Memory effects in $AlPO_4$-5 nanoporous material: Computational evidences

Efectos de memoria en el material nanoporoso $AlPO_4$-5: Evidencias computationales

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ABSTRACT. Reversible amorphization and memory effects of both dense and open frameworks have received large attention due to their prospective industrial applications. In this paper, we present the results of a computational study related to phase transition and memory effects at high external pressure in $AlPO_4$-5 nanoporous material. Energy minimization technique by classical potentials was used to study the behavior of the $AlPO_4$-5 unit cell at high external pressures. A combination of complex interatomic potentials was used to describe the crystalline structure of the aluminophosphate. According to our simulations crystalline order is lost at a pressure about 3.5 GPa. The behavior of the simulated infrared spectra of compressed structures is an unambiguous evidence of the loss of structural order. Also, an abrupt change in the slope of the unit cell volume *vs*. pressure curve was obtained. At $P \leq 3.5$ GPa the process was found reversible. Contrary to what has been reported in other aluminosilicate systems the final crystalline state of $AlPO_4$-5 at the simulated highest pressure was not amorphous. According to our knowledge this is a first evidence of a reversible phase transition in AlPO- family materials. This result could be important in future industrial and catalytic applications of these materials.

Keywords: A. Microporous material, B. phase transition, D. Lattice Dynamics

INTRODUCTION

The static pressure-induced amorphization (PIA) in zeolites, inorganic materials with well defined pores and cavities, has been in focus of numerous investigations.[1-12] Particular attention has received the PIA in LTA-type zeolite. Depending on the initial applied pressure the process has been reported reversible.[4-6,9,11,12]

Aluminophosphates are microporous materials with properties similar to that of zeolites.[13] Due to the flexibility of the aluminophosphate framework they can be made

catalytically active by introducing other elements like metal centers. Metal-aluminophosphates are prospective materials to be used as catalyst in fine chemistry reactions.[14-16]

Previous researches in α-AlPO (berlinite) showed that this structure undergoes a phase transition from crystalline to amorphous at 15 $\pm$ 3 GPa.[17] Moreover, the high-pressure amorphous phase recrystallizes under decompression, conserving both the structure and the crystallographic orientation of the original crystal. This process was studied by molecular dynamics by Tse and Klug.[18] However, in a very complete Raman study P. Gillet et al[19] shown that the memory-glass effect is not a reversible crystal-amorphous phase transition, as was reported originally,[17] but instead correspond to a reversible first-order crystal-crystal. Nevertheless, the memory effects could be very important in practical applications of these materials.

In this paper, we present the results of a computational study about the phase transition and the memory effects in $AlPO_4$-5 nanoporous material at high external pressures. Energy minimization technique by classical potentials was used to study behavior the $AlPO_4$-5 unit cell upon high external pressures.

The organization of this note is as follow: In section II, we present a general description of both the model used to study the $AlPO_4$-5 structure and the numerical method used in the simulations. In section III, we present the main results of our research and the discussion of them.

COMPUTATIONAL METHODOLOGY

Details of the used approximation have been extensively reported elsewhere,[20-22] therefore, we just highlight the most important issues. The software package GULP [23] was used in energy minimization calculations. GULP uses interatomic potentials that combine long-range electrostatic with short-range pair interactions. Electrostatic

interactions were calculated via the Ewald method. [24] The potential parameters for the $AlPO_4$-5 are reported in reference 25. Polarizability of the oxygen atoms was treated using a shell model developed by Dick and Overhauser.[26] To simulate the partial covalence of the framework relaxation a three-body term was included. Atomic coordinates and cell parameters were optimized to zero force using the Broyden, Fletcher, Golfard and Shanno (BFGS) procedure.[27] If the minimized structure presented imaginary phonon modes then the Rational Function Optimization (RFO)[28] was employed to remove them. The simulations were performed starting from the orthorhombic Pcc2 unit cell.[29] To simulate interactions in $AlPO_4$-5 the empirical parameters of Gale and Henson were used.[30]

Two different computational experiments were performed. In the first one, a abrupt compression from 10^{-4} GPa (room pressure) up to a final pressure = 1, 2,…., 7 GPa was carried out. After that the maximum pressure was reached, every structure was abruptly decompressed up to room pressure. In the second one, a step-to-step compression (increasing pressure in every step 1 GPa) up to reach the maximum value (1,2, …, 7 GPa) was performed. After that, a decompression returning through the same pressures was carried out. The key idea of both experiments was to evaluate the effect of the dynamics of compression/decompression processes on the $AlPO_4$-5's crystalline state under high external pressure conditions.

RESULTS AND DISCUSSION

In Table 1, the simulated crystallographic coordinates of the $AlPO_4$-5 in condition of abrupt compression (from the room pressure up to the final pressure, $\leq$ 7 GPa) are shown. Up to 3 GPa, the simulated crystallographic parameters remain intact essentially. Above this pressure a decrease of the unit cell parameters was observed, but the unit cell symmetry is conserved. At 4 GPa the unit cell parameters are so far from the initial crystal symmetry. The behavior of the volume under compression is

presented in Fig. 1 and it shown a decrease of the volume on the order of the 10% between 3 and 4 GPa. Also a slight change in the slope of the total energy vs. pressure curve is observed similarly to that observed in the molecular dynamics study on $AlPO_4$-α[17] and in our previous studies in aluminosilicates (LTA system).[6,12]

The loss of crystalline order is also evident from the observation of the infrared (IR) spectra of compressed structures (Fig. 3). The Al-O stretching band about 800 cm^{-1} (that we observe about 720-740 cm^{-1}) presents is broadened in the most disordered crystalline state (at 7 GPa). Also, the intensity of the main IR bands decreases when the pressure increases. A similar behavior was reported in LTA zeolites and it has been related to the structural disorder of the crystalline framework. However, in AlPO system, the intensity of IR bands decrease less than in LTA zeolites (aluminosilicates).[1-6, 12]

On the other hand, the abrupt decrease of the volume indicates a phase transformation[4,12, 17] at ~3.5 GPabut it is not necessarily leads to the amorphization of the crystal. As it was expected, this pressure is 4 times less than that observed in a dense framework ($AlPO_4$-α)[17] and it is on the order of than that found in LTA zeolites.[6,12]

In the abrupt compression experiment the final unit cell volume obtained after decompression (at ≤ 3 GPa) is the same that the starting structure at ambient pressure, supporting the complete crystallization of the $AlPO_4$-5 structure. At 4 GPa the final unit cell is a 10% less than the structure at ambient pressure (Fig. 1). Also, the unit cell angles (particularly γ) arrived to values so far of 90°.

Also, the behavior of the IR spectra shows that at ≥ 4 GPa, the intensity of the bands decrease and they are larger comparing to those at ambient pressure. In several

experimental and theoretical papers this fact has been related with the loss of crystallinity of the zeolite.

In spite of the observed loss of crystallinity, the structures at high pressures conserved the crystalline order. Therefore, in contrast with those found in LTA system,[4,12] the phase transition is not from crystalline to amorphous state (it is first-order crystal-crystal phase transition). This result is in agreement with previous experimental and theoretical results in berlinite.[17]

Table 1. Unit cell parameters of $AlPO_4$-5 upon rapid compression at different external pressures

P_{ext}	a/ Å	b/ Å	c/ Å	α/°	β/°	γ/°	gnorm
10^{-4}	13.7584	23.9075	8.4215	90.00	90.00	90.00	10^{-5}
1.0	13.6158	23.7507	8.3237	90.00	90.00	90.00	$2\ 10^{-4}$
2.0	13.4536	23.5896	8.2292	90.00	90.00	90.00	$5\ 10^{-4}$
3.0	13.2792	23.4009	8.1380	90.05	89.99	90.01	$6\ 10^{-4}$
4.0	12.8361	22.3727	7.9865	90.12	89.94	90.40	$4\ 10^{-2}$
5.0	13.8821	19.8192	7.8790	88.707	90.00	89.21	$9\ 10^{-2}$
6.0	12.6668	21.8080	7.8421	90.15	89.72	92.59	0.1(*)
7.0	12.6790	22.2213	7.870	90.67	90.13	89.63	0.1(*)

* Both minimized structures presented one imaginary mode

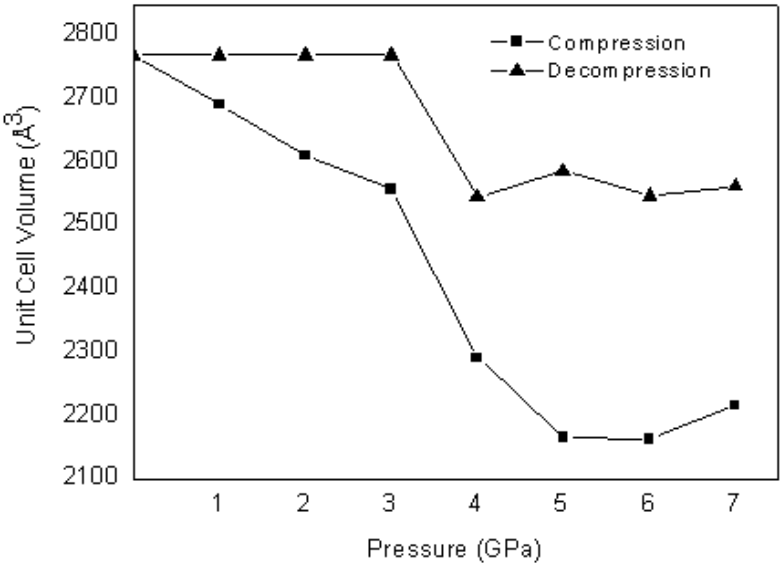


Fig. 1. Dependence of the simulated $AlPO_4$-5's unit cell volume on the external pressure under abrupt compression and decompression conditions. The unit cell volume at ambient pressure is 2770 Å.

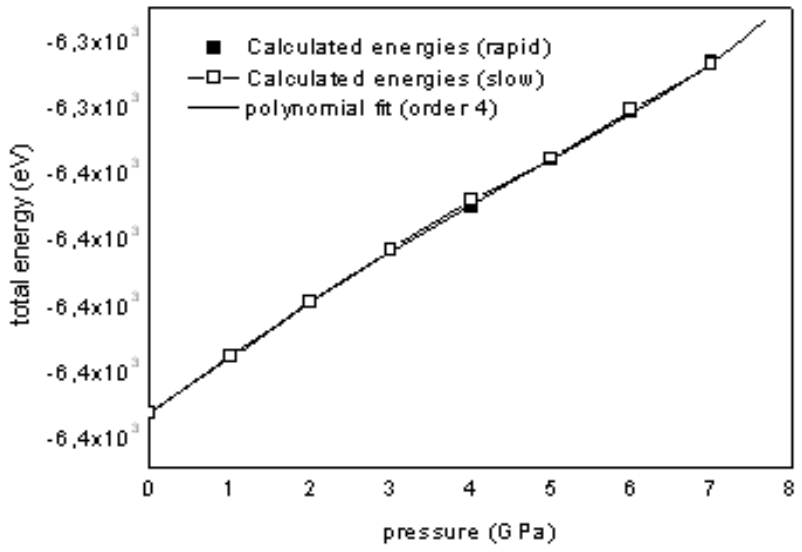


Fig. 2. Total energy vs. pressure

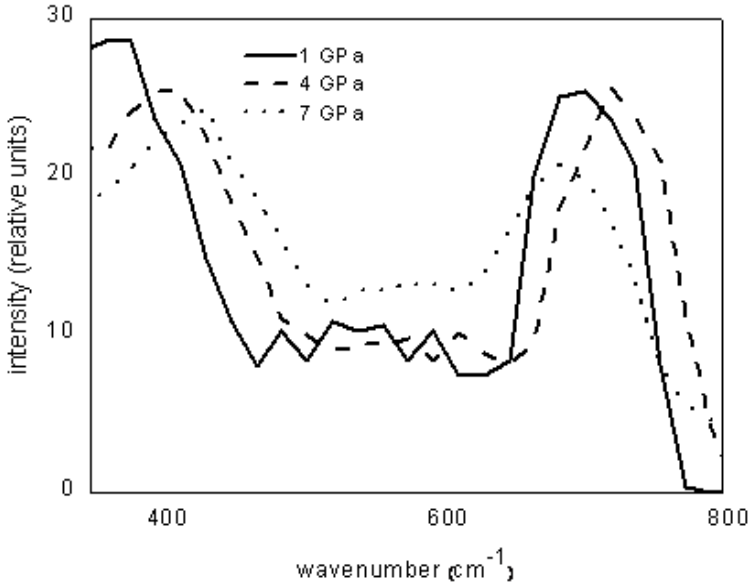


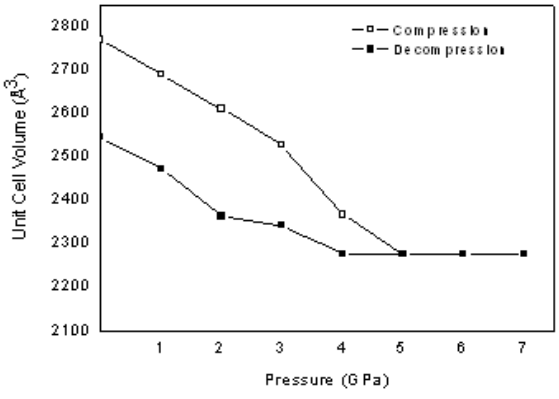
Fig. 3. IR- spectra of $AlPO_4$-5 under compression at three selected pressures.

Table 2. Unit cell parameters of $AlPO_4$-5 upon decompression (up to P_{ext}= 10^{-4} GPa) at different external pressures.

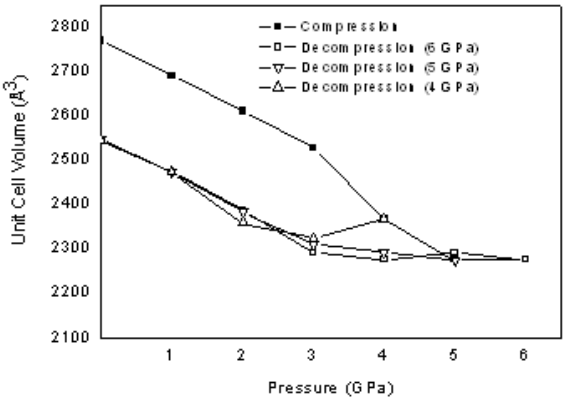
P_{ext}	a/ Å	b/ Å	c/ Å	α/°	β/°	γ/°	gnorm
1.0	13.7569	23.9093	8.4212	90.00	90.00	90.00	6 10^{-4}
2.0	13.7583	23.9077	8.4214	90.00	90.00	90.00	3 10^{-5}
3.0	13.7562	23.9116	8.4212	90.00	90.00	90.00	2 10^{-3}
4.0	13.2360	23.1039	8.3294	90.00	90.00	90.00	5 10^{-5}
5.0	14.0799	22.0710	8.3276	89.85	89.84	88.99	4 10^{-2} (**)
6.0	13.2390	23.1063	8.3298	89.97	89.98	89.95	5 10^{-4}
7.0	13.2447	23.3462	8.2907	90.04	90.10	90.40	4 10^{-2} (*)

In our second experiment, a similar behavior of the unit cell volume vs. external pressure (at the highest pressure, 7 GPa) was obtained (Fig. 4 a). However, now the decrease of the unit cell volume at 4 GPa is lesser than in the first case. When the decompression was from 7 GPa, 6 GPa, 5 GPa, and 4 GPa, a very similar final crystalline state was obtained and, a hysteresis curve is observed (figures 4a and 4b). Therefore, the complete recovering of the $AlPO_4$-5 structure was not reached.

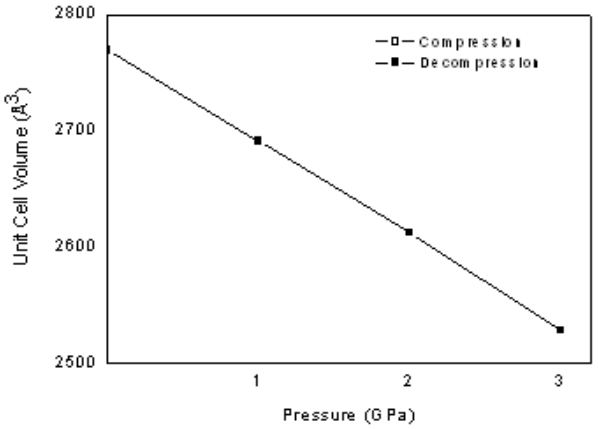
On the contrast, at ≤ 3 GPa the hysteresis disappeared and the recovering of the initial crystalline was reached.



a)



b)



c)

Fig. 4. Simulated dependence of unit cell volume of the $AlPO_4$-5 on the external pressure upon slow compression and decompression conditions (the pressure step of 1 GPa). The maximum pressure reached is:

a) 7 GPa

b) 6, 5 and 4 GPa

c) 3 GPa

CONCLUSIONS

The main result of this paper is to find evidences about the existence of a phase transition in the $AlPO_4$-5 structure at pressures close to 3.5 GPa. Depending on the final compression pressure and the pressure-step in the decompression process, the recovering of the initial geometry can be reached. In this sense, we found that when the compression is up to 3 GPa, the $AlPO_4$-5 structure remains essentially intact. At $\geq$ 4 GPa an abrupt decrease of the unit cell volume and significant variations in the bands of infrared spectra were obtained. Considering the previous studies in aluminosilicates, we conclude that a phase transition to a low-order crystalline state occurs. In contrast with the results reported in LTA system, in $AlPO_4$-5 the final crystalline state is not amorphous. This fact favored the recovering of the initial geometry when the external

pressure is retired. The computational experiment performed shows the possibility to use the memory effects in different applications of the aluminophosphates.

ACKNOWLEDGMENT

This research is supported by University of Informatics Sciences (UCI), La Habana, Cuba and the Alexander von Humboldt Foundation (Germany).

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