detector, which allows the detection of light elements. The carbon/nitrogen content was also evaluated by standard combustion analysis (Carbo Erba Elemental Analizer 1108) with a precision of 0.2%.

Angle-dispersive x-ray diffraction (ADXRD) experiments at RT and HP were carried out at beamline I15 of the Diamond Light Source using a diamond-anvil cell (DAC) and a monochromatic x-ray beam ($\lambda = 0.4246$ Å). Samples were loaded in a 100-μm hole of a rhenium gasket in a DAC with diamond-culet sizes of 300 μm. Pressure was determined using ruby fluorescence.[10] For Fe_3Mo_3C a second experiment was carried out using gold as pressure marker.[11] Both scales are reliable and allow determining pressure *in situ*. As we will see below, the choice of one pressure scale or the other does not influence the results. A 16:3:1 methanol-ethanol-water mixture was used as pressure-transmitting medium.[12,13] The x-ray beam was focused down to $30 \times 30\ \mu m^2$. A pinhole placed before the sample position was used as a clean-up aperture. The images were collected using a MAR345 image plate located at 350 mm from the sample. The diffraction patterns were integrated and corrected for distortions using FIT2D. The structural analysis was performed using POWDERCELL and GSAS.

At ambient pressure, the obtained diffraction patterns for Pd_2Mo_3N, $Ni_2Mo_3C_{0.52}N_{0.48}$ (space group $P4_132$),[5] $Co_3Mo_3C_{0.62}N_{0.38}$, and Fe_3Mo_3C (space group $Fd\bar{3}m$, η-carbide structure)[9] correspond to the known cubic structures, which are shown in Fig. 1. The obtained unit-cell parameters are summarized in Table I, showing good agreement with previous data.[3,5,9] Both structures have been already extensively described, their basic framework being formed by polyhedral units with short Mo-N (or Mo-C) bond distances. Figure 2 shows ADXRD data for $Ni_2Mo_3C_{0.52}N_{0.48}$ and Fe_3Mo_3C at selected pressures. Under compression, the only changes we observed in the XRD patterns are the shift of Bragg peaks toward high 2θ angles and the typical broadening of DAC experiments.[14,15] Similar evolution of diffraction

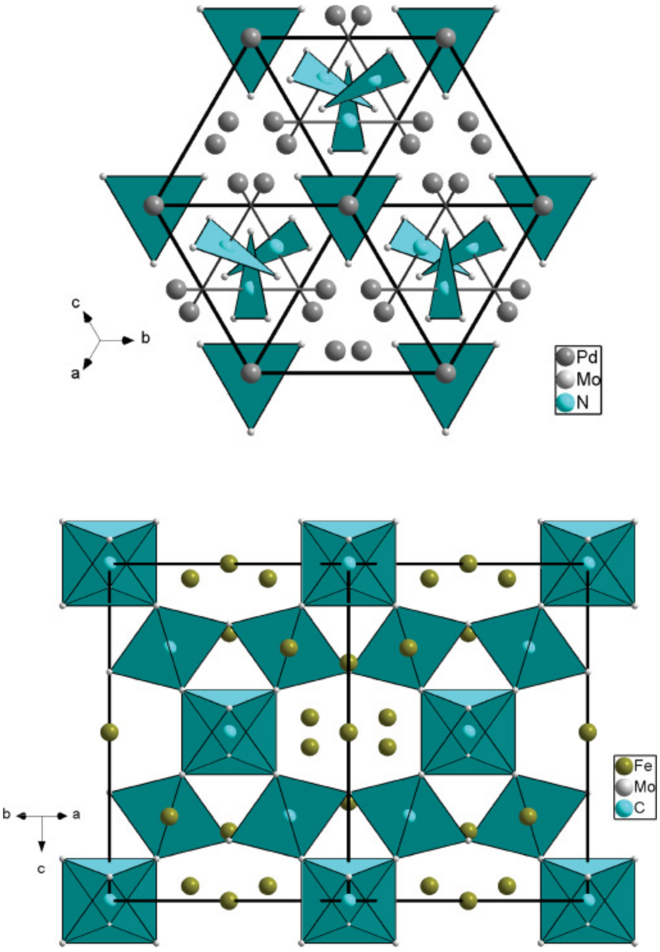

FIG. 1. (Color online) Schematic view of the crystal structures of Pd_2Mo_3N and Fe_3Mo_3C.

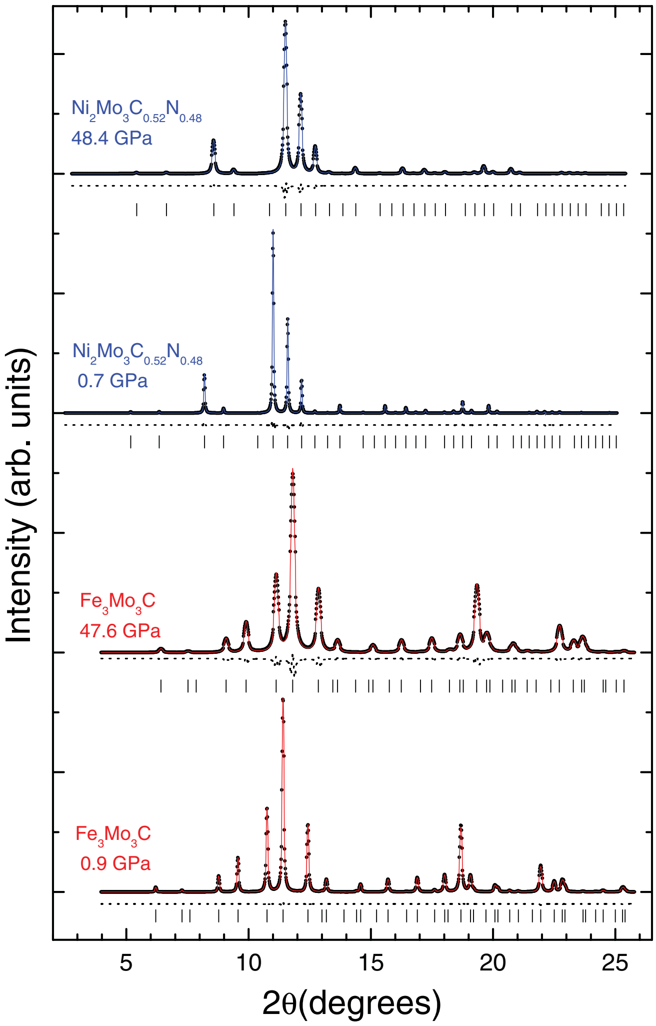

FIG. 2. (Color online) ADXRD data of $Ni_2Mo_3C_{0.52}N_{0.48}$ and Fe_3Mo_3C at selected pressures and RT. Measured (dots) and calculated (solid lines) patterns are shown together with the difference curve (dashed lines) and calculated positions of Bragg reflections (tick marks).

patterns upon compression is found in the other compounds. For Pd_2Mo_3N and $Ni_2Mo_3C_{0.52}N_{0.48}$, all measured XRD patterns can be indexed within the ambient-pressure structure. For $Co_3Mo_3C_{0.62}N_{0.38}$ and Fe_3Mo_3C, all measured patterns can be assigned to the η-carbide structure. No evidence of pressure-induced phase transition or chemical decomposition is detected in any of the experiments and the ambient-pressure XRD patterns are fully recovered upon decompression.

Before continuing the discussion of the results, we would like to comment on possible nonhydrostatic effects in our experiments. It is known that 16:3:1 methanol-ethanol-water is not a hydrostatic pressure medium beyond 11 GPa.[13] This typically induces peak broadening, which in our case can be noticed in Fig. 2. However, in previous experiments, it has been established that nonhydrostatic stresses do not influence, at least up to 50 GPa, the structural stability of isomorphic compounds.[4] In particular, we have here checked that the lattice parameters obtained from multiple diffraction lines of the same compound agree within their experimental uncertainties. Therefore, the possibility of a pressure-induced tetragonal or rhombohedral distortion of the cubic structure[16] caused by nonhydrostatic stresses can be excluded.

TABLE I. EOS parameters and unit-cell parameter (a) determined at ambient pressure.

Compound	a (Å)	V_0 (Å^3)	B_0 (GPa)	B_0'
Pd_2Mo_3N	6.817(5)	316.9(2)	333(3)	4.3(2)
$Ni_2Mo_3C_{0.52}N_{0.48}$	6.645(5)	293.4(2)	344(4)	4.2(2)
$Co_3Mo_3C_{0.62}N_{0.38}$	11.069(8)	1356(0.5)	353(4)	4.7(3)
Fe_3Mo_3C	11.099(8)	1368(0.5)	374(3)	4.1(3)

From the refinement of the diffraction patterns, we obtained the pressure evolution of unit-cell parameters (and volume) in all compounds. We also refined the internal atomic positions and found that their change with pressure is comparable to experimental uncertainty. Therefore, we decided to neglect the pressure effect on atomic positions. As can be seen in Fig. 2, good fittings are obtained in the refinements. Comparable results were obtained at different pressures in the four studied compounds. The pressure dependence of the unit-cell volume is plotted in Fig. 3. There it can be seen that the compounds here studied are highly incompressible. The pressure-volume data have been analyzed using a third-order Birch-Murnaghan

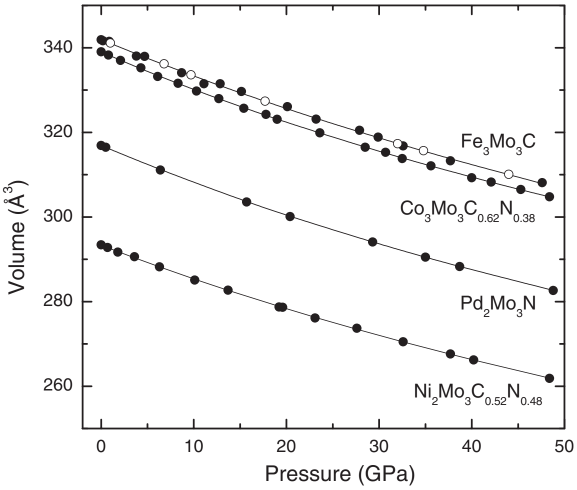

FIG. 3. Unit-cell volume versus pressure for studied compounds. Experimental data: Solid (empty) symbol ruby (gold) scale. Lines: Reported EOS. For Fe_3Mo_3C and $Co_3Mo_3C_{0.62}N_{0.38}$ we plotted $V/4$ to facilitate comparison with Pd_2Mo_3N and $Ni_2Mo_3C_{0.52}N_{0.48}$.

equation of state (EOS). The obtained volume at ambient pressure (V_0), bulk modulus (B_0), and its pressure derivative (B_0') are summarized in Table I. The bulk modulus of $Ni_2Mo_3C_{0.52}N_{0.48}$ (344 ± 4 GPa) is 4% larger than that of Ni_2Mo_3N (330 ± 8 GPa).[4] The bulk modulus of Pd_2Mo_3N (333 ± 3 GPa) is around 6% larger than theoretical values (312–313 GPa)[4,17] and comparable to the bulk modulus of Ni_2Mo_3N.[4] The bulk modulus of $Co_3Mo_3C_{0.62}N_{0.38}$ (353 ± 4 GPa) is 1% larger than that of Co_3Mo_3N (350 ± 8 GPa).[4] The bulk modulus of Fe_3Mo_3C (374 ± 3 GPa) is 2% larger than that of Fe_3Mo_3N (368 ± 9 GPa).[4] In particular, Fe_3Mo_3C turns out to be as incompressible as cubic BN. Note that for Fe_3Mo_3C two independent experiments were performed using different pressure scales (gold and ruby) and similar results were obtained (see Fig. 3). According with the above summarized results, apparently substitution of N by C produces an increase of the bulk modulus. This effect is most evident when comparing $Ni_2Mo_3C_{0.52}N_{0.48}$ with Ni_2Mo_3N, since in other compounds the B_0 increase is comparable with the standard deviation of this parameter. An important point to mention here is the trade-off effect of the bulk modulus and its pressure derivative when comparing the compressibility of different compounds. For $Co_3Mo_3C_{0.62}N_{0.38}$ and Co_3Mo_3N the same B_0' (4.7) is obtained and for Fe_3Mo_3C ($B_0' = 4.1$) and Fe_3Mo_3N ($B_0' = 4.2$) the difference in the pressure derivative is 2%; therefore it is clear that the effect of carbon/nitrogen substitution is not an artifact of the EOS fitting. Finally, for $Ni_2Mo_3C_{0.52}N_{0.48}$ $B_0' = 4.2$ whereas for Ni_2Mo_3N $B_0' = 4.5$. In this case, to check the carbon-content influence in compressibility we made an EOS fit assuming $B_0' = 4.5$ also for $Ni_2Mo_3C_{0.52}N_{0.48}$ obtaining $B_0 = 338 \pm 4$ GPa, a value still 3% larger than the bulk modulus of Ni_2Mo_3N.

As described, the four studied materials are found to be quite incompressible. In particular, they are less compressible than MoN,[18] cubic Hf_3N_4,[19] and cubic Si_3N_4[1] and as incompressible as cubic BN,[6] showing a bulk modulus only 16% smaller than diamond. The incompressible and nondeformable character of the studied compounds is related with the common features of their crystalline structures.[20] In all bimetallic nitrides (carbides), the Mo-N (Mo-C) bond distance is pretty similar to the Mo-N distance in rocksalt MoN (2.095 Å);[21] e.g., Mo-N is 2.079(7) Å in $Ni_2Mo_3C_{0.52}N_{0.48}$. However, in our compounds, as a distinctive feature, the NMo_6 octahedra not only form a three-dimensional network, but additionally are interpenetrated by NPd_5 (NNi_5) trigonal dipyramids or NFe_4 (NCo_4) tetrahedra forming a very strong three-dimensional network, which gives them their particular incompressibility. In particular, from our structural refinements we concluded that the Mo-N bond is quite incompressible, consequently making the bimetallic nitrides ultra-incompressible. The estimated bond compressibility in $Ni_2Mo_3C_{0.52}N_{0.48}$ is $\chi_{\text{Mo-N}} = -\partial \ln(d)/\partial P = 7.5(5) \times 10^{-4}$ GPa^{-1}, where d represents the Mo-N bond distance. This bond compressibility is smaller than that observed for the incompressible Mo-O bonds in several molybdates,[22–24] supporting our hypothesis. Regarding the Mo-C bond, we obtained from the structural refinements of Fe_3Mo_3C that $\chi_{\text{Mo-C}} = 6.4(4) \times 10^{-4}$ GPa^{-1}. Thus, apparently this bond is even less compressible than the Mo-N bond, which is consistent with the fact that the substitution of N by C may produce a decrease of compressibility in the studied materials. This observation is also consistent with conclusions previously obtained for noble-metal nitrides and carbides.[25]

In the past, based on the calculated shear modulus (G),[4] interstitial nitrides have been considered as good candidates for hard materials. In the present case the shear modulus can be estimated using the determined bulk modulus. For an isotropic system G can be directly related to B_0 according to $G = \frac{3}{2}B_0(1-2\nu)/(1+\nu)$ where ν is the Poisson's ratio, the value of the ratio of the transverse strain to the corresponding axial strain. For the compounds here studied a good approximation is to consider $\nu = 0.3$.[4] Under such approximation, for Fe_3Mo_3C, $G = 172$ GPa is obtained. Then, employing the correlation between shear modulus and the Vickers hardness reported by Teter,[26] a hardness of 23.3 GPa is estimated for Fe_3Mo_3C. This value is larger than the Vickers hardness of cubic Si_3N_4,[1] thus pointing to a larger resistance of Fe_3Mo_3C to plastic deformations. Therefore, the compounds here studied can be as hard as superhard nitrides. However, they are in the low hardness boundary for superhard materials.

In summary, we have studied experimentally the compressibility and structural properties of bimetallic nitrides, carbides, and carbonitrides. They are stable in their cubic structure under extreme compression and have large bulk moduli. In particular Fe_3Mo_3C has a bulk modulus comparable to cubic BN. We also found evidence suggesting that the substitution of N by C reduces the compressibility of the bimetallic family studied. The reported incompressibility is a consequence of the framework of short and strong Mo-N (Mo-C) bonds of the materials. The known correlation between shear modulus and hardness suggests that refractory interstitial nitrides and carbides are good candidates for ultrahard materials. A Vickers hardness of 23.3 GPa is estimated for Fe_3Mo_3C. A possibility to explore in order to further reduce compressibility is the substitution of Mo by W. This fact is known to enhance incompressibility in transition-metal nitrides.[27] An advantage of interstitial nitrides and carbides is that they can be synthesized in large amounts without the use of high-pressure conditions. Another interesting fact is their peculiar magnetic properties, caused by the narrow *d* band they have sitting at around the Fermi level.[28] We hope that this work will stimulate further research on this interesting family of compounds.

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