Density functional theory studies on the electronic, structural, phonon dynamical and thermo-stability properties of bicarbonates MHCO_3 , $\text{M} = \text{Li, Na, K}$

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Abstract

The structural, electronic, phonon dispersion and thermodynamic properties of MHCO_3 ($\text{M} = \text{Li, Na, K}$) solids were investigated using density functional theory. The calculated bulk properties for both their ambient and the high-pressure phases are in good agreement with available experimental measurements. Solid phase LiHCO_3 has not yet been observed experimentally. We have predicted several possible crystal structures for LiHCO_3 using crystallographic database searching and prototype electrostatic ground state modeling. Our total energy and phonon free energy (F_{PH}) calculations predict that LiHCO_3 will be stable under suitable conditions of temperature and partial pressures of CO_2 and H_2O . Our calculations indicate that the HCO_3^- groups in LiHCO_3 and NaHCO_3 form an infinite chain structure through $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds. In contrast, the HCO_3^- anions form dimers, $(\text{HCO}_3^-)_2$, connected through double hydrogen bonds in all phases of KHCO_3 . Based on density functional perturbation theory, the Born effective charge tensor of each atom type was obtained for all phases of the bicarbonates. Their phonon dispersions with the longitudinal optical–transverse optical splitting were also investigated. Based on lattice phonon dynamics study, the infrared spectra and the thermodynamic properties of these bicarbonates were obtained. Over the temperature range 0–900 K, the F_{PH} and the entropies (S) of MHCO_3 ($\text{M} = \text{Li, Na, K}$) systems vary as $F_{\text{PH}}(\text{LiHCO}_3) > F_{\text{PH}}(\text{NaHCO}_3) > F_{\text{PH}}(\text{KHCO}_3)$ and $S(\text{KHCO}_3) > S(\text{NaHCO}_3) > S(\text{LiHCO}_3)$, respectively, in agreement with the available experimental data. Analysis of the predicted thermodynamics of the CO_2 capture reactions indicates that the carbonate/bicarbonate transition reactions for Na and K could be used for CO_2 capture technology, in agreement with experiments.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Alkali metal bicarbonates are vital components of the pH buffering systems of the human body to regulate pH in the digestive system and to maintain acid–base homeostasis; 70%–75% of CO₂ in the body is converted into carbonic acid (H₂CO₃), which can quickly turn into bicarbonate (HCO₃[−]) with the help of the enzyme (carbonic anhydrase). Such reaction can be accelerated by the enzyme and the reaction rate of the enzyme is amazingly high ($\sim 10^{-6}$) [1]. The most common of the bicarbonate ion is sodium bicarbonate (NaHCO₃), which is used as baking soda. The flow of bicarbonate ions from rocks weathered by the carbonic acid in rainwater is an important part of the carbon cycle. Since the alkali bicarbonates can be decomposed into carbonates to release CO₂ and H₂O over a relatively low-temperature range (for example, NaHCO₃ at 70–250 °C), they could be used for CO₂ capture in post-combustion technology. Hence alkali bicarbonates have been the subject of several recent studies [2–20].

The HCO₃[−] groups in alkali metal bicarbonates form a hydrogen bonding network characteristic of their salt structures. Several previous studies have reported evidence of the existence of ‘proton disorder’ structures in these bicarbonates containing O–H $\cdots$ O hydrogen bonds [21–28]. Each bicarbonate has a different hydrogen bonding scheme. In NaHCO₃ and NH₄HCO₃, the hydrogen bonds are arranged in the form of chains while KHCO₃ contains (HCO₃[−])₂ dimers [29, 30]. In the crystal structure of KHCO₃ at low temperatures all OH $\cdots$ O hydrogen bonds are equivalent and virtually parallel to each other [24]. The structural transition of KHCO₃ from an ordered *P*2₁/*a* structure to a disordered *C*2/*m* structure at 340 K has been observed [22]. Lee and Kim [31] observed thermal decomposition of KHCO₃ to K₂CO₃ around 459 K. Wylock *et al* investigated carbonic gas absorption in a brine of NaHCO₃ and Na₂CO₃ and found that the CO₂ absorption is coupled with several chemical reactions taking place in the liquid phase [32]. It has been noted that MHCO₃, M = Li, Na, K, can exist in a molten ternary eutectic mixture at high temperature (>560 °C) [33].

Although the chemical and physical properties of alkali metal bicarbonates have been measured experimentally [16, 34–36], there are, to the best of our knowledge, no systematically theoretical studies reporting the electronic and phonon thermodynamic properties of these systems. In this study, we combine density functional theory with lattice phonon dynamics to investigate the electronic, structural, and phonon dispersion properties of alkali metal bicarbonates, MHCO₃ (M = Li, Na, K).

At this time there is no reported crystal structure for LiHCO₃. It has been claimed that LiHCO₃ exists only in solution at ambient conditions [37]. However, our previous calculated Li–C–O–H phase diagram shows that LiHCO₃ could exist as solid phase [3]. In this study, we have explored possible ground state crystal structures of LiHCO₃ using the prototype electrostatic ground state approach [38] and a database search of similar compounds. Furthermore, we have identified the conditions of temperature and partial pressures

of CO₂ and H₂O under which the LiHCO₃ crystal is expected to be stable.

2. Theoretical methods

The calculations performed in this work were based on first-principles density functional theory (DFT) with plane-wave basis sets and the pseudo-potential approximation to describe the electron–ion interactions. The Vienna *ab initio* simulation package (VASP) [39, 40] was employed in this study to calculate the electronic structures of bicarbonates MHCO₃ (M = Li, Na, K) and the corresponding carbonates. Previous tests to determine the proper choice of the pseudo-potential and the exchange–correlation functionals for oxides and salts [8, 41–43] suggested that the PAW pseudo-potential and the PW91 exchange–correlation functions are appropriate for use in all of the calculations of this study [44]. Plane-wave basis sets were used with a kinetic energy cutoff of 500 eV and an augmentation charge cutoff of 605.4 eV. The *k*-point sampling grids of $n_1 \times n_2 \times n_3$, obtained using the Monkhorst–Pack method [45], were used for these bulk calculations, where n_1 , n_2 , and n_3 were adjusted to give a spacing of about 0.028 Å^{−1} along the axes of the reciprocal unit cells. All atom positions and unit cell parameters were relaxed in the optimization calculations. For the high-pressure phase calculations, the volume and the atoms in the cell were relaxed subject to a Pulay stress (input parameter PStress in VASP), which was set to the experimentally measured pressure value.

The Born effective charge tensor of each atom type in the MHCO₃ structures and the macroscopic static dielectric tensor including local field effects of the MHCO₃ crystals were evaluated based on density functional perturbation theory (DFPT) [46–48] and were used in phonon calculations to obtain the infrared absorption spectrum and the longitudinal optical–transverse optical (LO–TO) splitting features of the solids [49].

A useful thermodynamic description of the phase stability and transition behavior for crystalline materials can be found based on calculation of the phonon frequencies. In this study, we employed the PHONON software package [50], in which the forces are calculated via the Hellmann–Feynman theorem, using the formalism derived by Parlinski *et al* [51]. Similar to our previous approach [3, 8, 20, 42, 43, 52], the phonon dispersion and the thermodynamic properties (zero-point energy, free energy, entropy, heat capacity) were computed for each crystal. In the phonon calculations, the $3 \times 1 \times 1$ supercells of MHCO₃ and the $4 \times 3 \times 1$, $1 \times 3 \times 5$ and $2 \times 2 \times 3$ supercells of three phases (space groups 14, 12 and 2 as shown in table 1) of KHCO₃ were created from their optimized unit cell structures. Displacements of ± 0.03 Å of the non-equivalent atoms in the supercells were used to generate the required input for the PHONON package [50] to calculate the phonon dispersions and density of states. The thermodynamic properties for each crystal as a function of temperature were generated from this formalism.

For the band structure and phonon dispersion calculations, the symbols and coordinates of the high symmetry

Table 1. The experimental and optimized crystal structural parameters of bicarbonates MHCO_3 , $\text{M} = \text{Li, Na, K}$.

Crystal	Space group and reference	Z	Experimental structures		Optimized structures	
			Lattice constants (Å)	Atomic fractional coordinates	Lattice constants and deviations (%)	Atomic fractional coordinates
LiHCO_3	$P12_1/c1$ (#14) ^a	4	N/A	N/A	4.242 21 8.985 44 7.666 62 117.714°	Li(0.215 92, 0.011 09, 0.704 76) C(0.192 28, 0.229 19, 0.967 18) O(0.132 30, 0.365 34, 0.981 08) (0.983 50, 0.149 66, 0.827 50) (0.496 70, 0.163 59, 0.109 61) H(0.677 78, 0.246 04, 0.196 97)
NaHCO_3	$P12_1/c1$ (#14) ^b	4	$a = 3.51$ $b = 9.71$ $c = 8.05$ $\beta = 111.85^\circ$	Na(0.4285, 0.0044, -0.2855) C(0.2123, 0.2384, -0.0767) O(0.1893, 0.3666, -0.0767) (-0.0104, 0.1619, -0.2046) (0.4959, 0.1705, 0.0592) H(0.669, 0.252, 0.143)	3.53(0.66) 9.76(0.50) 8.12(0.83) 112.7°(0.77)	Na(0.423 49, 0.005 00, 0.712 88) C(0.212 46, 0.239 77, 0.923 79) O(0.192 80, 0.369 36, 0.928 70) (0.984 59, 0.164 25, 0.793 93) (0.495 16, 0.172 20, 0.061 53) H(0.690 24, 0.241 91, 0.151 48)
KHCO_3	$P12_1/a1$ (#14) ^c	4	$a = 15.1725$ $b = 5.6283$ $c = 3.7110$ $\beta = 104.631^\circ$	K(0.165 33, 0.021 77, 0.295 33) C(0.119 67, 0.515 0, -0.143 63) O(0.193 29, 0.529 15, 0.094 82) (0.082 21, 0.319 98, -0.273 53) (0.077 61, 0.727 72, -0.274 48) H(0.011, 0.682, -0.465)	15.45(1.86) 5.72(1.52) 3.77(1.55) 105.9°(1.19)	K(0.165 30, 0.022 99, 0.287 26) C(0.119 77, 0.511 49, 0.845 15) O(0.194 43, 0.526 83, 0.086 63) (0.081 26, 0.319 28, 0.713 12) (0.077 93, 0.716 98, 0.717 60) H(0.014 34, 0.688 11, 0.542 05)
	$C12/m1$ (#12) ^d	4	$a = 15.1803$ $b = 5.6302$ $c = 3.7219$ $\beta = 104.77^\circ$	K(0.165 06, 0.000 0, 0.296 70) C(0.119 34, 0.5000, 0.856 43) O(0.193 59, 0.5000, 0.096 39) (0.079 87, 0.301 53, 0.727 91) H(0.019 01, 0.312 49, 0.554 80) ^e	15.45(1.81) 5.72(1.51) 3.77(1.26) 105.9°(1.06)	K(0.165 30, 0.022 99, 0.287 26) O(0.194 43, 0.526 83, 0.086 63) (0.081 26, 0.319 28, 0.713 12) (0.077 93, 0.716 98, 0.717 60) C(0.119 77, 0.511 49, 0.845 15) H(0.985 66, 0.311 89, 0.45795) ^f
	$P\bar{1}$ (#2) ^g ($P = 5.5$ GPa)	2	$a = 6.1443$ $b = 5.2974$ $c = 4.2133$ $\alpha = 95.106^\circ$ $\beta = 100.743^\circ$ $\gamma = 108.934^\circ$	K(0.2992, 0.1343, 0.290 58) C(0.2300, 0.5737, 0.9057) O(0.2073, 0.7774, 0.747 1) (0.1054, 0.3326, 0.7682) (0.3693, 0.6405, 0.1718) H(0.0659, 0.6921, 0.5524)	6.32(2.85) 5.37(1.36) 4.18(-0.69) 94.7°(-0.44) 100.6°(-0.19) 109.3°(0.34)	K(0.305 24, 0.139 08, 0.287 68) C(0.229 68, 0.578 77, 0.899 75) O(0.199 43, 0.778 27, 0.741 53) (0.110 38, 0.336 31, 0.765 01) (0.375 22, 0.646 22, 0.167 78) H(0.067 52, 0.706 29, 0.528 02)

^a No experimental structure data available.^b From [55].^c From [58].^d From [60].^e H sites half occupied.^f Half of the H sites fully occupied. However, the optimized crystal symmetry becomes $P21/c$ (#14).^g From [61].

Figure 1. The crystal structures of bicarbonates $M\text{HCO}_3$, $M = \text{Li, Na, K}$. The metal atoms M are represented in purple, O atoms in red, C atoms in dark gray and H atoms in white and green. (a) NaHCO_3 with space group $P121/n1$ (#14), (b) KHCO_3 with space group $P121/c1$ (#14), (c) KHCO_3 with space group $P\bar{1}$ (#2), (d) KHCO_3 with space group $C12/m1$ (#12), in which the H atoms in white and green are half occupied.

points in the first Brillouin zone of the crystals are taken from Bradley and Cracknell's definitions [53].

Given that no experimental crystal structure exists for LiHCO_3 , we carried out database search to identify possible candidate structures for the ground state. This was done by searching the inorganic crystal structure database (ICSD) for crystals having ABCX_3 composition. The following structures were investigated: NaHCO_3 ($P2_1/c$), PbAgSbS_3 ($P2_1/c$), NaLiCO_3 ($P\bar{6}m2$), BaErAgS_3 ($C2/m$), RbAgHfTe_3 ($P2_1/m$), BaLaCuTe_3 ($Pnma$), PbCuAsS_3 ($Pmn2_1$), CsAgUS_3 ($Cmcm$), LiEuAsS_3 ($P2_1/c$). Two structures for each prototype were used to accommodate the ambiguity for the Li and H atom positions.

In addition to the ICSD structure search, the PEGS (prototype electrostatic ground states) method [38] was used to produce prototype structures for LiHCO_3 . The PEGS method uses a simplified Hamiltonian consisting of electrostatic interactions and soft-sphere repulsion, combined with Metropolis Monte Carlo global optimization and potential energy smoothing to produce prototype structures for evaluation using DFT. Details of the method can be found elsewhere [38].

3. Results and discussions

3.1. Structural and bulk properties of $M\text{HCO}_3$ ($M = \text{Li, Na, K}$)

As shown in figure 1(a), the crystal structure of NaHCO_3 was determined to be monoclinic with space group $P121/n1$ [54] (or $P121/c1$ [55]). Each Na atom is surrounded by six O atoms with Na–O bond lengths 2.35–2.57 Å in the first sphere of coordination. The H atom is bonded with two O atoms from two different carboxyl groups. Under ambient conditions, as

shown in figure 1(b), KHCO_3 has a monoclinic structure with space group $P121/a1$ (#14, form I-kalinite) [56–58]. Above 318 K the crystal structure changes to a high-temperature phase, which is monoclinic with space group $C2/m$ (#12, form II) [57, 59, 60]. The lattice constants and the atomic coordinates for form I and form II are similar to each other. The main difference is that some atom positions in form II are half occupied [57, 59, 60]. Kashida *et al* [57] determined that all atoms in the KHCO_3 crystal with space group $C12/m1$ (#12) occupy each of the eight possible sites with half occupancy, while Machida *et al* [60] found that only the H atoms in the KHCO_3 crystal have sites with half occupancy, while all the other atomic sites in the crystal are fully occupied, as shown in table 1 and figure 1(d). In this study we avoid fractional occupation by assuming that the H atoms occupy the sites denoted by either the white or green balls in figure 1(d) with full occupancy. Recent high-pressure studies at ambient temperature showed that kalinite undergoes a structural phase transition between 2.8 and 4.6 GPa [61]. This new high-pressure phase (form III) is still in monoclinic with space group $P\bar{1}$ (#2) as shown in figure 1(c). The main difference between form I and form III is that in the $P21/a$ form I structure the K^+ ions are coordinated to eight O atoms from six HCO_3^- anions with K–O bond lengths <3.2 Å, while in the $P\bar{1}$ form III structure, the K^+ ions are coordinated with ten O atoms from a total of seven HCO_3^- anions, including two $\text{O}\cdots\text{O}$ contacts from a single $(\text{HCO}_3^-)_2$ dimer [61]. Although there are two other phases (forms IV and V) of KHCO_3 reported in the literature, their crystal structures have not been determined [56].

As previously mentioned, there are no experimental crystal structures for LiHCO_3 . Moreover, it has been reported that LiHCO_3 exists only in solution at ambient conditions [37]. We have therefore employed an ICSD

Figure 2. The calculated total energy versus the relative cell volume. (a) LiHCO₃ (circles) and NaHCO₃ (squares). (b) KHCO₃, form I, #14 (triangles), form II, #12 (circles), form III, #2 (squares).

database search and the PEGS method to generate prototype structures for LiHCO₃. The ICSD structures having the lowest total free energy were NaHCO₃, and the isostructural PbAgSbS₃ with $P2_1/c$ symmetry, with H on the Ag site and Li on the Pb site. Both H and Li atoms occupy the Wyckoff 4e positions. The LiEuAsS₃ structure had the next lowest energy of 11 kJ/mol f.u. (formula unit) above the lowest energy structure.

For the PEGS method, we modeled the CO₃²⁻ molecular ion as a rigid structure and allowed rotations and translations. The Li⁺ and H⁺ ions were allowed to translate and swap positions with one another, subject to ionic radii constraints. The cell contents were initialized randomly in a cubic box, however, unit cell lattice vectors and angles were optimized along with atomic coordinates in the total energy optimizations. No *a priori* cell symmetry was assumed. Born effective charges for the constituent atoms in the PEGS method were calculated using NaHCO₃ ($P2_1/c$) as the structure prototype. The charges used in PEGS calculations were: $Q_{\text{Li}} = 1.1 e$, $Q_{\text{H}} = 0.8 e$, $Q_{\text{C}} = 2.0 e$, and $Q_{\text{O}} = -1.3 e$. These values were roughly the average of the diagonal elements of the charge tensor (as shown in table S1 of supplementary data available at stacks.iop.org/JPhysCM/24/325501/mmedia), with small adjustments made to obtain overall charge neutrality in the PEGS simulation cell. Interatomic minimum distances for soft-sphere repulsion were taken from the $P2_1/c$ structure as well: C–C = 3.92 Å, C–H = 1.96 Å, C–Li = 2.94 Å, H–H = 4.0 Å,

Table 2. Static, total first-principles energies of structural candidates for LiHCO₃ identified through a combined ICSD database and PEGS search.

Structure type	Symmetry	Space group	$E - E_0$ (kJ/mol f.u.)	Density (g/cc)
NaHCO ₃	$P2_1/c$	14	0	1.88
LiEuAsS ₃	$P2_1/c$	14	11.1	1.76
PEGS	$C1c1$	9	16.0	1.74
PEGS	$P3_2$	145	26.1	1.87

Li–H = 2.52 Å, Li–Li = 2.79 Å, O–C = 1.26 Å, O–H = 1.03 Å, O–Li = 1.93 Å, and O–O = 2.22 Å. The resulting PEGS structures took symmetries in space groups $P1$ (#1), $P\bar{1}$ (#2), $P1211$ (#4), $P1c1$ (#7), $C1m1$ (#8), $C1c1$ (#9), $P2_1/m$ (#11), and $P3_2$ (#145). The lowest energy PEGS structure had $C1c1$ symmetry and a total energy 16 kJ/mol f.u. above the NaHCO₃-type structure in $P2_1/c$, while the highest symmetry PEGS structure had $P3_2$ symmetry and a total energy of 26 kJ/mol f.u. above the $P2_1/c$ structure. Phonon vibrational spectra were calculated using the linear response formalism in VASP. The calculated total free energies for the three competing structures as shown in figure S1 of supplementary data (available at stacks.iop.org/JPhysCM/24/325501/mmedia) indicate that the $P2_1/c$ structure is favored at all temperatures. The relative energies of the four lowest energy structures found through the combined ICSD and PEGS search are shown in table 2. It is evident that the PEGS method was unable to identify the lowest energy structure in the case of LiHCO₃. This may be due to several factors, including non-optimal ionic charges and interatomic distance restrictions. The simple electrostatic Hamiltonian used in PEGS does not capture dispersion and other forces that may play a larger role in the true potential energy surface for this compound.

Table 1 summarizes the experimentally measured as well as our optimized crystal structures of MHCO₃ with M = Li, Na, K. Among them, three phases of KHCO₃ (forms I, II, III) are investigated in this study. From figure 1 and table 1, one can see that overall the optimized structures are in good agreement with experimental data. We note that the high-temperature phase of KHCO₃ (form II) changes upon optimization from space group $C12/m1$ (#12) to space group $P12/c$ (#14). As noted above, experiments indicate fractional occupation in form II [57, 59, 60]. This indicates that methods that can explicitly deal with fractional occupation, such as virtual crystal approximation [62, 63], may be needed to explore the symmetry change to a higher degree of accuracy.

The equations of state for MHCO₃ with M = Li, Na, and K are plotted in figure 2, where it can be seen that the unit cell energy and the cohesive energy (shown in table 3) for MHCO₃ increase from Li to K. For KHCO₃, the high-pressure phase (form III, #2) has a cohesive energy that is smaller in magnitude than the corresponding low-temperature (form I, #14) and high-temperature (form II, #12) phases. We have fitted the DFT data in figure 2 to the Birch–Murnaghan

Table 3. The calculated bulk modulus, cohesive energy (E_{coh}), and the fitted parameters of Birch–Murnaghan equation of state for bicarbonates MHCO_3 , $M = \text{Li, Na, K}$.

Crystal		E_0 (eV/cell)	B_0 (eV $\text{\AA}^{-3}$)	B'_0	V_0 ($\text{\AA}^3$)	Bulk modulus (GPa)	E_{coh} (eV)
LiHCO_3		−155.36 (−155.28) ^a	0.062	3.466	288.8 (285.5) ^a	9.90	−31.74
NaHCO_3		−152.21 (−152.20) ^a	0.185	3.487	261.9 254.7 ^b	29.59	−29.78 (−28.40) ^c
KHCO_3	$P12_1/a1$ (#14)	−151.79 (−151.75) ^a	0.113	3.484	328.0 306.6 ^d	18.10	−29.67 (−28.34) ^c
	$C12/m1$ (#12)	−151.80 (−151.75) ^a	0.127	3.502	336.5 307.6 ^e	20.42	−29.67
	$P\bar{1}$ (#2)	−70.84 (−70.84) ^a	0.199	3.500	136.0 125.8 ^f	60.84	−27.15

^a Obtained from full optimization.^b From [55].^c Obtained by subtracting the atom formation energy from the experimental formation energy of the bicarbonates at 298.15 K [35, 36].^d From [58].^e From [60].^f From [61].**Table 4.** The calculated band gaps and valance band widths of the bicarbonates MHCO_3 , $M = \text{Li, Na, K}$ (unit: eV).

Crystal		VB_3 width	$\text{VB}_3 \sim \text{VB}_2$ gap	VB_2 width	$\text{VB}_2 \sim \text{VB}_1$ gap	VB_1 width	Band gap
LiHCO_3		0.49	2.10	1.10	8.64	9.67	5.77 (indirect)
NaHCO_3		0.48	2.05	0.60	9.06	9.67	5.35 (direct)
KHCO_3	$P12_1/a1$ (#14)	0.28	2.41	0.76	7.6	11.37	4.97 (direct)
	$C12/m1$ (#12)	0.28	2.41	0.76	7.11	11.32	5.02 (direct)
	$P\bar{1}$ (#2)	0.49	2.34	0.76	7.40	11.09	5.69 (direct)

equation of state [64, 65], given by

$$E(V) = E_0 + \frac{9B_0V_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 \times B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \times \left[6 - 4 \times \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}. \quad (1)$$

The fitted parameters (E_0 , V_0 , B_0 , B'_0) for MHCO_3 are listed in table 3. The bulk modulus B is defined as $B = B_0 + B'_0 \times P$ in this scheme, where P is the pressure and set to 1 atm for ambient conditions and 5.5 GPa for the high-pressure phase of KHCO_3 . We constrained B'_0 to lie in the range [2,6] in the fitting routine, since most values of B'_0 fall in this range. The fitted equation of state curves are also plotted in figure 2. The cohesive energy (E_{coh}) is calculated by subtracting the total bulk energy (E_0 in table 3) from the sum of total energies of the isolated spin-polarized atoms (Li, Na, K, O, C, H) using the same level calculations. These isolated atom energies are $E_{\text{Li}} = -0.27065$ eV/atom, $E_{\text{Na}} = -0.20469$ eV/atom, $E_{\text{K}} = -0.15544$ eV/atom, $E_{\text{H}} = -1.11573$ eV/atom, $E_{\text{C}} = -1.21255$ eV/atom, and $E_{\text{O}} = -1.49139$ eV/atom.

3.2. Electronic structures of MHCO_3 ($M = \text{Li, Na, K}$)

The calculated band structures of MHCO_3 ($M = \text{Li, Na, K}$) solids are shown in figure 3. It can be seen that the band

structures of these bicarbonates have some similarities. They have roughly three valence bands (VBs). The first band, VB_1 , is just below the Fermi energy and has several small gaps, which separate VB_1 into several sub-bands. In each case, the gap between VB_1 and VB_2 is larger than that between VB_2 and VB_3 , and the bandwidth of VB_1 is much larger than that of VB_2 and VB_3 . Comparing the band structures of LiHCO_3 and NaHCO_3 , from figures 3(a) and (b), respectively, one can see that the major difference is that NaHCO_3 has a direct band gap of 5.35 eV while LiHCO_3 has an indirect band gap located between Γ and Z high symmetry points with the value of 5.77 eV. The band structures of the low- and high-temperature phases of KHCO_3 are very similar, as can be seen from figures 3(c) and (d). Both have very similar direct band gaps of 4.97 and 5.02 eV respectively. Table 4 summarizes the calculated band gaps and valance band widths. We see that the band gap decreases when going from Li to Na to K. As previously noted [41, 49], band gaps computed from DFT are typically smaller than the experimental values. We therefore have a high degree of confidence that these bicarbonates are indeed all insulators.

Figure 4 shows the calculated total density of states (TDOS) and the corresponding atom partial density of states (PDOS) for LiHCO_3 and NaHCO_3 . As demonstrated in figures 4(a) and (b), the lowest band (VB_3) is mainly formed by the s orbitals of O, C and H, while orbitals of Li and Na do not contribute to VB_3 . The VB_2 band is mainly formed by

Figure 3. The calculated band structures of MHCO_3 , $M = \text{Li, Na, K}$. (a) LiHCO_3 , (b) NaHCO_3 , (c) KHCO_3 in $P12_1/a1$ (#14) phase, (d) KHCO_3 in $C12/m1$ (#12) phase.

the p orbitals of Li and C, with the s orbitals of O and H. In both systems, the s orbitals of H and C have more contribution to the lower portion of VB_1 , while their p orbitals have larger contribution to the upper portion of VB_1 . The p orbitals of O mainly contribute to VB_1 . The conduction bands (CB) in both cases are mainly formed by the p orbitals of C and O and s and p orbitals of H and Li (Na). As one can see from figure 4, the main difference between LiHCO_3 and NaHCO_3 is in the role of Li and Na. In LiHCO_3 , the p orbitals of Li have a larger contribution to VB_1 , VB_2 and CB than the s orbitals. In contrast, the s and p orbitals of Na in NaHCO_3 play similar roles in VB_1 and CB. In contrast to Li in LiHCO_3 , the orbitals of Na in NaHCO_3 have almost no contribution to the VB_2 .

Figure 5 shows the TDOS and PDOS of two phases of KHCO_3 (forms I and II). One can see that overall their DOS are very similar to each other. As with LiHCO_3 and NaHCO_3 (figure 4), the s orbital of H has a larger contribution to the VBs than its p orbitals, while the p orbitals of C and O have larger contributions to the VB_1 and CB than their s orbitals. In contrast to LiHCO_3 and NaHCO_3 , the p orbitals of K mainly contribute to VB_2 and both the s and p orbitals of K do not contribute to VB_1 and CBs. This difference in electronic structure results in different bonding behavior and structures. From figures 3(c), (d) and 5, one can see that the low-temperature phase of KHCO_3 (#14) and the high-temperature phase of KHCO_3 (#12) are similar to each other, and therefore, their electronic properties are expected to be similar.

The band structure and DOS of the high-pressure phase of KHCO_3 (form III) are shown in figures 6(a) and (b)

respectively. From figure 6(a) one can see that at high-pressure (5.5 GPa), the band gap is direct with a value of 5.69 eV, which is larger than the corresponding low- and high-temperature phases. As summarized in table 4, the valence bandwidths and gaps among VBs in this high-pressure phase are close to the other two phases of KHCO_3 (forms I and II in figures 3(c) and (d)). Comparing the TDOS and PDOS of this high-pressure phase of KHCO_3 (figure 6(b)) with other two phases of KHCO_3 (figure 5), one can see that they are similar to each other, which indicates that the pressure of 5.5 GPa does not greatly affect the electronic structure of KHCO_3 .

We present the optimized HCO_3^- structures for each of the MHCO_3 compounds in figure 7 in order to examine the hydrogen bonding network in these materials. We note that DFT does not always accurately describe hydrogen bonding, but Tsuzuki and Lüthi [66] showed that DFT calculations with PW91 generalized gradient functional can reproduce Møller–Plesset and coupled-cluster *ab initio* results for energies and geometries of hydrogen bonded species. This is indeed the case for the systems we consider here, giving us some confidence in the reliability of our results. It can be seen that the HCO_3^- groups are connected with each other forming infinite chain structures in LiHCO_3 and NaHCO_3 . Each chain is surrounded with Li or Na atoms. The optimized bond lengths of the O–H and C–O bonds in MHCO_3 are listed in table 5. Due to the different coordination environments, the hydrogen bonds between two HCO_3^- groups have unequal bond lengths. In LiHCO_3 these two bond lengths (r_1 , r_2 in figure 7, top) are 1.056 Å and 1.471 Å, respectively, while

Figure 4. The calculated density of states of MHCO_3 , $M = \text{Li, Na, K}$. (a) LiHCO_3 , (b) NaHCO_3 .

Table 5. The optimized bond lengths in bicarbonates MHCO_3 , $M = \text{Li, Na, K}$.

Crystal		Bond length ($\text{\AA}$)				
		r_1 (O–H)	r_2 (O–H)	r_3 (C–O)	r_4 (C–O)	r_5 (C–O)
LiHCO_3			1.056	1.471	1.269	1.343
NaHCO_3			1.040	1.526	1.268	1.349
			1.07 ^a	1.56 ^a	1.249 ^a	1.345 ^a
KHCO_3	$P12_1/a1$ (#14)		1.036	1.529	1.262	1.364
			1.005 ^b	1.587 ^b	1.244 ^b	1.332 ^b
			0.929 ^c	1.662 ^c	1.245 ^c	1.334 ^c
	$C12/m1$ (#12)		1.037	1.527	1.262	1.363
			0.762 ^c	1.835 ^c	1.225 ^c	1.387 ^c
	$P\bar{1}$ (#2)		1.049	1.449	1.253	1.352
			1.022 ^d	1.516 ^d	1.221 ^d	1.350 ^d

^a From [55].

^b From [58].

^c From [60] at 301 K (#14) and 353 K (#12).

^d From [61].

in NaHCO_3 they are 1.040 $\text{\AA}$ and 1.526 $\text{\AA}$, respectively. The C–O bond lengths in the HCO_3^- groups in the infinite chain (figure 7, top) are not all uniform. The C–O bond denoted r_5 , in which the O also forms a hydrogen bond $\text{H} \cdots \text{O}$ (r_2), has a shorter bond length than C–O (r_4), in which the O atom has a shorter H–O bond length denoted, r_1 . The remaining O atom not bonded to an H atom has a C–O bond (r_3) with a double bond character. These optimized structures are in good

agreement with the results reported by Sharma [55], but differ from early experimental data reported by Zachariassen [54] in which the two hydrogen bonds were determined to have the same bond length of 1.275 $\text{\AA}$. It can be seen from figure 7 and table 5 that overall the bonding structures and bond lengths in LiHCO_3 are very similar to those in NaHCO_3 .

The HCO_3^- groups form dimers rather than chains in all phases of KHCO_3 , as shown in figure 7. The dimers are

Figure 5. The calculated density of states of KHCO_3 , (a) KHCO_3 in $P12_1/a1$ (#14) phase, (b) KHCO_3 in $C12/m1$ (#12) phase.

formed through a double hydrogen bond structure. The K atoms coordinate with and separate these dimers, as depicted in figure 7. Due to the different bonding environments, these two hydrogen bonds (r_1 , r_2 in figure 7, bottom) between two HCO_3^- groups have unequal bond lengths. In turn, the three C–O bonds (r_3 , r_4 , r_5 in figure 7, bottom) of the HCO_3^- group also have different bond lengths. In table 5 we list the calculated bond lengths and the available experimental data for all three phases of KHCO_3 [57, 67, 68]. As one can see that for both low-temperature and high-temperature phases of KHCO_3 , the differences in the two hydrogen bonds from the optimized structures are smaller than those from the experimental findings. This may be due to proton disorder [21–25].

3.3. Phonon dynamical properties of crystals MHCO_3 ($M = \text{Li}, \text{Na}, \text{K}$)

As shown in table 1, the high-pressure phase of KHCO_3 ($P1$), contains two f.u. in its primitive cell while the other bicarbonates have four f.u. in their primitive cells. Therefore, there are 36 phonon modes in the high-pressure phase of KHCO_3 and 72 phonon modes in the other phases of bicarbonates. The calculated phonon dispersions of MHCO_3 are shown in figures 8(a)–(d) respectively. In

table S2 (as supplementary data available at stacks.iop.org/JPhysCM/24/325501/mmedia) we summarize our calculated phonon frequencies for these bicarbonates together with the corresponding irreducible representations. Because the crystal point groups are quite low (C_{2h} or C_2), all of the vibrational modes are non-degenerate (A_g , B_g , A_u , B_u) and half of them are Raman active, while the other half are infrared active, as shown in table S2 (available at stacks.iop.org/JPhysCM/24/325501/mmedia). Bertoluzza *et al* [69] found O–H vibrational frequencies peaks of $2660(\text{R}) \text{ cm}^{-1}$, $2542(\text{I}) \text{ cm}^{-1}$, $2450(\text{I}) \text{ cm}^{-1}$ with strong and medium intensities in NaHCO_3 . These correspond to the three highest frequencies listed in table S2 (available at stacks.iop.org/JPhysCM/24/325501/mmedia). Since LiHCO_3 has the same structure as NaHCO_3 , the phonon dispersions have some similarities as shown in figures 8(a) and (b). There is one phonon soft mode in both systems along $\mathbf{Z}-\Gamma-\mathbf{E}$ and $\mathbf{E}-\mathbf{C}-\mathbf{Y}$ wavevector axis. By analyzing the intensity of phonon dispersion of each type of atom, this soft mode is identified as originating mainly from one type of O atom in HCO_3^- vibrating along the x axis direction. This type of O is not involved in formation of $-\text{O}-\text{H}-\text{O}-$ chains as shown in figure 7. Instead, it is only connected to C atom and forms a C=O bond. Similarly, one soft mode also was found in the low-temperature phase of KHCO_3 ($P12_1/a1$ (#14)) along

Figure 6. The calculated electronic band structure (a) and density of states (b) for KHCO_3 $P1$ phase at $P = 5.5$ GPa.

$Z-E$ and $Y-\Gamma$ wavevector axis as shown in figure 8(c). In the high-temperature phase of KHCO_3 ($C12/m1$ (#12)) as shown in figure 8(d), several soft modes were found. These soft modes are mainly from the O atom of C=O bond (as shown in figure 7) of HCO_3^- vibration along z and x axis directions as well as small contributions from K vibrations.

The long-range electric fields associated with long-wave longitudinal phonons are responsible for the phenomenon of the longitudinal optic (LO)—transverse optic (TO) splitting, which removes the degeneracy between the LO and TO phonons at the Brillion zone center [70]. As one can see from

figure 8, LO–TO splitting occurs at Γ symmetry points in all phases of MHCO_3 .

The calculated total phonon density of states (TPDOS) of MHCO_3 $M = \text{Li, Na, K}$ are shown in figure 9. Overall, one can see that along the frequency axis the TPDOS is separated into several peaks (branches in figure 8), which represent different atomic vibrational modes. The calculated projected phonon density of states (PPDOS) (not shown) indicates that the vibrational amplitudes along each principal axis direction for each type of atom are different because of the asymmetric bonding environments. The highest frequency band (>60 THz) is from the H atom vibrations and the lowest frequency band (<10 THz) is mainly from vibrations of O, Na, and K atoms. In the case of LiHCO_3 , the Li vibration band is mainly in the range of 5–15 THz because its mass is lighter than Na and K. Interestingly, in all cases the alkali metal atom only has only one frequency band, while the other atom types (O, C, H) have several bands distributed over a range of frequencies (<50 THz for C and O, <85 THz for H). In LiHCO_3 and NaHCO_3 , the displacements of H atoms along x , and respectively y and z directions lead to frequency contributions in PPDOS centered around 30 THz, respectively ranging between 35–50 THz and 60–80 THz. However, in KHCO_3 , the contributions to PPDOS of H atoms displaced along the x , y , z directions are totally different: around 28–35 THz for x , between 40–50 THz for y , and above 70 THz for z . These results indicate the bonding environments of H in the KHCO_3 dimer structure are quite different from those in the LiHCO_3 and NaHCO_3 chain structures.

Figures 10(a) and (b) present the phonon dispersion relations and TPDOS of the high-pressure phase of KHCO_3 at $P = 5.5$ GPa. Obviously, there are several soft modes along all high symmetry points, which indicate that the high-pressure phase is unstable at ambient conditions. Except for the higher amplitudes of the soft modes shown in figure 10(b) (in the negative frequency range), the other vibrational motions are similar to the $P12_1/a1$ phase of KHCO_3 . Again, the highest frequency peaks (>70 THz) are from H atom vibrations.

The calculated phonon free energies and entropies of MHCO_3 as a function of temperature are plotted in figures 11(a) and (b), respectively. The zero-point energy is the phonon free energy at $T = 0$ K. As can be seen, the zero-point energies of MHCO_3 are significant and must be included when predicting thermodynamic properties. The calculated thermodynamic properties of these bicarbonates at 300 K are given in table 6, along with available experimental data. As shown in figure 11(a), the phonon free energy decreases with increasing temperatures. The calculated free energies of both low-pressure phases of KHCO_3 are similar to each other over the entire temperature range. The phonon free energies (F_{PH}) follow the trend $F_{\text{PH}}(\text{LiHCO}_3) > F_{\text{PH}}(\text{NaHCO}_3) > F_{\text{PH}}(\text{KHCO}_3)$ over the entire temperature range. It has been previously shown that the entropies of solids computed from the phonon calculations are generally in good agreement with experimental data [3, 8, 42, 43]. We see from figure 11(b) that the calculated entropies (S) are ordered as follows: $S(\text{KHCO}_3) > S(\text{NaHCO}_3) > S(\text{LiHCO}_3)$. These data can be used to determine the thermodynamic stabilities of the materials, as described in section 3.5.

Figure 7. Hydrogen bonding structures in MHCO_3 , $M = \text{Li, Na, K}$.

Figure 8. The calculated phonon dispersion relations with LO-TO splitting. (a) LiHCO_3 , (b) NaHCO_3 , (c) KHCO_3 with space group $P121/a1$, (d) KHCO_3 with space group $C12/m1$.

3.4. Infrared absorption spectra of MHCO_3

We have used density functional perturbation theory (DFPT) [46–48] to calculate the Born effective charge tensor of each atom type in MHCO_3 and the macroscopic static dielectric tensors for each of the bicarbonates; these values are listed in table S1 (as supplementary data available at stacks.iop.org/JPhysCM/24/325501/mmedia). These param-

eters were used in conjunction with the calculated phonon data to calculate the infrared (IR) absorption spectrum. The calculated infrared spectra of MHCO_3 are shown in figure 12.

We see from figure 12(a) that the calculated IR spectrum of LiHCO_3 is similar to that of NaHCO_3 over the frequency range 15–60 THz. However, at low frequency (<15 THz), the absorption peaks of NaHCO_3 appear at lower frequencies than those of LiHCO_3 , while at high frequencies (>60 THz)

Table 6. The calculated zero-point energy (E_{ZP}), heat capacity (C_p), phonon free energy (F_{PH}) and entropy (S) of bicarbonates $M\text{HCO}_3$ ($M = \text{Li, Na, K}$) at $T = 300$ K. Experimental data also shown where available.

Crystal	E_{ZP} (kJ mol ⁻¹)	Entropy (J mol ⁻¹ K ⁻¹)	Heat capacity (J mol ⁻¹ K ⁻¹)	F_{PH} (kJ mol ⁻¹)
LiHCO_3	78.4	86.6	79.6	66.0
NaHCO_3	75.4	104.0	84.8	60.1
KHCO_3	$P12_1/a1$ (#14)	101.7 ^a	87.6 ^a	54.0
		122.1	86.6	
	$C12/m1$ (#12)	115.5 ^a	90.4 ^a	53.5
		121.7	86.3	
$P\bar{1}$ (#2)	70.5	104.5	73.5	54.2

^a From HSC chemistry [34] thermodynamic package. **Figure 9.** The calculated phonon total density of states (PTDOS) of $M\text{HCO}_3$, $M = \text{Li, Na, K}$.

the absorption peaks of NaHCO_3 appear at higher frequencies than those of LiHCO_3 .

By comparing the IR spectrum of the high-temperature phase of KHCO_3 (#12) with that of the low-temperature phase of KHCO_3 (#14) as shown in figure 12(b), one can see that the frequencies of their IR modes are similar, but that they have different absorption intensities. The high-temperature phase has higher intensity around 80 THz, while the low-temperature phase has higher intensity around 35 THz. The IR spectrum of the high-pressure phase of KHCO_3 is also shown in figure 12(b). The high frequency peak (~ 82 THz) in the low-pressure phases is shifted to lower frequency (~ 75 THz) for the high-pressure phase, while the three peaks in the frequency range 40–50 THz are grouped together in the high-pressure phase relative to the low-pressure phases, as seen in figure 12(b).

Analysis of our results reveals that the O–H stretching vibration corresponds to the highest frequency mode in figure 12, while the O–H $\cdots$ O vibration corresponds to the second lowest frequency mode. Experimentally measured $\nu(\text{OH})$ and $\nu(\text{OH}\cdots\text{O})$ modes in NaHCO_3 and KHCO_3 are reported to be 2540 cm⁻¹ (76.2 THz), 240 cm⁻¹ (7.2 THz), 2630 cm⁻¹ (78.9 THz) and 234 cm⁻¹ (7.0 THz), respectively [71]. These data are close to the corresponding

Figure 10. The calculated phonon dynamic properties with LO–TO splitting of $\text{KHCO}_3 P\bar{1}$ phase at $P = 5.5$ GPa; (a) phonon dispersion curve; (b) phonon density of states.

Figure 11. The calculated phonon free energies including zero-point energies and entropies of MHCO_3 , $M = \text{Li, Na, K}$, as a function of temperature.

Figure 12. The calculated infrared absorption spectra of MHCO_3 , $M = \text{Li, Na, K}$.

results in figure 12 with corresponding values of 74.4, 6.8, 80.0, and 7.7 THz.

3.5. Thermodynamic stabilities of MHCO_3

As discussed previously, the low-temperature phase of KHCO_3 converts to the high-temperature phase having

Figure 13. The calculated free energy change for the low- and high-temperature phases of KHCO_3 having space groups $P121/a1$ (#14) and $C12/m1$ (#12), respectively.

fractional occupancy [57, 59, 60] above 318 K. We can obtain the free energy of the solid by combining the DFT energy with phonon free energy. Figure 13 shows the calculated Helmholtz free energy change (ΔA) of the two phases of KHCO_3 ($A(\#12) - A(\#14)$) as a function of temperature. We note that if we do not include the configurational entropy due to fractional occupancy no phase transition occurs, i.e., $\Delta A > 0$ for all T . A simple approximation for including the fractional occupancy configurational entropy is given by Kim and Sholl [72]. Assuming that all the H atom sites in the high-temperature phase are occupied gives a configurational entropy term of $k_B \ln(2.0)$, where k_B is the Boltzmann constant. Inclusion of this term in the difference of the free energy plot in figure 13 gives a phase transition at about 60 K, which is much lower than the experimental value of 318 K. One possible reason for the large discrepancy between our calculated phase transition temperature and the experimental value is that the energy differences are very small, less than 1 kJ mol^{-1} over the entire temperature range considered, whereas the calculated free energy changes of multi-phase reactions from DFT are not expected to give results more accurate than about 10 kJ mol^{-1} relative to the corresponding experimental data [20, 73]. Errors in the DFT energies are therefore likely to be at least partly responsible for the error in the predicted transition temperature.

Figure 14 shows the calculated equilibrium conditions for the reactions $\text{M}_2\text{CO}_3 + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g}) = 2\text{MHCO}_3$ as a function of temperature assuming ideal gas behavior of CO_2 and H_2O in the gas phase. The equilibrium constant $P_{\text{CO}_2} P_{\text{H}_2\text{O}} / P_0^2$ where P_0 is the reference pressure (1 bar), and P_{CO_2} , $P_{\text{H}_2\text{O}}$ are the partial pressures of CO_2 and H_2O , respectively. The plots in figure 14 indicate that above the curve the bicarbonate phase is thermodynamically favored, whereas below the curve the carbonate phase is favored. By way of example, at a value of $P_{\text{CO}_2} P_{\text{H}_2\text{O}} / P_0^2 = 1$ (dashed horizontal line in figure 14) our calculations predict that LiHCO_3 is favored below 195 K, while NaHCO_3 and KHCO_3 are stable below 405 K and 445 K, respectively. These latter

Figure 14. The equilibrium phase diagrams for the reactions $M_2CO_3 + H_2O(g) + CO_2 \rightleftharpoons MHCO_3$, where $M = Li, Na, K$, as computed from DFT with phonon contributions.

two values are close to the values of 415 and 435 K from HSC Chemistry database [34] calculations. We note that good agreement between DFT and HSC data is not generally the case for carbonates, as noted previously [3, 20], and this is also the case with these systems. The good agreement between HSC and DFT data for $NaHCO_3$ and $KHCO_3$ at $P_{CO_2}P_{H_2O}/P_0^2 = 1$ is fortuitous. The discrepancy can largely be traced to DFT errors in predicting the experimental heats of formation of the compounds [3, 20]. Figure 14 illustrates the utility of the bicarbonate/carbonate reaction for CO_2 capture, since the thermodynamic equilibrium point occurs at reasonable conditions of temperature and partial pressures of CO_2 and H_2O for both the Na and K systems.

Given that crystalline $LiHCO_3$ has not been experimentally observed [37], we have examined in more detail the conditions of temperature and partial pressures of CO_2 and H_2O under which one might expect to observe crystalline $LiHCO_3$ based on our DFT and phonon free energy calculations. In figure 15 we have plotted three stability curves for $LiHCO_3$ and Li_2CO_3 as a function of temperature and P_{CO_2} , each at different fixed values of P_{H_2O} . The values of P_{H_2O} are (from left to right) 10^{-4} , 10^{-3} , and 10^{-2} bar, while the vertical lines are the ice sublimation or boiling temperatures at each of those values of pressure. Hence, the required partial pressure of water will likely only be available above these temperatures on each of the curves. Thus, our calculations predict that $LiHCO_3$ should be observable at a temperature of 280 K when the pressure of CO_2 is above about 1000 bar and the pressure of water is at least 0.01 bar. The $LiHCO_3$ phase should also be stable at lower pressures of CO_2 , but only at lower temperatures. Figure 15 provides guidance on the experimental conditions to explore in order to synthesize and characterize $LiHCO_3$.

4. Summary and conclusions

We have presented the structural, electronic, phonon, and thermodynamic properties of $MHCO_3$ ($M = Li, Na, K$)

Figure 15. The $LiHCO_3$ – Li_2CO_3 phase diagram at different partial pressures of H_2O . The bicarbonate phase is thermodynamically favored above the curves (at higher partial pressures of CO_2). The values of P_{H_2O} are 10^{-4} , 10^{-3} , and 10^{-2} bar for the circles, squares, and triangles, respectively. The red dashed vertical line is the ice sublimation temperature at 10^{-4} bar. The green dotted vertical line is the ice sublimation temperature at 10^{-3} bar. The purple dashed vertical line is the water saturation temperature at 10^{-2} bar.

calculated from a combination of density functional theory and phonon dynamical calculations. The calculated bulk properties, including the bulk moduli, cohesive energies and optimized lattice constants, are in good agreement with the available experimental measurements and other theoretical findings.

We have predicted the ground state structure of $LiHCO_3$ through a combination of a crystallographic database search and the PEGS method. Surprisingly, the database search yielded a lower energy structure than the PEGS approach. We have computed the band structures of all solids and found that all systems investigated are insulators. The corresponding band gaps decrease when going from Li to Na to K. In $LiHCO_3$ and $NaHCO_3$, there are three main valence bands (VB_3 , VB_2 , VB_1). The lowest band (VB_3) is primarily formed by the s orbitals of O, C and H, while the orbitals of Li and Na do not contribute to VB_3 . The VB_2 band was mainly formed by p orbitals of Li and C with s orbitals of O and H, while the VB_1 bands were formed by interactions among all orbitals.

We have characterized different bond lengths found in the infinite chain structure of the hydrogen bonded HCO_3^- groups in $LiHCO_3$ and $NaHCO_3$. We have also studied the HCO_3^- dimer structures found in all phases of $KHCO_3$. The two types of hydrogen bonds in the $KHCO_3$ dimer could result in proton transfer from one CO_3 group to another CO_3 group by simultaneous barrier crossing and interchange of the $O \cdots H$ bonds within the dimer.

The infrared spectra for all the bicarbonates investigated in this study have been computed from density functional perturbation theory. We found reasonably good agreement with available experimental data. We also identified LO–TO splitting at the Γ symmetry points in all phases of $MHCO_3$.

The thermodynamic properties of the bicarbonates were computed from the lattice phonon dynamics. The phonon free energies (F_{PH}) follow the trend $F_{\text{PH}}(\text{LiHCO}_3) > F_{\text{PH}}(\text{NaHCO}_3) > F_{\text{PH}}(\text{KHCO}_3)$ and the calculated entropies (S) of MHCO_3 are ordered as $S(\text{KHCO}_3) > S(\text{NaHCO}_3) > S(\text{LiHCO}_3)$. Our calculated entropies and heat capacities are in good agreement with available experimental data.

We present the equilibrium phase diagrams for the family of reactions $\text{M}_2\text{CO}_3 + \text{H}_2\text{O}(\text{g}) + \text{CO}_2 = 2\text{MHCO}_3$ for $\text{M} = \text{Li}, \text{Na}, \text{and K}$ as a function of temperature. These data are useful for examining the suitability of these materials for CO_2 capture applications. We have also identified the thermodynamic conditions (partial pressures of CO_2 and H_2O and temperatures) where LiHCO_3 is expected to be thermodynamically favored relative to Li_2CO_3 , and could therefore be observed experimentally for the first time.

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