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Structural, Elastic and Thermodynamic Properties of Ag-Based Oxides *X*AgO (*X* = Li and Na): An *ab initio* Study

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ABSTRACT

Structural parameters, elastic constants and thermodynamic properties of the tetragonal ternary Ag-based oxides LiAgO and NaAgO are investigated theoretically for the first time using the plane-wave ultra-soft pseudopotential method [1] based on the density functional theory [2,3]. The optimized lattice parameters and atomic positions agree well with the available theoretical and experimental counterparts. Pressure dependence of the structural parameters is also explored. Pressure dependences of the single-crystal elastic constants *Cij* for LiAgO and NaAgO are explored. The elastic wave velocities propagating along the principal crystallographic directions are numerically estimated. The elastic anisotropy is estimated and further illustrated by 3D-direction-dependent of the Young's modulus. A set of some macroscopic elastic moduli, including the bulk, Young's and shear moduli, Poisson's coefficient, average elastic wave velocities and Debye temperature, were calculated for polycrystalline LiAgO and NaAgO from the *Cij* via the Voigt-Reuss-Hill approximations [4–6]. Through the quasiharmonic Debye model [7], which takes into account the phonon effects, the temperature and pressure dependencies of the bulk modulus, unit cell volume, volume thermal expansion coefficient, Debye temperature and volume constant and pressure constant heat capacities of LiAgO and NaAgO are explored systematically in the ranges of 0–20 GPa and 0–1200 K.

COMPUTATIONAL METHODS

The present calculations are carried out through the pseudopotential plane-wave method (PP-PW) as implemented in the CASTEP code [8]. The exchange-correlation interactions is treated by the PBEsol version of the generalized gradient approximation (the so-called GGA-PBEsol) [9]. An ultra-soft Vanderbilt-type pseudopotential is used to model the potential created by the nucleus and frozen electrons which applied to valence electrons. The Li: $1s^2 2s^1$, O: $2s^2 2p^4$, Ag: $4d^{10} 5s^1$ and Na: $2s^2 2p^6 3s^1$ electrons are treated as valence electrons. The plane-wave (PW) basis set, in which the electron wave functions are expanded, are truncated at a maximum plane-wave energy (E_{cut}) of 400 eV. The Brillouin zone is sampled by Monkhorst–Pack special *k*-mesh.

The optimized structural parameters are reached through the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique geometries [10]. The optimization convergence for energy change, maximal force, maximal stress and maximal displacement are fixed at 5×10^{-7} eV/atom, 0.01 eV/Å, 0.02 GPa and 5.0×10^{-4} Å, respectively. Gaussian scheme with a smearing width equal to 0.1 eV is used for the smearing of the electronic occupation. The finite strain-stress method is used to obtain the monocrystalline elastic constants (C_{ij}s) from which the polycrystalline elastic moduli are derived via the Voigt-Reuss-Hill approximation.

RESULTS

STRUCTURAL PROPERTIES

Table 1: Calculated equilibrium lattice parameters (a_0 and c_0, in Å), internal coordinates (y_X, x_{Ag} and x_O), bulk modulus (B_0, in GPa), bulk modulus first pressure derivative (B') and bond lengths (Ag–O and X–O, in Å) for the ternary Ag-base oxides: LiAgO and NaAgO.

Parameter	Materials			
	LiAgO		NaAgO	
	Present	Expt.	Present	Expt.
a	9.176	9.248[c]	9.429	9.522[c]
			9.670[b]	9.520[d,e]
c	3.816	3.75[c]	4.655	4.602[c]
			4.699[b]	4.599[d]
y_X	0.415		0.493	4.617[e]
			0.486[b]	0.483[d]
				0.49[e]
x_{Ag}	0.138		0.161	0.159[e]
	0.162		0.158	0.306[e]
x_O	0.322		0.310	
B_0	71.34		47.18	
			64[b]	
B'	4.79		5.28	
d_0(Ag-O)	2.0936		2.0737	
d_0(X-O)	2.0663		2.3503	

[b] Ref. [11], [c] Ref. [12], [d] Ref. [13], [e] Ref. [14].

ELASTIC PROPERTIES

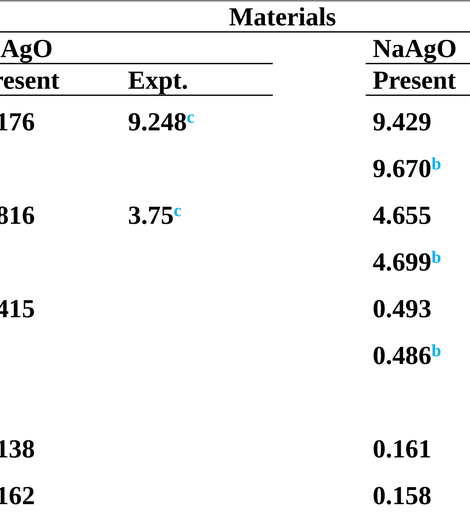

Fig. 1: Calculated pressure dependence of the elastic constants Cij and bulk modulus B for the LiAgO and NaAgO materials. The symbols are the calculated results and the continuous lines are the second-order polynomial fits to the results

Table 2: Calculated elastic constants (C_{ij}, in GPa), Bulk modulus (B, in GPa), shear modulus (G, in GPa), Pugh's indicator (B/G), Young's modulus (E, in GPa), Poisson's ratio (σ), Lamé's. coefficient (λ, in GPa), longitudinal, transverse and average sound velocities (V_l, V_t and Vm, respectively, in m/s), and Debye temperature (θ_D, in K) for the LiAgO and NaAgO materials. B is obtained from the C_{ij}s. The C_{ij}s of the isostructural compounds are given for comparison.

Parameter	Materials			
	LiAgO	LiCuO	NaAgO	NaCuO
C_{11}	116.1	125.5[a]	82.9	86.4[a]
C_{33}	95.976	94.3[a]	76.4	73.8[a]
C_{44}	15.8	25.1[a]	13.6	15.4[a]
C_{66}	60.9	58.7[a]	34.6	34.7[a]
C_{12}	83.3	72.7[a]	51.0	41.8[a]
C_{13}	41.1	40.0[a]	21.7	21.3[a]
B_R	69.4		46.5	
B_V	73.2		47.9	
B_H	71.3		47.2	
G_R	21.6		18.5	
G_V	29.3		22.2	
G_H	25.5		20.4	
B_H/G_H	2.8		2.32	
E	68.2		53.4	
σ	0.341		0.311	
λ	53.7		33.1	
V_l	4418.4		3970.9	
V_t	2172.6		2077.9	
V_m	2439.6		2324.4	
θ_D	340.1		288.7	

THERMODYNAMIC PROPERTIES

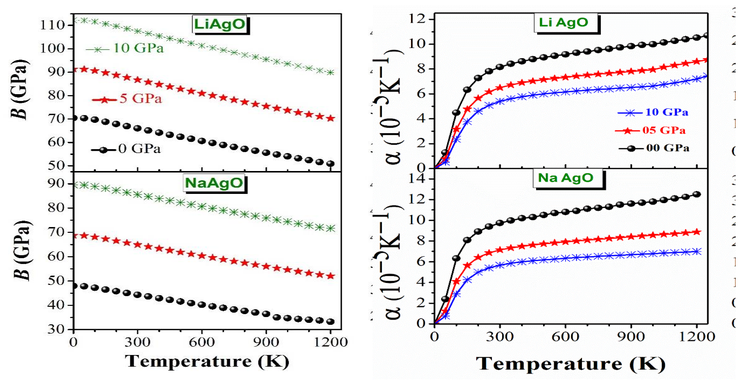

Fig. 2: Temperature dependence of the bulk modulus and the volume thermal expansion coefficient under the various pressures for LiAgO and NaAgO.

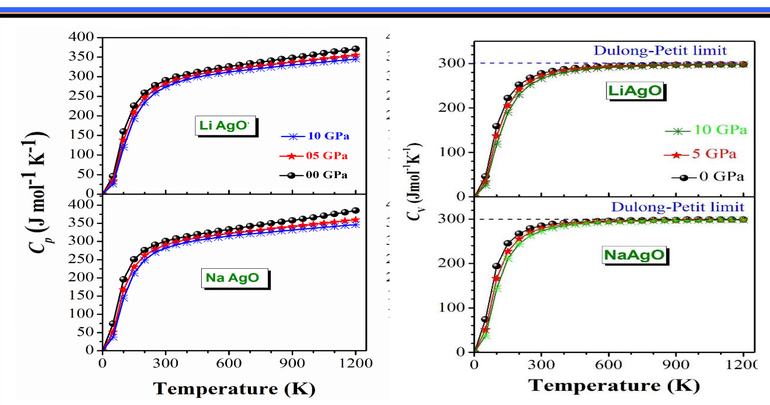

Fig. 3. Temperature dependence of the constant pressure heat capacity and the constant volume heat capacity under the various pressures for LiAgO and NaAgO.

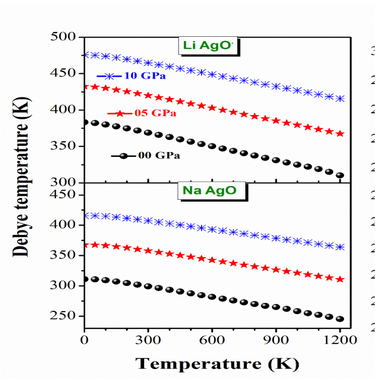

Fig. 4. Temperature dependence of the Debye temperature under the various pressures for LiAgO and NaAgO.

CONCLUSION

- ✓ *Ab initio* calculations of the structural, elastic and thermodynamic properties for the Ag-based oxides *X*AgO (X = Li and Na) have been performed in the present work.
- ✓ Good agreement is found between the optimized lattice parameters and the existing experimental values. An anisotropic behavior of the pressure dependence of the lattice constants is also found.
- ✓ All studied materials are mechanically stable at zero pressure with a strong elastic anisotropy.
- ✓ According to Pugh's criterion, all studied materials behave in a brittle manner.
- ✓ The temperature and pressure dependencies of the bulk modulus, unit cell volume, heat capacity, volume thermal expansion coefficient and Debye temperature are also studied in 0-1200 K and 0-20 GPa ranges via the quasi-harmonic Debye model.

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