Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
an open access publisher
http://ansinet.com

Journal of Applied Sciences 12 (16): 1726-1729, 2012
ISSN 1812-5654 / DOI: 10.3923/jas.2012.1726.1729

Effect of Least Variations in the Lattice Constant in the Lattice Dynamics of Nanostructured CdO

[1]Lakshmi Narasimha Acharya Kandala, [1]John Bosco Balaguru Rayappan, [1]Jeyaprakash Beri Gopalakrishnan, [2]Stalin Mano Gibson Manasai and [3]Lawrence Nallathambi
[1]Center for Nanotechnology and Advanced Biomaterials (CeNTAB),
School of Electrical and Electronics Engineering, SASTRA University, Thanjavur 613 401, India
[2]R.D. Government Arts College, Sivaganga 630 561, India
[3]Department of Physics, St. Joseph's College (Autonomous), Tiruchirapalli 620 002, India

Abstract: Lattice vibrational dynamics of nanostructured CdO lattice with two slightly different lattice constants (4.69 and 4.61 Å) has been investigated using Born von Karman model. CdO materials were prepared as thin film form on glass substrate by spray pyrolysis technique. An aqueous solution of 0.05 M Cadmium acetate is sprayed as fine mist on the preheated glass substrate at two different temperatures to form CdO thin film. The CdO films obtained at 220°C and 260°C have lattice constants of 4.69 and 4.61 Å, respectively. Born von Karman model was employed to obtain the dispersion relations of phonons and frequency density of states of the face centered cubic structured CdO crystals. Born Mayer potential was used to estimate the force constants of inter-atomic interactions between first five neighbors for both the CdO lattices. The dynamical matrix was constructed with the estimated force constants and hence eigen values and vectors were determined for a set of 73 wave vector points obtained from reciprocal lattice. The density of phonon states found to be accumulated in the higher frequency region. The amplitude of lattice vibration that is Debye Waller factor and lattice contribution to the specific heat capacity was estimated for various temperatures. A significant change in phonon dispersion, specific heat capacity and Debye Waller factor values have been observed between the nanostructured CdO crystals of different lattice constants.

Key words: Lattice dynamics, specific heat capacity, phonon dispersion, Debye Waller factor, nanostructured CdO

INTRODUCTION

In the recent past nanostructured metal oxide materials in thin film form have attracted major attention due its wide spread applications in gas sensors, optoelectronic devices, temperature controllers in satellites, etc. (Maity and Chattopadhyay, 2006). Among the different members of the metal oxide family, CdO is having attracted many researchers because of its wide range of applications in the fields of solar cells, smart windows, flat panel display, Phototransistors etc., (Mane *et al.,* 2006). CdO crystallizes in the rock salt structure and it is an n type semiconductor.

In spite of the technological importance of CdO, the vibrational properties of this compound have not been further investigated. Hence lattice dynamics of CdO has been studied by employing Born von Karman formalism (Born and Huang, 1954).

MATERIALS AND METHODS

Cadmium acetate [Cd $(CH_3COO)_2.2H_2O$] precursor of various concentration was sprayed on glass substrate using spray pyrolysis technique. The precursor solution was sprayed on the preheated glass substrate at an optimized deposition conditions. The structural characteristics of the films were studied using X-ray diffractometer (PANalytical Model X'per PRO) with Ni-filtered CuKα radiation (l = 1.5148 Å).

Method of calculation: The nanostructured CdO crystallizes with the FCC structure. In the adiabatic and harmonic approximation, the phonon frequencies of the normal modes of vibration of a cubic crystal are calculated by solving the secular equation:

$$\left|D(q) - \omega^2(q)I\right| = 0 \quad (1)$$

Corresponding Author: John Bosco Balaguru Rayappan, Center for Nanotechnology and Advanced Biomaterials (CeNTAB), School of Electrical and Electronics engineering, SASTRA University, Thanjavur 613 401, India

Table 1: Computed force constant parameters of CdO nanostructured thin films

Position of atoms (Å)	Force constant parameters	Force constant value (dynes cm^{-1}) For lattice constant 4.61 Å	For lattice constant 4.69 Å
$\left(\frac{1}{2}\frac{1}{2}0\right)$	A_1	1.1608	0.9859
	B_1	-0.740	-0.0718
	C_1	1.2348	1.0568
(100)	A_2	0.0226	0.0176
	B_2	0.0363	0.0289
$\left(1\frac{1}{2}\frac{1}{2}\right)$	A_3	0.0015	0.0011
	B_3	-0.00037	-0.00028
	C_3	0.0021	0.0016
	D_3	-0.00018	-0.00014
(110)	A_4	0.00015	0.00011
	B_4	-0.000059	-0.00004
	C_4	0.000021	0.00015
$\left(\frac{3}{2}\frac{1}{2}0\right)$	A_5	0.000011	0.000008
	B_5	-0.000004	-0.000003
	C_5	0.000024	0.000017
	D_5	0.000026	0.000018

where, I is the unit matrix and D is the dynamical matrix which is given by:

$$D\begin{pmatrix} q & \\ k & k' \end{pmatrix} = \frac{1}{\sqrt{m_k m_{k'}}} \sum_{l'} \Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix} \exp(iq.(R(l') - R(l))) \qquad (2)$$

where, q is the wave vector, m_k is the mass of the kth atom in the lth unit cell, $m_{k'}$ is the mass of the k'th atom in the l'th unit cell:

$$\Phi_{\alpha\beta}\begin{pmatrix} l & l' \\ k & k' \end{pmatrix}$$

is the atomic force constant, R(l) and R(l')are the position vectors. The average atomic mass of the alloy A_xB_{1-x} is determined from the relation:

$$M_{A_xB_{1-x}} = xM_A + (1-x)M_B \qquad (3)$$

The dynamical matrix elements were evaluated by employing Born-von Karman formalism extending to fifth neighbor interaction and are given Table 1. These force constants were evaluated using Born Meyer Potential (Born and Mayer, 1932):

$$U_{ij} = A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) \qquad (4)$$

where, r_{ij} is the separation between ions I and j, A_ij = 951.88 eV and ρ_{ij} = 0.34856 Å^{-1}(Chroneos and Busker, 2005) are the potential parameters specific to ions i and j.

With the evaluated force constants the dynamical matrix was constructed and the diagonalization of this matrix was carried out for a set of 73 wave vector points of the FCC lattice. The phonon frequency dispersion is calculated by solving Eq. 1 using the computed force constant parameters given in Table 1.

RESULTS AND DISCUSSION

The phonon frequencies have been calculated by using a set of 73 wave vectors by uniformly dividing the Brillouin zone for nanostructured CdO having a slight difference in lattice constants (4.69 and 4.61 Å). The frequency distribution curves g(x) versus x =ω/ω_{max} are drawn and shown in Fig. 1.

The frequency distribution shows that large number of frequencies is distributed in the high frequency region resulting in the prominent scattering of electrons due to which the conductivity is expected to decrease. The computed force constants for both the lattice constants (4.69 and 4.61 Å) are fed to the dynamical matrix and then to the characteristic equation from which the phonon dispersion relations are obtained. The results thus obtained are plotted in Fig. 2. with the dashed lines indicating the phonon dispersions of lattice constant 4.61 Å and the solid lines for the phonon dispersions of higher lattice constant (4.69 Å) which are in good agreement with the experimental data (Popovic *et al.*, 1991).

The specific heat capacity of the solids for a range of 0 to 1000 K was computed using the Einstein's model (Einstein, 1907), the computed values have been plotted in Fig. 3. Where, the dotted line indicates the specific heat capacity of the solid with lower lattice constant (4.61 Å) and the solid line for the higher lattice constant (4.69 Å). The plot shows that initially all atoms vibrate in their respective phonon modes, while as the temperature reaches 400 K all the atoms in crystals with both the

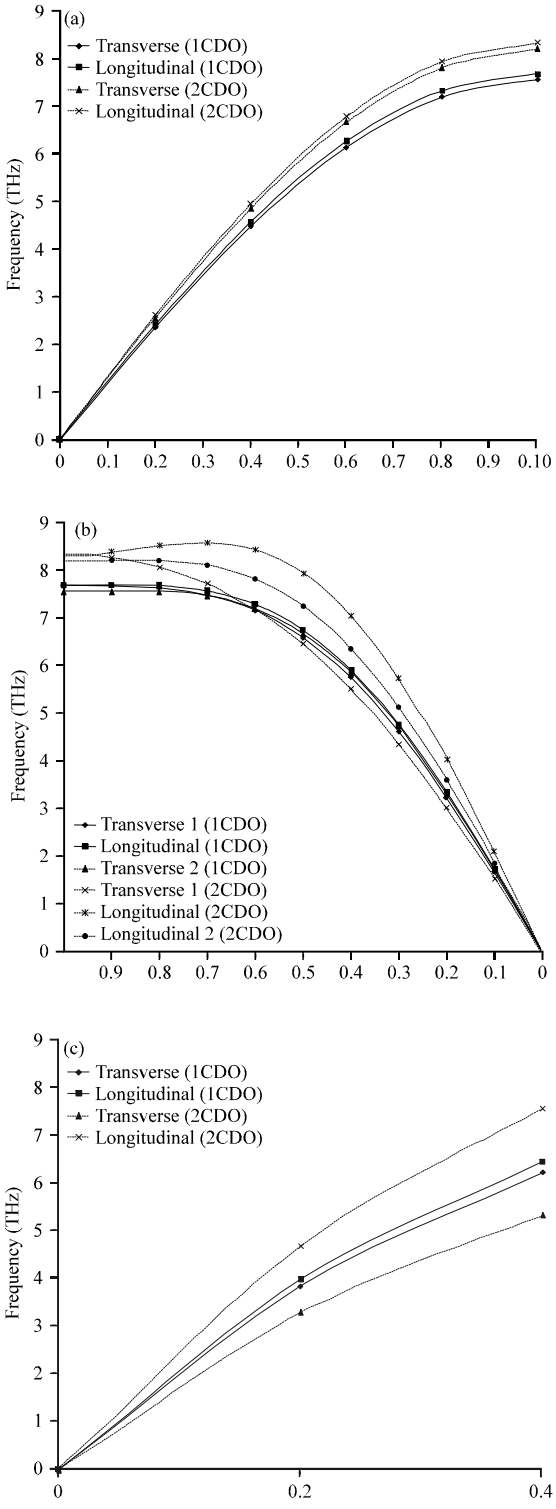

Fig. 1(a-c): Phonon dispersion curve for CdO crystal for lattice constants 4.69 Å and 4.61 Å along; (a) 100, (b) 110 and (c) 111 orientation

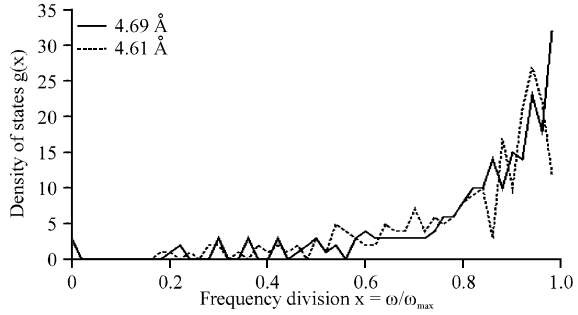

Fig. 2: Phonon frequency distribution curve for CdO crystal for different lattice constants

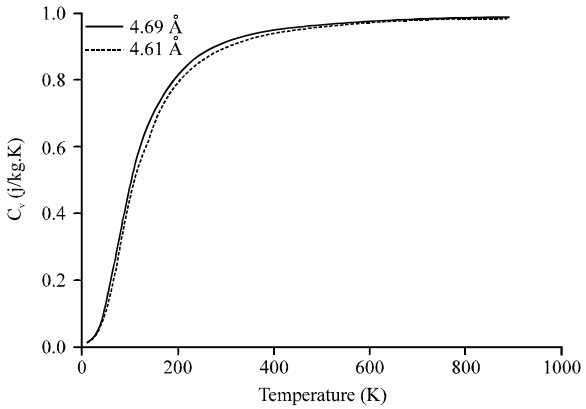

Fig. 3: Specific heat capacity curve for CdO crystal for different lattice constants

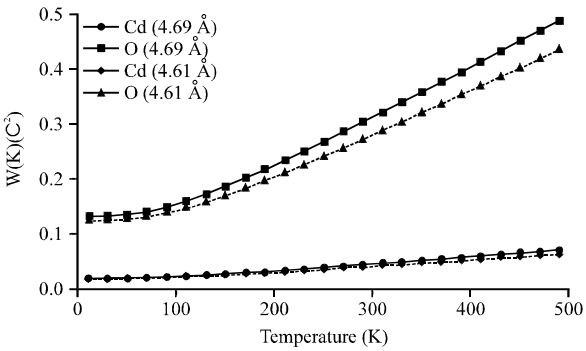

Fig. 4: Debye-Waller factor for Cd and O atoms for different lattice constants

lattice constants (4.69 and 4.61 Å) vibrate in normal modes. The difference so seen at the lower temperatures between the specific heat of both the lattice constants is due to the change in the phonon frequencies.

The Debye-Waller factor has been computed for the Cd and O atoms for both the lattice constants (4.69 and 4.61 Å) have been computed and plotted in Fig. 4.

The values thus obtained reveal that Cd atoms displace less when compared to O atoms which is due to the higher mass of Cd atoms than the mass of O atoms, whilst the atoms of crystal with lattice constant (4.69 Å) displaces more when compared to the atoms of lattice constant (4.61 Å) which happens to be in good agreement with the data obtained by Mariammal *et al*. (2011).

CONCLUSION

Lattice dynamics of nanostructured CdO thin films having slightly different lattice constants have been investigated using Born von Karman formalism. The phonon dispersions of both the films are reported. Based on the computed phonon frequency distribution, thermal properties namely specific heat capacity and Debye Waller factor have been reported. The difference in the lattice constant has influenced the estimated thermal properties. And the same has been highlighted.

REFERENCES

Born, M. and J.E. Mayer, 1932. Lattice theory of ionic crystals. Z. Phys., 75: 1-18.

Born, M. and K. Huang, 1954. Dynamical theory of crystal lattices. Acta Cryst., 9: 837-838.

Chroneos, A. and G. Busker, 2005. Solution mechanisms for LiO_2 in Sc_2O_3, Y_2O_3 and La_2O_3. Acta Chem. Slov., 52: 417-421.

Einstein, A., 1907. Plank's theory of radiation and the theory of specific heat. Ann. Phys. Lpz., 22: 180-190.

Maity, R. and K.K. Chattopadhyay, 2006. Synthesis and characterization of aluminum doped CdO thin films by sol-gel process. Sol. Energy Mat. Sol. Cells, 90: 597-606.

Mane, R., H. Pathan, C. Lokhande and S. Han, 2006. An effective use of nanocrystalline CdO thin films 3 in dye-sensitized solar cells. Sol. Energ., 80: 185-190.

Mariammal, R.N., V.M. Susila and K. Ramachandran, 2011. On the Debye-Waller factor and debye temperature of CdO nanoparticles. Cryst. Res. Rechnol., 46 : 979-985.

Popovic, Z.V., G. Stanisic, D. Stojanovic and R. Kostic, 1991. Infrared and raman spectra of CdO. Phys. Sat. Sol., 165: K109-K112.