Journal of Non-Crystalline Solids 463 (2017) 64–67

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

High-density amorphous phase of CdO

Murat Durandurdu

Department of Materials Science & Nanotechnology Engineering, Abdullah Gül University, Kayseri 38080, Turkey

ARTICLE INFO

Article history:
Received 11 January 2017
Received in revised form 23 February 2017
Accepted 1 March 2017
Available online 6 March 2017

Keywords:
Amorphous-to-amorphous
CdO
Pressure

ABSTRACT

An amorphous CdO model is densified up to a theoretical pressure of 200 GPa. A continues phase transformation from a low-density amorphous (LDA) phase to a high-density amorphous (HDA) phase is observed through the simulation. Associated with the phase transformation, the average coordination raises progressively from ~5.5 to ~7.0. The sevenfold coordination is the most abundant motifs in the HDA state. Therefore its short-range order differs principally from that of the known CdO crystals. Upon pressure release, an amorphous state being intermediate between the LDA structure and the HDA phase is recovered with a mean coordination number of 5.9.

1. Introduction

High-pressure research is one of important fields in Materials Science, Condensed Matter Physics and Geological Science. Materials undergo structural phase transformations to densely packed states at significantly high pressure [1–7]. Accompanied by phase transformations, their physical, chemical, mechanical and electronic properties can be altered [1–7].

During compression, structurally ordered materials exhibit crystal-to-crystal phase modifications [1–7] or crystal-to-amorphous phase transformations so called pressure-induced amorphization [8–11]. Indeed pressure-induced phase changes in most crystalline materials under hydrostatic condition and at room temperature have been well established. Nonetheless new transformation mechanisms and hence novel high-pressure phases could be uncovered at different temperature and pressure environments [12–15]. For the case of amorphous systems, the situation is little complex because they are thermodynamically metastable. In amorphous materials, amorphous-to-crystal [16–20] or amorphous-to-amorphous phase transitions [20–28] have been shown to occur with increasing pressure. Later ones are one of current interests of the high pressure community and are commonly observed in open structured amorphous systems (mostly tetrahedrally coordinated) [21–28]. Yet recent experimental investigations have exposed that such a phase transformation can occur in more closed packed materials as well, for example, metallic glasses [29–30]. The characteristic of amorphous-to-amorphous phase transformations in the tetrahedral materials and metallic glasses appears to be complicated and different [31–32].

At ambient condition, CdO has the NaCl-type crystal and it transforms to a CsCl-type structure at around 90 GPa [33] with the application of pressure. Consequently its structure and high-pressure behavior are substantially different from the other II–VI semiconductors although its electronic structure is someway analogous to that of the semiconductors [34].

In the present work, we explore, for the first time, the high-pressure behavior of amorphous CdO (*a*-CdO), an intermediate material between open structured tetrahedral amorphous networks and more closed packed metallic glasses. Studying *a*-CdO can be beneficial to understand not only the high-pressure behavior of other octahedrally coordinated amorphous systems but also a phase transformation from a sixfold coordinated high density amorphous (HDA) phase to a very high density amorphous (VHDA) proposed for some materials as well [35]. Our simulation reveals that *a*-CdO continuously transforms from a low density amorphous (LDA) phase to a HDA phase between 15 and 70 GPa but the local structure of HDA phase is different than that of the high-pressure phase of CdO crystal because the average coordination number of the HDA state is roughly 7.

2. Method

We performed *ab initio* simulations using the density functional theory (DFT) code SIESTA [36]. We used the pseudopotentials constructed using Troullier and Martins scheme [37], the GGA of Perdew, Burke, and Ernzerhof [38] and the double-ξ plus polarized orbitals. All calculations were done at Γ point. The amorphous model was created by using the melt and quench method and the NPT ensemble and consisted of 216 atoms with periodic boundary conditions (see Ref. [39] for more information). In the present work, however, all simulations were performed within the NPH ensemble that was effectively employed to explore pressure induced phase transformations in various amorphous and

---

E-mail address: murat.durandurdu@agu.edu.tr.

http://dx.doi.org/10.1016/j.jnoncrysol.2017.03.003
0022-3093/

crystalline systems including CdO crystal [40]. In this ensemble both the atomic positions and the simulation cell shape and size were optimized such that the maximum force was smaller than 0.01 eV/Å^3. We used the Parrinello and Rahman approach [41] to control pressure and increased it progressively with an increment of 5, 10 and 20 GPa.

3. Results

The amorphous model was gradually compressed to 200 GPa because in our preceding work on the CdO crystal using the same simulation technique, a phase alteration from the NaCl type crystal to a CsCl type crystal was observed at 150–175 GPa (see Ref. [40] for more information). Fig. 1 exhibits the pressure-volume relation of the crystal and amorphous phases on compression and of the amorphous state on decompression from 200 GPa. As perceived from the figure, the volume of *a*-CdO changes smoothly except a small fluctuation between 10 and 15 GPa. This fluctuation might be coupled with the finite size of the system or might exemplify a first order-like phase transformation at this pressure. Upon pressure release from 200 GPa, the model did not return its initial volume (density), demonstrating the occurrence of a pressure-induced densification in *a*-CdO.

We next probe the partial pair distribution functions (PPDFs) provided in Fig. 2 to have comprehensive information about the local structural changes induced by pressure. Several important conclusions can be straightforwardly inferred from the PPDFs analysis. *i*) The system remains amorphous at the highest pressure researched. This means that *a*-CdO undergoes an amorphous-to-amorphous phase transformation. The ball and stick representation of the model produced by the VESTA program [42] at preferred pressures is shown in Fig. 3. *ii*) The system preserves chemical order during the entire pressure treatment. *iii*) The average Cd—O bond length has a trend to decrease with increasing pressure as shown in Fig. 4 in spite of an increase in the coordination number. This is indeed different than our expectation because to accommodate extra O or Cd atoms into the first coordination shell, the Cd—O distances are anticipated to elongate.

Fig. 5 shows the average coordination number and the coordination distribution of Cd and O atoms as a function of pressure. The coordination number is estimated using the first minimum of the Cd—O correlation function. The mean coordination number rises severely from ~5.5 to ~7.0 between 15 GPa and 70 GPa. Beyond 70 GPa, the amendment in the average coordination number is not substantial, implying that the amorphous-to-amorphous phase transformation happens between 15 and 70 GPa in CdO. As understood from the coordination distribution, the model consists of different coordination environments at each applied pressure. At ambient condition, the fivefold and sixfold coordinated configurations (~47%) are the most privilege motifs. As the external pressure is increased, the fraction of the fivefold coordination gradually decreases and vanishes at 70 GPa. On the other hand, the proportion of the sixfold coordination initially grows and reaches a maximum value of about 65% at 25 GPa for O atoms and 45 GPa for Cd atoms. After these pressures, their fraction decreases noticeably and becomes roughly 25% beyond 70 GPa. The amount of the sevenfold-coordinated configurations significantly increases between 15 GPa and 70 GPa and more than half of the atoms are sevenfold coordinated at 70 GPa. The eightfold coordination becomes visible above 60 GPa with a fraction of ~20%.

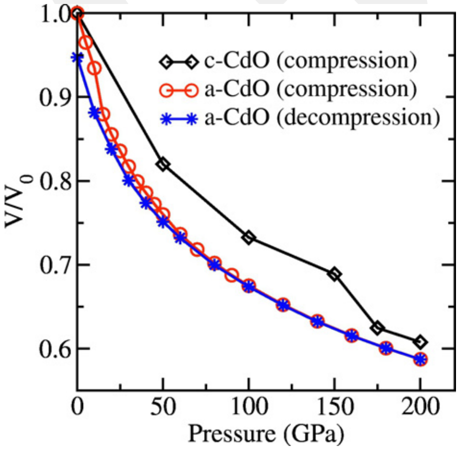

Fig. 1. Pressure-volume relation of the NaCl type CdO (c-CdO) on compression and of *a*-CdO on compression and decompression. A phase transformation from the NaCl type crystal to a CsCl type crystal occurred at 150–175 GPa in our MD simulation Ref. [40].

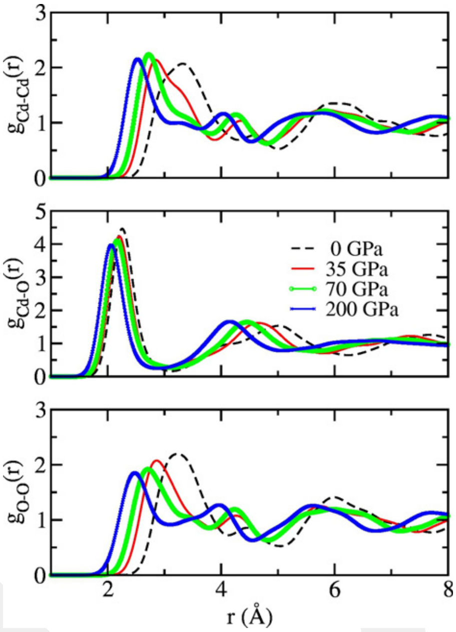

Fig. 2. Partial pair distribution functions (PPDFs) during the compression.

During the pressure release, a dramatic decline in the average coordination number takes place below 30 GPa but the initial coordination number is not recovered. The decompressed model involves fivefold (24%), sixfold (61%) and sevenfold (16%) coordinated configurations and it appears that these distributions are considerably different than those (47%, 47% and 2%) of the uncompressed model. Note the persistence of nonnegligible amount of the high-pressure sevenfold coordination in the decompressed network. On the basis of these observations, we propose that decompressed model is an intermediate state between the LDA and HDA states and the LDA-HDA phase change is irreversible.

We also consider the influence of pressure on the electronic properties of *a*-CdO. The computed electron density of states of *a*-CdO at certain pressures and the NaCl- and CsCl-type crystals at zero pressure is given in Fig. 6. For the fully relaxed *a*-CdO model using the NPH ensemble, the HOMO-LUMO band gap is predicted to be about 1.35 eV at ambient pressure. As seen from Fig. 6, the band gap of *a*-CdO fluctuates up to 70 GPa at which point it begins to decrease but the metallization does not occur at the highest pressure achieved in the present study. From a linear fit of the band gap above 70 GPa, the metallization is roughly estimated to happen at a theoretical pressure of 370 GPa if and only if the pressure-induced structural changes proceed in this manner. This prediction is somehow similar to what has been proposed for the crystalline CdO. Namely the pressure-induced metallization is expected to occur much beyond the NaCl-to-CsCl transition pressure according to the full potential linear muffin-tin orbital (FP-LMTO) method [43]. The band gap of the decompressed amorphous system is ~1.36 eV.

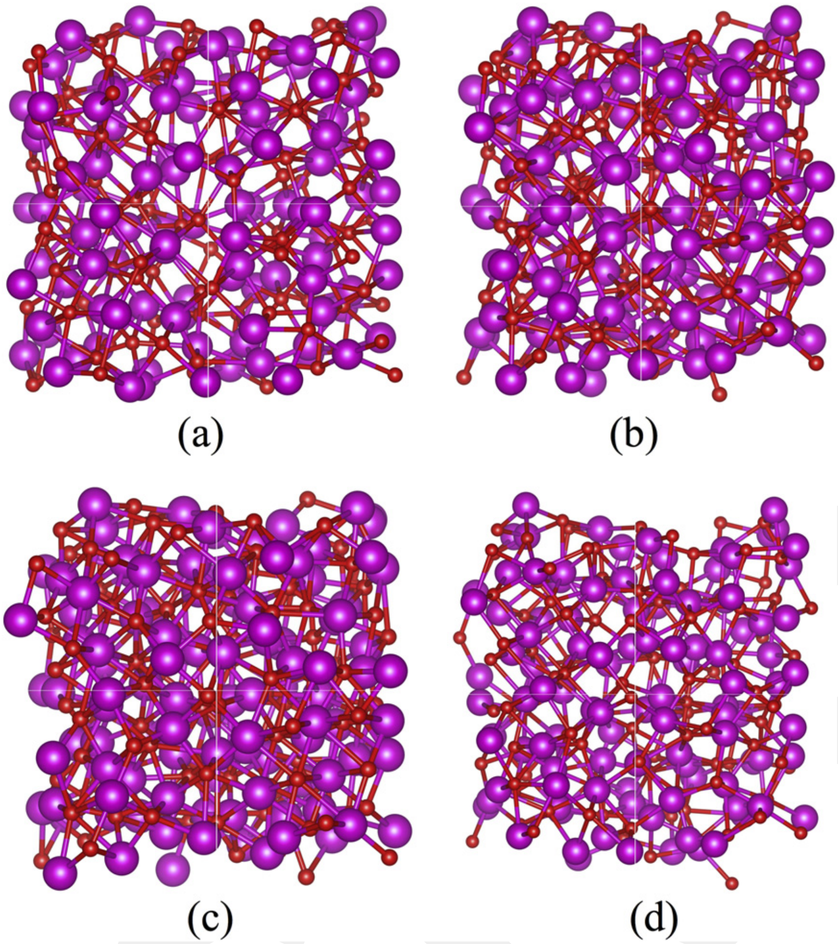

Fig. 3. Ball and stick representation of *a*-CdO at (a) zero GPa (b) 70 GPa on compression (c) 200 (GPa) on compression and (d) zero GPa on decompression. Cd and O atoms are represented by large and small spheres, respectively.

4. Discussion

It is clear from Fig. 1 that *a*-CdO is more compressible than the RS crystal. Such an observation is indeed anticipated because the *a*-CdO model has structural defects i.e., angular distortions, coordination defects and bond-length disorder, in a contrast to the crystal, which lead to a more compressible behavior in *a*-CdO. Yet one unexpected result

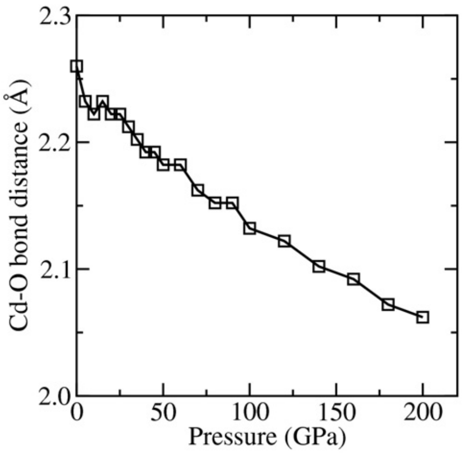

Fig. 4. Variation of Cd—O bond distance under pressure.

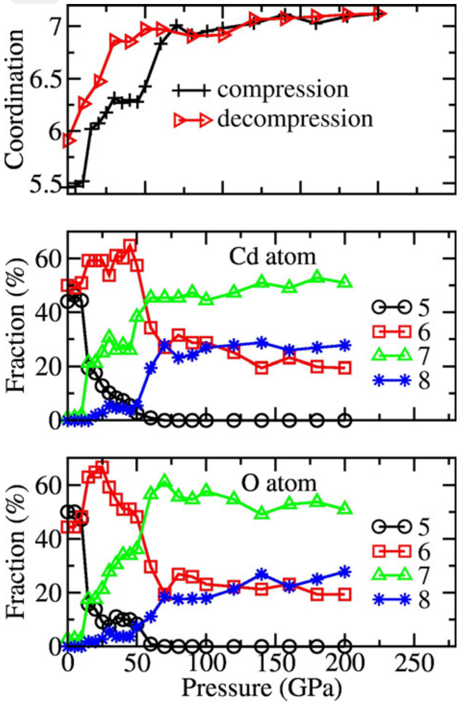

Fig. 5. Modification of mean coordination number and coordination distribution of Cd and O atoms as a function of pressure.

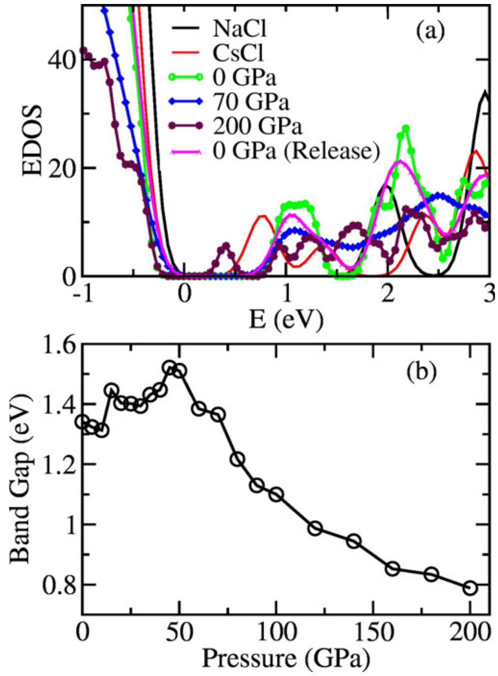

Fig. 6. (a) Electron density of states of *a*-CdO at some pressures and the NaCl- and CsCl-type crystals at zero pressure. (b) Variation of band gap energy of *a*-CdO under pressure.

is that although *a*-CdO transforms to a denser state than the CsCl state beyond 160 GPa, its average coordination does not reach eight.

The present work proposes the existence of a pressure induced amorphous-to-amorphous phase change in CdO. This phase transformation is inferred as a gradual phase transformation since the coordination modification occurs over a wide pressure range. On the basis of the modification in the coordination number, one can see that the phase transformation starts at 15 GPa and completes at 70 GPa in the simulations since there is apparently no substantial variation in the coordination number above 70 GPa. In experiments, however, the starting and completion pressures are expected to be lower than these values because they are generally overestimated due to the various limitations (the size effect, time scale, surface effects etc.) in the dynamical simulations.

Perhaps the most interesting observation is the formation of the dominated sevenfold coordinated clusters in the HDA phase and the persistence of some of them upon pressure release. Such sevenfold-coordinated motifs do not form in the crystal at high pressures. Consequently the HDA phase is proposed to be locally different from the known CdO crystals.

Generally the average coordination number of the HDA phase of tetrahedrally coordinated materials nearly parallels to that of their high-pressure crystalline polymorph. However this is not the case for CdO. At higher pressures, a transformation into an eightfold coordinated amorphous state or into a CsCl type phase is likely to occur in CdO.

5. Conclusions

Pressure-induced densification of an *a*-CdO model is investigated using an *ab initio* technique. An irreversible phase change to a HDA structure is predicted through the simulation. During the phase change, the mean coordination increases from ~5.5 to ~7.0. The HDA phase consists of differently coordinated configurations and the sevenfold coordination is the most privilege ones. Consequently the local structural arrangement in the HDA phase differs from that of the known CdO crystals.

Acknowledgements

The author acknowledges a financial supported from the Abdullah Gül University Support Foundation. The simulations were run on the TÜBİTAK ULAKBİM, High Performance and Grid Computing Center (TRUBA resources).

References

[1] G.J. Ackland, Rep. Prog. Phys. 64 (2001) 483.
[2] U. Schwarz, Z. Krist. 219 (2004) 376.
[3] F.J. Manjón, D. Errandonea, Phys. Status Solidi Basic Res. 246 (2009) 9.
[4] O. Degtyareva, High Pressure Res. 30 (2010) 343.
[5] S.B. Zhang, M.L. Cohen, Phys. Rev. B 35 (1987) 7604.
[6] G.J. Ackland, I.R. Macleod, New J. Phys. 6 (2004) 1.
[7] P. Bhardwaj, S. Singh, Cent. Eur. J. Chem. 10 (2012) 1391.
[8] A.K. Arora, Solid State Commun. 115 (2000) 665.
[9] E.G. Ponyatovskii, O.I. Barkalov, Mater. Sci. Forum 88 (1992) 431.
[10] P. Richet, P. Gillet, Eur. J. Mineral. 9 (1997) 907.
[11] D.N. Sanz, P. Loubeyre, M. Mezouar, Phys. Rev. Lett. 89 (2002) 245501.
[12] P.F. McMillan, Nat. Mater. 1 (2002) 19.
[13] P. McMillan, High Pressure Res. 23 (2003) 7.
[14] L.S. Dubrovinsky, et al., Phys. Earth Planet. Inter. 143 (2004) 231.
[15] J.H. Kim, T. Fukuda, T. Kakeshita, Scr. Mater. 54 (2006) 585.
[16] T. Yoshino, K. Maruyama, H. Kagi, M. Nara, J.C. Kim, Cryst. Growth Des. 12 (2012) 3357.
[17] F. Ye, K. Lu, Phys. Rev. B 60 (1999) 7018.
[18] K. Yang, et al., J. Phys. Condens. Matter 19 (2007) 425220.
[19] E.N. Rissi, E. Soignard, K.A. McKiernan, C.J. Benmore, J.L. Yarger, Solid State Commun. 152 (2012) 390.
[20] M. Popescu, F. Sava, A. Velea, A. Lorinczi, J. Non-Cryst. Solids 355 (2009) 1820.
[21] F. Coppari, et al., Phys. Rev. B 80 (2009) 115213.
[22] S.K. Deb, M. Wilding, M. Somayazulu, P.F. McMillan, Nature 414 (2001) 528.
[23] D. Lacks, Phys. Rev. Lett. 84 (2000) 4629.
[24] V.P. Prakapenka, G. Shen, L.S. Dubrovinsky, M.L. Rivers, S.R. Sutton, J. Phys. Chem. Solids 65 (2004) 1537.
[25] L. Properzi, A. Di Cicco, L. Nataf, F. Baudelet, T. Irifune, Sci. Rep. 5 (2015), 10188. .
[26] M. Wu, Y. Liang, J. Jiang, J. Tse, Sci. Rep. 5 (2012), 15343. .
[27] C. Yildirim, et al., Sci. Rep. 6 (2016), 27317. .
[28] T. Loerting, et al., J. Non-Cryst. Solids 407 (2015) 423.
[29] H.W. Sheng, et al., Nat. Mater. 6 (2007) 192.
[30] L. Belhadi, et al., Appl. Phys. Lett. 103 (2013) 111905.
[31] Q.S. Zeng, et al., J. Phys. Condens. Matter 22 (2010) 375404.
[32] Q.S. Zeng, et al., Phys. Rev. Lett. 104 (2010) 10.
[33] H. Liu, H.K. Mao, M. Somayazulu, Y. Ding, Y. Meng, D. Häusermann, Phys. Rev. B 70 (2004) 094114.
[34] L.F.J. Piper, et al., Phys. Rev. B 77 (2008) 125204.
[35] J.L. Finney, D.T. Bowron, A.K. Soper, T. Loerting, E. Mayer, A. Hallbrucker, Phys. Rev. Lett. 89 (2002) 205503.
[36] J.M. Soler, et al., J. Phys. Condens. Matter 14 (2002) 2745.
[37] N. Troullier, J.L. Martins, Phys. Rev. B 43 (1991) 8861.
[38] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[39] M. Durandurdu, J. Non-Cryst. Solids 412 (2016) 18.
[40] M. Durandurdu, Europhys. Lett. 84 (2008) 66003.
[41] M. Parrinello, A. Rahman, J. Appl. Phys. 52 (1981) 7182.
[42] K. Momma, F. Izumi, J. Appl. Crystallogr. 44 (2011) 1272.
[43] J. Jesse Pius, C. Nirmala Louis, A. Amalraj, Orbital: Electron. J. Chem. 8 (2016) 325.