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Ab initio-assisted assessment of the CaO-SiO₂ system under pressure

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ABSTRACT

We present the results of an *ab initio*-assisted assessment of melting and subsolidus phase relations in the system CaO-SiO₂ up to high pressure conditions. All solid compounds known to nucleate in the system have been treated as purely stoichiometric and the liquid resolved in the framework of a simple polymeric model. Mixing properties of the binary liquid phase are fully described by a single-parameter purely enthalpic chemical interaction plus a strain energy contribution. The latter is required to predict liquid immiscibility of SiO₂-rich liquid compositions at ambient conditions and becomes irrelevant at $P > 2$ GPa. A detailed survey of thermodynamic properties of silica polymorphs and calcium oxide and silicates in a broad range of P-T conditions reveals quite controversial stability relations and melting behavior. First-principles calculations on CaO and SiO₂ pure liquid components and solid phases (lime and stishovite) have been used, along with a sound assessment of first- and second-order phase transitions, to reconcile thermochemical data with topological details of the observed phase diagrams. A physically-consistent coupling between thermodynamic and thermoelastic properties (viz. compressibility and thermal expansion) turns out to be of fundamental importance to infer reliable stability relations both at subsolidus and melting conditions. Pressure effects shift the composition of the main invariant points in the CaO-SiO₂ system and also change the melting behavior of the CaSiO₃ metasilicate in a complex manner.

1. Introduction

The substantial improvements in computing capability and the development of accurate computational codes render nowadays feasible the investigation of periodic structures by *ab initio* all-electron approaches. The adoption of appropriate Gaussian expansions, coupled with hybrid functionals, ensures that the static energy of the investigated crystals at the variational state plus zero-point and thermal corrections returns extremely accurate values of the absolute thermodynamic magnitudes which can be rapidly converted to the conventional ones by standard procedures [1]. The effect of thermal energy is appropriately accounted for by vibrational calculations and the ensuing parameterization in terms of heat capacity is so precise that a $C_p=f(T)$ Shomate's function generated from *ab-initio* data can often be hardly recognizable from the best interpolant of calorimetric data of reference standard materials [2]. The mode-gamma analysis of the Hessian eigenvectors in the quasi-harmonic approximation is finally the main road toward an accurate account of the thermodynamic properties of any crystalline solid. All these procedures are nowadays routine. Concerning the substances that lack long-range periodicity, their *ab-initio* characterization is still at an embryonic stage, but the observation that silicate liquids may be treated as polarized continua in the

framework of Tomasi's Polarized Continuum Model [3] (and, as such, parameterized [4–6]) opens new perspectives toward a complete *ab initio* prediction of melting relations in chemically complex systems [7]. Having the various aggregation states of interest been resolved by first-principles, it follows that the magnitudes connected to the solid/liquid state transition acquire new emphasis in the attempt to reconcile theory with observations. We present hereafter a first attempt toward an *ab initio*-assisted assessment of melting relations and sub-solidus phase equilibria in the system CaO-SiO₂. This system is prototypical in many aspects because the two limiting components have quite contrasting extrinsic stability limits in the crystalline state. The most refractory one (CaO) has the same cubic structure (B1) up to very high pressure [8,9], while extensive polymorphism is exhibited by silica (at least eight polymorphs of SiO₂ exist if one considers 2nd order transitions and disregards those on which there is poor consensus) [10,11]. The two components form also an orthosilicate and a metasilicate (as many other binary systems with SiO₂ as component) and all phases may be treated as purely stoichiometric with reasonable accuracy. Because this system is of importance not only in Material Science but in the Earth Sciences as well, particular emphasis is devoted to the effects of pressure (P) as an intensive variable. Since few and, in some cases, controversial data exist on melting behavior

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Table 1

Thermodynamic properties of the pure liquid components in the CaO–SiO₂ system. $H_{f,298}^{\circ}$ = enthalpy of formation from the elements at $T_f=298.15$ K, $P_f=1$ bar; S_{298}° = standard state entropy ($T_f=298.15$ K, $P_f=1$ bar); C_p = isobaric heat capacity ($C_p = a + bT + cT^{-2} + dT^{-1/2} + eT^{-3} + fT^2 + gT^3 + hT^{-1}$). (1) this work; (2) Belmonte et al. [7].

Component	$H_{f,298}^{\circ}$ (J/mol)	S_{298}° (J/mol×K)	a	$b \times 10^3$	$c \times 10^{-5}$	d	$e \times 10^{-8}$	$f \times 10^6$	$g \times 10^9$	$h \times 10^{-4}$	Reference
CaO	−569918.0	56.0067	66.181	3.4509	14.209	−561.38	−3.6202	0.38087	−0.10247	0.26810	(1)
SiO ₂	−911746.2	33.887	88.455	−3.00137	−48.527	−114.33	7.2829	0.71332	0.0059239	0.0	(2)

and phase relations in the CaO–SiO₂ system, the main goals of this work are: (i) to assess a physically-consistent dataset of thermodynamic and thermophysical properties of liquid and solid phases in a broad range of P–T conditions; (ii) to define a theoretical framework (or, at least, some guidelines based on first principles) to properly combine thermodynamic with thermoelastic properties and account for first- and second-order (lambda) phase transitions; (iii) to compute relevant phase diagrams up to several tens of GigaPascals (GPa) and infer reliable stability relations both at subsolidus and melting conditions.

2. *Ab initio*-assisted thermodynamic modeling of pure solid and liquid phases

2.1. First-principles end-member properties

2.1.1. Liquid and glassy SiO₂

A computational investigation with *ab-initio* procedures of the structure-energy and vibrational properties of silica clusters in a dielectric continuum with dielectric constant $\epsilon=3.8$ has shown that an aggregate of D_{6h} network units and $[\text{SiO}_4]^{4-}$ monomers, locally ordered in the short-medium range and in a mutual arrangement lacking of spatial continuity in the glassy state, reproduces satisfactorily both the experimentally observed low-T isobaric heat capacity and the deviation from the Debye T^3 law [12]. At the glass transition (T_g) the rotational and translational components generate a heat capacity gap only partly counterbalanced by the loss of coherent motion of all atoms in the ensemble [12]. The computation of the vibrational, translational and rotational components of the macroscopic partition function of the liquid, by assuming negligible anharmonicity, returns appropriate isochoric heat capacity values (C_V) at all T conditions within the homogeneity range of the substance. The discrete values may be then retrieved in terms of a modified Shomate's equation within a given T range (here arbitrarily expanded from 298.15 to 5000 K, or to 7000 K for solid and liquid CaO), i.e. $C_V = a + bT + cT^{-2} + dT^{-1/2} + eT^{-3} + fT^2 + gT^3 + hT^{-1}$. Thermoelastic properties (i.e. isothermal bulk modulus, K_T ; volume thermal expansion coefficient, α_V ; and molar volume at discrete temperatures, V) are then required to calculate the anharmonic contribution to the heat capacity (i.e. $TV\alpha_V^2K_T$), hence the isobaric heat capacity ($C_P = C_V + TV\alpha_V^2K_T$). Thermoelastic properties of the pure SiO₂ liquid were optimized on the basis of the low- to high-pressure melting curve of the substance by Belmonte et al. [7], along the guidelines discussed in Ottonello et al. [13]. The substance was initially assumed to behave in a strictly harmonic way to reproduce the univariant curves experimentally observed at various P,T conditions. In the case of SiO₂, for instance, the liquidus was constrained to attain the melting point depicted by the experiments of Dalton and Presnall [14] at 5 GPa and to give melting temperatures roughly consistent with the experiments of Shen and Lazor [15] at higher pressures. Initial guess values of the standard state molar volume (i.e. fictive liquid at $T = 298.15$ K and $P = 1$ bar), bulk modulus at the athermal limit (K_0) along with its baric and thermal derivatives (K'_0 and dK/dT , respectively), thermal expansion coefficient (represented as a polynomial expansion on T, $\alpha_V = \alpha_0T + \alpha_1 + \alpha_2T^{-1} + \alpha_3T^{-2} + \alpha_4T^{-3}$) were necessary to this purpose. The anharmonic contribution generated by the inverse procedure was retrieved in terms of a , c , f , and g coefficients of the Shomate's equation and then added to C_V in order to obtain C_P .

Calculations were iteratively refined to attain univariant loci consistent with the experimental observations. In this work we refined again the thermophysical properties of the liquid silica on the basis of a new *ab initio*-assisted assessment of the thermodynamic properties of α -cristobalite, coupled with the effects of the α/β lambda transition (see Section 2.1.4.4 and Section 4.1). To achieve consistency with experiments over the entire P-range of interest (i.e. from 0 to 70 GPa) some thermophysical properties of liquid silica have been slightly changed with respect to our recent assessment [7]: the molar volume of the fictive liquid at standard state was lowered from 2.782 J/bar to 2.6 J/bar and the baric derivative of the bulk modulus was set to $K'_0 = 12.8$ (instead of 15.8). All the remaining thermodynamic and thermo-physical parameters necessary to depict the properties of the liquid are the same as Belmonte et al. [7] (Tables 1, 2).

2.1.2. Liquid CaO

As observed by Bajgain et al. [16] through first principles molecular dynamics (FPMD) calculations carried out in the framework of Density Functional Theory (DFT) with plane-waves and pseudo-potentials, liquid CaO undergoes progressive structural changes with varying T and P. At low pressure the analysis of the partial Radial Distribution Function (RDF) suggests a mean coordination number around 5 for Ca–O first neighbours. This value progressively rises to RDF = 8 with the increasing pressure. According to the same Authors [16] the isochoric heat capacity of liquid CaO at 3000 K is $C_V = 44.90 \pm 1.83$ J/(mol×K). Based on the listed thermo-physical parameters at the same temperature, the anharmonic correction is $TV\alpha_V^2K_T = 21.77 \pm 2.75$ J/(mol×K), which gives an isobaric heat capacity $C_P = 66.67 \pm 4.58$ J/(mol×K) if added to the isochoric value. This value is consistent, within error, with the NIST-JANAF estimates [17], which assign to liquid CaO a constant heat capacity of 62.76 J/(mol×K). The melting temperature at 1-bar pressure is quite controversial. As emphasized by Eriksson et al. [18], older literature agrees in locating the melting point of CaO at $T_f = 2868 \pm 35$ K [19]. This value is accepted by a number of thermodynamic assessments [18,20–23], although other assessments [24,25] adopted a higher melting point at 1-bar pressure according to different experimental results (i.e. $T_f = 3200 \pm 50$ K [26] and $T_f = 3172$ K [27]). A recent experimental investigation by Manara et al. [28] confirms this higher melting temperature of lime (i.e. $T_f = 3222 \pm 25$ K at 1-bar pressure). The only molecular dynamics simulation made so far on CaO [29] adopts $T_f = 3200$ K and suggests a marked increase of the melting temperature with pressure (see later). The solid-liquid transition is poorly constrained also from the energy point of view. In the NIST-JANAF tabulations [17] the entropy of fusion of lime is

Table 2

Thermophysical properties of the pure liquid components in the CaO–SiO₂ system. V_{298}° = standard state molar volume ($T_f = 298.15$ K, $P_f = 1$ bar); K_0 = bulk modulus at the athermal limit (i.e. $T = 0$ K; $P = 0$ GPa); $K'_0 = (dK/dP)_0$ = pressure derivative of the bulk modulus (assumed independent on T); $(dK/dT)_P$ = temperature derivative of the bulk modulus; α_V = volume thermal expansion coefficient ($\alpha_V = \alpha_0T + \alpha_1 + \alpha_2T^{-1}$).

Component	V_{298}° (cc/mol)	K_0 (GPa)	K'_0	$(dK/dT)_P$ (bar/K)	$\alpha_0 \times 10^7$ (K ^{−2})	$\alpha_1 \times 10^7$ (K ^{−1})	$\alpha_2 \times 10^3$
CaO	16.2	36	4.5	−45	0.0	1110	0.
SiO ₂	26.0	5.0	12.8	0.0	−0.3611	843.1	0.

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