Non-empirical study on pressure dependence of ruby bond length

M Novita1,*, N Cholifah2 and K Ogasawara3

1Faculty of Engineering and Informatics, Universitas PGRI Semarang, Jl. Sidoandri-Timur No.24 Semarang, Central Java 50232, Indonesia
2Lembaga Penelitian dan Pengabdian Kepada Masyarakat, Universitas PGRI Semarang, Jl. Sidoandri-Timur No.24 Semarang, Central Java 50232, Indonesia
3School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen Sanda, Hyogo 669-1337 Japan

*novita@upgris.ac.id

Abstract. Due to its potential application in luminescence technologies, the complete understanding on pressure dependence of ruby is especially important. Up to recently, the theoretical prediction on the structural properties of ruby under pressure has been made involving the empirical parameters. Therefore, here we performed a non-empirical study on the pressure dependence of ruby bond length. Due to the Ca substitution and the applied external pressure, the local structure of α-Al2O3: Cr3+ was changed. We estimated this effect by performing the first-principles band-structure calculations using Cambridge Serial Total Energy Package (CASTEP) method and compared with the Shannon’s crystal radii method. The two different bond lengths; Cr-1st nearest neighbour oxygen (d1) and Cr-2nd nearest neighbour oxygen (d2) were investigated in detail. The results show that under 0-110 GPa the d1 and d2 decreased ca. 0.172 and 0.145 Å, respectively. These results were slightly smaller than the d1 and d2 decreases in the case of pure α-Al2O3 crystal, they were observed to be ca. 0.167 Å for d1 and 0.177 Å for d2. In the other words, the d1-d2 differences were larger at the higher pressure, ca. 0.052-0.080 Å for 0-110 GPa.

1. Introduction

Ruby (α-Al2O3: Cr3+) is a beautiful red gemstone and known as the first solid-state laser ever invented. The alumina (α-Al2O3) itself has been widely used as pressure calibrant in high-pressure experiment. Many researchers have been investigating the structural, optical, electronics properties of alumina under pressure [1,2]. On the other hand, ruby has been utilized for secondary pressure standard in the diamond-anvil cell (DAC) experiments and called as "ruby pressure scale". The first DAC was hand-held size made by Charles E Weir and his group. However, the first-DAC has no precise method for determining on how much the pressure being exerted on the sample. Thanks to the strong and red shifted R-line energy (2E→ 4A2) under pressure [3-6], DAC was refined utilizing a very small amount of ruby crystal (ca. 1%) as the internal pressure sensor. Now it became de facto standard for measuring pressure in a DAC.

The reports on the structural and optical properties of ruby under pressure have also been made by several authors both experimentally and theoretically [3-9]. However, the theoretical prediction on the
structural and optical properties of ruby under pressure reported up to recently involves empirical parameters. Therefore, here we performed an investigation on the ruby bond length under pressure without referring to any experimental parameter. The lattice-relaxation effects due to the Cr$^{3+}$ substitution in the Al$^{3+}$ site and due to the applied pressure were studied thoroughly.

2. Methods

![Figure 1. α-Al$_2$O$_3$: Cr$^{3+}$ model cluster consisting of one Cr$^{3+}$ surrounded by six O$^{2-}$ (CrO$_6^{9-}$). The bond length between Al -1$^{st}$ nearest neighbour oxygen ($d_1$) is 1.855 Å while the bond length between Al - 2$^{nd}$ nearest neighbour oxygen ($d_2$) is 1.971 Å [10].](image)

Figure 1 shows the illustration of α-Al$_2$O$_3$: Cr$^{3+}$ model cluster consisting of one Cr$^{3+}$ surrounded by six O$^{2-}$. There are two different bond lengths; Al - 1$^{st}$ nearest neighbour oxygen ($d_1$), and Al - 2$^{nd}$ nearest neighbour oxygen ($d_2$). As reported by Sawada et al., the pure α-Al$_2$O$_3$ crystal at 0 pressure has $d_1 = 1.855$ Å and $d_2 = 1.971$ Å [10]. Since the local structure of α-Al$_2$O$_3$ changed not only due to the Cr$^{3+}$ substitution but also due to the applied external pressure, the investigation on the lattice-relaxation effect is very important. Therefore, in this work we estimated the lattice relaxation effect using two different methods.

2.1. Cambridge Serial Total Energy Package (CASTEP) method

The first-principles band-structure calculations were carried out using Cambridge Serial Total Energy Package (CASTEP) code [11-13] in Material Studio 6.0. The Vanderbilt [14] ultrasoft pseudopotentials were used. The exchange-correlation potential was taken into account within the Generalized Gradient Approximation (GGA) proposed by Perdew, Burke, and Ernzerhof (PBE) [15]. The GGA-PBE exchange-correlation potential has been known for its general applicability and gives rather accurate results for a wide range of systems. In the first step, the structural optimizations on the pure α-Al$_2$O$_3$ crystal were carried out. The procedure employed here is similar with those used in Ref. 16. Here the calculations of the physical forces on the ion and the integrated stress on the unit cell were performed using the Hellmann-Feynman Theorem. We applied the external pressure from 0 to 110 GPa into the optimized α-Al$_2$O$_3$ crystal obtained in the structural optimization step. Next, one Cr$^{3+}$ ion was substituted in the Al$^{3+}$ site for each optimized α-Al$_2$O$_3$ crystal under pressure which then followed by the geometry optimization step. We obtained the lattice-relaxation ratio of α-Al$_2$O$_3$: Cr$^{3+}$ under 0-110 GPa for $d_1$ and $d_2$ ca. 104.71-108.86% and 100.92-102.77%, respectively.
2.2. Shannon’s crystal radii method

Shannon’s crystal radii method is one of the simplest approaches to estimate the lattice relaxation effect [17,18]. We have reported some studies employing this method for oxide and fluoride materials [19-22]. The estimated bond length can be calculated by equation (1).

\[
d(\text{Cr} - \text{O})_{\text{relaxed}} = \frac{S(\text{Cr}^{3+}) + S(\text{O}^{2-})}{S(\text{Al}^{3+}) + S(\text{O}^{2-})} \times d(\text{Al} - \text{O})_{\text{unrelaxed}}
\]  

(1)

The Cr-O relaxed bond length can be estimated by using the ratio of Cr-O and Al-O Shannon’s crystal radii multiplies with the Al-O unrelaxed bond length. Since Cr\(^{3+}\) has six coordination number \((S(\text{Cr}^{3+}) = 0.755 \text{ Å})\), Al\(^{3+}\) has six coordination number \((S(\text{Al}^{3+}) = 0.675 \text{ Å})\) and O\(^{2-}\) has four coordination number \((S(\text{O}^{2-}) = 1.24 \text{ Å})\), the ratio of Cr-O and Al-O Shannon’s crystal radii was found to be 104.18\%. In this case, we estimated the lattice relaxation effect of α-Al\(_2\)O\(_3\) crystals having applied external pressure 0 GPa [10], 0.001 GPa [23], 1.1 GPa [23], 2.1 GPa [23], 2.8 GPa [23], 2.855 GPa [24], 3.5 GPa [23], 4.6 GPa [24], 4.283 GPa [23], 7.446 GPa [24], 8 GPa [23], 8.26 GPa [23], 9.117 GPa [24], 20.8 GPa [25], 23.8 GPa [25], 26.9 GPa [25], 30.9 GPa [25], and 108 GPa [26].

3. Results and discussion

![Figure 2](image_url)

**Figure 2.** The Al-O bond length estimated from CASTEP code are indicated by circle (●). The experimental data reported from Refs. 23-26 are indicated by triangle (▲). Two different types of Al-O bond length \(d_1\) and \(d_2\) are shown by solid and dashed lines, respectively.

Figure 2 shows the Al-O bond length estimated from structural optimization using CASTEP code. The experimental data of the observed Al-O bond length reported from Refs. 23-26 were shown together for comparison. Two different types of Al-O bond length \(d_1\) and \(d_2\) are indicated by solid and dashed lines, respectively. As the increasing pressure from 0 to 110 GPa, the estimated Al-O bond length decreased following the tendency of the experimental data [23-26]. This tendency is caused by the changes in the local structure with pressure.

Figure 3 shows the comparison between Cr-O bond length estimated from CASTEP and Shannon’s crystal radii methods. In this case, the Cr-O bond lengths of α-Al\(_2\)O\(_3\): Cr\(^{3+}\) at 0 pressure were estimated to be 1.96 and 2.01 Å. These results are in good agreement with the Extended X-Ray Absorption Fine Structure (EXAFS) experiment performed by Kizler et al. [27]. The observed Cr-O bond lengths are 1.97 and 2.00 Å. As the pressure increase, the Cr-O bond length estimated from both methods, CASTEP and Shannon’s crystal radii methods, decreased rapidly. However, if we see carefully the difference
between $d_1$ and $d_2$ become larger in the results using CASTEP method. This tendency is understandable since the Shannon’s crystal radii method is a simple estimation to calculate the lattice relaxation effect. On the other hand, CASTEP method involves many variables therefore estimate the lattice relaxation effect more accurately. However, since the observed Cr-O bond length under pressure has not been reported to our knowledge, our results needs to be confirmed further such as investigating the molecular orbital energy and the multiplet energies.

4. Conclusion
We have successfully estimated the lattice-relaxation effect of ruby bond length under pressure without referring to any experimental parameter. The lattice relaxation effects were calculated by two different methods i.e., the first-principles band-structure calculations using CASTEP method and the Shannon’s crystal radii method. The results show that by using the CASTEP method, the lattice-relaxation ratios of $\alpha$-Al$_2$O$_3$: Cr$^{3+}$ under 0-110 GPa for $d_1$ and $d_2$ were ca. 104.71-108.86% and 100.92-102.77%, respectively. On the other hand, by using the Shannon’s crystal radii method, the lattice-relaxation ratio of $\alpha$-Al$_2$O$_3$: Cr$^{3+}$ under 0-108 GPa was ca. 104.18%. All of the calculated bond-length shows the decreasing tendency against the applied pressure. However, compared to the Shannon’s lattice relaxation estimation, the $d_1$-$d_2$ difference obtained by CASTEP method was increased as the pressure increases.

Acknowledgement
The authors gratefully acknowledge the support from Direktorat Riset dan Pengabdian Masyarakat, Direktorat Jenderal Penguatan Riset dan Pengembangan, Kementrian Riset, Teknologi, dan Pendidikan Tinggi, Indonesia

References
[1] W Duan, R M Wentzcovitch and K T Thomson 1998 Phys. Rev. B 57 10363
[2] W Duan, G Paiva, R M Wentzcovitch and A Fazioz 1998 Phys. Rev. Lett. 81 3267
[3] R A Forman, G J Piermarini, J D Barnett and S Block 1972 Science 176 284
[4] J H Eggert, K A Goettel and I F Silvera 1989 Phys. Rev. B 40 5724
[5] J H Eggert, K A Goettel and I F Silvera 1989 Phys. Rev. B 40 5733
[6] J H Eggert, F Moshary, W J Evans, K A Goettel and I F Silvera 1991 Phys. Rev. B 44 7202
[7] R A Forman, B A Weinstein and G Piermarini 1977 in Spectroscopie des Elements de Transition et des Elements Lourds dans les solides (Lyon: Centre National de la Recherche Scientifique) pp
[8] D R Stephens and H G Drickamer 1961 J. Chem. Phys. 35 427
[9] W Duan, B B Karki and R M Wentzcvovitch 1999 Am. Mineral. 84 1961
[10] H Sawada 1994 Mat. Res. Bull. 29 127
[11] M C Payne, M P Teter, D C Allan, T A Arias and J D Joannopoulos 1992 Rev. Mod. Phys. 64 1045
[12] M D Segall, P J D Lindan, M I J Probert, C J Pickard, P J Hasnip, S J Clark and M C Payne 2002 J. Phys. Condens. Matter 14 2717
[13] S J Clark, M D Segall, C J Pickard, P J Hasnip, M I J Probert, K Refson and M C Payne 2005 Z. Kristallogr. 220 567
[14] D Vanderbilt 1990. Phys. Rev. B 41 7892
[15] J P Perdew, K Burke and M Ernzerhof 1996 Phys. Rev. Lett. 77 3865
[16] M Novita, H Nagoshi, A Sudo and K Ogasawara 2018 IOP Conf. Ser.: Mat. Sci. Eng. 299 012060
[17] R D Shannon and C T Prewitt 1969 Acta Cryst. B 25 925
[18] R D Shannon 1976 Acta Cryst. A 23 751
[19] M Novita and K Ogasawara 2012 J. Phys. Soc. Jpn. 81 104709
[20] M Novita and K Ogasawara 2012 Jpn. J. Appl. Phys. 51 022604
[21] M Novita, T Honma, B Hong, A Ohishi and K Ogasawara 2016 J. Lumin. 169 594
[22] M Novita, H Yoshida and K Ogasawara 2013 *ECS Transactions* **50** 9
[23] L W Finger and R M Hazen 1978 *J. Appl. Phys.* **49** 5823
[24] H d’Amour, D Schiferl, W Denner, H Schulz and W B Holzapfel 1978 *J. Appl. Phys.* **49** 4411
[25] J K Zajonz, S Werner and H Schulz 1999 *Z. Krist.* **214** 331
[26] B Xu, H Stokes and J J Dong 2010 *J. Phys. Condens. Matter* **22** 315403
[27] P Kizler, J He, D R Clarke and P R Kenway 1999 *J. Am. Ceram. Soc.* **79** 3