Journal of Materials Science and Engineering B 1 (2011) 365-371
Formerly part of Journal of Materials Science and Engineering, ISSN 1934-8959

Simulation on Thermal Conductivity of MgO and PbTe by Molecular Dynamics Method

Hassakorn Wattanasarn[1], Tosawat Seetawan[1], Nuansiri Chansrinuang[1], Chanchana Thanachayanont[2] and Prasarn Chainaronk[3]

1. Thermoelectrics Research Center and Program of Physics, Faculty of Science and Technology, Sakon Nakhon Rajabhat University, 680 Nittayo Rd., Sakon Nakhon 47000, Thailand

2. National Metal and Materials Technology Center, National Science and Technology Development Agency, 114 Thailand Science Park, Phahonyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand

3. Program of Physics, Faculty of Science, Ubonratchathani Rajabhat University, 2 Ratchathani Rd., Ubon Ratchathani 34000, Thailand

Received: February 24, 2011 / Accepted: March 23, 2011 / Published: August 25, 2011.

Abstract: Thermal properties of materials were obtained by molecular dynamics (MD) simulation method. The thermal properties were consisting of linear thermal expansion coefficient, heat capacity and thermal conductivity. In this study, we investigated the thermal conductivity in the temperature range of 300-2,000 K for MgO and 300-800 K for PbTe at below melting points at which the temperatures and pressures were controlled. The interatomic interaction used the Lenard-Jone potential into pair ions. The atom velocities were calculated by Verlet algorithm. The potential parameters were added for Bushing-Ida function for the investigation of two body potential. The systems of 4 × 4 × 4 cells on 512 ions (256 cations and 256 anions) were performed for MgO and PbTe. We obtained the simulated values of the linear thermal expansion coefficient which have not been experimentally measured, where the thermal conductivity of MgO and PbTe have been evaluated on only phonon contribution together with literature data.

Key words: Thermal conductivity, MgO, PbTe, molecular dynamics.

1. Introduction

The thermal conductivity is very important for material application at a high temperature. However, it is difficult to measure. In this study, molecular dynamics simulation method [1] is proposed to be an appropriate method for thermal property study, particularly for the thermal conductivity. Magnesium oxide (MgO) is mantle earth and NaCl structure type, the researchers are interested and had many investigated methods to physical properties at high temperature and high pressure, particularly the thermal conductivity is decreased from 30 $Wm^{-1}K^{-1}$ at room temperature to 8 $Wm^{-1}K^{-1}$ at high temperature [2]. The MgO has thermal and electrical insulating properties with its cubic structure. Interatomic interaction at high temperature with add-on particle position and phonon vibration using MD has been demonstrated [3, 4]. Lead tellulide (PbTe) is a thermoelectric material with a maximum dimensionless figure of merit (ZT) in temperature range of 600-700 K [5] and a low thermal conductivity [6]. In this study, the interested difference of thermal conductivity of MgO and PbTe at varies temperature. The thermal conductivity and electrical conductivity were calculated using Wiedemann-Frantz law. The thermal conductivity reduction decreased the mean free path of phonon following the lattice thermal conductivity (κ_{lat}) given by,

$$\kappa_{lat} = C_P \nu l / 3$$

where C_V is the specific heat capacity, ν is the average

Corresponding author: Tosawat Seetawan, assistant professor, research field: physics. E-mail: t_seetawan@snru.ac.th.

phonon velocity, l means free path of phonon [7, 8]. The thermal conductivity is effected by free electron and lattice vibration. In this study, we investigated the thermal conductivity from phonon contribution affected by the number of particles, pressure, and temperature at a constant volume of MgO and PbTe by MD simulation.

2. MD Processes

In the MD simulation, the partial ionic model with Lenard-Jone potential into pair ions is used. The simulation was carried out by MXDORTO program [9]. The Verlet's algorithm integrated the atom motion and velocity integration on time per step 2×10^{-15} s. was used. The EMD simulation used a controlled temperature range of 300-2,000 K and controlled pressure at 0.1 MPa, 0.75 and 1.5 GPa. The desirable temperature and pressure made at 10,000 steps at equilibrium for lattice parameter into linear thermal expansion coefficient study. The interatomic interaction of many atoms has expressed the potential summation with ij being ion pairs and ijk being ion i, j and k, respectively.

$$U(r) = \sum_{ij} U_{ij}(r) + \sum_{ijk} U_{ijk}(r) + \sum_{ijkl} U_{ijkl}(r) + \ldots (1)$$

In this study, the potential parameters were determined by the lattice parameters fit to the experimental data of materials. The parameters add-on Bushing-Ida function [10] was used for the investigation of the interaction of 2 body potential.

$$U_{ij}(r_{ij}) = \frac{z_i z_j e^2}{r_{ij}} + f_0(b_i + b_j)\exp\left(\frac{a_i + a_j - r_{ij}}{b_i + b_j}\right) - \frac{c_i c_j}{r_{ij}^6} + D_{ij}\left\{exp\left[-2\beta_{ij}\left(r_{ij} - r_{ij}^*\right)\right] - 2\,exp\left[-\beta_{ij}\left(r_{ij} - r_{ij}^*\right)\right]\right\} \quad (2)$$

where z_i and z_j are the effective partial electronic charges on the i and j ion, e is the electric charge, r_{ij} is the atom distance, r_{ij}^* is the bond length of anion-cation pairs in vacuum, $f_0 = 4.186$; D_{ij} and b_{ij} are the depth and shape of this potential. In this function, the first term is coulomb interaction, the second term is the short range repulsive potential, a_i and a_j are the radii, b_i and b_j are hardness, c_i and c_i are Van Der Waals constant of ions i and j respectively. The third term is represented by the Van Der Waals interaction which arises from dipole and the last term is the Morse type potential [11]. The potential parameter of Mg^{2+}, O^{2-} and Pb^{4+}, Te^{2-} in this study are shown in Table 1. Since the lattice constant of MgO is about 4.207 Å [12] and the lattice constant of PbTe is about 6.462 Å [13]with cubic structure, the unit cell was arranged at $4 \times 4 \times 4$, composed of 512 ions (216 cations and 216 anions) and controlled at constant pressure at 0.1 MPa with varying temperature. From this MD simulation, the lattice parameter of MgO about 4.212 Å and PbTe about 6.455 Å at 300 K were obtained as shown in Fig. 1 and Fig. 2 together with Ref. [13-15]. The lattice parameter increases with increasing temperature according to Vegard's law, because the lattice parameter of PbTe is larger than the lattice parameter of MgO. The lattice parameter slightly increases with an increase in temperature and the lattice parameter increases with increasing pressure from 0.001, 0.75 to 1.5 GPa. The potential parameter with add-on potential function indicates that the lattice parameter increases with an increase in temperature.

3. Results and Discussion

3.1 Linear Thermal Expansion Coefficient

The variation of lattice parameter with temperature was calculated for the linear thermal expansion

Table 1 The potential parameters table for MD simulation in this study.

Ions	z	a	b	c	pairs	D_{ij}	β_{ij}	r_{ij}
O	−1.2	1.813	0.142	21.00	O-Mg	10.0	1.76	1.938
Mg	1.5	1.320	0.142	0.00				
Te	−1.2	2.038	0.080	0.00	Te-Pb	13.0	1.56	2.339
Pb	2.4	1.728	0.080	0.00				

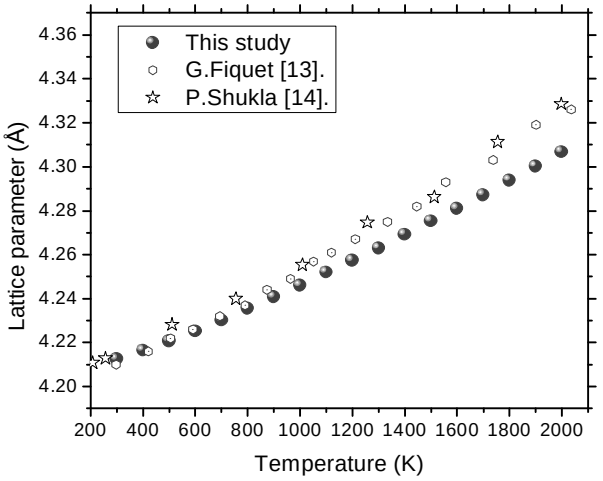

Fig. 1 Lattice parameter of MgO at temperature range of 300-2,000 K together with values from Ref. [13, 14].

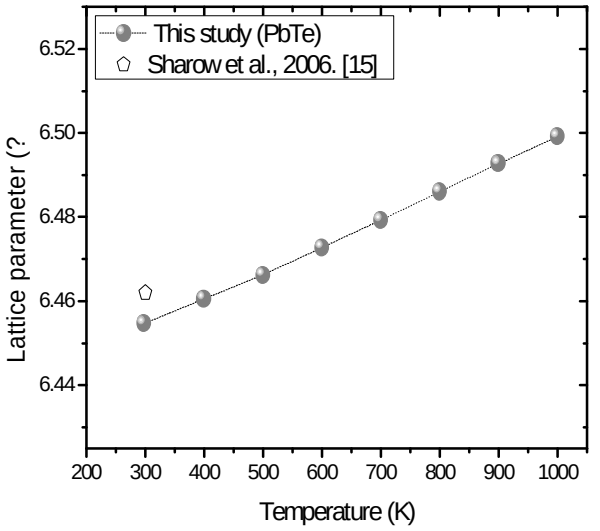

Fig. 2 Lattice parameter of PbTe at temperature range 300-1,000 K together with Ref. values [15].

coefficient (a_{lin}) due to the heat initiated by the lattice expansion that effects an interatomic distance average with temperature, following a_{lin} equation which is relative to lattice parameter values.

$$a(T) = a_0 \left[1 + a_{lin}(T)T \right] \quad (3)$$

$$a_{lin} = \frac{1}{a(T_0)} \left(\frac{\partial a(T)}{\partial T} \right)_P \quad (4)$$

a(T) is the lattice parameter at temperature *T*(K), *a(P)* is lattice parameter at pressure *P*(Pa), T_0 is room temperature. The MD result showed that the linear thermal expansion coefficient increased with increasing temperature. The MD simulation results are shown in Fig. 3 and Fig. 4. The a_{lin} of MgO increases with increasing temperature from 8.5×10^{-6} K^{-1} to 12.07×10^{-6} K^{-1} at 400-1,500 K and the a_{lin} values of PbTe increases with increasing temperature from 10.74×10^{-6} K^{-1} to 11.24×10^{-6} K^{-1} at 400-800 K. The a_{lin} of PbTe is different from the a_{lin} of MgO due to the lattice parameter of PbTe is much more than MgO.

3.2 Heat Capacity

The interatomic interaction of 2-body potential initiated the internal energy *E(T)* at temperature *T* which can determine heat capacity at a constant volume (C_V) with temperature following

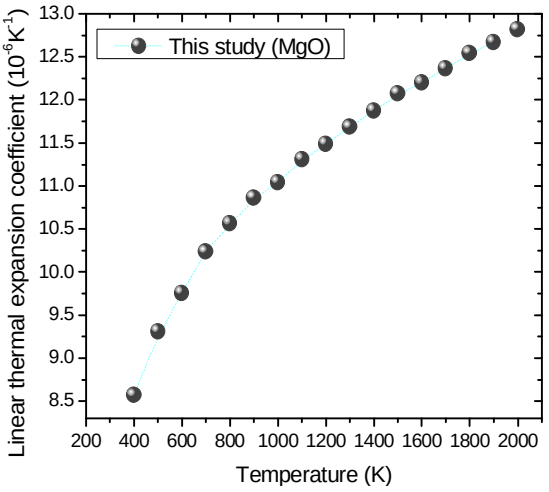

Fig. 3 Linear thermal expansion coefficient via temperature range of 300-2,000 K of MgO.

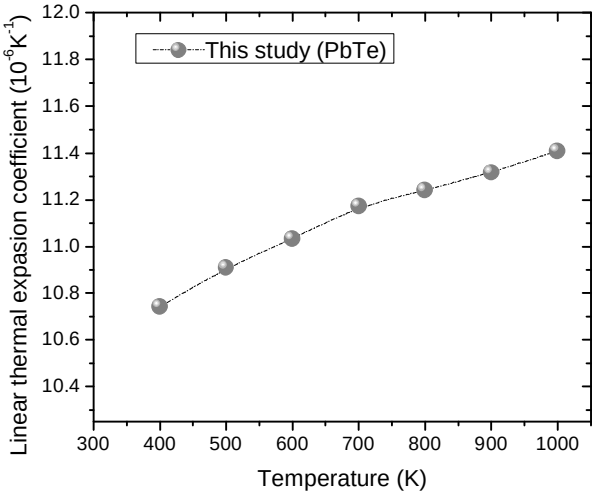

Fig. 4 Linear thermal expansion coefficient via temperature range of 400-800 K of PbTe.

$$C_V = \left(\frac{\partial E(T)}{\partial T} \right)_V \quad (5)$$

The lattice vibrates due to heat transfer. The average interatomic distance average raises. The heatcapacity of lattice dilation (C_d) follows

$$C_d = \frac{\left(3a_{lin}\right)^2 VT}{\beta} \quad (6)$$

Where β is compressibility, V is molar volume, and heat capacity at constant pressure (C_P) which is estimated by

$$C_P = C_V + C_d + C_{el} \quad (7)$$

where C_{el} is the heat capacity of the electronic conduction term which is neglected since some value in C_{el} term could not be calculated in this study. Then we calculated C_V and C_d using the MD simulation. The C_P values of MgO increase with the temperature increasing until about 800 K, which is in agreement with literature data [16-18] as shown in Fig. 5. The calculation of PbTe was shown in Fig. 6 with Ref. [19]. The C_P increases with increasing temperature below literature data at low temperature and according at high temperature because C_P had been related between C_V and C_d. Therefore, the C_P of PbTe had tendency in agreement with literature at high temperatures.

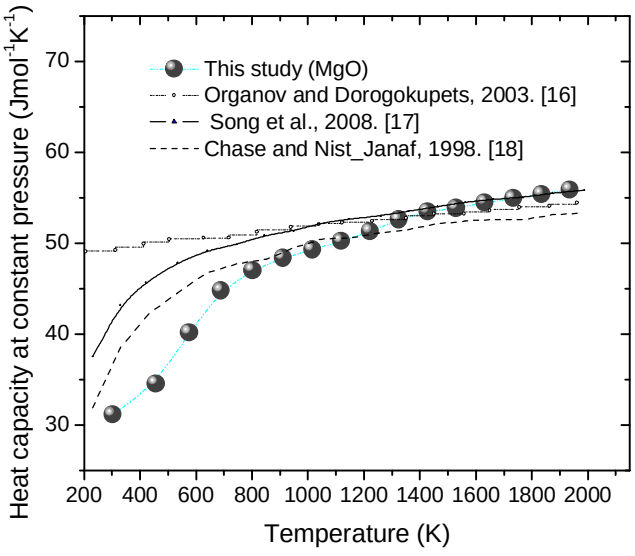

Fig. 5 Heat capacity at constant pressure of MgO via temperature range of 300-2,000 K with Ref. [16-18].

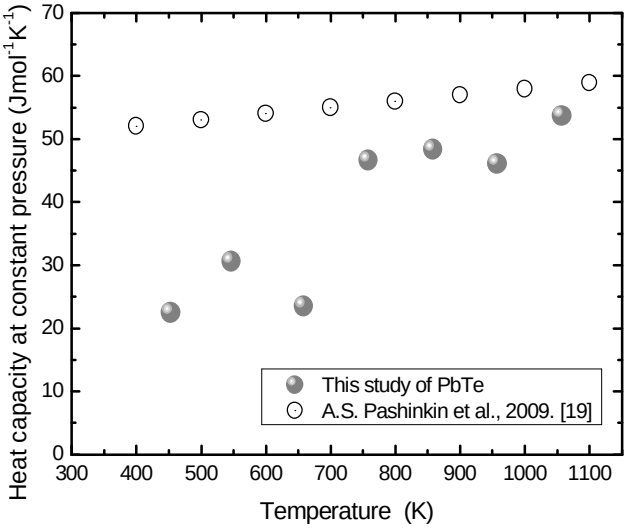

Fig. 6 Heat capacity at constant pressure of PbTe via temperature range of 300-800 K with Ref. [19].

3.3 Thermal Conductivity

The thermal conductivity was investigated from MD simulation which could be calculated by the autocorrelation function of energy current and expressed with statistical mechanics by Green-Kubo relation for thermal conductivity [20] following

$$k_l = \frac{V}{3k_B T^2} \int_0^\infty \langle S(t) \cdot S(0) \rangle \, dt \quad (8)$$

where k_l is the thermal conductivity of lattice contribution, $S(t)$ is the energy current for MD simulation, k_B is Boltzmann constant, V is volume, T is absolute temperature, the energy current used the following equations,

$$S(t) = \frac{1}{V}\left[\sum_j E_j v_j + \frac{1}{2} \sum_j \sum_{i \neq j} r_{ij} \left(f_{ij} . v_j \right) \right] \quad (9)$$

$$E_j = \left\{ \frac{1}{2} m_j v_j^2 + \frac{1}{2} \sum_{i \neq j} U_{ij}\left(r_{ij}\right) \right\} - E_{av} \quad (10)$$

where E_K is instantaneous excess energy of ion j, m_j, v_j are mass and velocity of ion j, f_{ij}, r_{ij}, $U(r_{ij})$ are force, interatomic distance, potential energy between i , j ions and E_{av} is the energy average of system. The autocorrelation function of energy current was calculated with 1×10^5 steps [21]. They have been

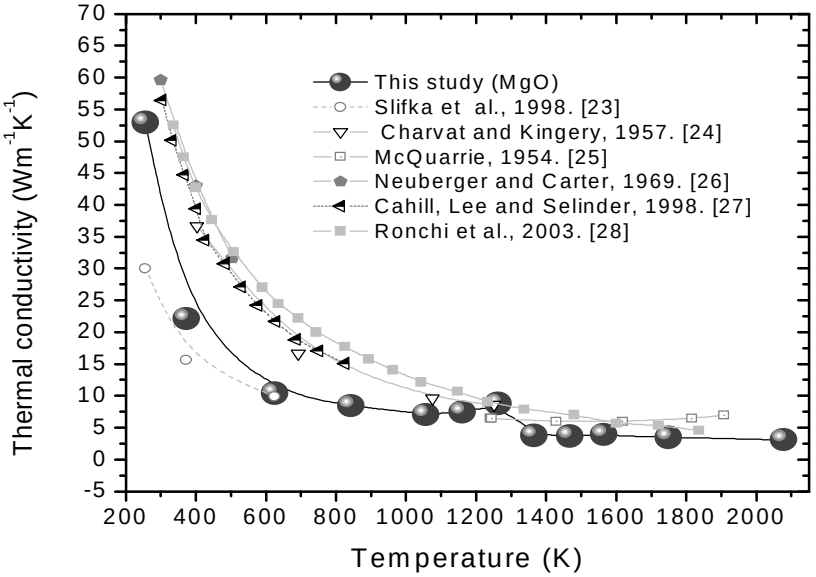

Fig. 7 Thermal conductivity of MgO via temperature range of 300-2,000 K together with Ref. [23-28].

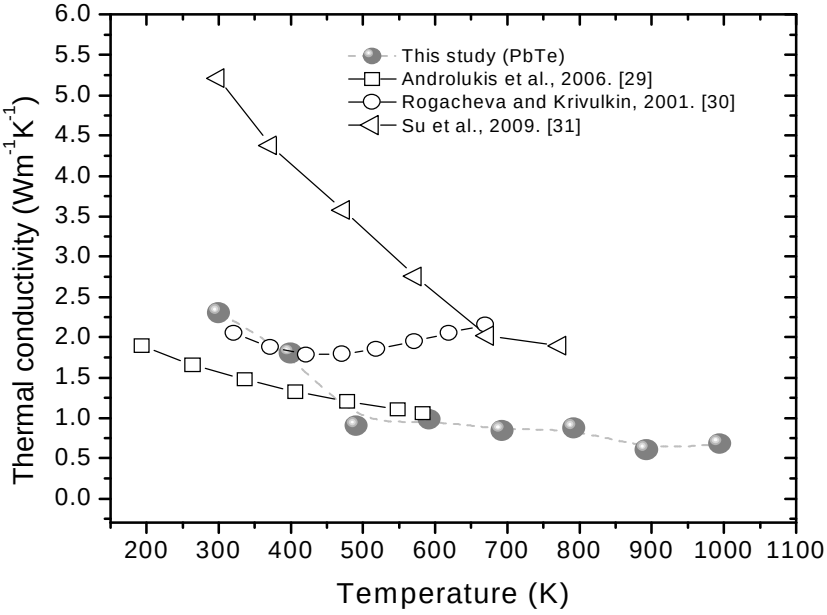

Fig. 8 Thermal conductivity of PbTe in temperature range of 300-800 K together with Ref. [29-31].

calculated from the relaxation time of the energy and current between $S(t)$ and $S(0)$ would approach amean value of thermal conductivity at temperature of MD simulation [22]. In this study, the thermal conductivity by MD simulation is obtained from lattice vibration and electron conduction. The thermal conductivity of MgO is shown in Fig. 7. The thermal conductivity is about 53 $Wm^{-1}K^{-1}$ at 270 K and decreases with increasing temperature in agreement with literature data above 500 K. The thermal conductivity of PbTe decreased from 2.3 $Wm^{-1}K^{-1}$ at 300 K to 0.87 $Wm^{-1}K^{-1}$ at 800 K, as shown in Fig. 8, with differential literature data at low temperature, in addition to the k_l values of PbTe decreases with increasing temperature. It is very interesting for thermoelectric material application. The thermal conductivity at high temperature would decrease, because electron mobility was obstructed from phonon-phonon interaction. Deflect of atoms affects the thermal conductivity and electron conductivity,

hence, they had low values at high temperature. Therefore, MD simulation can be used to calculate the thermal conductivity of MgO and PbTe at room temperature to high temperatures.

4. Conclusions

The simulated thermal properties of MgO and PbTe composing of lattice parameter and linear thermal expansion coefficient and heat capacity have been found to increase with increasing temperature and the thermal conductivity of MgO and PbTe decrease with increasing temperature in agreement with literature. Therefore, MD simulation can be used to evaluate the thermal properties of materials from low to high temperature.

Acknowledgments

The author would like to thanks Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan for usage of the MXDORTO program. Financial support was provided by the Research and Development Institute, Sakon Nakhon Rajabhat University.

References

[1] T. Seetawan, G. Wong-Ud-Dee, C. Thanachayanont, A. Vittaya, Molecular dynamics simulation of strontium titanate, Chin. Phys. Lett. 27 (2010) 0260501.

[2] J.A. Slifka, D.K. Filla, J.M. Phelps, Thermal conductivity of magnesium oxide from absolute, steady-state measurements, J. Res. Natl. Inst. Stand. Technol. 103 (1998) 357.

[3] X. Sun, Q. Chen, Y. Chu, C. Wang, Properties of MgO at high pressure: shell-model molecular dynamics simulation, Physica B. 370 (2005) 187-188.

[4] B.G. Dick, A.W. Overhauser, Theory of the dielectric constants of alkali halide crystals, Phys. Rev. 112 (1958) 90.

[5] J. Yang, T. Caillat, Thermoelectric materials for space and automotive power generation, MRS Bull. 31 (2006) 224.

[6] Z.H. Dughaish, Lead telluride as a thermoelectric material for thermoelectric power generation, Physica B. 322 (2002) 205.

[7] H. Muta, K. Kurosaki, S. Yamanaka, Thermoelectric properties of reduced and La-doped single-crystalline $SrTiO_3$, J. Alloys Compd. 392 (2005) 306-392.

[8] C. Kittel, Introduction to Solid State Physics, 4th ed., Wiley, London, 1971.

[9] S. Yamasaki, T. Arima, K Idemitsu, Y. Inagaki, Thermophysical properties of rare-earth-stabilized zirconia and zirconate pyrochlores as surrogates for actinide-doped zirconia, Int. J. Thermophys. 28 (2007) 663-665.

[10] Y. Ida, Interionic repulsive force and compressibility of ions, Phys. Earth Planet Inter. 13 (1976) 97.

[11] P.M. Morse, Diatomic molecules according to the wave mechanics: part 2, vibrational levels, Phys. Rev. 34 (1929) 57.

[12] P. Haas, F. Tran, P. Blaha, Calculation of the lattice constant of solids with semilocal functionals, Phys. Rev. B 79 (2009) 085104.

[13] G. Fiquet, P. Richet, G. Montagnac, High-temperature thermal expansion of lime, periclase, corundum and spinel, Phys. Chem. Miner. 27 (1999) 103-177.

[14] P. Shukla, T. Watanabe, J.C. Nino, J.S. Tulenko, S.R. Phillpot, Thermal transport properties of MgO and $Nd_2Zr_2O_7$ pyrochlore by molecular dynamics simulation, J. Nucl. Mater. 380 (2008) 1-7.

[15] M.K. Sharow, O.B. Yatsenko, Y.A. Ugai, Lattice parameter of $PbTe_{1-x}Cl_x$ solid solutions, Inorganic Matter. 43 (2006) 133.

[16] A.R. Organov, P.I. Dorogokupets, All-electron and pseudopotential study of MgO: equation of state, anharmonicity and stability, Phys. Rev. B. 67 (2003) 224110.

[17] T. Song, X.W. Sun, Y.X. Liu, Z.J. Liu, Q.F. Chen, C.W. Wang, Comparative study of the structural and thermodynamic properties of MgO at high pressures and high temperatures, J. Alloys Compds. 461 (2008) 279-284.

[18] M.W. Chase, J.N. Janaf, Thermochemical Tables, J. Chem. Ref. Data Monograph, 9 (1998) (Am. Chem. Soc., Am. Inst. Phys., Natl. Inst. Stand. Technol.).

[19] A.S. Pashinkin, M.S. Mikhailova, A.S. Malkova, V.A. Fedorov, Heat capacity and thermodynamic properties of lead selenide and lead-telluride, Neorganicheskie Materialy 45 (2009) 1226-1229.

[20] R. Zwanzing, Time-correlation functions and transport coefficients in statistical mechanics, Ann. Rev. Phys. Chem. 16 (1965) 67.

[21] K. Kurosaki, K. Yamada, M. Uno, S. Yamanaka, K. Yamamoto, T. Namekawa, Molecular dynamics study of mixed oxide fuel, J. Nuclear Matter. 294 (2001) 160-167.

[22] T. Arima, S. Yamasaki, Y. Inagari, K. Idemitsu, Evaluation of thermal properties of UO_2 and PuO_2 by equilibrium molecular dynamics simulations from 300 to

2000 K, J. Alloys Compds. 400 (2005) 43-50.

[23] A.J. Slifka, B.J. Filla, J.M. Phelps, Thermal conductivity of magnesium oxide from absolute, steady-state measurements, J. Res. Natl. Inst. Stand. Technol. 103 (1998) 357-368.

[24] F.R. Charvat, W.D. Kingery, Thermal conductivity XIII: effect of microstructure on conductivity of single phase ceramics, J. Am. Ceram. Soc. 40 (1957) 306-315.

[25] M. McQuarrie, Thermal conductivity: part 5, high temperature method and results for alumina, magnesia, and beryllia from 1000 to 1800 °C, J. Am. Ceram. Soc. 37 (1954) 84-88.

[26] M. Neuberger, D.B. Carter, Magnesium Oxide, Hughes Aircraft Co., Electronic Properties Information Center, Culver City, CA., 1969.

[27] D.G. Cahill, S.M. Lee, T.I. Selinder, Thermal conductivity of κ-Al_2O_3 and α-Al_2O_3 wear-resistant coatings, J. Apply Phys. 83 (1998) 5783.

[28] C. Ronchi, J.P. Ottaviani, C. Degueldre, R. Calabrese, Thermophysical properties of inert matrix fuels for actinide transmutation, J. Nuclear Matter. 320 (2003) 54.

[29] J. Androlukis, K.F. Hsu, R. Pcionek, H. Kong, C. Uher, J.J. D'Angelo, et al., Nanostructure and high thermoelectric efficiency in p-Type $Ag(Pb_{1-y}Sn_y)_m SbTe_{2+m}$, Adv. Matter. 18 (2006) 1771.

[30] E.I. Rogacheva, I.M. Krivulkin, Isotherms of thermal conductivity in PbTe-MnTe solid solutions, Phys. Solid State 43 (2001) 1033.

[31] T. Su, X. Jia, H. Ma, J. Guo, Y. Jiang, N. Dong, et al., Thermoelectric properties of nonstoichiometric PbTe prepared by HPHT, J. Alloy. Compds. 468 (2009) 410.