



First-principles study of anhydrite, polyhalite and carnallite



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ABSTRACT

We report density functional calculations of the structures and properties of anhydrite (CaSO_4), polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). Densities of states are systematically investigated and phonon analysis using density functional perturbation theory is performed at constant equilibrium volume for anhydrite and polyhalite in order to derive their isochoric thermal properties. Thermal properties at constant atmospheric pressure are also calculated using the quasi-harmonic approximation. The computed molar entropy and isobaric heat capacity for anhydrite reproduce experimental data up to 800 K to within 3% and 10%, respectively, while further experimental work is needed to assess our theoretical predictions for polyhalite.

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1. Introduction

Salt minerals are of importance in numerous fields of research and technology. Knowledge of the structure–properties relationship of salt minerals is crucial, for example, to gain a better understanding of natural evaporite deposits [1–3], nuclear waste disposal or gaseous/liquid hydrocarbons storage in geological repositories in salt formations [4], salt hydrate phase change materials for latent heat storage [5], or metal production using electrochemical methods [6].

Marine evaporites tend to form thick salt dome basins or bedded salts deposits. All evaporites are ionic salts containing the major ions Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , SO_4^{2-} , and CO_3^{2-} in varying proportions, along with structural water and other less common ionic constituents (e.g., Ba^{2+} , Sr^{2+} , Br^- , Li^+ , I^- and $\text{B}(\text{OH})_4^-$) with various degrees of coordination. Approximately eighty different salt minerals have been identified in evaporite deposits, although only a few are considered important rock formers [7,8]. The most representative salts in these chemogenic deposits can generally be divided among three major mineral classes: the carbonates (e.g., dolomite, calcite, magnesite), the sulfates (e.g., anhydrite, gypsum, kieserite, polyhalite), and the chlorides (e.g., halite, sylvite, carnallite, kainite, bischofite). Minerals precipitate from sea water in reverse order of their solubilities, carbonate minerals first, followed by sulfate minerals, and finally chloride minerals. Among these salts, anhydrite (CaSO_4) and the triple salt polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are inversely related, and the polyhalite disappearance coincides with the formation of the double salt carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) [3].

In this Letter, we report first-principles calculations of the structures and properties of anhydrite, polyhalite and carnallite using density functional theory (DFT). Details of our computational approach are given in the next section, followed by a discussion of our results for the crystal structures, electronic and thermodynamic properties.

2. Computational methods

Total-energy calculations were performed using DFT, as implemented in the Vienna *ab initio* simulation package (VASP) [9]. The exchange–correlation energy was calculated using the generalized gradient approximation (GGA), with the parameterization of Perdew, Burke, and Ernzerhof (PBE) [10]. The interaction between valence electrons and ionic cores was described by the projector augmented wave (PAW) method [11,12]. The $\text{Ca}(3p^6, 4s^2)$, $\text{Cl}(3s^2, 3p^5)$, $\text{K}(3p^6, 4s^1)$, $\text{Mg}(2p^6, 3s^2)$, $\text{O}(2s^2, 2p^4)$ and $\text{S}(3s^2, 3p^4)$ electrons were treated explicitly as valence electrons in the Kohn–Sham (KS) equations and the remaining core electrons together with the nuclei were represented by PAW pseudopotentials. The KS equation was solved using the blocked Davidson iterative matrix diagonalization scheme [13]. The plane-wave cutoff energy for the electronic wavefunctions was set to 500 eV, ensuring the total energy of the system to be converged to within 1 meV/atom. Unit cells were optimized with periodic boundary conditions applied. Ionic relaxation was carried out using the quasi-Newton method and the Hellmann–Feynman forces acting on atoms were calculated with a convergence tolerance set to 0.01 eV/Å. Structural optimizations and properties calculations were carried out using the Monkhorst–Pack special k -point scheme [14]. The following k -point meshes were used for integrations in the Brillouin zone (BZ) of bulk systems: $3 \times 5 \times 3$ for anhydrite, $3 \times 3 \times 3$ for

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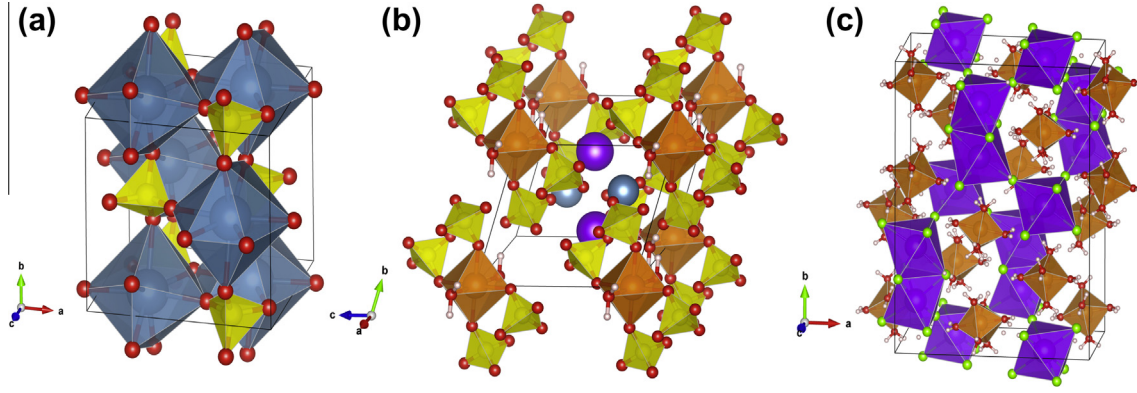


Figure 1. Crystal unit cells of (a) anhydrite (CaSO_4 ; Cmc , $Z = 4$), (b) polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; $P\bar{1}$, $Z = 1$) and (c) carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; $Pnma$, $Z = 12$) optimized at the GGA/PBE level of theory. Color legend: K, purple; Ca, blue; Mg, orange; O, red; Cl, green; H, white; S, yellow. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Crystallographic data calculated at the GGA/PBE level of theory (experimental data are given between parenthesis).

Name Sp. gp.	Anhydrite Cmc	Polyhalite $P\bar{1}$	Carnallite $Pnma$
Z	4	1	12
a (Å)	7.08 (6.993) ^a	7.09 (6.975) ^b	16.28 (16.119) ^c
b (Å)	7.09 (6.995) ^a	7.10 (6.984) ^b	22.83 (22.472) ^c
c (Å)	6.28 (6.245) ^a	8.96 (8.899) ^b	9.59 (9.551) ^c
α (°)	90 (90) ^a	103.9 (104.01) ^b	90 (90) ^c
β (°)	90 (90) ^a	100.6 (101.19) ^b	90 (90) ^c
γ (°)	90 (90) ^a	114.6 (114.10) ^b	90 (90) ^c
V (Å ³)	315.64 (305.481) ^a	377.14 (362.337) ^b	3564.13 (3459.622) ^c

^a Ref. [17].

^b Ref. [20].

^c Ref. [21].

polyhalite, and $2 \times 2 \times 3$ for carnallite. The tetrahedron method with Blöchl corrections was used for BZ integrations [15]. Ionic and cell relaxations of the bulk structures were performed simultaneously, without symmetry constraints.

Phonon calculations for anhydrite and polyhalite were carried out using density functional perturbation theory (DFPT) with VASP. Phonon analysis was performed at constant equilibrium volume in order to derive isochoric thermal properties. The Helmholtz free energy was calculated using the formula:

$$F = \frac{1}{2} \sum \hbar\omega + k_B T \sum \ln [1 - e^{-\beta\hbar\omega}], \quad (1)$$

where $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the temperature of the system and $\hbar\omega$ is the energy of a single phonon. The entropy was computed using the expression:

$$S = -k_B \sum \ln [1 - e^{-\beta\hbar\omega}] - \frac{1}{T} \sum \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}. \quad (2)$$

The heat capacity at constant equilibrium volume was calculated using the formula:

$$C_V = k_B \sum (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{[e^{\beta\hbar\omega} - 1]^2}. \quad (3)$$

Further analysis from a set of phonon calculations in the vicinity of each computed equilibrium crystal structure was carried out to

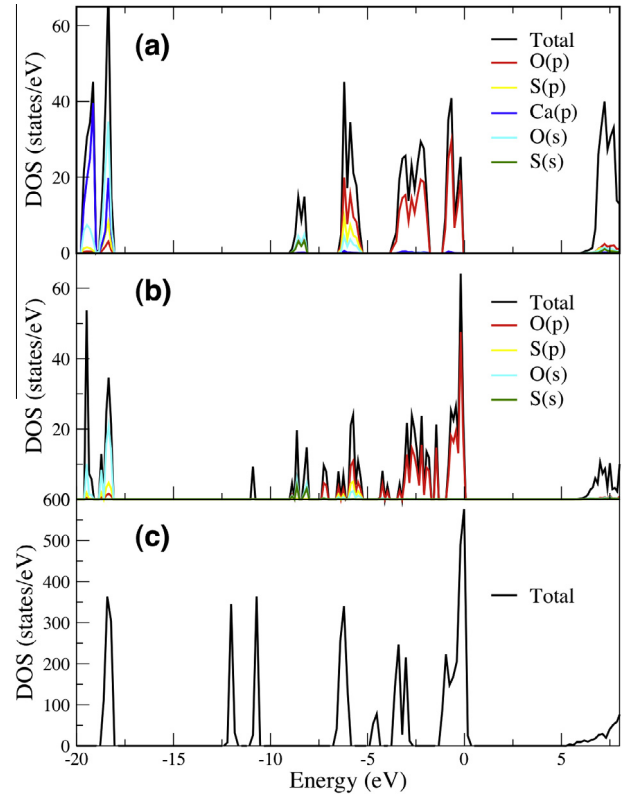


Figure 2. Total and partial densities of states (DOS), per unit cell, of (a) anhydrite, (b) polyhalite, and (c) carnallite, computed at the GGA/PBE level of theory. The Fermi energy is set to zero.

obtain thermal properties at standard pressure (1 bar) within the quasi-harmonic approximation (QHA). The QHA introduces a volume dependence of phonon frequencies as a part of anharmonic effect [16]. The Gibbs free energy is defined at a constant pressure by the transformation [16]:

$$G = \min_V [U(V) + F(T, V) + pV], \quad (4)$$

where \min_V [function of V] corresponds to a unique minimum of the expression between brackets with respect to the volume V , U is the total energy of the system, and p is the pressure applied. The isobaric heat capacity was also derived as follows:

$$C_P = -T \frac{\partial^2 G}{\partial T^2}. \quad (5)$$

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