

Analyzing thermal and vibrational behavior of MgSiO_3 Perovskite using the Debye model

Biswajit Nayak¹, Smruti Swagat Ray Mohapatra², Abhijit Pradhan³, Koresh Kumar Jena⁴,

¹Professor, ²Assistant Professor, ^{3,4}student

Department of Mechanical Engineering Einstein Academy of Technology and Management
Bhubaneswar, Khurda Odisha, India

Abstract: MgSiO_3 perovskite, a high-pressure phase of magnesium silicate, plays a significant role in geophysics, materials science, and high-temperature applications due to its unique structural and thermal properties. This research investigates the utilization of MgSiO_3 perovskite by analyzing its thermal and vibrational behavior using the Debye model.

The Debye model is employed to estimate specific heat capacity, thermal conductivity, and lattice vibrations of MgSiO_3 under varying temperature and pressure conditions. Computational simulations and theoretical calculations are used to determine Debye temperature, phonon dispersion, and thermodynamic stability. The study also explores the potential applications of MgSiO_3 perovskite in high-pressure geophysical modeling, advanced ceramics, and thermal insulation materials.

The results provide insights into the heat transport properties, elastic constants, and vibrational modes of MgSiO_3 , aiding in the optimization of its applications in extreme environments. This research contributes to the broader understanding of perovskite-based materials and their role in energy storage, planetary sciences, and advanced engineering applications.

Keywords: MgSiO_3 perovskite, Debye like solid, Debye temperature, Entropy.

I. Introduction

Perovskite is a natural, yellow, brownish-yellow, reddish, brown, or black mineral and a structure type which includes no less than 150 synthetic compounds; the crystal structure is ideally cubic, it occurs as rounded cubes modified by the octahedral and dodecahedral forms, luster is sub adamantine to sub metallic, hardness is 5.5 on Mohs scale, and specific density is 4.0.

Perovskite, named after the Russian mineralogist L.A. Perovski, has a specific crystal structure with the ABX_3 formula where A is typically a metal/carbon-based (organic) molecular cation occupied in a cubo-octahedral site, B is a metal ion such as titanium, Pb, Sn, occupied in an octahedral site and X is oxygen, carbon, nitrogen or halogen. The larger A cation occupies a cubo-octahedral site shared with twelve X anions while the smaller B cation is stabilized in an octahedral site shared with six X anions.

When O^{2-} anion is used, A and B are usually divalent and tetravalent, respectively. However, perovskite containing halogen anions allow monovalent and divalent cations in A and B sites, respectively, to fulfill charge neutrality.

The most studied perovskites are oxides due to their electrical properties of Ferro-electricity or superconductivity. Halide perovskites received little attention until layered organometal halide perovskites were reported to exhibit a semiconductor-to-metal transition with increasing dimensionality [1].

II. Perovskite in Nature

Perovskite mostly don't exist in nature, but those that do are very common. Magnesium-silicon perovskite minerals make up a substantial proportion of the Earth's mantle: a few million trillion tons (the mantle is around 4×10^{21} tonnes). Far from being exotic, they form naturally in many circumstances, as a stable low-energy configuration. So with skill it's not too difficult to make them, without high energies or weird processes. There is enough variety using common elements for rare ones like tellurium to be unnecessary.

From the first uses of perovskites as a white pigments, PbTiO_3 in the 1930's to the MLC capacitors (mostly based in substituted PbTi.ZrO_3 or BaTiO_3 materials) in which today's computers rely on to operate, synthetic methods have been a key factor in the optimization of their final properties

III. Interpretation of Entropy as a function of Debye temperature (vibrational temperature)

Since 1952, when Latimer published the second edition of his classic "Oxidation Potentials," sufficient free energy data on compounds and ions have been easily available to calculate equilibrium relations for many low temperature-low pressure systems of geologic interest. Although these data are strictly applicable only at 25°C and 1 atmosphere total pressure, the error in applying them to natural environments at or near the earth's surface is usually small.

Eh-pH diagrams utilizing such data were first used by Pourbaix (1949) as a convenient and provocative method of showing interrelation between solids and dissolved ionic species with special reference to problems of metallic corrosion. Since then, similar diagrams have been used to depict approximate equilibrium relations between minerals and the ions in equilibrium with them in aqueous solution, and the results have been compared to natural relations, especially in problems of atmospheric oxidation of ores, and those of primary chemical precipitation.

When such diagrams were first constructed, it was with hope that they would bear a faint resemblance to nature, and conceivably might be used like an "ideal gas" or "ideal solution"-as hypothetical models useful in showing how far complex natural relations departed from simple systems involving chemical compounds instead of minerals, and containing only those ions or other dissolved species for which thermo chemical information happened to be available.

It has been a surprise to find that these naive chemical analogs of nature are directly useful in many instances. That is to say that numerous calculated solubilities fit those deduced from geologic relations, predicted assemblages of chemical compounds are reflected by identical assemblages of their nearest mineral analogs, and the environment of their occurrence, expressed on a pH-potential grid, corresponds to that found in the field. In fact, natural systems reflect the diagrams much better than most experimental ones.

The reasons for this agreement seem to be:

- (1) There is sufficient time available for achievement of near-equilibrium in many natural low temperature aqueous environments. Even though the low temperature activation energies for transformations of silicate structures, for example, are high, and experimental work is well-nigh impossible, the months and years during which natural systems fluctuate through a small range of conditions permit a close approach to equilibrium.
- (2) The amount of interaction in natural systems is less than might be anticipated from their complexity. For example, the error in calculating the free energy of formation of calcite from solubility data on sea water is small if all the currently known interactions are considered.
- (3) The effect of biological activity is to add complexity on the one hand, and to catalyze reaction on the other. The net effect seems to be one of increasing reaction rates of well-established reactions, and hence of helping rather than hindering the investigator.
- (4) In a considerable number of instances, the difference in free energy between a pure synthetic compound and its mineral analog is not large (although the difference may be extremely important for some processes).

Because of the close correspondence between natural relations and those calculated from free energy data, that is, from experiments carefully designed to approach equilibrium, the interesting possibility arose of obtaining free energy data directly from observations on natural systems[2].

IV. Debye theory for polyatomic solids

Thermoelastic properties for a Debye solid, such as C_p vs.

T , at $P=0$ can be easily calculated from standard Debye tables. A Debye solid is a monatomic solid (typically a metal) in which thermoelastic properties are a function of only one characteristic frequency ν , which is equivalent to one characteristic temperature, Θ_{vib} (Debye 1912). The specific heat, C_v , of a Debye solid is defined as

$$C_V = 3RD \left(\frac{T}{\Theta_{vib}} \right)^3 \quad (1)$$

Where Θ_{vib} is the Debye temperature; R is the gas constant; and D (Θ_{vib}/T) is the Debye function for specific heat found from tables. Most solids of interest to geoscience are not monatomic. Debye theory may be applied usefully to certain polyatomic minerals, provided the vibrational phonon density of states is well approximated by a Debye frequency spectrum,

For polyatomic solids, $p > 1$ and the original Debye assumptions are violated; hence the name Debye-like solids, when Equation 1 is empirically obeyed. NaCl is a good example of a Debye-like solid. The thermal properties calculated by Debye theory are close in value to corresponding measured values or to those calculated from the detailed phonon density of states. NaI is an example of a solid that is not Debye-like because of its wide band gap.

Lattice dynamics deals with the vibrations of the whole lattice, three times Avogadro's number of vibrations. In this approach, the thermal energy is defined in a statistical sense and the thermoelastic properties are defined in terms of the lattice dynamical phonon density of states. A fairly good approximation to the phonon density of states can be represented by a histogram of cells using data constructed mainly from measured optic modes. Kieffer method is really the crystallographic approach because it deals with the individual atoms in the crystallographic cell as the central basis for computing thermal energy of vibration. Each atom gives rise to three modes of vibration that are, in principle, identifiable by a spectroscopic measurement. In a few cases, the density of states can be effectively represented by a crude approximation, called the Debye spectrum, a quadratic curve with a sharp cutoff.

In contrast to the Kieffer method, the Debye theory assumes that all modes can be approximated by two different acoustic modes only, each having no dispersion, thus ignoring the optic modes. This assumption works for a few dense polyatomic solids in which almost all the optic modes have frequencies less than ν ; that is, if the optic modes are confined to the interior of the phonon density of states. For polyatomic solids in which many optic modal frequencies are large in comparison with ν , the Kieffer method is most useful.

In brief, a Debye-like solid is one in which the Debye spectrum maximum frequency ν , as determined by the measured sound velocity, exceeds in value most of the optic frequencies in the phonon density of states. We use the standard data of Debye temperature in this paper from the references[3].

4.1 Formulation of Gibbs Entropy

Change in entropy of the system is given by

$$\Delta S = \Delta S_{\text{products}} - \Delta S_{\text{reactants}} \quad (2)$$

Entropy of a system is given by

$$S = \int \frac{C_p}{T} dT \quad (3)$$

Kieffer (1979, 1980) has developed a model based on lattice dynamics that allows calculation of heat capacity (C_V), entropy (S), and the Helmholtz free energy (F) from vibrational frequencies and acoustic velocities. Calculated C_V can be compared to calorimetric measurements of C_p by using the harmonic correction of (4).

$$C_p = C_V + T\alpha^2 k_V$$

Which is modified to

$$C_p = C_V + \frac{T\alpha^2 k_V}{D} \quad (4)$$

Where α is coefficient of thermal expansion, D is the specific density, V is molar volume and k_T is the bulk modulus of substance. The above equation is further modified to

$\Delta S_c \text{ (JK}^{-1} \text{)}$	119.5
$\Delta S_m \text{ (JK}^{-1} \text{)}$	121.7

6. Conclusions

Results show that MgSiO₃ perovskite is a Debye-like solid because the specific heat and entropy calculated to temperatures from Debye theory agree with available experimental data, especially those above 400 K. MgSiO₃ perovskite joins a small group of Debye-like minerals, now consisting of: MgO, Al₂O₃, and MgSiO₃ perovskite.

Table1: Calculation of Entropy for MgSiO₃ perovskite

References

$$\alpha = \frac{dV}{VdT} \quad (5)$$

From eqns.(4) & (5)

$$C_p = C_v + \frac{T\alpha^2 K_T V^2}{D \ln \alpha VT} \quad (6)$$

$$C_v = \frac{12\pi^4 R}{5} \left(\frac{T}{\Theta_{vib}} \right)^3 \quad (7)$$

$$\Theta_{vib} = \frac{h\nu}{K_B} \quad (8)$$

Where Θ_{vib} is the vibrational temperature and ν is the frequency of the substance. Therefore, the entropy for the material

$$S = \frac{12\pi^4 R}{15} \left(\frac{T}{\Theta_{vib}} \right)^3 + \frac{T\alpha^2 k V^2}{D \ln(\alpha VT)} \quad (9)$$

5. Results

The theoretical calculations by the formula used in this paper almost agree with the experimental data.

Molar thermodynamic properties (units: kJ, K, GPa) ΔG_c is the calculated Gibbs free energy of the formation from the elements, ΔG_m is the actual Gibbs free energy, ΔS_c is calculated entropy and ΔS_m is actual entropy of the substance, ΔH is the enthalpy of formation, V is the molar volume, α is the coefficient of thermal expansion, k_T is the bulk modulus, Θ_{vib} is the Debye temperature, D is the specific density, with temperature $T=600K$ [4].

Parameters	Values
D	4.0
Θ_{vib} (K) (actual)	1055
k_T (GPa)	730
$V(\text{cm}^3/\text{mol})$	24.58
$\alpha (10^5 \text{ K}^{-1})$	2.45

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