

Density functional theoretical study of lattice-specific heat and thermal properties of magnesium nitride

Venu Mankad · Sanjeev K. Gupta ·
Himadri R. Soni · Prafulla K. Jha

29th STAC-ICC Conference Special Chapter
© Akadémiai Kiadó, Budapest, Hungary 2011

Abstract A comprehensive first principle study of thermodynamic properties of MgN is reported within the density functional theory scheme. The ground state properties such as lattice constant, Bulk modulus etc. of MgN in rock-salt (RS) phase have been determined. The thermodynamical properties have been analyzed in the light of phonon density of states of MgN and its constituent atoms. The variation of lattice-specific heat with temperature obeys the classical Dulong–Petit’s law at high temperature while at low temperature it obeys Debye T^3 law. The phonon spectrum shows the presence of all positive phonons and zero phonon density of states at zero energy confirming a dynamically stabilized structure of MgN in RS phase.

Keywords Thermodynamical properties · Magnesium nitride · Phonon density of states · Density functional theory

Introduction

The early transition metal mononitrides are well known for their outstanding physical properties including hardness, mechanical strength, high melting points, and electrical conductivity. Because of these interesting features, they have wide applications in optical coatings, wear-resistance coating, etc. Recently, these materials are also being investigated to understand their potential application in thermoelectric [1, 2]. Nitrides are identified as primary

advanced nuclear fuels because of their high density, high breeding ratio, high thermal conductivity, and their compatibility with sodium coolant [3–6]. Nitrides are becoming interesting class of ceramic fuel because of their use in the development of fast nuclear reactors. In addition, the nitrides are known to possess the good reprocessing behavior i.e., easy to dissolve in nitric acid [5–8]. Thus, the characterization of thermophysical properties play a key role in assessing performance and safety purpose related to their usefulness in the nuclear fuel system. Recent study of Basim et al. [9] and Ciriello et al. [10] provided new experimental data concerning thermophysical properties of zirconium nitride. Nitrides can be used as homogeneous diluents for plutonium (Pu) [11] because of its chemical and thermodynamic compatibility with the actinide and also with the liquid metal coolant. Furthermore, the nitrides are expanding to thermoelectric; we present a comparative theoretical study of various thermal properties. Many mononitrides like HfN and ZrN are the proposed nitride metal/semiconductor superlattices which can act as phonon filters for reducing lattice thermal conductivity [12]. MgN is among the mononitrides having strong application in the spintronics [13]. Since thermodynamic functions of a solid are determined mostly by the vibrational degrees of freedom of the lattice. Also, the electronic degrees of freedom play a noticeable role for only metals at low temperature; the knowledge of entire of BZ is required to understand the thermal properties like specific heat, entropy, Helmholtz energy, etc.

This article presents a comprehensive study on the thermodynamical properties using lattice dynamical calculation. The thermodynamical properties including phonon contribution to the Helmholtz free energy ΔF , the phonon contribution to the internal energy ΔE , the entropy S , and the constant-volume-specific heat C_v are calculated

V. Mankad · S. K. Gupta · H. R. Soni · P. K. Jha (✉)
Department of Physics, Bhavnagar University,
Bhavnagar 364022, India
e-mail: pkj@bhavuni.edu; prafullaj@yahoo.com

within the harmonic approximation. These properties are obtained using the plane-wave pseudopotential approach within the framework of density functional perturbation theory (DFPT) [14, 15]. The density functional calculations have considerably expanded our ability to predict the stability, thermodynamical properties, and thermal decomposition process in many complex systems due to the enormous improvement in computational power [16, 17]. The remainder of this article is organized as follows: in “Computational details” section, we briefly give the first principle computational method and structural optimization. In the following section, we present and discuss the thermodynamical properties of MgN. The conclusions are given in the final section.

Computational details

Our calculations are based on the implementation of plane wave density functional theory (DFT) in the Kohn–Sham framework using ABINIT simulation package.¹ The wave functions describe only the valence and the conduction electrons, while the core electrons are taken into account for pseudopotentials. For the exchange–correlation functional, we have employed the generalized gradient approximation (GGA) functional developed by Perdew, Burke, and Ernzerhof (PBE) [18] since, it is known that GGA gives better results than the simpler local density approximation (LDA) when describing the structural properties of transition metal compounds [19]. The electron–ion interactions are described through the use of Troullier and Martins type pseudopotentials [20]. A set of convergence tests have been performed to choose correctly the mesh of k -points and the cut-off kinetic energy (e_{cut}) of plane waves to start the ground state and linear response calculations. The kinetic energy cut-off for the plane wave basis is set to 59 Ha for the rock-salt (RS) phase of MgN. The Brillouin zone is sampled by $6 \times 6 \times 6$ Monkhorst–Pack mesh of k points [21]. As aim in this study is to calculate the constant-volume-specific heat, the entropy, the phonon contribution to internal energy, and Helmholtz free energy as a function of temperature, these properties have been calculated using phonon spectrum obtained from DFPT. The phonon band structure and phonon density of states first have been obtained through out Brillouin zone. The phonon density of states is an important dynamical property as its computation needs frequencies in the entire Brillouin zone and can be defined as [22–25]

$$g(\omega) = \frac{1}{N} \int_{\text{BZ}} \sum_j \delta[\omega - \omega_j(\vec{q})] d\vec{q}, \quad (1)$$

where N is a normalization constant that $\int g(\omega) d\omega = 1$. $g(\omega) d\omega$ is the ratio of the number of Eigen states in the frequency interval $(\omega, \omega + d\omega)$ to the total number of Eigen states, $\omega_j(q)$ is the phonon modes. Using phonon density of states obtained using Eq. 1, the phonon contribution to Helmholtz free energy ΔF , the phonon contribution to the internal energy ΔE , as well as the constant-volume-specific heat C_v , and the entropy S , at temperature T can be calculated from the following expressions within the harmonic approximation [25]

$$\Delta F = 3nNk_{\beta}T \int_0^{\omega_{\max}} \ln \left\{ 2 \sinh \frac{\hbar\omega}{2k_{\beta}T} \right\} g(\omega) d\omega \quad (2)$$

$$\Delta E = 3nN \frac{\hbar}{2} \int_0^{\omega_{\max}} \omega \coth \left(\frac{\hbar\omega}{2k_{\beta}T} \right) g(\omega) d\omega \quad (3)$$

$$S = 3nNk_{\beta}T \int_0^{\omega_{\max}} \left[\frac{\hbar\omega}{2k_{\beta}T} \coth \frac{\hbar\omega}{2k_{\beta}T} - \ln \left\{ 2 \sinh \frac{\hbar\omega}{2k_{\beta}T} \right\} \right] g(\omega) d\omega \quad (4)$$

$$C_v = 3nNk_{\beta} \int_0^{\omega_{\max}} \left(\frac{\hbar\omega}{2k_{\beta}T} \right)^2 \csc^2 \left(\frac{\hbar\omega}{2k_{\beta}T} \right) g(\omega) d\omega \quad (5)$$

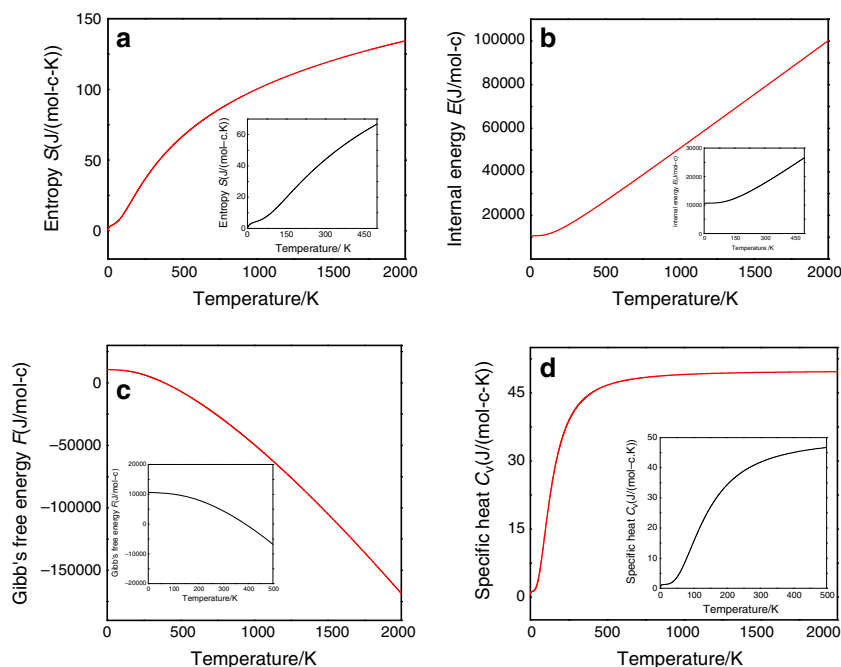
Results and discussion

As a first step, we have performed the structural optimization of MgN in RS phase. The structural optimization has been performed under the minimum condition of the total energy and the force acting on atoms. As a result we obtained the equilibrium values of the lattice constant and cell volume. The equilibrium lattice constant, $a_0 = 8.37$ Bohr, bulk modulus, $B = 114.263$ GPa, and cell volume $V = 146.646$ Bohr³, are in good agreement with available theoretical data [13]. The bulk modulus has been computed minimizing the crystal total energy for different values of lattice constant by means of Birch–Murarghan equation of state [26].

Figure 1 presents the variation of thermal properties such as Helmholtz free energy (ΔF), entropy (S), the constant-volume lattice-specific heat (C_v), and internal energy (ΔE) with temperature obtained using the Eqs. 1–5. The figure depicts that while the entropy (Fig. 1a) and internal energy (Fig. 1b) increases with temperature, Helmholtz energy (Fig. 1c) decreases with temperature. The constant-volume lattice-specific heat C_v , presented in Fig. 1d increases and temperature dependent until 500 K

¹ The Abinit code is a common project of the University Catholique de Louvain, Coming Incorporated, and other contributions <http://www.abinit.org>.

Fig. 1 Calculated Helmholtz free energy, internal energy, entropy and lattice-specific heat at constant volume as a function of temperature



and then it gets saturated at around 50 J/mol-c-k ($6 NK$ where N is Avogadro number and K is the Boltzmann's constant) the classical value as per Dulong–Petit's law. This is due to the anharmonic approximation of the Debye model. However, at higher temperatures the anharmonic effect on C_v is suppressed. The inset in all figures shows the behavior at very low temperatures. The low temperature behavior of lattice-specific heat at constant volume satisfies a T^3 law in the temperature limit and is in accordance with Debye specific heat law at low temperature. This can be attributed to the good structural optimization and stable acoustic phonon modes. The entropy varies linearly until 2000 K. The increase, however, is faster at lower temperatures. To see the dynamical stability of optimized

structure, we present phonon density of states in Fig. 2. It is clear from this figure that the whole phonon spectrum is positive and it is divided in two regions optical and acoustical with a clear gap of about 64.2 cm^{-1} . The lower frequency region which is due to acoustic phonons arises from Mg-atom vibrations. Further, the zero temperature values of internal and free energies do not vanish due to zero point motion [25] and can be calculated from the asymptotic expressions of Eqs. 2 and 3

$$\Delta F_0 = \Delta E_0 = 3nN \int_0^{wL} \frac{\hbar\omega}{2} g(\omega) d\omega. \quad (6)$$

The value of ΔF_0 is $49.55 \text{ (J/(mol-c-K))}$. The higher frequency distribution observed in the phonon spectra is responsible for the low internal energy at low temperature as the atoms have low thermal energy and hence they vibrate less. But at the higher temperature the case is reverse.

Conclusions

In summary, we have investigated the thermodynamical properties as a function of temperature for the RS MgN using the phonon spectrum obtained from the DFPT calculation. Within the harmonic approximation, Helmholtz free energy, entropy, and specific heat and internal energy have been calculated and analyzed with the help of frequencies and their distribution in phonon spectrum. The whole phonon spectrum is positive which reflects the dynamical stability and good optimization of the geometry

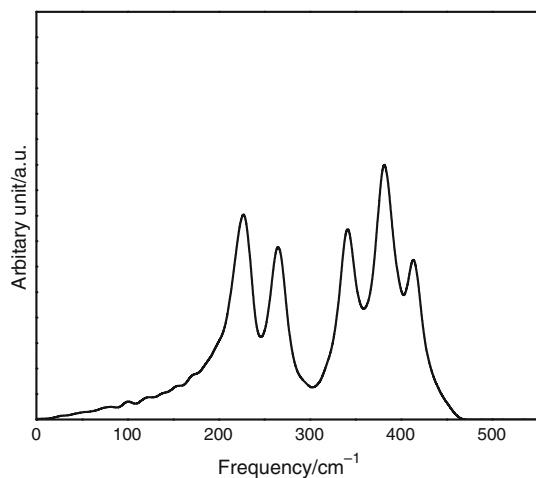


Fig. 2 The phonon density of states for MgN in RS phase

of the structure. The internal energy and entropy increases with temperature while Helmholtz free energy decreases. The lattice-specific heat obeys the T^3 law of Debye theory of specific heat at lower temperatures. At higher temperatures due to the suppression of anharmonic effect the C_v approaches to the saturation value of 50 J/(mol-c-k).

Acknowledgements The authors are thankful to University Grants Commission, New Delhi and Department of Science and Technology (DST) Govt. of India for the financial assistance.

References

1. Zebajadi M, Bian Z, Singh R, Shakourie A, Wortman R, Rawat V, Sands T. Thermoelectric transport in a ZrN/ScN super lattice. *J Electron Mater.* 2009;38:960–3.
2. Rawat V, Koh Y, Cahill D, Sands T. Thermal conductivity of (Zr, W)N/ScN metal/semiconductor multilayers and superlattices. *J Appl Phys.* 2009;105:0249091–6.
3. IAEA-TECDOC-1374, Development status of metallic, dispersion and non-oxide advanced and alternative fuels for power and research reactors. IAEA, 2003.
4. Rogozkin BD, Stepennova NM, Proshkin AA. Mononitride fuel for fast reactors. *Atomic Energy.* 2003;95(3):624–36.
5. Burghartz M, Ledergerber G, Hein H, van der Laan RR, Konings RJM. Some aspects of the use of ZrN as an inert matrix for actinide fuels. *J Nucl Mater.* 2001;288:233–6.
6. Rogozkin BD, Stepennova NM, Bergman GA, Proshkin AA. Thermochemical stability, radiation testing, fabrication, and reprocessing of mononitride fuel. *Atomic Energy.* 2003;95(6):835–44.
7. Blank H. Non-oxide ceramic nuclear fuels. In: Frost BRT, editor. *Materials science and technology*, vol 10A. Weinheim: Wiley; 2005. p. 191–363.
8. Ogawa T, Crawford D, Konings RJM, Pillon S, Schram RPC, Verwerft M, Wallenius J. In: *Proceedings of the GLOBAL 2005*, No. 316, Tsukuba, Japan, October 2005, p. 9–13.
9. Basini V, Ottaviani JP, Richaud JC, Streit M, Ingold F. Experimental assessment of thermophysical properties of (Pu, Zr)N. *J Nucl Mater.* 2005;344:186–90.
10. Ciriello A, Rodinella VV, Staicu D, Somers J. Thermophysical characterization of nitrides inert matrices: preliminary results on zirconium nitride. *J Nucl Mater.* 2007;371:129–33.
11. Kleykamp H. Selection of materials as diluents for burning of plutonium fuels in nuclear reactors. *J Nucl Mater.* 1999;275:1–11.
12. Saha B, Acharya J, Sands T, Waghmare U. Electronic structure, phonons, and thermal properties of ScN, ZrN, and HfN: a first-principles study. *J Appl Phys.* 2010;107:033715 1–9.
13. Droghetti A, Baadji N, Sanvito S. MgN: a possible material for spintronic applications. *Phys Rev B.* 2009;80:235310 4–6.
14. Gonze X, Lee C. Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory. *Phys Rev B.* 1997;55:10355–68.
15. Baroni S, de Gironcoli S, dal Corso A, Giannozzi P. Phonons and related crystal properties from density-functional perturbation theory. *Rev Mod Phys.* 2001;73:515–62.
16. Koleżyński A, Malecki A. First principles studies of thermal decomposition of anhydrous zinc oxalate. *J Therm Anal Calorim.* 2009;96(2):645–51.
17. Koleżyński A, Malecki A. Theoretical approach to thermal decomposition process of chosen anhydrous oxalates. *J Therm Anal Calorim.* 2009;97(1):77–83.
18. Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Phys Rev Lett.* 1996;77:3865–8.
19. Raybaud P, Kresse G, Hafner J, Toulhoat H. Ab initio density functional studies of transition-metal sulphides: I. crystal structure and cohesive properties. *J Phys Condens Matter.* 1997;9:11085–106.
20. Troullier N, Martin JL. Efficient pseudopotentials for plane-wave calculations. *Phys Rev B.* 1991;43:1993–2006.
21. Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. *Phys Rev B.* 1976;13:5188–92.
22. Jha PK. Phonon spectra and vibrational mode instability of MgCNi₃. *Phys Rev B.* 2005;72:214502.
23. Jha PK, Sanyal SP. A lattice dynamical study of the role of pressure on Raman modes in high- T_c HgBa₂CuO₄. *Phys C.* 1996;261:259–62.
24. Jha PK, Sanyal SP. Phonon spectrum, lattice specific heat of the HgBa₂CuO₄ high-temperature superconductor. *Phys C.* 1996;271:6.
25. Lee C, Gonze X. Ab initio calculation of the thermodynamic properties and atomic temperature factors of SiO₂ α -quartz and stishovite. *Phys Rev B.* 1995;51:8610–3.
26. Murnaghan FD. The compressibility of media under extreme pressures. *Proc Natl Acad Sci.* 1944;30(9):244–7.