Temperature Dependence of the Electronic Structure of Oxides: MgO, MgAlO$_4$ and Al$_2$O$_3$

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Abstract

We have studied the room temperature optical reflectivity of MgO, MgAlO$_4$, and Al$_2$O$_3$ from 5 to 40 eV using a novel spectrophotometer with a laser plasma light source. Structure in the imaginary component of the dielectric constant is observed in each compound. The region of the major transitions in MgO and MgAlO$_4$ is determined using an ab initio pseudopotential band structure calculation [7] of MgO. The exciton reflectivity has been studied in these materials at temperatures between 4 K and 150 K, and exciton-photon coupling appears to increase from MgO to Al$_2$O$_3$. The temperature dependence of the higher lying interband transitions in MgO has been determined by 4 K, and we find that while the temperature dependence of the peak transitions at 7 K and 3 K are nearly identical (1.2–2.2 meV/K) at 7 K, higher lying transitions have very different temperature dependences. Furthermore, with increasing temperature the X point valence band gap increases at a rate of 0.3 meV/K, while the conduction band separation at 7 K decreases at 0.4 meV/K.

1. Introduction

New and demanding applications have generated intense interest in the electronic structure of oxide materials. While the alkali halides have been extensively studied using optical techniques, and covalent semiconductors studied using optical and electron spectroscopies, the more complex oxide materials have not seen such thorough investigations. This is in part due to the passive roles these materials play in traditional technological applications. However, there is increasing interest in MgO and Al$_2$O$_3$ as substrate materials for thin film growth, Al$_2$O$_3$ and MgAlO$_4$ as tunable laser materials, and more complex oxides as nonlinear optical media. Thus a more fundamental understanding of the basic electronic structure of oxide materials is desirable.

The room temperature electronic structure of MgO has been studied previously using optical spectroscopy [1] and band structure methods [2]. Previous optical reflectivity measurements of Al$_2$O$_3$ [3] have not allowed careful interpretation, and there is no consensus on the fundamental electronic structure of this material. There is very little information available on the more complex oxide MgAl$_2$O$_4$ spinel. In addition, the effect of temperature on the band states is important in many applications. For example, the processing and applications of these oxide materials all involve elevated temperatures. While the temperature dependence of the electronic structure of semiconductors has been studied [8], only recently have investigations in the VUV begun to uncover the effect of temperature on excitonic and band gap transitions in Al$_2$O$_3$ [5] and MgO [6]. In this paper we present the room temperature reflectivity and imaginary component of the dielectric response for MgO, MgAlO$_4$, and Al$_2$O$_3$ from 5 to 40 eV. The origins of the major transitions in MgO and MgAlO$_4$ are assigned to critical points based on an ab-initio pseudopotential (PSF) band structure calculation [7] of MgO. We then use the exciton line shape analysis developed by Toyozawa [8] to study the temperature dependence of the 7 K exciton observed at the band gap energy. The temperature dependence of the higher lying interband transitions of MgO has been determined from 50 K to 100 K, and is used to identify temperature induced changes in the band structure.

2. Experimental

Reflectivity measurements have been performed at room and elevated temperature from 5 to 40 eV using a Laser Plasma Light Source [9]. A high power, nanosecond pulse from a Nd: YAG laser is focused onto the surface of a Samarium metal target producing a high intensity pulse of continuum radiation extending from the visible to the X-ray region. The plasma light enters a spectrophotometer, which is the subject of another paper [10]. The wavelength resolution is 0.3 nm above and 0.1 nm below 10 nm, and reflectivity magnitudes are reproducible to within \(\Delta R/R = 5\%\).

MgO single crystals [11] are cleaved under nitrogen and transferred into the spectrophotometer with minimal exposure to air. Synthetic boehmite spinel MgAlO$_4$ and MgAl$_2$O$_4$, powders [12] lack simple cleavage planes and are polished with a 15 μm diamond paste followed by a colloidal silica based chemical polish. Samples are heated with a 10.6 μm, 150 Watt CO$_2$ laser incident on the sample and temperatures are measured by thermocouples embedded in the sample or optical pyrometers. In some cases the reflectivities are multiplied by a constant to agree with the known refractive index in the visible.

3. Electronic Structure of MgO, MgAlO$_4$, and Al$_2$O$_3$

The measured reflectivities of single-crystal MgO, MgAlO$_4$, and Al$_2$O$_3$ are shown in Fig. 1. The data has not been smoothed. The materials are all transparent in the visible, and the excitonic transitions associated with the fundamental absorption edge increases in the series from 7.6 to 9.1 eV. As expected, the predominantly ionic MgO exhibits the strongest structure throughout the VUV. However, the MgAlO$_4$ reflectivity is very similar to MgO, showing prominent high energy features at 10.0, 14.3, and 19.0 eV. Al$_2$O$_3$ displays the broadest reflectivity features, but the six high lying features are observed. At photon energies above 23 eV the reflectivity

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Fig. 2. Reflectivity of (a) MgO, (b) MgAl₂O₃, and (c) α-Al₂O₃, obtained using a laser plasma light source.

Fig. 3. Imaginary component \( \varepsilon_2 \) of the dielectric response of (a) MgO, (b) MgAl₂O₃, and (c) α-Al₂O₃.

Magnitudes begin to decrease. Except for small features near 32 eV from O 2s states, the interband transitions are exhausted by 40 eV; the reflectivity drops by less than 1%. Shown in Fig. 2 are the imaginary components of the dielectric constant \( \varepsilon_2 \) for the three materials, determined using an FFT-based Kramers-Kronig technique [13]. Using semianalytic curve fitting we can identify the critical point structure in \( \varepsilon_2 \). In all three materials the exonic and interband states are nearly degenerate, making an exact determination of the fundamental gap difficult.

3.1. MgO

The reflectivity and calculated \( \varepsilon_2 \) of MgO agree very well with previously published results [13]. Shown in Fig. 3 is the PES band structure of MgO calculated using the local density approximation (LDA). The experimental and calculated interband transition energies for MgO are listed in Table 1. The LDA band gap energy of MgO is 4.6 eV, yet we have found the best correspondence between the critical point energies and the LDA band energies using the as-calculated band energies. This may arise because the reduced LDA band gap leads to increased hybridization and suppression of the conduction bands. Clearly, the fundamental absorption is a \( \Gamma_2 \rightarrow \Gamma_6 \) transition, and the increase in \( \varepsilon_2 \) at 9 eV is due to transitions from \( \Gamma_10 \) to \( \Gamma_1 \). The rest of the higher lying features in \( \varepsilon_2 \) can be accounted for by transitions either at or near the \( X \) point. The peak near 10.7 eV is associated with a \( X \) to \( \Gamma_1 \) transition, and the sharp structure at 14 eV arises from the

Table 1. Room temperature critical point energies for MgO

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<th>( E ) (exp)</th>
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<th>Assignement</th>
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<tr>
<td>( \Gamma_1 )</td>
<td>7.5 (MeV)</td>
<td>4.6</td>
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<tr>
<td>( \Gamma_7 )</td>
<td>8.8 (MeV)</td>
<td>8.8</td>
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<tr>
<td>( \Gamma_2 )</td>
<td>10.5 (MeV)</td>
<td>13.9</td>
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<tr>
<td>( \Gamma_6 )</td>
<td>11.0 (MeV)</td>
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<td>( \Gamma_10 )</td>
<td>14.3 (MeV)</td>
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<tr>
<td>( \Gamma_5 )</td>
<td>16.5 (MeV)</td>
<td>17.1</td>
</tr>
<tr>
<td>( \Gamma_7 )</td>
<td>17.8 (MeV)</td>
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Another significant feature arises from $X_{2}$ to $X_{1}$ transitions starting at 16.1 eV. The differences in the critical point energies given by $E_{C}$, $E_{E}$, and $E_{M}$, and their assignments allow us to determine a $X_1 - X_3$ valence band separation of 2.8 or 2.9 eV, respectively, which compares nicely with the calculated separation of 3.2 eV. Similarly, we determine the $X_1 - X_3$ conduction band separation from $E_{C} - E_{C}$ and $E_{M} - E_{M}$ to be 7.7 or 2.8 eV, in agreement with the PSF calculation of 3.9 eV. Although there are other higher lying features their assignment is more difficult due to the possibility of many overlapping transitions. While the PSF calculation does not predict the band gap accurately, the agreement between the transition energies and band separations at $A$ is good.

The agreement between the optical data presented here and the previous results of Reesler and Walker is excellent. However, conflicts between the two band structure calculations used to account for the optical data give rise to different valence assignments. There is agreement in the assignment of the fundamental gap and the increase between 9 and 11 eV due to transitions at $L$. However, the empirical pseudopotential calculation [2] overestimates the $K$ point transition energies relative to our calculation. Thus, Reesler and Walker attribute the increase at 13.2 eV to a $X_5 - X_5$ point transition along the $X_5 - X_5$ line, and the decrease at 13.3 eV to the $M_{3}$ point transition along the $X_5 - X_3$ line. They also attribute the increase at 16.1 eV to $X_3 - X_3$ transitions. Our calculation places these transitions at lower energies, and we have used transitions from $X_2$ to account for the $M_{3}$ point transition at 13.1 eV and the $M_{3}$ point at 16.6 eV. While identification of the specific band transitions differs due to conflicts in the calculations, there is good agreement that a majority of the higher lying optical activity is due to band parallelism near $X$.

3.2. MgAlO$_{3}$

In addition to MgO we have studied the related oxide material MgAlO$_{3}$. This material also has cubic symmetry but a more complex unit cell consisting of tetrahedrally coordinated Mg and octahedrally coordinated Al. The reflectivity and $\rho$ are shown in Figs 1(a) and 2(b), respectively. MgO and MgAlO$_{3}$ have very similar features, seen by comparing the optical data. An excitonic transition is followed by a gradual increase in $\rho$, followed by a sharp drop, and then another sharp peak. The observed critical points are tabulated in Table II. We have not yet calculated the band structure of MgAlO$_{3}$, but we can assume similar assignments for the two materials, in which the optical activity is due in large part to transitions at $X$. Using the energies from Table II, we derive conduction band separations analogous to a $X_{1} - X_{3}$ separation of 3.2 $\pm$ 0.2 eV, and a valence band separation analogous to a $X_{1} - X_{3}$ separation of 3.8 $\pm$ 0.2 eV. The increase in valence band $X_{1}$ point separation is appealing since MgAlO$_{3}$ is more covalent than MgO, and using high resolution valence band X-ray Photoelectron Spectroscopy we measure a valence band width increase from 7.5 eV in MgO to 8.1 eV in MgAlO$_{3}$. Furthermore the valence band peak separation increases from 2.6 eV in MgO to 4.1 eV in MgAlO$_{3}$ in very good agreement with the optically determined $X$ point valence band separation. Thus, the electronic structure of MgAlO$_{3}$ can be predicted fairly accurately from a comparison to MgO.

3.3. $\pi$-AlO$_{3}$

The measured reflectivity of (0001) oriented $\pi$-AlO$_{3}$ is shown in Fig. 1(c). The data displays weaker structure than the Mg-containing oxides, expected due to increased covalency. The $\pi$-AlO$_{3}$ reactivity exhibits an excitonic transition at 9.1 eV followed by higher energy reflectivity peak at 32 eV associated with transitions from the O 2s state. Previous results from 8.5 to 28.5 eV show only a broad reflectivity band peaked at 13 and 20 eV with no other features resolved [3]. Shown in Fig. 2(c) is $\rho$, calculated from the optical data. We resolve six critical points above the excitonic transition, as listed in Table II. We have calculated the band structure of $\pi$-AlO$_{3}$[5], but the large number of states in the unit cell and low symmetry make simple critical point assignments difficult. We are in the process of calculating the first principles optical response using the PSF method and the detailed analysis of $\pi$-AlO$_{3}$ will be the subject of a future publication.

4. Excton temperature dependence

MgO, MgAlO$_{3}$ and $\pi$-AlO$_{3}$ exhibit excitonic transitions associated with the $\pi$ point band gap. These excitons have small binding energies due to the large dielectric constants, and are therefore nearly degenerate with the fundamental absorption edge. Shown in Fig. 4 are the background subtracted exciton reflectivities of MgO from room temperature.

| $E_1$ | 7.8 (M) | 8.7 (M) |
| $E_2$ | 9.0 (M) | 9.7 (M) |
| $E_3$ | 11.0 (M) | 11.3 (M) |
| $E_4$ | 11.9 (M) | 11.9 (M) |
| $E_5$ | 14.0 (M) | 12.9 (M) |
| $E_6$ | 14.7 (M) | 14.7 (M) |
| $E_7$ | 18.5 (M) | 17.0 (M) |
| $E_8$ | 19.5 (M) | 19.5 (M) |
to almost 1500 K. The exciton shifts to lower energy and broadens as temperature increases. If the temperature dependence of the exciton binding energy is assumed to be small, the exciton follows the fundamental edge, giving us a simple probe of the band gap temperature dependence important for the high temperature conductivity behavior of oxide materials. Similar data was obtained for $\alpha$-Al$_2$O$_3$ and MgAl$_2$O$_4$, and the spectra are omitted for the purposes of brevity. Shown in Fig. 3 are the exciton peak positions for the three oxides vs. temperature. The temperature coefficients vary linearly with temperature and are: $-0.91$, $-0.78$, and $-1.0$ meV/K for MgO, MgAl$_2$O$_4$, and $\alpha$-Al$_2$O$_3$, respectively. These coefficients are larger than observed in the covalent semiconductors, and the same magnitude as in the alkali halides. The exciton half width and line shape in a material are dependent on the strength of the exciton-photon coupling. The framework developed by Tsyaplyaev predicts that weak coupling causes Lorentzian line shapes and widths that vary linearly with $T$, while strong coupling causes Gaussian line shape and widths that vary as $T^2$. Shown in Fig. 6 are the temperature dependence of the exciton halfwidths of MgO and $\alpha$-Al$_2$O$_3$. The MgO half width increases linearly with temperature, while the $\alpha$-Al$_2$O$_3$ exciton half width increases as the square root of temperature, though scatter in the data permits a linear fit. The MgO line shape changes from Lorentzian to Gaussian near 800 K, arising from intermediate exciton-phonon coupling at 300 K with strong coupling seen at high temperature. MgO and MgAl$_2$O$_4$ exhibit Gaussian behavior throughout the temperature range studied, suggesting that exciton-phonon coupling is stronger in more covalent oxides; however, it is important to note that defects present in the polished surfaces may affect the observed exciton-phonon coupling. MgAl$_2$O$_4$ crystals with high antisite defect concentrations exhibit excitons with very wide (0.4 eV half width) Gaussian line shapes, a further indication of defect induced strong coupling. Continuing measurements to low temperatures allow a determination of the effective optical phonon coupling strength [14].

5. High temperature interband transitions

The sharp optical spectra of MgO make it an attractive candidate on which to perform high temperature electronic structure studies. Reducing the temperature has a minimal effect on sharpening the observed optical spectra of MgO, and the only observed change between 300 K and 77 K is a small shift and spin-orbit splitting of the exciton peak [15]. However, large changes are associated in the higher lying interband transitions at elevated temperatures. Shown in Figs. 7 are the 293 K and 1073 K $\chi_0$ of MgO determined from the measured reflectivities. Data was also obtained at 773 K but is omitted from the figure. The difference between room temperature and 1000 K is striking; the major peaks in $\chi_0$ all shifting to lower energy and broadening out considerably. Critical point analysis of the elevated temperature data allows us to determine the temperature dependence of the higher lying transitions and some of the critical points. Shown in Fig. 8 are the experimentally determined shifts in

![Image](image-url)
We previously pointed out differences between our optical assignments and the previous interpretation of the MgO optical data by Roeoeler and Walker. Their assignments of the optical transitions combined with our measurements of the temperature dependence of the critical points lead to several conflicting results. Roeoeler and Walker assign the onset of the 14eV peak in $\tau$ to an $M_1$ transition from $\lambda$ to $\lambda'$ and an $M_1$ point along $\Delta_2 - \Delta_1$ near $\lambda$. We measure a temperature shift of $-1.71$ meV/K for the M point. We did not account for our optical data using an $M_1$ point at $12.8$ eV, but the temperature shift of the valley before the peak, which is essentially the position of the M point, is only $-0.61$ meV/K. This is a very large difference in temperature dependence if the transitions are between the same bands. Furthermore, these points are very close together in the Brillouin zone, and to account for the observed temperature behavior one must invoke large temperature dependent changes in dispersion near $\lambda$. Furthermore, since the $\Gamma$ point separation is decreasing at $-1.22$ meV/K but the $X$ point separation at only $-0.61$ meV/K, dispersion changes from $\Gamma$ to $X$ are needed to account for the observed temperature behavior. Thus our assignments in MgO are more consistent with the calculated energies and the observed temperature dependence.

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References