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High-pressure transformation of N_2/O_2 mixtures into ionic compounds

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We report the neutral-ionic transformation of N_2/O_2 mixtures above 5 GPa at 300 K. The reaction is photoinduced with a Nd:YAG laser irradiation. The ionic compounds are characterized by Raman and infrared spectroscopic and synchrotron x-ray diffraction measurements. We show by Raman analysis that the $NO^+NO_3^-$ compound can trap a large fraction of O_2 molecules, thus forming an O_2 clathrate. But no N_2 molecule can be included in this nitrosonium nitrate compound. We propose an orthorhombic unit cell with 10 $NO^+NO_3^-$ in it.

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I. INTRODUCTION

The pressure-induced transformations in simple molecular gases under pressure have been found particularly interesting for H_2, O_2, and N_2. Indeed, rich phase diagrams have been disclosed for these three systems.[1–3] Up to recently, the main efforts to induce by pressure bonding changes in these van der Waals systems were aimed at the observation of a metallic state. Above 96 GPa, solid oxygen transforms into a molecular metal with superconducting properties.[4] Solid N_2 (Ref. 5) and solid H_2 (Ref. 6) have been turned into black solids by the decrease of their electronic gap, a precursor sign to their metallization, respectively, up to 240 GPa and up to 320 GPa. However, recent high-pressure studies have revealed other interesting changes of the bonding in these molecular solids. Solid oxygen in the epsilon phase above 12 GPa may be formed of paired oxygen molecules into O_4 units.[7] By coupling high pressure and laser heating, solid N_2 transforms into a cubic single-bonded nitrogen structure.[8]

Comparatively few studies have been devoted to the phase transformations under pressure in mixtures of O_2, N_2, and H_2. The phase diagrams of O_2/H_2 (Ref. 9) and O_2/N_2 (Refs. 10 and 11) mixtures have been measured. Interestingly, the existence of van der Waals compounds has been observed, $(O_2)_3(H_2)_4$,[9] or suggested, $(N_2)_3O_2$ and $N_2(O_2)_2$.[11] In this study, we present the pressure-induced transformation of O_2/N_2 mixtures into an ionic compound formed with the NO^+ and NO_3^- ions. This confirms that the nitrosonium (NO^+) nitrate (NO_3^-) compound, which has been previously observed by applying pressure on nitrogen oxides (N_2O_4, N_2O),[12–15] is the stable high-pressure phase of systems formed with N/O atoms. Also, we propose an orthorhombic unit cell for the compound from the x-ray data. Finally, we demonstrate by Raman measurements that this compound can host a large fraction of O_2 molecules, so forming a new type of clathrate.

II. EXPERIMENT

The binary phase diagram of N_2/O_2 mixtures has been recently determined[11] under pressure at 300 K. The same experimental procedure for loading the membrane diamond anvil cell and measuring the concentration of the mixtures has been used here. We used diamonds with culets of 500 μm. BeCu gaskets were used to confine the sample and the sample chamber at 10 GPa was typically 100 μm in diameter and 30 μm thick. In the present study, we took advantage of the almost total miscibility of O_2 and N_2 molecules in the solid phase above solidification. This phase, is based on the δ-N_2 structure (cubic $Pm3n$ structure with eight molecules in the unit cell), showing almost ideal substitution of O_2 molecules and a spontaneous growth of single crystals filling the whole sample chamber. The chemical transformation of the solid mixture into an ionic solid, characterized below as $NO^+NO_3^-$, is triggered under the continuous Nd:YAG laser irradiation (typically about 2 watts focused in a 10 μm spot at the center of the sample chamber during about 10 seconds to a few minutes). This transformation has been studied for three initial single crystals, with O_2 concentrations, respectively, of 25, 66, and 75 mol %. A total of 12 different samples were studied to test the reproducibility of the observations at each concentration. For O_2 concentrations of 66 mol % and 75 mol % the reaction is total and the sample chamber is observed totally deep reddish brown, as shown in Fig. 1. In this case, by starting at 6 GPa, a drop of pressure of 1 GPa is measured after transformation. This was observed reproducibly on five samples. Since this reaction takes place under quasi-isochoric condition, the volume per molecule in the $NO^+NO_3^-$ compound at 5 GPa is estimated equal to the one of the N_2/O_2 alloy at 6 GPa, as recently measured.[11] The $NO^+NO_3^-$ compound formed is thus denser than the O_2/N_2 alloy. It should be noted that the transformation could not be induced for O_2 concentrations lower than 10 mol %, even after a laser irradiation of 1 hour at 10 watts. But the reaction was still easily induced with less than 5 mol % N_2 in the initial mixture. Finally, we observe the reaction propagating throughout the sample when it is a single crystal. On the contrary, the reaction remains local when samples are powders. It shows that the mesoscopic state (single crystal or powders) of the initial sample is important for the propagation of the locally induced reaction to the whole sample as a phonon assisted reaction.[16]

III. RESULTS

The effect of photoinduction with a Nd: YAG laser is understood by noting that the transition from the ground triplet state of the O_2 molecule $^3\Sigma_g^-$ to the first excited singlet state $^1\Delta_g$ is made possible by a resonance condition with the 1064 nm wavelength of the laser and by transition dipoles

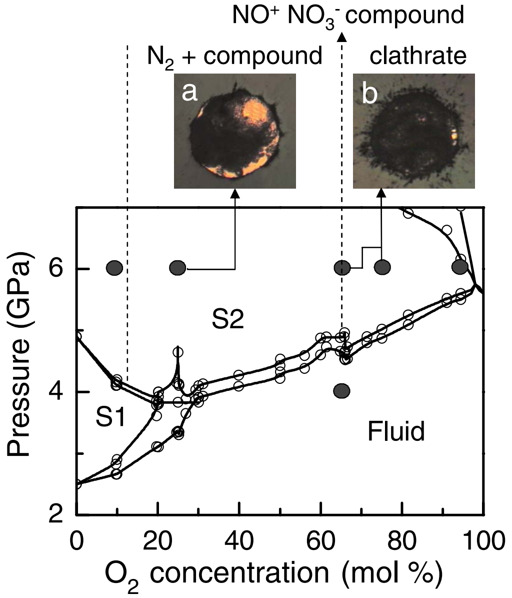

FIG. 1. (Color online) Part of the phase diagram of N_2/O_2 mixtures under pressure (Ref. 11) and microphotographies of the transformation of N_2/O_2 mixtures under Nd: YAG laser irradiation at 6 GPa and 300 K. (a) Equilibrium between $NO^+NO_3^-$ compound (deep reddish brown part) and pure solid N_2 for an initial concentration of 25 mol % O_2. (b) Homogeneous reddish brown compound filling the whole sample chamber for initial concentrations of 66 and 75 mol % O_2, corresponding, respectively, to a pure $NO^+NO_3^-$ compound and to a O_2 clathrate.

induced by intermolecular forces. The ${}^3\Sigma_g^- \rightarrow {}^1\Delta_g$ electronic transition has been reported in the different phases of oxygen, near ambient pressure.[17] However, the pressure redshift of the ${}^3\Sigma_g^- \rightarrow {}^1\Delta_g$ transition could destroy this resonance condition. We have verified by fluorescence measurements that a significant concentration of $O_2({}^1\Delta_g)$ can still be populated at 6 GPa under Nd: YAG laser irradiation. Since the ${}^1\Delta_g$ singlet state is known to have a high chemical activity and a long lifetime, its population could help to crossover the energy barrier of the transformation into a ionic compound. Indeed, it has been demonstrated before that a laser irradiation can be viewed as a method to force a pressure-induced transformation at a much lower pressure than where it should normally occurs.[18] Similarly, in the present case, a 1 eV electronic excitation (i.e., corresponding to the 1064 nm photon energy) could be given to the O_2 molecule by a pure compression to 60 GPa. But, at this pressure, the O_2/N_2 mixture is totally phase separated and consequently the pure pressure-induced neutral-ionic transformation of the O_2/N_2 mixtures would not be observed.

Raman measurements were realized with an XY DILOR spectrometer using a Ar-Kr laser as excitation wavelength (514.5 nm and ~100 mW). The spectra were collected on a CCD detector cooled with liquid nitrogen. Infrared measurements were achieved with a Perkin Elmer infrared Fourier transform spectrometer using a KBr beamsplitter. The spectra were collected on a mercury-cadmium-telluride (MCT) quantum detector cooled with liquid nitrogen. Raman diffusion and infrared absorption measurements show a spectroscopic signature of the formation of the known $NO^+NO_3^-$ compound. This is observed for the three different initial O_2 concentrations studied here. A typical Raman spectrum of the product of the transformation in an O_2/N_2 mixture with an O_2 concentration almost equal to 66 mol % is presented in Fig. 2(a). The peak at 2240 cm^{-1} corresponding to the N-O

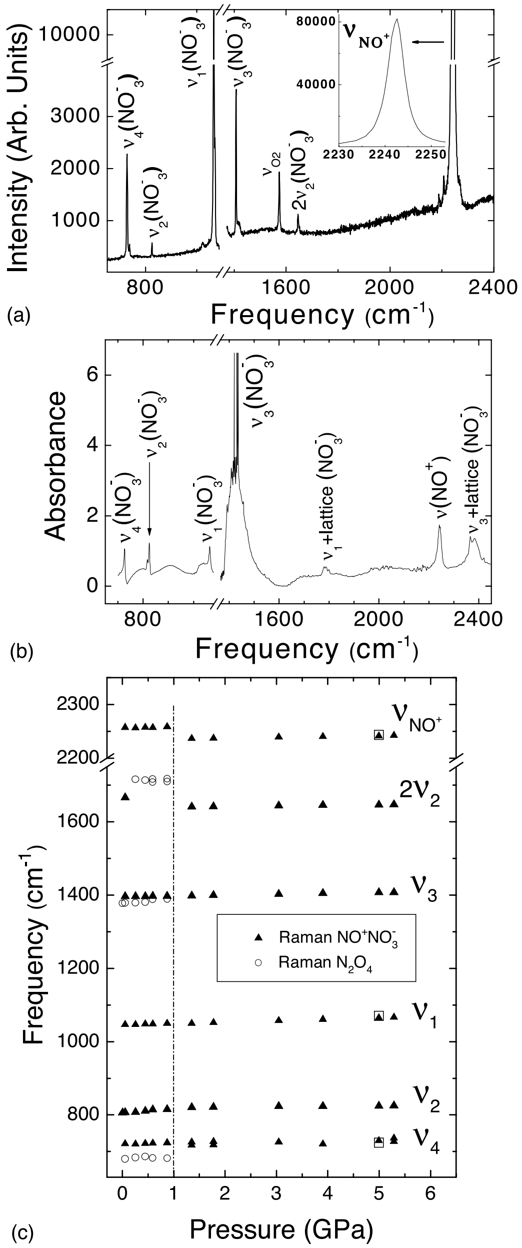

FIG. 2. Raman (a) and infrared (b) spectra of the $NO^+NO_3^-$ compound at 5.5 GPa. The same modes, as identified in the text, are observed in the two spectra. The weak O_2 Raman vibron peak is due to an initial mixture slightly in excess to 66 mol % O_2. (c) Evolution of the Raman frequencies versus pressure. Only the characteristic modes of NO_3^- and NO^+, as triangles, are observed down to 1 GPa. Below 1 GPa, associated to the visual transformation of the sample, the characteristic modes of N_2O_4, as circles, are observed in addition to the modes of NO_3^- and NO^+. Raman data obtained by Yoo *et al.* for $NO^+NO_3^-$ transformed from N_2O at high pressure are represented at 5 GPa by open squares (Ref. 15).

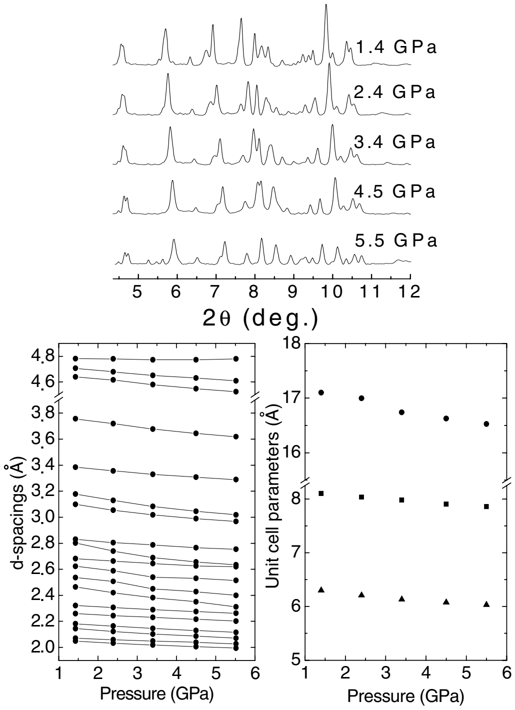

FIG. 3. Evolution of the x-ray spectra, the *d*-spacings and the unit cell parameters versus pressure of the $NO^+NO_3^-$ compound that is formed from N_2/O_2 mixtures. The evolution of the x-ray patterns show that the ionic compound keeps the same structure down to ≃1 GPa.

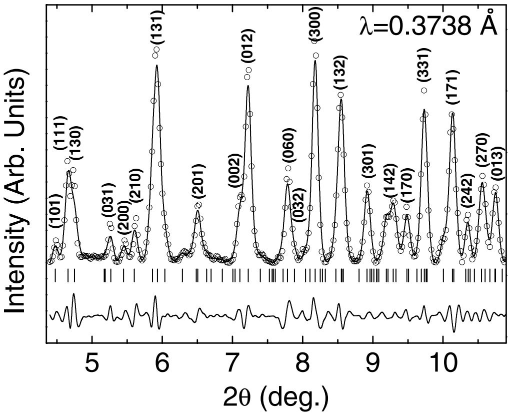

FIG. 4. Determination of the structure of the $NO^+NO_3^-$ compound at 5.5 GPa. Open circles represent the integrated spectra obtained from angular dispersive x-ray diffraction with a monochromatic beam at 0.3738 Å; the solid line is the LeBail refinement of the unit cell, giving an orthorhombic unit cell with parameters $a=7.863(1)$ Å, $b=16.519(3)$ Å, $c=6.031(1)$ Å, and $V=783.4(2)$ Å^3/cell. The lower line is the difference between the experimental and the calculated spectra that best index the x-ray pattern.

stretch for NO^+ is particularly intense. The NO_3^- group is also clearly identified with its intense peak at nearly 1050 cm^{-1} corresponding to the ν_1 (symmetric stretch) mode, and with the other peaks associated to the ν_2 (out-plane bend) mode around 820 cm^{-1}, the ν_3 (antisymmetric stretch) mode around 1390 cm^{-1}, and the ν_4 (in-plane deformation) mode around 720 cm^{-1}. Infrared absorption measurements with intense absorption bands [Fig. 2(b)] confirm the ionic character of the compound. The same N-O stretch mode for NO^+ and the ν_1, ν_2, ν_3, and ν_4 fundamental modes of NO_3^- are also identified. The coincidence of the Raman and infrared lines implies either that the structure of the compound is noncentrosymmetric or that NO^+ and NO_3^- species are not ordered on some sites.

The pressure dependence of the Raman frequency of these modes, as reported in Fig. 2(c), is in good agreement with the Raman data of the $NO^+NO_3^-$ compound obtained from high *P*-*T* transformation of N_2O and N_2O_4.[15,19] Also, the stability of the ionic compound has been studied upon decompression. Down to ~1 GPa, no phase transition is observed. There is a continuous shift of the frequencies, as seen in Fig. 2(c). Similarly, a continuous increase of all the *d*-spacings is observed from x-ray diffraction (Fig. 3). At 1 GPa, a transition occurs in the sample associated with a partial conversion of $NO^+NO_3^-$ to bulk molecular N_2O_4 and probably with a mixture of phases. A similar transition at 1 GPa has been reported upon decompression of the $NO^+NO_3^-$ compound synthesized from N_2O at high *P*-*T*.[19]

The structure of the $NO^+NO_3^-$ compound obtained from an initial O_2 concentration of 66 mol % was studied by synchrotron x-ray diffraction experiments at the ESRF with angle-dispersive monochromatic x-ray diffraction ($\lambda=0.3738$ Å). Two different samples were studied with identical results. The same diffraction peaks were observed but with a slightly different distribution of intensity between them that can be ascribed to some preferred orientation of the powder samples. In order to improve over the degree of crystallinity in the solid, the diamond anvil cell was rocked with an angle of ±15°. The diffraction patterns were angularly integrated with a maximum 2θ angle of 20°. A Le Bail extraction,[20] based on profile matching, was performed with the Fullprof software[21,22] to refine the unit cell parameters determined previously with the Crysfire software.[23] The peak shape was modeled by a Gaussian profile, and the background was manually adjusted. The experimental spectrum at 5.5 GPa, the calculated one from the Le Bail extraction and their difference are shown in Fig. 4. The measured *d*-spacings and the results of the refinement are presented, respectively, in Tables I and II.

This pattern is best indexed by an orthorhombic unit cell with cell parameters $a=7.863(1)$ Å, $b=16.519(3)$ Å, $c=6.031(1)$ Å, and $V=783.4(2)$ Å^3/cell. The Le Bail extraction was performed with several space groups. For four of them (*P*222, *P*222$_1$, *Pmm*2, *Pmmm*) equivalent results were obtained (cell parameters, Rp, Rwp, GoF). The difference on cell parameters is less than 0.002 Å. The results obtained for the space group of the highest symmetry, *Pmmm*, are reported. Moreover, knowing the volume per molecule of the $NO^+NO_3^-$ compound, under the assumption that the transformation from the initial alloy is quasi-isochoric, we have estimated that this unit cell contains 10±0.2 $NO^+NO_3^-$ entities. We have tried to perform a Rietveld refinement of the data in order to determine the atomic positions. The Rietveld refinement was unsuccessful, mainly because the overlap of the peaks is too important. Song *et al.*[14] and Yoo *et al.*[15] have

TABLE I. Analysis of the x-ray diffraction pattern for the $NO^+NO_3^-$ compound at 5.5 GPa, obtained from a N_2/O_2 initial mixture with 66 mol % O_2. Observed *d*-spacings of the ionic compound $NO^+NO_3^-$. The calculated *d*-spacings obtained from a LeBail refinement are corresponding to an orthorhombic unit cell with parameters $a=7.863(1)$ Å, $b=16.519(3)$ Å, $c=6.031(1)$ Å, and $V=783.4(2)$ Å^3/cell.

hkl	d_{obs} (Å)	d_{obs}-d_{calc}	*hkl*	d_{obs} (Å)	d_{obs}-d_{calc}
101	4.7794	−0.0060	032	2.6348	−0.0101
111	4.6072	0.0107	300	2.6197	−0.0013
130	4.5226	0.0122	132	2.5086	0.0018
031	4.0724	0.0060	301	2.3991	−0.0047
200	3.9179	−0.0142	142	2.3108	−0.0155
210	3.8091	−0.0156	170	2.2618	0.0015
131	3.6182	0.0062	331	2.2026	−0.0004
201	3.2884	−0.0051	171	2.1160	−0.0005
002	3.0174	0.0019	242	2.0712	0.0009
012	2.9673	0.0008	270	2.0276	0.0043
060	2.7546	0.0014	013	1.9943	−0.0013

inferred a different structure for the $NO^+NO_3^-$ compound synthesized at high *P* and *T* from solid N_2O. It has also an orthorhombic structure but with a smaller unit cell and with a speculated aragonite type arrangement, i.e., similar to classical ionic structures, with NO^+ and NO_3^- grouped in pairs close to a N_2O_4 conformation. We could not explain our observed diffracted *d*-spacings with the structure proposed by Song *et al.* even after a Le Bail refinement of cell parameters: a unit cell with higher parameters is necessary to index all the diffracted peaks. This solution does not fit all the observed peaks of the diffraction pattern of the present study, with very intense peaks not being adjusted. At 5.5 GPa, these peaks correspond to the following *d*-spacings in ångstroms (with our indexing in parentheses): 4.7794 (101), 4.6072 (111), 3.6182 (131), 3.2884 (201), 2.9673 (012), 2.7546 (060), 2.5086 (132). This implies either the ionic compound synthesized from N_2/O_2 mixtures has a different structure than the one obtained from the N_2O system, due to a topochemical effect, or that the present data being sensitive to larger d-spacings than previously reported give a larger unit cell.

TABLE II. Analysis of the x-ray diffraction pattern for the $NO^+NO_3^-$ compound at 5.5 GPa, obtained from a N_2/O_2 initial mixture with 66 mol % O_2. Crystallographic data and refined parameters from powder x-ray diffraction for $NO^-NO_3^-$. The Le Bail extraction was performed using the orthorhombic symmetry and the *Pmmm* space group with a unit cell containing 10 $NO^+NO_3^-$ molecules.

	$NO^+NO_3^-$
System	Orthorhombic
Space group	*Pmmm*
Lattice parameters (Å)	$a=7.863(1)$ $b=16.519(3)$ $c=6.031(1)$
Cell volume (Å^3/cell)	783.4(2)
Z	10
Experimental points	737
Refined parameters	4
Rp	9.96%
Rwp	12.9%
Goodness of fit	10.52

IV. DISCUSSION

We have investigated the influence of the initial O_2 concentration of the O_2/N_2 alloy on the nature of the product of the photoinduced transformation. We have thus characterized by Raman and infrared spectroscopies and by x-ray diffraction the compound obtained from two other initial O_2 concentrations, respectively, 25 and 75 mol %. For 25 mol % O_2, a phase separation is observed between the $NO^+NO_3^-$ compound and pure N_2 solid [see photo (a) of Fig. 1]. It should be noted that the vibron peak of N_2 was not detected in the Raman spectra of the compound, even though an extensive mapping of its entire volume had been done. The x-ray diffraction pattern of this compound leads to the same LeBail extraction of the unit cell parameters, as described above for 66 mol % O_2 initial concentration. In contrast, for 75 mol % O_2, a homogeneous product is obtained, as evidenced by optical observation, Raman microprobe and x-ray measurements. The same diffraction peaks are obtained as with a starting concentration of 66 mol % O_2, and the same unit cell could reproduce the diffraction data, although with a slight volume expansion. Furthermore, two new peaks are measured in the Raman spectra of the compound. The first peak around 1560 cm^{-1}, as seen in Fig. 5(c), corresponds to the vibron of the O_2. molecule This rules out a tempting interpretation that the O_2^+ molecules, with a vibron frequency expected around 1843 cm^{-1},[24] could be substituting the NO^+ molecule in the ionic compound. The evolution of the O_2 vibron frequency in the compound is plotted versus pressure in Fig. 5 and it is compared to the one measured in pure

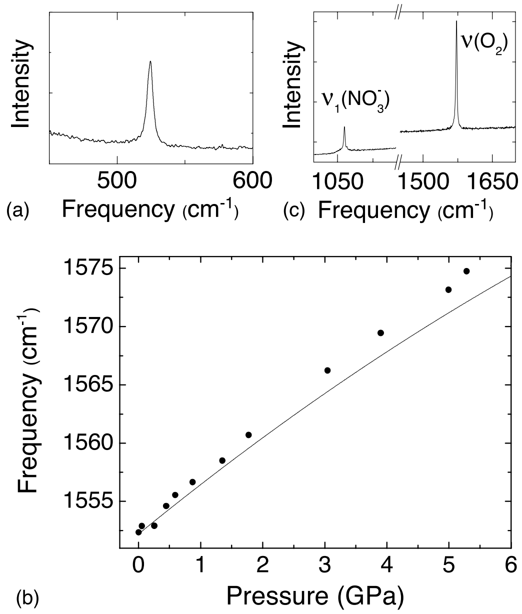

FIG. 5. Raman signature of O_2 molecules in the clathrate formed from an initial O_2 concentration of 75 mol %. (a) The cage mode of O_2 molecules in the $NO^+NO_3^-$ lattice at 5 GPa. (b) Comparison of the O_2 vibron frequency versus pressure for pure O_2 at 300 K, represented as the line, and for the clathrate, as dots. The clathrate was stable down to 0.3 GPa. (c) The O_2 vibron mode at 5 GPa. The intensity of the ν_1 mode of NO_3^- is shown for comparison.

oxygen. The difference between the two curves shows that the vibron of O_2 molecules cannot be attributed to the one of a hypothetical pure O_2 phase in equilibrium with the compound. The second peak is measured around 525 cm^{-1}, as shown in Fig. 5(a). Its frequency is near the one of the ν_6 mode of the N_2O_4 molecule but none of the other intense intramolecular modes of N_2O_4 has been detected. This peak can possibly be attributed to the cage mode of the O_2 molecule in the compound. In fact, its frequency is of the order of the frequency of the libron modes of solid O_2 in the ϵ phase.[1] In summary, these are strong evidences that the O_2 molecules are hosted in the $NO^+NO_3^-$ ionic compound. In this case, a large amount of O_2 can be stored in the $NO^+NO_3^-$ compound because the guest/host molecular ratio is around $R \sim 1/3$, quite a high value for a clathrate. The observation that no N_2 molecules could be trapped in the ionic compound is also puzzling. The fact that N_2 molecule has a steric effect larger than the one of O_2 by about 6% may be part of the interpretation but certainly not a fully satisfying one.

V. CONCLUSIONS

In conclusion, we have observed a neutral-ionic transformation in O_2/N_2 solid solutions under pressure. The transformation is forced in a pressure domain of miscibility by employing a Nd:YAG laser irradiation. From angular dispersive x-ray data, an orthorhombic unit cell is obtained. This unit cell is larger than the one of the structure proposed previously for $NO^+NO_3^-$ at high pressure.[14,15] A large amount of O_2 molecules can be trapped in the lattice of the ionic compound. This kind of clathrate obtained by the pressure transformation in mixtures of gases could have broad applications: In the synthesis of energetic materials; in geophysics, since a similar structure could be the high pressure form of carbonate;[25] in astrophysics, since the compound could be found in meteorites and interplanetary dust.[26] Finally, the present data should stimulate theoretical works to understand the stability and the structure of the compound and also, why and how O_2 but no N_2 molecules can be trapped in.

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