

REVIEW PAPER ON EQUATION OF STATE OF OLIVINE

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Abstract: To determine the equation of state for olivine is of great interest to study the physical state and the chemical composition of region of the earth's interior. Olivine is magnesium iron silicate and it is found in earth's subsurface. The composition of molecule Mg_2SiO_4 is 90% and molecule Fe_2SiO_4 is 10%. It is found in green color. Olivine has high crystallization temperature as compared to other minerals found in earth surface. It is first mineral to be altered by weathering. Its hardness is between 6.5 and 7.0, as compare to surrounding rocks, olivine is usually harder. Here the occurrence of olivine, its properties, its experimental as well as some theoretical status, about its application and also about its equation of state is discussed. Here elasticity of olivine and thermal expansion of the minerals is also discussed. Many scientifically research has been done, so here we talk about that research.

Index terms: olivine, equation of state, elasticity, thermal expansion, San Carlos olivine.

Introduction

The equation of state is described as the relationship between temperature, pressure and volume of a given substance or a mixture of substance. It's very useful to describe the state or properties of a mixture. The simplest equation of state is ideal gas law. In many fields of science ideal gas law is used extensively. To find the equation of state of a material or a substance so it can be determined by static diamond anvil cell and dynamic shock wave experiments at high pressure and a high temperature. The idea of equation of state of a material is one of the information which is essential for pressure calibration. So the main aim of present review is to find the equation of state of olivine.

Studying what is happening inside the earth is impossible task so to understand what is happening inside the earth's interior scientist must be creative. By many experiments scientists comes to know more about the earth's interior. One of the basic mineral that is found inside the earth's interior is olivine. Use of olivine is very vast.

Olivine is a major component that found in upper mantle and olivine is a magnesium iron silicate. Olivine is a common mineral that found in earth's surface. Olivine comes in a category of nesosilicate. The term olivine is also applied to a group of minerals with related crystalline structure. These include tephroite (manganese silicate), monticellite (calcium magnesium silicate) and kirschsteinite (calcium iron silicate).

General formula of olivine is $(\text{Mg, Fe})_{2}\text{SiO}_4$. Olivine is in orthorhombic structure. Olivine is green in color but it can also be found in yellow-green, greenish yellow or brown. As compare to the surrounding rocks olivine is usually harder. There are many people who are familiar with olivine because it is very famous gemstone and it is very famous in jewelry. Olivine as a game stone mostly mined at a San Carlos reservation in Arizona. Gemstone is also known as Peridot. Peridot is also a birthstone for the month of august. Olivine show poor cleavage property.

In earths surface most of the olivine found in dark colored igneous rock. As compared to other minerals olivine has high crystallization temperature. Sometime crystal of olivine found during metamorphism of dolomitic limestone. Olivine becomes an important mineral in earth's mantle. The ratio of magnesium to iron is varies between its two end members: forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). Melting temperature of forsterite is high about 1900 degree Celsius at atmospheric pressure while fayalite is low about 1200. Specific gravity of forsterite is 3.2 and fayalite is 4.3.

The refractive index of olivine is 1.64– 1.70 and has double refraction. Olivine is considered as an important mineral. Forsterite is used to clear the impurities from steel. Olivine is also used to make refractory brick. For basic refractories olivine is used as a raw material. Olivine has an excellent resistance against metals and slag penetration. Olivine is used as a gemstone. In metallurgical process also olivine is used. As olivine has high crystallization temperature so when magma is cooled crystal of olivine is formed, and after the formation it settles to the bottom of the chamber because of its high temperature.

Olivine found mostly in an oceanic crust [1]. Mainly olivine is a major component in most basic rocks and it is one of the widely distributed mineral in the earth's crust [2] [3]. In many parts of the world olivine rocks are found, but only two main types of rocks are exploited [4]. Dunite is such type of rock where 90% of the volume is made up of olivine [$(\text{Mg, Fe})\text{SiO}_4$]. Norway, which was considered to be 1.7 billion years old contain more than 90% olivine with about 50% MgO content [5]. 60% of the world's olivine production is produced by Norway (about 6.3 million tons per year) and it is the largest supplier of olivine. Olivine supplying countries are Spain (supplier Pasek Espana SA), Italy (supplier Nuova Cives SrL), Austria (supplier Magnolithe GmbH), Sweden, USA (supplier Olivine Corpn), Japan (supplier Toho Olivine Industrial Co Ltd) etc. In India [6] this mineral is found in Salem district of Karnataka and Keonjhar district of Orissa. In Norway olivine has the highest MgO and least iron content, which is most applicable for refractory purpose. In Norway olivine has a production of 3.3 million tons per annum. The component of MgO and SiO_2 of this olivine consists about 89-93 wt%, which tells that the mineral is highly pure. Whereas, in Indian olivine material has least MgO content and higher iron content. As olivine has the highest melting point, specific gravity and shows good hardness, such type of properties make olivine a good candidate for refractories industry.

Because of its advantageous properties olivine is used for variety of applications as given below:

1. As there is no free crystalline silica, so it is not hazardous to health and environment.
2. There is no polymorphic transformation.
3. As there is no tendency to hydration, so for storage no special attention is required.
4. It has good insulating characteristic and low heat conductivity.
5. Due to Low thermal expansion it results to thermal shock.
6. Due to high content of forsterite it has a high refractoriness.
7. For heat storage material high volume heat capacity is useful. It has High abrasion resistance. Its Specific gravity is from 3.26-3.4 and its bulk density is from 1.5-2.0 g.cm⁻³.
8. Its price is favorable.

As it is mentioned that olivine is low priced material and it competes with higher priced materials of same chemistry. The area of uses of olivine is very wide. Olivine used in many field. Most of the Metallurgical industries are the largest consumer of olivine products. Europe is considered as the major consumer of olivine products. As a slag conditioner olivine material is also used in iron and steel industries. For a blast furnace it is considered as a basic raw material [7] because there is the availability of oxides of magnesium, silicon and iron, which is essential for slag conditioning. There are some other reasons why steel industries prefer olivine and they are:

- (a) It has good sintering capacity and good product quality.
- (b) It also reduced energy consumption.
- (c) It can also reduce slag conditioner consumption as well as slag production.
- (d) It reduced the amount of fines and also reduces favourable environmental effects.

One of the major applications of olivine is moulding sand. It has the advantage of easy applicability and it can be recycled and reused without any type of difficulty. Olivine can produce clean surfaces and it required minimum finishing; and it is not a dangerous material. For the casting of manganese steel and non-ferrous metals it is most suitable. Olivine material is also used for making coatings [8]. In alloy steel manufacturing industries olivine- graphite coating and olivine- magnesite coating are very important.

To produce forsterite refractories olivine is considered as an excellent raw material as it can replace costly magnesite refractories in slag belt of the steel ladles, steel casting nozzles, soaking furnaces, etc [9]. As in the presence of higher amount of fayalite or FeO in olivine, it can reduce refractory properties and

olivine contain 12-15 wt% FeO which cannot be used for refractories. One of the major applications of Olivine is that it is used for the manufacturing of cordierite kiln furniture by the addition of clay to the system.

Due to hardness, sharp edged grains, high specific gravity (which increases its impact), conchoidal fracture and non-hazardous character olivine is considered as an important abrasive grit-blasting material. For the manufacture of fire retardant mineral wool and mineral wool insulating product olivine is utilized as a raw material. In Europe, olivine mineral wool is marked as "environmentally friendly mineral wool". For under water pipes and cables olivine sand is as ballast and covering material having high relative density, high hardness and favourable price make it is suited for such type of application.

For many applications olivine is considered as an important material besides hot metal and refractory industries. Its favourable conditions, particularly for the environmental and health issues, will give thrust for a wider use of olivine. On the hot metal industries olivine consumption is still depend, but new applications of olivine as well as increasing ecological considerations will also increase a demand of olivine products. Use of olivine is increasing day by day. It is a most suitable mineral that found in earth crust. Olivine is used as a larger production such as dolomitic and serpentine marble is mined in Myanmar and Pakistan. Beside all these advantage olivine has a bad impact on environment. As mining mineral olivine emit sulphur dioxide which cause an increase in global warming which greatly affect the environment.

Review of Literature

It is important to determine the thermodynamic properties of the common minerals in the Earth's interior for the better understanding of the composition and dynamics of the mantle [10][11][12]. For mantle minerals thermodynamic parameters like heat capacity and thermal expansion are both related to geodynamics and mineral physics, and controlling the Earth's internal evolution their values at high pressure are major factors [13]. Thermal expansion of the minerals depends on temperature and pressure, which can be arised from experimental measurements on volume [14]. By using calorimetric experiments heat capacity at ambient pressure can be obtained [15] [16] [17] and theoretical calculations [18] [19] [20].

The most often forms of solid equations of state used in geophysics are Murnaghan and Birch. The Murnaghan equation of state is come from the theory of finite strain, [21]. For a solid in a pressure range above 0.5K the theory of Murnaghan equation of state should not be applicable for this. Due to high pressure the use of Murnaghan equation of state lead to overestimate of density and seismic parameter [22]. For the use of the Murnaghan equation of state at high pressures Macdonald presented many other limitation he give conclusion from thermodynamics that the Murnaghan equation produces finite negative pressure due to which the density leads to a finite value which does don't gives an acceptable result [23][24]. For the olivine-transformed spinels Birch equation of state is used. By integrating a Taylor expansion of the bulk

modulus in pressure, the Murnaghan equation of state was found while Birch equation of state is totally based on the Taylor expansion of strain energy with respect to the Eulerian strain components

To derive the equation of state (EoS) Davis and Gordon introduced a numerical procedure [25]. In order to test the feasibility of mineral San Carlos olivine is used. San Carlos olivine is that is located in San Carlos, Arizona having Mg: Fe ratio of 9:1 [(Mg_{0.9}Fe_{0.1})₂SiO₄] [26]. Olivine is an important mineral of the upper mantle [27], and its thermodynamic properties is one of the most important themes in mineral science [28]. By using different experimental methods the sound velocities of San Carlos olivine have been investigated [29] [30] [31] [27] [32] [33]. The high temperature elastic moduli for Fe-bearing olivine was first reported by Isaak, which gives the various parameters as a function of temperature at ambient pressure [31]. Zhang and Bass determined the highest temperature and pressure range data which was used the Brillouin spectroscopy with CO₂ laser-heating and at 16.5 GPa at room temperature and 12.8 GPa at 1300K the sound velocity of San Carlos olivine is to be found. The elastic properties of the olivine provide useful information in a wide range of P–T conditions. By using stimulated laser scattering method to measured the room temperature volume of equation of state of San Carlos olivine at 17 GPa by and later, by using Brillouin spectroscopy to 30 GPa [29][34].

Shock wave experiments was carried out using a 54-mm one-stage and a 25-mm two –stage light gas gun. By the method of Brillouin scattering and X-ray diffraction under room temperature obtained ambient pressure adiabatic bulk modulus and pressure derivatives of San Carlos olivine [34]. In the elastic moduli of iron –bearing olivine there is no big difference given by the researchers in the literatures (129.4 GPa, 131.1 GPa, 130.3 GPa) [35] [31] [27]. By In situ synchrotron X-ray diffraction measurements, the thermal equation of state of olivine is obtained and the density of polycrystalline olivine at 873K is extended to 35GPa [27] [36].

For the elasticity of olivine there is abundant literature concerned.

1. First derivatives of P and S wave velocities with respect to pressure and temperature.
2. First pressure and temperature derivative of shear and bulk moduli.
3. Pressure and temperature derivatives of Poisson's ratio.

At room temperature and ambient pressure the densities of San Carlos olivine are given as 3353 kg m⁻³ and it was measured by using the Archimedes immersion technique [31]. Then it was reported that the density of San Carlos olivine is given as 3355 kg m⁻³ by using the buoyancy method, and this result is close to the 3360 kg m⁻³ [29]. Then the density is measured by using X-ray diffraction method and a value of 3343 kg m⁻³ is found [34]. At ambient pressure the heat capacity of San Carlos olivine was also given by Isaak it was determined by the end-member heat capacity data [16]. With increased in temperature Richet

presented a method to obtain the heat capacity of the silicate glass and the value is depended on the composition of the silicate glass [37].

In the rock forming minerals the accurate data of thermal expansion have a great importance in theoretical and experimental methods to clarify the equation of state of the earth's interior. Dilatometric method was used to measure the thermal expansion of olivine with a temperature range from room- level to 1000 degree celcius. Olivine from the calculated thermal expansion coefficients is given in a range of temperature from -250 to 1500 degree celcius which is based on the Gruneisen's theory of thermal expansion. The large single crystals of chrysolite and fayalite were measured by the dilatometric method [38] [39]. By X-ray powder method, lattice parameters of olivine were measured at high temperature [40]. The heat capacity data between 50 and 300K for olivine was 780K which was calculated from Debye temperature [41].

For investigating low- symmetry materials such as olivine single- crystal X- ray diffraction method is used. The olivine structure was measured by X- ray diffraction method to 48 GPA. The third- order Birch-Murnaghan equation of state gives the volume- pressure data at 48 GPA. The ambient- pressure adiabatic bulk modulus of olivine has been well described from ultrasonic, resonance, and Brillouin measurement and has a mean value of 128 GPA [42] [43]. The theoretical studies of olivine using density functional theory, values for the pressure derivative of the bulk modulus range from 4.0- 4.3[44] [45] [46]. Two new Raman bands were observed above 30 GPA in a non- hydrostatic Raman spectroscopy study at 50 GPA [47]. On a Fe- bearing olivine the additional non-hydrostatic powder X-ray is also compatible with the lattice parameter and unit-cell volume trends [48] [49]. For Mg- rich olivine it shows that the shock compression data of a mixed- phase region which indicate a high- pressure phase transition starting from about 50GPa[50].

In the olivine lattice result in a systematic decrease in the velocity of P and S waves for the iron substitution for magnesium [51]. An iron-rich olivine become more compact, iron increases the density but slightly reduces the bulk modulus of olivine. In olivine the velocity of the compressional and shear waves is a function of density and also of the Fe/ (Mg+Fe) ratio. The density of an olivine with a specific Fe/ (Mg+Fe) ratio is increase through a steady decrease in mean atomic volume. Olivine transforms into a spinel structure at a high pressure with an increase density of about 10% [52]. Successfully a fayalite was transformed into spinel sample and measured by the compressional velocity as a function of pressure to about 6 kb [53]. MgSiO spinel shows a 45% increase for the values of bulk modulus and Fe₂SiO₄- spinel shows a 60% increase from the respective bulk moduli in the olivine form. The bulk modulus and the volume per atom at zero pressure show a relationship for all solids. One can estimate its velocity knowing the end density of the spinel of given composition.

Conclusion

This review paper is based on equation of state of olivine. This paper also includes application of olivine as well as its properties. Many equation of state is discussed here like Birch Murnaghan etc. Here thermal expansion of the minerals and elasticity of olivine is also discussed. The information of elasticity contain (i) Wave velocities of P and S with respect to pressure and temperature, and their first derivatives (ii) The first pressure and temperature derivatives of shear and bulk moduli and (iii) The pressure and temperature derivatives of poisson's ratio. In a temperature range from 1 to 1000°C by dilatometric method thermal expansion of olivine is measured. With the help of perfect thermal expansion information, it provides a good judgement of elastic wave velocities and other physical constants, which are very useful in the learning of the equation of state of the interior of earth mantle. To calculate different parameters of San Carlos olivine numerical method is used, which was useful to liquid only. Molar volume, adiabatic bulk modulus, and shear modulus can be derived with sound velocities at high pressure from heat capacity and density at ambient pressure. For both temperature and pressure thermal expansion and heat capacity is its function, but with increasing in pressure it also proposed the variations in heat capacity.

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