Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 25(2015) 4080−4088
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

# Atomistic simulation of defected magnesium hydroxide as flame retardants

Dong-yun ZHANG[1,2,3], Ping YANG[1], Zheng DU[2], Qiu-hua YUAN[1], Shen-hua SONG[3], Xiang-zhong REN[1], Pei-xin ZHANG[1]

1. College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China;
2. National Supercomputing Center in Shenzhen, Shenzhen 518055, China;
3. School of Materials Science and Engineering, Harbin Institute of Technology Shenzhen Graduate School, Shenzhen 518055, China

Received 18 May 2015; accepted 12 October 2015

**Abstract:** The mechanical properties and the point defect energy of magnesium hydroxide ($Mg(OH)_2$) were studied using the molecular dynamics. Moreover, the microelectronic structure of $Mg(OH)_2$ with point defects in the bulk and on its surface were investigated using the first principles. The simulation results indicate that $Mg(OH)_2$ was easily modified by other cations because of its strong, favorable interstitial and substitution defects via point defect energy calculation. $Mg(OH)_2$ can provide high-efficiency flame retardancy because of the strong OH (OH Schottky defect) or H bond (H Frenkel defect and Schottky defect). The potential model of $Mg(OH)_2$ was established, and molecular dynamics simulation was used to investigate the relations between the crystal structure and the mechanical properties. $Mg(OH)_2$ with special morphology such as nano-sheets was a prior consideration to maintain the composite mechanical properties. The detailed electronic structures of $Mg(OH)_2$ with defects were determined. This work may provide theoretical guidance for choosing dopant element and reveal the element doping mechanism of $Mg(OH)_2$.
**Key words:** $Mg(OH)_2$; density functional theory; molecular dynamics; defects; electronic structure

## 1 Introduction

Magnesium hydroxide ($Mg(OH)_2$) is an important inorganic material that has many important industrial applications [1]. It is widely used in polymer materials as an environment-friendly additive-type flame retardant [2,3]. Flame retardants are additives that inhibit or resist the spread of fire when they are used in polymer products, such as plastics, rubber, fibers, woods, and textiles. Flame retardant technology is gaining increased attention because of the social requirements for safety in the use of polymer materials. $Mg(OH)_2$ is a non-halogenated flame retardant that shows excellent properties, such as suitability for plastics at higher processing temperatures, smoke suppression, no evolution of hazardous by-products, and fire-retarding properties [4]. There are a lot of researches showing that the morphology and size of $Mg(OH)_2$ can significantly influence the mechanical properties of doped polymer materials [5,6], and $Mg(OH)_2$ can be better applied in various flame retardants by purification, micronization, and surface modification [7−9].

Different particle sizes and shapes of $Mg(OH)_2$ can be synthesized by solvent molecules [10] or introducing cations with diverse valents [11], which results in defect formation. PANG et al [11,12] produced lamellar (nano-sheets), rose-like, and torispherical $Mg(OH)_2$ by introducing cations of varying valents ($Zn^{2+}$, $Al^{3+}$, and $Sn^{4+}$), and they proposed valence bonding to the cations as the differentiating mechanism. Defect problems are critical to modern solid science and technology. The formation of an interface defect is easy because of the large specific surface area and high surface energy of nano-$Mg(OH)_2$, which results in the decline of some polymer functions. Therefore, point defect is an important factor affecting many flame retardant properties, from phase stability to morphology to usage [13]. The existence of defects in condensed matter can be experimentally detected and measured by positron annihilation techniques, extended X-ray absorption fine-structure, X-ray absorption near-edge spectroscopy,

**Foundation item:** Projects (51174138, 20971088) supported by the National Natural Science Foundation of China; Project (JCYJ20130329102720840) supported by Shenzhen Government's Plan of Science and Technology, China
**Corresponding author:** Pei-xin ZHANG; Tel: +86-755-26733136; E-mail: pxzhang@szu.edu.cn
DOI: 10.1016/S1003-6326(15)64058-4

and neutron diffraction [14−17]. However, these techniques are not widely used because of their complexity process and comparatively high cost. Meanwhile, computations can contribute to the understanding of point defects [18−20]. To the best of our knowledge, the defects of $Mg(OH)_2$ have not yet been investigated from this perspective.

In the present work, the detailed microstructures of $Mg(OH)_2$ containing point defects both in the bulk and on its surface were determined using density functional theory. The crystal and electronic structures of $Mg(OH)_2$ with ions dopants were studied to provide theoretical direction to selecting the modified ions. Furthermore, molecular dynamics (MD) simulation was used to investigate the mechanical properties and the effects on defect energies of different defects [21,22]. The purpose was to provide technical guidance for modifying and using composite $Mg(OH)_2$, and provide methods and scientific basis for looking for other high-efficiency flame retardants. Moreover, a detailed study on the elastic constants of $Mg(OH)_2$ can provide important information for the mechanical performances of $Mg(OH)_2$ combined with polymer materials too.

## 2 Computational methods and theory

$Mg(OH)_2$ (trigonal, space group $P\bar{3}m1$, No. 164, $Z$=1) has a layered $CdI_2$-type structure. The layer structure has one layer of Mg and two layers of hydroxyl (OH) groups. The OH groups are bonded to three Mg cations (Fig. 1) [23].

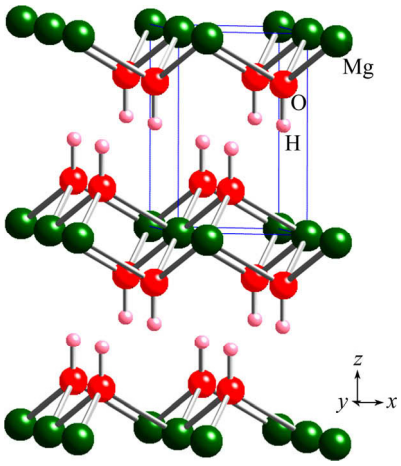


**Fig. 1** Structure of magnesium hydroxide (Big green ball represents Mg, medium red ball represents O, and small pink ball represents H)

### 2.1 Model with point defects using MD

All of these calculations were performed on supercomputers in National Supercomputing Center in Shenzhen. MD was used to investigate the point defects energies and the mechanic properties of $Mg(OH)_2$. The calculation used the Mott−Littleton method implemented in the General Utility Lattice Program (GULP) [24]. This method partitions the crystal lattice surrounding the defect into two spherical regions. In the inner sphere, the ions are strongly displaced by the defect; thus, the interactions are explicitly treated and the ions are allowed to relax completely. By contrast, the ions in the outer region are implicitly treated as a dielectric continuum. The obtained radii of the inner and outer spheres were 10 and 20 Å, i.e., regions I and II contained ~750 and ~5100 ions, respectively.

The interactions between ions in the crystalline $Mg(OH)_2$ compose long-range Coulombic and short-range interaction components. The interatomic potentials of O and H from 0 Å to 1.2 Å are expressed as Morse forms as Eq. (1):

$$V(r_{ij}) = D_e[(1-\exp(-a_0(r_{ij}-r_0)))^2 - 1] \quad (1)$$

where $r_{ij}$ is the distance between atoms $i$ and $j$, and $D_e$ (eV), $a_0$, and $r_0$ (Å) are the empirical parameters.

Other short-range interactions, including the interaction of O and H from 1.2 Å to 10.0 Å, are modeled using the Buckingham potential function given by Eq. (2):

$$V(r_{ij}) = A\exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C}{r^6} \quad (2)$$

where $A$ (eV), $\rho_{ij}$ (Å), and $C$ (eV·Å$^6$) are the empirical parameters. The interatomic potentials for $Mg^{2+}$, $H^+$, and $O^{2-}$ are fitted based on the study of GALE [25] on oxide materials (Table 1).

**Table 1** Parameters of general interatomic potentials for $Mg(OH)_2$

| Interaction | Potential | $D_e$/eV | $a_0$ | $r_0$/Å | Cutoffs range/Å | |
|---|---|---|---|---|---|---|
| | | | | | Min | Max |
| H—O | Morse | 5.539 | 2.3669 | 0.966 | 0 | 1.2 |

| Interaction | Potential | $A$/eV | $\rho_{ij}$/Å | $C$/(eV·Å$^6$) | Cutoffs range/Å | |
|---|---|---|---|---|---|---|
| | | | | | Min | Max |
| H—O | Buckingham | 616.71 | 0.25 | 0 | 1.2 | 10 |
| O—O | Buckingham | 22764.3 | 0.149 | 30.72 | 0 | 18 |
| Mg—O | Buckingham | 1862.9 | 0.2747 | 0 | 0 | 10 |
| Ca—O | Buckingham | 2100 | 0.302 | 0 | 0 | 10 |

The $Mg(OH)_2$ structure was optimized under constant pressure (0 Pa). The charges of O, H, and Mg were set to −1.59, 0.59 and 2.0, respectively, based on the atomic population analysis in the Mulliken area through first principles calculation. The unit-cell parameters and bond lengths obtained were compared with the experimental values and ab initio calculations in Table 2 and good agreement had been achieved. The