خواص اپتیکی اکسید اسپینل $MgAl_2O_4$

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چکیده- خواص اپتیکی اکسید اسپینل $MgAl_2O_4$ نظیر تابع دی الکتریک، ضریب انعکاس، ضریب شکست و تابع اتلاف با استفاده از نظریه تابعی چگالی محاسبه شده است. محاسبات بکمک روش پتانسیل کامل امواج تخت تقویت شده و با تقریب شیب تعمیم یافته شده انجام گردید. خواص اپتیکی در دامنه انرژی ۴۰eV-۰ محاسبه شده است. نشایج محاسبات نشان می دهد که این مواد اکسیدی در ناحیه نور مرئی شفاف هستند و تغییرات ضریب شکست در طول موجهای بلند تقریبا خطی است و مقدار آن به شدت در طول موجهای کوتاه افزایش می یابد. ضریب شکست آن در طول موج ۸۰۰nm در حدود ۱/۴۷۷ محاسبه شده است.

کلید واژه- ساختار اسپینل، $MgAl_2O_4$، خواص اپتیکی
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Optical properties of spinel $MgAl_2O_4$ oxide

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Abstract- The optical properties such as the dielectric function, the reflectivity, the refractive index and the loss function have been calculated for spinel $MgAl_2O_4$ oxide using density functional theory (DFT). The full potential linearized augmented plane wave (FL-LAPW) method was used with the generalized gradient approximation (GGA). Calculations of the optical spectra have been performed for the energy range ۰-۴۰eV. It is shown that the material is transparent in the visible wavelengths and dispersion curve of refractive index is fairly flat in the long wavelength region and rises rapidly towards shorter wavelengths. The refractive index value is ۱,۷۷۴ at ۸۰۰ nm near the visible region.

Keywords: Spinel structure, DFT, Optical properties

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۱. Introduction

The spinel structure (sometimes called garnet structure) is named after the mineral *spinel* ($MgAl_2O_4$); the general composition is AB_2O_4. The spinel has a close-packed face-centered-cubic structure space group $Fd\bar{3}m$ (number ۲۲۷), with eight $MgAl_2O_4$ units per cubic cell [۱]. The cations (usually metals) occupy ۱/۸ of the tetrahedral sites and ۱/۲ of the octahedral sites and there are ۳۲ O-ions in the unit cell. The anion sublattice is arranged in a pseudo-cubic close packed (ccp) spatial arrangement. Although some spinels possess almost-ideal ccp anion sublattice [۲].

However, to our knowledge, a few theoretical and experimental articles have been published on the optical properties of spinel $MgAl_2O_4$ oxide. Young-Nian Xu and W.Y. Ching [۳] have studied the electronic structure, the charge-density distribution, and the optical-absorption spectra in MgO, α-Al_2O_3 and $MgAl_2O_4$ crystal by orthogonalized linear combination of atomic orbitals method. P. Thibaudeau and F. Gervais [٤] have performed *ab-initio* calculation on infrared and Raman phonon modes in the normal cubic $MgAl_2O_4$ spinel at the first Brillouin zone centre using density functional theory with plane-wave basis and norm-conserving pseudopotentials. M. L. Bortz *et al.* [٥] have studied the room temperature optical reflectivity of MgO, $MgAl_2O_4$, and α-Al_2O_3 from ٥ to ٤۰eV using a novel spectrophotometer with a laser plasma light source.

In this paper the optical properties of $MgAl_2O_4$ have been calculated within the frame of random phase approximation using density functional theory.

۲. Method of calculation

The calculations and relaxation of the ionic positions were carried out using a FP-LAPW method in the framework of DFT along with the generalized gradient approximation (GGA) [٦, ۷] using Wien۲k codes [۸]. The calculation of complex dielectric tensor was performed with a fine k-mesh using ۱۰۰۰ *k*-

point in the irreducible wedge of first Brillouin zone. The values of other parameters are Rk_{max}=۷ (R is the smallest muffin-tin radius and k_{max} is the cut-off for the plane wave) for the convergence parameter and G_{max}=۱٤ (magnitude of largest vector in charge density Fourier expansion or the plane wave cutoff), R_{MT}(Mg)=۱,۸au, R_{MT}(Al)=۱,۹au and R_{MT}(O)=۱,۷٥au (muffin-tin radius). The iteration halted when the charge difference was less than ۰,۰۰۰۱e between steps as convergence criterion. The cut off energy, which defines the separation of valence and core states, was chosen -٦ Ry.

۳. Optical properties

The dielectric function of anisotropic material is a complex symmetric tensor. In the limit of linear optics, in the case of non-spinpolarized, and within the independent particle approximation, random phase approximation (RPA) the imaginary part of the dielectric tensor can be computed from the knowledge of the electronic band structure of a solid from the following well-known relation [۹]:

$$\mathrm{Im}\varepsilon_{\alpha\beta}(\omega)=\frac{4\pi^2}{m^2\omega^2}\sum_{c,v}\int d\mathbf{k}\langle c_{\mathbf{k}}|p^{\alpha}|v_{\mathbf{k}}\rangle\langle v_{\mathbf{k}}|p^{\beta}|c_{\mathbf{k}}\rangle\delta(\varepsilon_{c_{\mathbf{k}}}-\varepsilon_{v_{\mathbf{k}}}-\omega) \quad (۱)$$

where $|v_k\rangle$ and $|c_k\rangle$ are electron states in the valence and the conduction bands respectively, with the wave vector **k**. The real part of frequency dependent dielectric function $\varepsilon_{\alpha\beta}(\omega)$, is given by:

$$\mathrm{Re}\,\varepsilon_{\alpha\beta}(\omega)=\delta_{\alpha\beta}+\frac{2}{\pi}P\int_0^{\infty}\frac{\omega'\,\mathrm{Im}\,\varepsilon_{\alpha\beta}(\omega')}{\omega'^2-\omega^2}d\omega' \quad (۲)$$

which is P is the Cauchy principal value.

The refractive index, $n(\omega)$, and the extinction coefficient, $k(\omega)$, are given by [۱۰]:

$$n_{\alpha\beta}(\omega)=\left\{\frac{1}{2}\left[|\varepsilon_{\alpha\beta}(\omega)|+\mathrm{Re}\,\varepsilon_{\alpha\beta}(\omega)\right]\right\}^{1/2} \quad (۳)$$

$$k_{\alpha\beta}(\omega)=\left\{\frac{1}{2}\left[|\varepsilon_{\alpha\beta}(\omega)|-\mathrm{Re}\,\varepsilon_{\alpha\beta}(\omega)\right]\right\}^{1/2} \quad (٤)$$

At low frequency the static refractive index $n_{\alpha\beta}(۰)$ can be calculated using the following expression for nonmagnetic materials:

$$n^2_{\alpha\beta}(0)=\mathrm{Re}\,\varepsilon_{\alpha\beta}(\infty) \quad (٥)$$

where $\varepsilon_{\alpha\beta}(\infty)$ is the high-frequency dielectric constant. The spinel $MgAl_2O_4$ structure is isotropic, i.e., there is only one independent component (ε_{xx}).

٤. Results and Discussion

٤,۱ Band structure

The calculated electronic band structure for the spinel $MgAl_2O_4$ oxide along the high symmetry directions is shown in Fig. ۱. The overall band profiles are calculated in this work is consistent with other first-principles calculation results reported previously [۱۱, ۱۲]. The valence bands are separated by a ٥,۲eV direct gap at Γ point from the conduction band states. There are two indirect band gaps in the [۱۱۱] and [۱۰۱] directions, along Γ-L and Γ-X, with a value of ۷,٥eV and ۸,۲eV respectively.

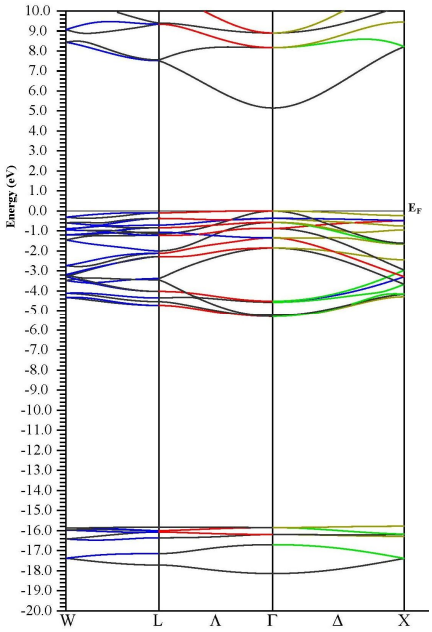

Fig. ۱ The band structure of spinel $MgAl_2O_4$ oxide.

٤,۲. Dielectric function

The real and the imaginary parts of the frequency dependent dielectric for the spinel $MgAl_2O_4$ structure is shown in Fig. ۲. The static dielectric permittivity tensor, $\varepsilon_{\alpha\beta}(۰)$, of a nonpolar material contains electronic, $\varepsilon(\infty)$, and ionic contribution. The electronic dielectric constant of spinel $MgAl_2O_3$ oxide is presented in Table ۲. The calculated $\mathrm{Im}\varepsilon(\omega)$ shows the first peak at about $E_.$=٦,۲۷eV this is due to the fundamental gap. This peak is related to the interband transition from the valence to the conduction band states along Γ–Γ direction.

For simplification of analysis of the other optical transitions spectra, the labels $E_.$, E_1 and E_2 have been used. The subscript ۰ in E refers to transition along [۰۰۰] and ۱ for transitions at points in [۱۱۱] direction and ۲ for transitions in the [۱۰۰] direction of **k** space. These notations are used based on those of Ref. [۱۳] to describe the reflectivity spectra of semiconductor of wurtzite and zinc blend structures. For the spinel structure with space group $Fd\bar{3}m$ (number ۲۲۷) the [۱۱۱] direction is along Γ-L and [۱۰۰] is from Γ-X respectively.

The most important contribution to the peaks E_1 and E_2 arises from the transitions the uppermost valence band to the first conduction band. The positions of five peaks in the imaginary part of the dielectric function calculated in this work are summarized in Table ۱.

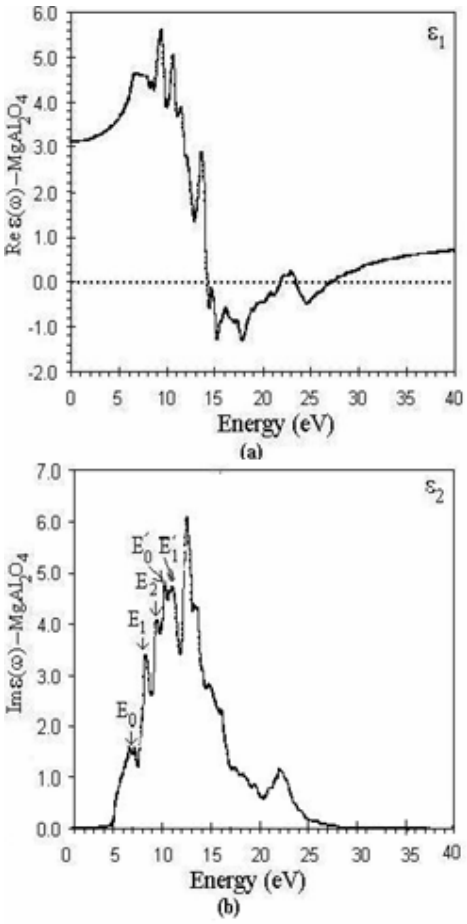

Fig. ۲ (a) Calculated real and (b) imaginary parts of the dielectric function for spinel $MgAl_2O_4$ oxide.

Table ۱ The peaks value of the imaginary part of spinel $MgAl_2O_4$ oxide for transition from uppermost valence to the conduction band.

Peak Energy (eV)	this work	Experimental
E_0 (Γ→Γ)	٦,٢٧	٧,٨ [٥]
E_0' (Γ→Γ)	٩,٤٢	١١,٠ [٥]
E_1(Γ→L)	٧,٤٤	
E_1' (Γ→L)	١٠,١٩	
E_2(Γ→X)	٨,٦١	

Table ۲ The refractive index and high-frequency dielectric constants for spinel $MgAl_2O_4$ oxide

Method	n(٠)	ε(∞)
Experimental:		
Bulk	١,٧١٢ – ١,٧٦٢ [١٤]	
٢,٨٩[١٥]		
Thin film	١,٦٩ – ١,٧٣ [١٦]	
Theoretical:	١,٧٣٢٠ [٤]	٣,٠٠ [٤]
This work	١,٧٦٣	٣,١١٢

In Fig. ۳ the refractive index, $n(\omega)$, and the reflectivity , $R(\omega)$, are shown for spinel $MgAl_2O_4$ structure. The material is transparent in the visible and the excitonic transition associated with the fundamental absorption edge increases in the series from ٦,٢٧ to ١٠,١٩eV. At phonon energies above ٢٤,٥eV the reflectivity magnitudes begin to decrease and the interband transitions are exhausted by ٤٠eV. The experimental spectra of reflectivity of $MgAl_2O_4$ from ٥ to ٤٠eV using a novel spectrophotometer with a laser plasma light source is plotted in Fig. ۳ [٥].

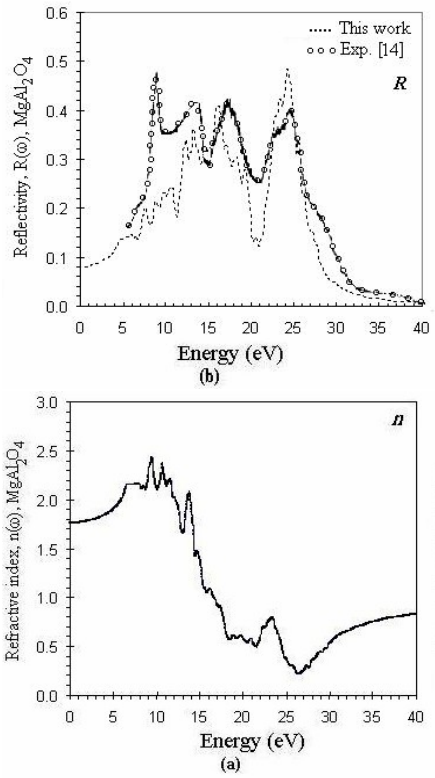

Fig. ۳ (a) Refractive index and (b) reflectivity for spinel $MgAl_2O_4$ oxide.

The refractive index is obtained from equation (١٠) $n(0) \approx 1.763$ which is close to the experimental value ١,٧١ [١٤]. The static refractive index is summarized in Table ۲.

٤,٣ Dispersion of the refractive index

The dispersion curve of refractive index is shown in Fig. ٤. The curve is fairly flat in the long wavelength region and rises rapidly towards shorter wavelengths, showing the typical shape of dispersion curve near an electronic interband transition. The strong increase in the refractive index is associated with the fundamental band gap absorption. The refractive index is ١,٧٧٤ at ٨٠٠ nm near the visible region; the wavelengths of visible light are shaded.

٤,٣ Electron Energy Loss Spectroscopy

We can calculate the EEL spectrum from the following relations [۹]:

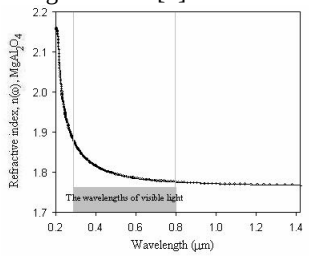

Fig. ٤ Wavelength dispersion curve of the refractive index spinel $MgAl_2O_4$ oxide.

$$\varepsilon_{\alpha\beta}(\omega)=\varepsilon_1+i\varepsilon_2 \quad \text{and} \quad L_{\alpha\beta}(\omega)=\mathrm{Im}[-1/\varepsilon_{\alpha\beta}(\omega)]=\frac{\varepsilon_2}{\varepsilon_1^2+\varepsilon_2^2} \qquad (٦)$$

In Fig. ٥ the energy loss function is plotted for spinel $MgAl_2O_4$ oxide. There are other peaks and features in this spectrum, in addition to the plasmon peak, associated with interband transitions. The plasmon peak is usually the most intense feature in the spectrum and this is at energy that the Reε(ω) goes to zero, after the zero-loss peak, the zero loss peak is absent in Fig. ٥.

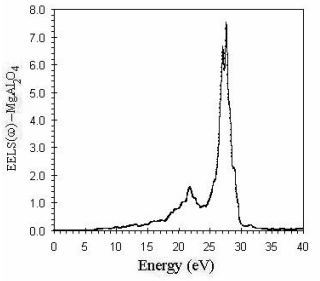

Fig. ٥ Loss functions for the spinel $MgAl_2O_4$ oxide.

The maximum peak energy of $\mathrm{Im}[-\varepsilon^{-1}(\omega)]$ at ۲۷,٦٦eV is assigned to the energy of volume plasmon $\eta\omega_p$. The various calculated energy loss values obtained in this study are corresponding to different transitions and associated with interband transitions. Some spectra also show a broad weak peak and we observe several peaks and a rather broad spectrum.

٥ Conclusions

We calculated and analyzed the optical constants spectra of spinel $MgAl_2O_4$ oxide as function of the incident photon energy. The calculated results show a ٥,۲eV direct band gap along Γ-Γ direction for this structure.

The material is transparent in the visible wavelengths and the excitonic transition associated with the fundamental absorption edge increases in the series from ٦,۲۷ to ۱۰,۱۹eV. The dispersion curve of refractive index is fairly flat in the long wavelength region and rises rapidly towards shorter wavelengths, showing the typical shape of dispersion curve near an electronic interband transition. The refractive index value is ۱,۷۷٤ at ۸۰۰ nm near the visible region.

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