The structural, electronic and mechanical properties of $M_2O_2S$ (M=Y, La, Ce) by first-principles calculations

SUN Liang$^{a,b}$, GAO Yimin$^a$, LI Yefei$^a$, KATSUMI Yoshida$^b$, WANG Wen$^c$

a. State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University
b. Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Japan
c. State Key Laboratory of Water Resources and Hydropower Engineering Science, Wuhan University

P.R.CHINA&JAPAN
tottirocket@hotmail.com

Corresponding author: LI Yefei E-mail address:yefeili@126.com

Abstract: The structural, electronic and mechanical properties of $M_2O_2S$ (M=Y, La and Ce) are calculated by using first-principles calculations which based on density functional theory (DFT). All the calculation results are all well corresponding with other theoretical and experimental results. The structural and electronic results represent that strong covalent bonds are among three compounds while Ce$_2$O$_2$S got great metallic property because of the electron in 4f orbit of Ce. The calculated elastic constants of each oxysulfide indicate that they are all mechanically stable. The greatest bulk moduli is Y$_2$O$_2$S which also shows the highest compressibility among three RE sulfuroxides.

Key-Words: First-principles calculations; Electronic properties; DFT; Elastic behavior; Bonding; Stability;

1 Introduction

In recent decades, it plays a special role in steelmaking using scrap steel as the main raw material for making steel which seems more environmental and renewable resources. However, it is inevitable that the contents of oxide and sulfide in the recycled steel might become higher than the original steel which always gathers on the grain boundary in the conventional process of steelmaking. The impurity elements tend to make the steel products deterioration. Therefore, there are lots of research works mainly on the removal mechanism of the oxide and sulfide impurities in steel.

The high chemical activity of rare-earth metals (REM) and their affinity for oxygen and sulfur are responsible for deeply removing oxide and sulfide impurities, thereafter reducing their segregation at grain boundaries [1]. It is also generally accepted [2] that the pitting corrosion of steel is always aroused by all types of inclusions, especially as the belonged MnS inclusions which can be replaced by small spherical RE sulfides or RE oxysulfides.

There are several researchers used DFT method to learn the electronic and mechanical properties of several RE oxides and oxysulfides. Pere Alemany etc [3] have learnt the lattice constants and bulk modulus B of La$_2$O$_2$S and Y$_2$O$_2$S by using both LDA and GGA methods and found the results are in good agreement with the earlier published papers using similar computational approaches. And Masayoshi Mikami etc [4] also used first-principles methods to learn the electronic structure of yttrium oxysulfide (Y$_2$O$_2$S) and found that it has an indirect band gap and the top of the valence bands shows anisotropic character which means anisotropic mass of the hole.

However, there are no theoretical or experimental findings on the electronic properties and mechanical properties of series of RE (Y, La, Ce) oxysulfides. The purpose of this paper is to present the results of our theoretical investigation of the M$_2$O$_2$S (M=Y, La, Ce), and to give discussions to relate the experimentally known facts to our results.

2 Calculation Models and Methods.

The crystal structures of M$_2$O$_2$S are shown in Fig. 1. It can be seen that M (Cerium, Yttrium, and Lanthanum) atoms are in capped trigonal antiprismatic coordination of four O atoms and three S atoms. The crystal structure consists of two-dimensional [M-O] layer stacked perpendicular to
the [001] direction [5] which will show great lubricating properties for their lay-like structure.

Fig.1. Crystal structures of M$_2$O$_2$S (M= Y, La and Ce).

Our calculations were carried out by using first-principles method based on density functional theory (DFT), which implemented in CASTEP code [6-8]. The ultrasoft pseudo potentials were employed to represent the interactions between ionic core and valence electrons and the valence electrons of Y, La, Ce, S, and O are: 4d$^5$5s$^2$, 5s$^2$5p$^5$5d$^5$6s$^2$, 4f$^5$5s$^2$5p$^5$5d$^5$6s$^2$, 2s$^3$p$^3$, 2s$^2$p$^4$, respectively. A special k-point sampling method was applied to the integration by setting as 14×14×7 for M$_2$O$_2$S with Monkhorst-Pack scheme in the first irreducible Brillouinzone [9].

Generalized gradient approximation (GGA) of PBE approach was used for exchange-correlation energy calculations [10]. A kinetic energy cut-off value of 410eV was used for plane wave expansions. The total energy changes during the optimization finally converged to less than 5×10$^{-7}$ eV and the forces per atom were reduced to 0.01eV/Å. The Broyden-Fletcher-Goldfarb-Shannon (BFGS) algorithm was applied to relax the whole structure to reach the ground state where both cell parameters and fractional coordinates of atoms were optimized simultaneously. All calculations were performed with the non-spin polarized density functional theory. For the reason that the magnetic states of these three compounds were considered to be paramagnetic and such postulate will only affect their properties slightly.

3 Results and discussions

3.1 Electronic structures

The rare earth sulfuroxides’ lattice parameters involved in the calculation are given in Table 1. It can be seen from the calculated lattice parameters of the M$_2$O$_2$S compounds are in a good agreement with other available experimental results from ICSD.

The TDOS and PDOS maps are shown in (Fig. 2) respectively and the result of electronic structure of three compounds will be discussed blow. It is illustrated that the d-states of RE (M=Y, La and Ce) atoms are not only overlapped with p-states of O atoms near Fermi level but also overlapped with p-states of S atoms can be explained as p-d hybridization both between RE-O atoms and RE-S atoms, individually.

Table 1 Lattice parameters (a, b, c, in Å) of M$_2$O$_2$S (M=Y, La and Ce)

<table>
<thead>
<tr>
<th>Species</th>
<th>Space group</th>
<th>Method</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_2$O$_2$S</td>
<td>P3M1</td>
<td>GGA-PBE</td>
<td>3.96(3.79)$^a$</td>
</tr>
<tr>
<td>La2O2S</td>
<td>P3M1</td>
<td>GGA-PBE</td>
<td>4.12(4.05)$^b$</td>
</tr>
<tr>
<td>Ce2O2S</td>
<td>P3M1</td>
<td>GGA-PBE</td>
<td>4.06(4.01)$^c$</td>
</tr>
</tbody>
</table>

Thus, there are some degree of covalence between the RE atoms and the anions atoms. However, the center gravity of RE p-states does not completely coincide with the S d-states, which, in some extent also indicates the ionic bonding in these compounds. The valley in DOS maps around the Fermi level is the pseudo gap and the DOS of these compounds below Fermi level is mainly due to the p and s states of the anions atoms. Moreover, the metallic aspect of the compounds can be attributed to the partially filled Y-4d state, 5d state of La and Ce, respectively. Especially, it can be seen that the partially filled f-state of the Ce atoms were coincided with Fermi level which indicated strong metallic property.

![Fig 2: The total density of states (TDOS) of M$_2$O$_2$S and Partial density of states (PDOS) of Y, La, Ce, S, O atoms.](image)

The black line represents the position of the Fermi surface.

Furthermore, it is generally accepted that more information on chemical bonding will be provided by population analysis results and Bond population analysis results in Table 2 and Table 3 below.
The electrons transferring in the bands of the compounds can be very clearly seen from Table 2. After defined the other two parameters to characterize the chemical bonds in these borides, the average bond length and the average overlap population will be easier to calculate from Eq. (1) and (2) below.

\[
\bar{L}(AB) = \frac{\sum L_i N_i}{\sum N_i} \quad (1)
\]

\[
\bar{n}(AB) = \frac{\sum n_i N_i}{\sum N_i} \quad (2)
\]

Here, \( \bar{L}(AB) \) and \( \bar{n}(AB) \) represent the average bond length and mean bond population, respectively; \( N_i \) is the total number of \( i \) bond in the cell and \( L_i \) is the bond length of \( i \) type and the results are discussed in Table 3.

Table 2 population analysis results of three compounds

<table>
<thead>
<tr>
<th>Species</th>
<th>Ion</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>f</th>
<th>total charges</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(2)</td>
<td></td>
<td>1.88</td>
<td>4.82</td>
<td>0</td>
<td>0</td>
<td>6.7</td>
</tr>
<tr>
<td>Y2O2S</td>
<td>S</td>
<td>1.86</td>
<td>4.83</td>
<td>0</td>
<td>0</td>
<td>6.69</td>
</tr>
<tr>
<td>Y(2)</td>
<td></td>
<td>0.28</td>
<td>0.17</td>
<td>1.5</td>
<td>0</td>
<td>1.95</td>
</tr>
<tr>
<td>O(2)</td>
<td></td>
<td>1.87</td>
<td>4.92</td>
<td>0</td>
<td>0</td>
<td>6.79</td>
</tr>
<tr>
<td>La2O2S</td>
<td>S</td>
<td>1.84</td>
<td>4.84</td>
<td>0</td>
<td>0</td>
<td>6.68</td>
</tr>
<tr>
<td>La(2)</td>
<td></td>
<td>2.25</td>
<td>6.27</td>
<td>1.35</td>
<td>0</td>
<td>9.87</td>
</tr>
<tr>
<td>O(2)</td>
<td></td>
<td>1.86</td>
<td>4.84</td>
<td>0</td>
<td>0</td>
<td>6.7</td>
</tr>
<tr>
<td>Ce2O2S</td>
<td>S</td>
<td>1.83</td>
<td>4.73</td>
<td>0</td>
<td>0</td>
<td>6.56</td>
</tr>
<tr>
<td>Ce(2)</td>
<td></td>
<td>2.23</td>
<td>6.21</td>
<td>1.42</td>
<td>1.16</td>
<td>11.02</td>
</tr>
</tbody>
</table>

Hexagonal structural compounds can be shown illustrated in table 4.

Table 3 Bond population analysis results of three compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bond</th>
<th>Electrons</th>
<th>Length(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y2O2S</td>
<td>Y-O</td>
<td>0.64</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>O-O</td>
<td>-0.09</td>
<td>2.92</td>
</tr>
<tr>
<td></td>
<td>Y-S</td>
<td>0.75</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>La-O</td>
<td>0.89</td>
<td>2.47</td>
</tr>
<tr>
<td>La2O2S</td>
<td>O-O</td>
<td>-0.07</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>La-S</td>
<td>0</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td>Ce-O</td>
<td>0.46</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td>Ce-S</td>
<td>0.63</td>
<td>2.99</td>
</tr>
<tr>
<td>Ce2O2S</td>
<td>O-O</td>
<td>-0.07</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>Ce-S</td>
<td>0.63</td>
<td>2.99</td>
</tr>
</tbody>
</table>

According to Born-Huang’s lattice dynamic theory, the mechanical stability criterions of hexagonal structural compounds can be shown below:

\[ C_{11} > 0, C_{44} > 0, (C_{11} - 2C_{44}) > 0, (C_{11} + C_{22})C_{33} > 3C_2 \]

The calculated elastic constants of each rear oxysulfide in Table 4 are all well satisfied the above corresponding criterion, indicating that three compounds are all mechanically stable. It can clearly be seen that the calculated \( C_{11} \) and \( C_{33} \) are larger than other elastic constants which certainly means that the compounds are very incompressible under uniaxial stress along x (\( \varepsilon_{11} \)) or z (\( \varepsilon_{33} \)) axis.

The reason is \( C_{11} \), \( C_{22} \) and \( C_{33} \) are the tensile strength along [100], [010], and [001] directions, respectively. Thus, among three compounds, because \( Y_2O_2S \) has the largest \( C_{11} \), it can be hardly tensile along [100] direction while along [001] direction, \( Ce_2O_2S \) is difficult to compress.
The other mechanical properties can be simulated by using Voigt-Ruess-Hill approximation [11] for elastic moduli. In this method, the bulk and shear moduli can be calculated by arithmetic average of Voigt and Reuss approximations. It is well known that Voigt-Ruess-Hill approach is the directional averages for all possible crystal orientations and generally used for characterizing the mechanical properties of bulk polycrystalline materials.

\[
\begin{align*}
B_{VRH} &= \frac{1}{2}(B_V + B_R) \\
G_{VRH} &= \frac{1}{2}(G_V + G_R)
\end{align*}
\] (3)

In equation (3), \( B \) and \( G \) are bulk and shear moduli, while \( V \) and \( R \) represents Voigt and Reuss approximations, individually. In the Voigt approximation, \( B_V \) and \( G_V \) are calculated from elastic constant matrix by the Eqs. (4).

\[
\begin{align*}
B_V &= \frac{1}{2}(2C_{11} + C_{12} + C_{13} + 4C_{44}) \\
C_V &= \frac{1}{30}(M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66}) \\
C &= C^2 / M \times G_k = \frac{15}{[(18B_c / C)^2 + (6/C_{11} - C_{12}) + (6/C_{44}) + (3/C_{66})]} \\
M &= C_{11} + C_{12} + 2C_{13} - 4C_{44}, C_c = (C_{11} + C_{12})C_{13} - 2C_{44}
\end{align*}
\] (4)

The main advantage of this method is because the bulk modulus (\( B_{VRH} \)), shear modulus (\( G_{VRH} \)) for polycrystalline crystal can be estimated within Voigt-Reuss-Hill methods [11] after evaluating the elastic constants; then the Young’s modulus and Poisson’s ratio can also be calculated as follows [12]:

\[
E = \frac{9B_{VRH}G_{VRH}}{3B_{VRH} + G_{VRH}}
\] (5)

\[
\nu = \frac{3B_{VRH} - 2G_{VRH}}{2(3B_{VRH} + G_{VRH})}
\] (6)

The bulk modulus (\( B \)), shear modulus (\( G \)), Young’s modulus (\( E \)) and Poisson’s ratio of \( M_2O_2S \) (\( M = Y, \ La, \ Ce \)) can be calculated by using the Voigt-Reuss-Hill approximations and the results are shown in Table 5 and Fig. 2 shows the variations of elastic parameters of three compounds.

Table 5 Elastic constants (B, G, E and Poisson’s ratio) of three compounds (in GPa)

<table>
<thead>
<tr>
<th>Spaces</th>
<th>Method</th>
<th>B</th>
<th>G</th>
<th>B/G</th>
<th>E</th>
<th>( \nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(_2)O(_2)S</td>
<td>Calculated</td>
<td>119.4</td>
<td>54.9</td>
<td>2.17</td>
<td>134</td>
<td>0.31</td>
</tr>
<tr>
<td>La(_2)O(_2)S</td>
<td>Calculated</td>
<td>99.61</td>
<td>50.3</td>
<td>1.98</td>
<td>113</td>
<td>0.31</td>
</tr>
<tr>
<td>Ce(_2)O(_2)S</td>
<td>Calculated</td>
<td>109.3</td>
<td>66.3</td>
<td>1.65</td>
<td>170</td>
<td>0.27</td>
</tr>
</tbody>
</table>

From Table 5 and Fig. 2 above, the calculated bulk modulus of \( Y_2O_2S \) is 119.4 Gpa which is the highest one comparing with the other compounds and is close to the value (118 Gpa) got by Pere Alemany [3]. The reason is according to the strong covalent bond in \( Y_2O_2S \). While the \( Ce_2O_2S \)’s \( G \) and \( E \) modulus is the maximum which comparatively leads to a similar tendency with \( C_{44} \) constant. This tendency can be discovered basically due to its strong covalent bond and metallic bond. The Poisson’s ratios (\( \nu \)) of all compounds are all around 1/3 which illustrates metallic property of this kind of materials.

Moreover, there is a semi-empirical theory that \( B/G \) can be a principle to predict the ductillity of the compound. It is indicated that for the brittle compound, \( B/G \) is smaller than 1.75 (for diamond \( B/G=0.8 \)) and for metallic compound \( B/G \) is greater than 1.75 (for Al \( B/G=2.74 \)). In our case, the calculated results clearly illustrated that \( Y_2O_2S \) (2.17) and \( La_2O_2S \) (1.98) indicating their ductile nature rather than the value of \( B/G \) of \( Ce_2O_2S \) is 1.65 which indicating is brittle property. This result is a well illustration of the strong covalent bond of \( Y_2O_2S \) and \( La_2O_2S \) while the metallic bond of \( Ce_2O_2S \).

The last part is to discuss the compressibility of these three compounds (\( Y_2O_2S, \ La_2O_2S, \ Ce_2O_2S \) by fitting the total-energy (\( E \)) as function of cell volume (\( V \)) using Birch-Murnaghan equation of state[13,14]. The calculation results are shown in Fig. 3.
Fig 3 the compressibility of three RE oxysulfides comparing with several other harden materials. Meanwhile, the statistics of diamond, Cr₂C₃ and α-Al₂O₃ are also shown for comparison. The hardest material (diamond) always situated in the upper part of the figure for its highest compressibility rather than Cr₂C₃ and α-Al₂O₃. And Y₂O₂S shows the highest compressibility among three compounds. This kind of compounds show several advantages, such as high hardness, advanced wear resistance and chemical stability.

4 Conclusion

By conclusion, we investigated the structural, electronic and mechanical properties of M₂O₂S (M=Y, La and Ce) by using first-principles calculations based on density functional theory (DFT). There are some summaries below:

1. The crystal structure of three compounds are all hexagonal which consists of two-dimensional [M-O] layer stacked perpendicular to the [001] direction which shows great lubricating properties for their lay-like structure.

2. There are strong covalent bonds among all three compounds between RE atoms and O atoms and C₂O₂S which shows strong metallic property because of the electron in 4f orbit.

3. The calculated elastic constants of each oxysulfide indicating that they are all mechanically stable and the highest bulk moduli is Y₂O₂S which also shows the highest compressibility among three RE sulfuroxides.

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