Electronic and optical properties of Y_2SiO_5 and $Y_2Si_2O_7$ with comparisons to α -SiO₂ and Y_2O_3

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The electronic structure and bonding in two complex crystals, yttrium oxyorthosilicate Y_2SiO_5 and yttrium pyrosilicate $Y_2Si_2O_7$, were studied by means of first-principles local density calculations. Both crystals are ionic insulators with large band gaps. It is shown that their electronic structure and bonding cannot be represented by the weighted sums of those of α -SiO₂ and Y_2O_3 . On average, the Si-O (Y-O) bond in the ternary crystals tends to be weaker (stronger) than the respective bond in α -SiO₂(Y_2O_3). It is further shown that the specific local atomic coordinations can lead to significantly different partial density of states that should be experimentally detectable. The bulk and optical properties of these two crystals were also calculated. We find the bulk modulus of $Y_2SiO_5(Y_2Si_2O_7)$ to be 134.8 GPa (140.2 GPa). The optical dielectric constants for the two crystals are estimated to be 3.11 and 3.44, respectively. In the absence of any experimental data, these values are presented as theoretical predictions.

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I. INTRODUCTION

 SiO_2 and Y_2O_3 are some of the most important binary oxides and are also fundamental ingredients of other more complex oxides. SiO₂ has many polymorphs with α -SiO₂ (quartz), the most well-known stable phase.¹ In contrast, Y_2O_3 has only one known phase with a bixbyte structure.² Many research groups have studied the electronic structure and bonding in crystalline SiO_2 in the past.^{1,3–7} Within the last decade, there has also been considerable attention paid to the electronic and optical properties of the Y_2O_3 crystal.⁸⁻¹¹ Between the SiO₂ and Y₂O₃ phase boundaries there are two well-established yttrium silicates, Y-oxyorthosilicate or $Y_2SiO_5(SiO_2+Y_2O_3)$ and Y-pyrosilicate or $Y_2Si_2O_7(2SiO_2+Y_2O_3)$. Conspicuously, there has been no study on the electronic structure and bonding of these two ternary crystals. There could be several reasons for the lack of such efforts. First, the crystal structures of these two crystals are much more complicated and their precise structures have not been determined until very recently.¹² Second, because of the complexity of these crystal structures, full ab initio electronic structure calculations still require considerable effort even in this era of rapid advancement in computational methods and techniques. Third, it is conceivable that there could be nothing spectacular in their electronic structure and bonding. Most likely, their properties are just the weighted averages of the two end members SiO_2 and Y_2O_3 .

 Y_2SiO_5 is an important laser crystal that has been synthesized since 1961.¹³ Most research activities connected with Y_2SiO_5 have been related to rare-earth (Ce³⁺, Eu³⁺, etc.) doped crystals to be used as blue phosphor^{14,15} or in Cr⁴⁺-doped Y_2SiO_5 to be applied as a saturable-absorber *Q*-switch laser.¹⁶ This is mainly because the substitution of Si⁴⁺ in Y_2SiO_5 by a Cr⁴⁺ ion entails no other chargecompensating ions and has the highest figure of merit,¹⁶ whereas in systems such as Cr⁴⁺ in $Y_3Al_5O_{12}$ (YAG), it requires the addition of Ca or Mg as charge-compensating ions, which could affect the laser operation.²⁰ Although there are many reports on the spectroscopic studies of doped Y_2SiO_5 , we are not aware of any studies of the fundamental properties of the host crystal itself. We have recently argued that for a proper understanding of laser operations in crystals such as $Y_3Al_5O_{12}$, $YAlO_3$, $BeAl_2O_4$, or $LiYF_4$,¹⁷⁻²⁰ the electronic structure and bonding of the host crystal must be understood first. On the other hand, study of Y₂Si₂O₇ is much less common. It is mostly recognized as a precipitated phase in the interlayers joining Si₃N₄ ceramics with Si₂N₂O or SiO_2 glass²¹ and is considered to be a critical phase in the SiO₂-Y₂O₃-Si₃N₄ phase diagram.^{22,23} Within the complex phase diagram of SiO_2 - Y_2O_3 - Si_3N_4 , there are a total of ten identified crystalline phases, three at the corners (SiO₂, Y_2O_3 , and Si_3N_4), three on the edges (Si_2N_2O between SiO_2 and Si_3N_4 , Y_2SiO_5 , and $Y_2Si_2O_7$ between SiO_2 and Y_2O_3), and four in the interior of the phase diagram. The quaternary crystals at the interior of the phase diagram are $Y_{10}[SiO_4]_6N_2$ (N-apatite), $Y_2Si_3N_4O_3$ (M-melilite), $Y_4Si_2O_7N_2$, (J-phase or N-YAM), and $YSiO_2N$ (Nwallastonite). $Y_2Si_2O_7$ is at the corner of what has been called the compatibility triangle (with corners at Si₂N₂O, Si_3N_4 and $Y_2Si_2O_7$), which may play some role in the formation of different phases during high-temperature sintering. There are claims that other polymorphs of Y2SiO5 and Y₂Si₂O₇ could exist,²⁴ but to our knowledge, no detailed information on their structures has been published. It is highly desirable to initiate a detailed study on the electronic structure and bonding in the two complex yttrium silicate crystals.

In this paper, we present a detailed calculation of the electronic structure and bonding, bulk, and optical properties of Y_2SiO_5 and $Y_2Si_2O_7$ crystals and compare them with similar calculations on α -SiO₂ and Y_2O_3 .²⁵ We are mostly concerned with the subtle differences in those properties that can be attributed to their specific crystal structure and local environment. Our calculations demonstrate that the naive notion that the properties of Y-Si-O systems can be described as the average of SiO₂ and Y_2O_3 is grossly inadequate. In the following section, we will describe the crystal structures of Y_2SiO_5 and $Y_2Si_2O_7$. The method of calculation is outlined





in Sec. III. The main results of the calculation are presented and discussed in Sec. IV. In the last section, some concluding remarks and a comment on the direction of future investigations are made.

II. CRYSTAL STRUCTURE

The crystal structures of $Y_2Si_2O_7$ and Y_2SiO_5 are sketched in Fig. 1. The lattice constants are listed in Table I. We used the crystal data recently reported by Leonyuk *et al.*¹² The single-crystal sample for Y_2SiO_5 is Cr doped while that of $Y_2Si_2O_7$ is undoped. They were grown by the Czochralski technique in a high-frequency heated iridium crucible. The crystal parameters determined are significantly different from the ones reported more than 30 years ago.^{26,27}

The crystal structures of Y_2SiO_5 and $Y_2Si_2O_7$ are fairly complicated. They both have a monoclinic lattice but with different space groups, B2/b for Y_2SiO_5 and $P2_1/c$ for $Y_2Si_2O_7$. In Y_2SiO_5 , the unit cell contains 32 atoms (Z =4) with two different Y sites Y1 and Y2, one Si site, and five O sites, which we will label as O1–O5. Y1 bonds to seven O ions with bond lengths (BL) ranging from 2.199 Å to 2.604 Å. Y2 bonds to only six O ions with ranging from 2.203 Å to 2.287 Å. Si is tetrahedrally bonded to four O's with two short bonds (BL=1.602 Å and 1.605 Å) and two longer bonds (BL=1.628 Å and 1.636 Å). O1 is the only O atom in Y_2SiO_5 that has no Si as a nearest neighbor (NN) and is loosely bonded to four Y ions with BL's ranging from

TABLE I. Crystal parameters and interatomic distances in Y_2SiO_5 and $Y_2Si_2O_7$ from Ref. 5.

Crystals	Y ₂ SiO ₅	$Y_2Si_2O_7$
Space group	C2/c	$P2_1/c$
Lattice constants		
a (Å)	14.371	4.694
<i>b</i> (Å)	6.71	10.856
<i>c</i> (Å)	10.388	5.588
β	122.17°	95.01°
Cation coordination	Y1-07, Y2-06	Y-06
	SiO4	Si-O4

2.199 Å to 2.373 Å. O2 bonds to three Y and one Si while O3, O4, and O5 all bond to one Si and two Y.

In $Y_2Si_2O_7$, there is only one Y site, one Si site, and four O sites. Y has six NN O ions with BL's ranging from 2.250 Å to 2.328 Å. Si is at the tetrahedral site with BL's slightly different from that in Y_2SiO_5 (1.616, 1.622, 1.631, and 1.637 Å). O1 is the only atom in a bridging position with two NN Si. O2, O3, and O4 all have two Y and one Si as NN's. For comparison, we recall that in α -SiO₂, O is in a bridging position while Si is tetrahedrally bonded with Si-O bond lengths of 1.605 Å and 1.614 Å. In Y_2O_3 , both Y1(8*a*) and Y2(24*d*) bond to six O atoms with BL's of 2.244 Å, 2.337 Å, and 2.268 Å. There is only one unique O (48*e*) site which bonds to four Y atoms similar to O1 in Y_2SiO_5 . We will further discuss the implications of these local structural configurations on the calculated electron density of states (DOS) in these two crystals in Sec. IV.

III. METHOD OF CALCULATION

We used the *ab initio* orthogonalized linear combination of atomic orbitals (OLCAO) method²⁸ for the electronic structure calculation. In the OLCAO method, the localized atomic basis is used in the expansion of the Bloch function. This localized description of the orbital basis is particularly effective in describing the bonding in complex crystals. The method has been well described in many recently published papers.^{17–20,29–35} Here, we briefly outline the details that are pertinent to the present calculation. In both crystals, the basis sets consist of Y 1s, 2s, 3s, 4s, 5s, 6s, 2p, 3p, 4p, 5p, 3d, 4d, 5d; Si $1\overline{s}$, $2\overline{s}$, $3\overline{s}$, $4\overline{s}$, 2p, 3p, $4\overline{p}$, $3\overline{d}$, O 1s, 2s, $\overline{3s}$, 2p, 3p atomic orbitals, which are expanded in terms of a Gaussian-type of orbital (GTO). These basis sets are generally referred to as full basis sets. The minimal basis sets will have Y 6s, Y 5d, Si 4s, 4p, 3d and O 3s, 3p removed from the full basis sets. The core orbitals (those underlined) were orthogonalized to the "non core" orbitals in the usual "frozen-core" approximation. The semi core Y 4p orbital was treated as a "none-core" orbital since its orbital energy is only slightly lower than that of O 2s. The crystal potentials were constructed according to the density functional theory with the local approximation (DFT-LDA).³⁶ Wignerinterpolation formula was employed to account for additional correlation effects in the LDA potential. The crystal poten-



FIG. 2. Calculated band structure of Y₂SiO₅ and Y₂Si₂O₇.

tials were expanded in terms of atom-centered analytic functions consisting of a combination of s-type Guassians. We used the experimental lattice parameters for the electronic structure and optical properties studies. In the case of ground state bulk properties, we used a total-energy minimization scheme for geometry optimization.^{37,38} Geometry optimization is necessary in order to obtain an accurate bulk modulus in which all crystal parameters are simultaneously varied when the crystal volume is compressed or dilated. The bonding properties are described in terms of Mulliken effective atomic charge and bond order values between nearestneighbor pairs. For these calculations, separate minimalbasis sets were used to obtain a more meaningful description since the Mulliken scheme³⁹ works best when the basis functions are more localized. For the optical properties calculation, the dipole transition matrices were included for transitions from the occupied valence band (VB) (including those of Y 4p) to the unoccupied conduction band (CB). To improve the accuracy of higher CB states, additional atomic obitals (Y 7s, 6p, 6d, Si 5s, 5p, 4d, and O 4s, 4p) were added to the basis set in the optical calculation, which is generally referred to as an extended basis set. Even with an extended basis set, the optical calculations were limited to transitions no higher than 35 eV since the accuracy of the wave functions of the high CB states cannot be fully guaranteed in a method based on the variational principle. A sufficiently large number of **k** points in the irreducible portion of the Brillouin zones (BZ) were used (64 and 54 for Y_2SiO_5 and Y₂Si₂O₇, respectively) both in the self-consistent iterations and in the final analysis of the DOS as well as in the optical properties calculations.

IV. RESULTS

A. Band structure and density of states

The band structures and the DOS of Y_2SiO_5 and $Y_2Si_2O_7$ were calculated using the OLCAO method. Fig. 2 shows the band structures of the two crystals along the high-symmetry lines of the BZ. These band structures are typical of ionic insulators with relatively large band gaps and flat-topped VB's. The gaps are direct, 4.82 eV for Y_2SiO_5 and 4.78 eV for $Y_2Si_2O_7$. The real gaps may be somewhat larger in both crystals since it is well known that LDA theory generally underestimates the band gaps of insulators. In both cases, the bottom of the CB is at Γ and consists of a single band of predominately Y 4*d* and Si 4*s* character. The top of the VB



FIG. 3. Calculated total DOS and atom-resolved PDOS of $Y_2 SiO_5\,.$

may not be exactly at the Γ point but the difference is so small that the gaps in both crystals can be considered to be direct band gaps.

The main electronic structure results of Y_2SiO_5 and $Y_2Si_2O_7$ are best illustrated by their total DOS and atomresolved partial DOS (PDOS) which are shown in Figs. 3 and 4, respectively. To facilitate discussion, the DOS and PDOS of α -SiO₂ and Y_2O_3 are also presented in Fig. 5. In both crystals, we can roughly divide the VB DOS into two regions. Those above -9.0 eV are derived mainly from O 2*p* orbitals and those below -14.0 eV are associated with the O 2*s* and Y 4*p* states. We note from Fig. 5 that the corresponding O 2*s* band in α -SiO₂ is at a lower energy than that of Y_2O_3 , and the O 2*p* band in α -SiO₂ (separated into



FIG. 4. Calculated total DOS and atom-resolved PDOS of $Y_2Si_2O_7$.

two segments) is much wider than the O 2p bands in Y_2O_3 . Focusing on Y_2SiO_5 , we can summarize our observations as follows: (1) The PDOS of O1 is totally different from the PDOS of the other four oxygens. It has a sharp O 2s peak at -15.1 eV and a narrow O 2p band. This is because O1 is not bonded to any Si atom but to four Y ions with much longer Y-O bonds. The PDOS profile has a great resemblance to the O PDOS of Y_2O_3 . This indicates that Y-O is a relatively weak bond in Y₂SiO₅. (2) The PDOS of O2, O3, O4, and O5 are all very similar. As discussed in Sec. II, the only difference among them is that O2 has three Y and one Si as NN whereas O3, O4, and O5 have two Y and one Si as NN. This small difference is reflected in the slight difference in the PDOS near the top of the VB. This reenforces the assertion that Y-O is a relatively weak bond and its main influence is at the top of the VB. (3) The PDOS for Y1 and Y2 are very similar. Their only difference is in the CB PDOS because Y1 has an extra O as NN atom. (4) The PDOS of Si, which is tetrahedrally coordinated, resembles to some extent the PDOS in α -SiO₂. Both the upper and the lower sections break into multiple segments.

Figure 4 shows the total DOS and PDOS of $Y_2Si_2O_{7,}$ which are quite different from that of Y_2SiO_5 . We summarize the results as follows: (1) the most prominent feature is



FIG. 5. Calculated total DOS and atom-resolved PDOS of (a) α -SiO₂ and (b) Y₂O₃.

a sharp peak at -8.0 eV, which comes from the bridging oxygen O1. Thus the PDOS of O1 is significantly different from those of other three O ions. (2) The PDOS of the other three Os, O2, O3, and O4 are very similar because they have the same local bonding configurations as pointed out in Sec. II. (3) The PDOS of Si is very different from that in Y_2SiO_5 even though they are both tetrahedrally bonded to four O's with comparable BL's. The upper VB does not have multiple segments as in Y_2SiO_5 . This underscores an important fact that the NN local bonding is not the only factor to distinguish the electronic structure of constituent atoms in complex oxides. In this case, the structure of the second NN, namely, O1, has a great influence on the PDOS of Si. (4) The PDOS of Y is only slightly different from that of Y2 in Y_2SiO_5 ; both have six NN O's. The minor difference in the lower CB region is obviously related to the different crystal symmetry

TABLE II. Calculated effective charge Q_{α}^* in Y_2SiO_5 and $Y_2Si_2O_7$. Also listed are the Q^* values in α -SiO₂ and Y_2O_3 , calculated in a similar fashion. For Y, the charge for the six 4p electrons are not included.

	Y ₂ SiO ₅	$Y_2Si_2O_7$	α -SiO ₂	Y ₂ O ₃
Y	1.972, 1.940	1.928	-	1.961, 1.978
Si	2.641	2.539	2.333	-
0	6.599, 6.714, 6.716, 6.721, 6.697	6.803, 6.709 6.716, 6.707	6.834	6.684

and slightly different Y-O BL's. It is clear from the above calculated DOS and PDOS of the two crystals that the electronic structures of Y_2SiO_5 and $Y_2Si_2O_7$ cannot be simply viewed as a superposition of those of SiO_2 and Y_2O_3 in Fig. 5. The sharp peaks at -15.1 eV in Y_2SiO_5 and -8.0 eV in $Y_2Si_2O_7$ should be easily detected experimentally using techniques such as x-ray photoelectron spectroscopy and resonant x-ray emission spectroscopy.

B. Effective charge and bond order

One of the great advantages of the local orbital methods is the ease with which the effective charges on each atom and the strength of the bonds between pairs of atoms can be quantified and compared in a simple and straightforward way provided the same computational method and basis set are used. This is particularly useful for comparative studies of crystals with complex structures. The differences are usually small and delineate the small differences in local bonding configurations. In accordance with the Mulliken scheme,³⁹ the effective charges Q^*_{α} on each atom α and the bond order $\rho_{\alpha\beta}$ for each pair of atoms (α,β) are given by

$$Q_{\alpha}^{*} = \sum_{i} \sum_{n,occ} \sum_{j,\beta} C_{i\alpha}^{*n} C_{j\beta}^{n} S_{i\alpha,j\beta}, \qquad (1)$$

$$\rho_{\alpha\beta} = \sum_{n,occ} \sum_{i,j} C^{*n}_{i\alpha} C^n_{j\beta} S_{i\alpha,j\beta}.$$
⁽²⁾

Here $C_{i\alpha}^n$ is the coefficient of the eigenvector of the *n*th band. $\alpha(i)$ specifies the atom (orbital) and $S_{i\alpha,j\beta}$ is the overlap matrix between the Bloch functions. Since the Mulliken scheme is more meaningful when the basis functions are more localized, we made separate calculations using minimal basis sets for both Y_2SiO_5 and $Y_2Si_2O_7$. The results are summarized in Tables II and III together with those of α -SiO₂ and Y₂O₃ for comparison.²⁵ In general, a larger charge transfer indicates a stronger ionic character of the crystal bonding. Table II shows that Y loses about one electron and Si about 1.4 or 1.5 electron in the charge transfer. For the O ions, O1 in Y_2SiO_5 ($Y_2Si_2O_7$) has a smaller (larger) Q^* than other O's. O1 in Y₂SiO₅ has no Si as NN and tends to be less ionic while O1 in $Y_2Si_2O_7$ is a bridging O with Q^* close to the Q^* of O in α -SiO₂. The variations of Q^* among the other O ions at different sites are generally less than 0.01 electron. The charge transfer from Y(Si) ion is slightly larger (smaller) than the respective charge transfer in the Y_2O_3 and SiO₂ crystals.

The bond orders (BO's) between each pair of atoms in the two crystals were calculated according to Eq. (2) and are listed in Table III. Also listed in the parentheses are the corresponding BL's. From the BO values, it is obvious that the Si-O bond is much stronger than the Y-O bond with BO values of almost twice that of Y-O. In Y_2SiO_5 , the largest Y-O BO is 0.191 for the Y2-O1 bond with a BL of 2.203 Å. The BO of Y1-O1 is only 0.187 even though the BL is actually slightly shorter (2.199 Å). The largest (smallest) Si-O BO is 0.318 for Si-O3 (Si-O2) with the BL of 1.602 Å (1.628 Å). It is also noted that Si-O5 has a BO of 0.305 even though it has the longest Si-O BL of 1.636 Å. So the BO values do not necessarily scale with BL. Apparently, the bond angle and the second NN effect also influence the strength of a given bond. In $Y_2Si_2O_7$ crystal, the variations of Y-O BO

TABLE III. Calculated bond order $\rho_{\alpha,\beta}$ in Y_2SiO_5 and $Y_2Si_2O_7$. The bond lengths in Å are listed in the parentheses.

Crystals				
Bond	Y_2SiO_5	$Y_2Si_2O_7$	α -SiO ₂	Y_2O_3
Y1-01	0.187(2.199) 0.130(2.373)	-		0.124(2.288) (6)
Y1-O2	0.137(2.374) 0.085(2.604)	0.181(2.252) 0.167(2.274)		
Y1-O3	0.168(2.319)	0.160(2.297) 0.191(2.251)		
Y1-04	-	0.185(2.250) 0.178(2.328)		
Y1-05	0.165(2.299) 0.165(2.317)	-		
Y2-01	0.191(2.203) 0.153(2.279)	-		0.142(2.244) (2)
Y2-O2	0.149(2.283)	-		0.105(2.337) (2)
Y2-O3	0.183(2.275)	-		0.133(2.268) (2)
Y2-O4	0.171(2.280) 0.160(2.287)		-	
Si-O1	-	0.309(1.631)	0.324(1.605) (2)	
Si-O2	0.286(1.628)	0.311(1.622)	0.299(1.614) (2)	
Si-O3	0.318(1.602)	0.305(1.616)	-	
Si-O4	0.295(1.605)	0.290(1.637)	-	
Si-O5	0.305(1.636)			-

TABLE IV. Calculated ground-state and electronic properties of Y_2SiO_5 and $Y_2Si_2O_7$.

Crystals	Y ₂ SiO ₅	$Y_2Si_2O_7$
a (Å)	14.099 (-1.90%)	4.712 (+0.38%)
<i>b</i> (Å)	6.807 (+1.45%)	10.862 (+0.06%)
<i>c</i> (Å)	10.722 (3.22%)	5.611 (0.41%)
β	119.46 (-2.22%)	95.14 (-0.90%)
V/V_0	1.027	1.008
B (GPa)	134.8	140.2
Β'	3.86	4.65
E_{σ} (eV)	4.82	4.78
Bandwidth	6.19	5.94
O 2 <i>p</i> (eV)		
$\varepsilon_1(0)$	3.11	3.44
$\omega_p ({\rm eV})$	14., 21., 30.9	20.5, 23.2, 27.3, 30.5

and BL are less than those in Y_2SiO_5 . The maximum BO is 0.185 for Y-O4 (BL=2.250 Å) and the minimum BO is 0.160 for Y-O3 (BL=2.297 Å). Likewise, the Si-O BO and BL values in $Y_2Si_2O_7$ fall between the limits for the Y_2SiO_5 crystal. Again, the largest Si-O BO of 0.311 for Si-O2 (BL =1.622 Å) is larger than that of the Si-O4 pair (BO=0.306) with a shorter BL of 1.616 Å. Comparing the BO values of the binary crystals α -SiO₂ and Y_2O_3 , we find the BO for Si-O bonds in Y_2SiO_5 and $Y_2Si_2O_7$ are slightly weaker than those in α -SiO₂, while the BO of Y-O bonds are slightly larger than those in Y_2O_3 .

C. Bulk properties

We used a total energy-minimization scheme within the OLCAO method^{37,38} to obtain the equilibrium geometry of Y_2SiO_5 and $Y_2Si_2O_7$ The results for the crystal parameters are listed in Table IV. Also shown are the percent deviations from the experimental values of Table I, which were used for the electronic structure calculation. In the optimization process, all internal parameters of the crystal (not shown) are simultaneously varied. It can be seen that in the case of $Y_2Si_2O_7$, the predicted crystal parameters are in excellent agreement with the measured ones with deviations in lattice constants of less than 0.41% and the deviation in the angle β of only 0.9%. In the case of Y_2SiO_5 , the deviations are considerably larger, but are still within the general level of agreements for LDA calculations. The main reason for the larger deviation in Y₂SiO₅ is probably due to the fact that the crystal sample in Ref. 12 is Cr doped. This certainly will affect the measured crystal parameters to a large extent. The corresponding deviation in the equilibrium volume is +0.9%for $Y_2Si_2O_7$ and +2.7% for Y_2SiO_5 .

We have calculated the bulk modulus *B* and the pressure coefficient *B'* of Y_2SiO_5 and $Y_2Si_2O_7$. The crystal volumes were expanded or contracted with the crystal symmetry maintained and all the internal parameters relaxed. By fitting the calculated total-energy versus volume data for the two crystals to the Murnaghan equation of states (EOS).⁴⁰ We have obtained *B* and *B'* for Y_2SiO_5 and $Y_2Si_2O_7$ which are



FIG. 6. Calculated optical properties of Y_2SiO_5 : (a) real part of the dielectric function, (b) imaginary part of the dielectric function, and (c) electron energy loss function.

listed in Table IV. The bulk moduli for Y_2SiO_5 and $Y_2Si_2O_7$ are very close, 134.8 GPa and 140.2 GPa, respectively. They are both smaller than the reported experimental B value for Y_2O_3 ranging from 150 GPa (Ref. 41) to 170 GPa (Ref. 42). They are much larger than the *B* value of 34 GPa in α -SiO₂ (Ref. 43) because of the flexible bridging O in α -quartz. On the other hand, the high-pressure polymorph of SiO_2 , or stishovite, has a bulk modulus B as high as 304.6 GPa and is sometime referred to as the second or third hardest material after diamond and BN. In stishovite, Si is octahedrally coordinated and all the octahedrons are edge sharing. In contrast, tetrahedrons in α -SiO₂ are all corner sharing linked at the bridging O site. Introduction of Y stabilizes the SiO₄ tetrahedrons (similar to the case of Y-stabilized ZrO₂), thereby resulting in a significant increase in its bulk modulus. We are not aware of any measured values of the bulk modulus for Y_2SiO_5 or $Y_2Si_2O_7$.

D. Optical properties

The interband optical transitions with all dipole matrix elements included were calculated for Y_2SiO_5 and $Y_2Si_2O_7$. To achieve higher accuracy, an extended basis set was used. The imaginary parts of the dielectric functions $\varepsilon_2(\omega)$ were calculated first and the real parts $\varepsilon_1(\omega)$ were obtained from the imaginary parts by Kramers-Kronig conversion. The energy loss functions were obtained from the inverse of the complex dielectric function or $Im\{[\varepsilon_1(\omega)+i\varepsilon_2(\omega)]^{-1}\}$. These results are presented in Figs. 6 and 7 for Y_2SiO_5 and $Y_2Si_2O_7$ respectively. For Y_2SiO_5 , $\varepsilon_2(\omega)$ rises swiftly from the threshold at 5.0 eV to reach a plateau at about 7.1 eV. It starts to drop at 9.2 eV until around 24 eV: it rises again with



FIG. 7. Calculated optical properties of $Y_2Si_2O_7$: (a) real part of the dielectric function, (b) imaginary part of the dielectric function, and (c) electron energy loss function.

a peak at 26. eV. The second peak at the higher energy is attributed to transitions from the semi core Y 4p levels to the CB. The gross features of the absorption spectrum of Y₂Si₂O₇ are similar to Y₂SiO₅ except it does not have a plateau in $\varepsilon_2(\omega)$ in the same energy range. $\varepsilon_2(\omega)$ actually peaks at 9.6 eV and the peak associated with transitions from Y 4p is at 26 eV, similar to that in Y₂SiO₅.

The calculated optical dielectric constant $\varepsilon_0 = \varepsilon_1 (\hbar \omega = 0)$ for the two crystals are found to be 3.11 and 3.44, respectively. ε_0 can be related to the measured refractive index for through $n = \sqrt{\varepsilon_0}$, so we estimate the refractive index for the two crystals to be about 1.76 and 1.85, respectively. Again, we find no reported experimental data for the optical constants in these two crystals. The peaks in the electron energy loss function are interpreted as the frequency ω_p for bulk plasma excitation. Figures 6(c) and 7(c) show that the main plasmon peaks for Y₂SiO₅ and Y₂Si₂O₇ are at 30.9 eV and 30.5 eV, respectively. However, additional peaks at 14.0 eV and 21.0 eV for Y₂SiO₅ and at 20.5 eV, 23.2 eV, and 27.3 eV for Y₂Si₂O₇ can also be identified. Because the plasmon peaks at high-energy region where the values of the dielectric function are usually small and

less accurate, the quoted plasmon frequencies for the two crystals need to be treated with caution. The plasmon frequencies and the optical dielectric constant values are listed in Table IV.

V. CONCLUSIONS

We have studied the electronic and the optical properties of two yttrium silicates, Y₂SiO₅ and Y₂Si₂O₇. Both are important ternary crystals either in laser technology or for a better understanding of structures of complex ceramic interfaces. It is shown that the electronic structure and bonding in these two complex crystals cannot be simply interpreted as the weighted average of α -SiO₂ and Y₂O₃. They depend on the crystal structure and the specific local bonding configurations. In particular, the local bondings of O1 in these two crystals are very different from each other and from that of other O ions, resulting in very different local PDOS spectra. The effective charge and the bond order calculations delineate the fine difference of the cations and anions in different local environments. It appears that in Y-Si-O compounds, the Si-O bond is slightly weakened (with respect to α -SiO₂) and the Y-O bond is somewhat strengthened (with respect to Y_2) O₃). Furthermore, the bulk properties and the optical properties of these two crystals are also calculated and compared. However, experimental data on these two crystals are nonexistent: we therefore view the present results as theoretical predictions to be confirmed later by actual experimental measurements. It is our intent to perform systematic and similar calculations on other crystalline phases related to the SiO₂-Y₂O₃-Si₃N₄ phase diagram in order to gain a deep insight on the structures and properties of the intergrannular glassy films in polycrystalline Si₃N₄ ceramics where different types of cation-anion bonding are exhibited. It is also desirable to carry out supercell calculations with rare-earth (Ce- or Er-) or Cr-doped Y_2SiO_5 such that the interactions between the metal ions and the crystalline host can be better understood. In particular, the issue of excited state absorption of Cr^{4+} in Y₂SiO₅, either to other localized states in the gap or to the states in the conduction band of the host, is a subject of current interest.¹⁸ Such calculations are currently under way⁴⁴ and will be reported elsewhere in the future.

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