Reststrahlen spectroscopy of MgAl₂O₄ spinel

N.N. Boguslavskaya¹, E.F. Venger¹, N.M. Vernidub², Yu.A. Pasechnik², K.V. Shportko²

¹ Institute of Semiconductor Physics, NAS of Ukraine, 45 prospect Nauky, 03028 Kyiv, Ukraine
² M.Dragomanov National Pedagogic University, 9 Pirogova St., 01030 Kyiv, Ukraine

Abstract. Using IR reflectance spectroscopy and surface polariton spectroscopy in the reststrahlen region, we investigated Czochralski-grown MgAl₂O₄ spinel. The computer analysis of variance made for spectra enabled us to get a mathematical model for reflection spectra of spinel. In our calculations we used consistent data for optical parameters (zero- and high-frequency permittivities, transverse optical phonon frequencies and corresponding damping coefficients) of spinel single crystals that have been obtained from comparison between the measured and calculated spectra. These data were used when studying attenuated total reflection spectra and dispersion curves for surface polaritons in MgAl₂O₄ spinel.

Keywords: reflectance spectroscopy, surface polaritons, spinel, reststrahlen, attenuated total reflection spectra.

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1. Introduction

Both natural and synthetic spinelides are promising materials for use in micro- and optoelectronics. That is why they often draw attention of researchers. However, investigation of their physico-chemical properties is complicated by the fact that in many cases their structure is unknown. The attempts to make the problem easier by arranging the samples studied in series of pseudo-binary solid solutions often have not met with success. The reason for this lies in the fact that there are some restrictions on compatibility, heterogeneity and multicomponent character of isomorphic mixtures.

Many authors have dealt with investigation of IR absorption spectra of natural and synthetic chemical compounds of spinel-like structure (see the review [1]). In [1] these spectra were studied in spinelides belonging to the set of (Mg, Fe)(Fe³⁺, Al, Cr)₂O₄ solid solutions. The authors of [1] have obtained both structural and spectroscopic characteristics of synthetic spinelides and proved, on the empirical level, that the model for independent vibrations of tetrahedral and octahedral "molecules" of spinel structure is inadequate. A comparison between the crystal-chemical and optical parameters of spinelides belonging to nine continuous sets of solid solutions enabled the authors of [1] to treat the spectra as resulting from vibrations of the spinelide lattice as a whole. The predominant role of the effect of octahedral isomorphic substitutions on the absorption spectral line positions also has been stressed in [1].

The MgAl₂O₄ spinel structure is typical for the X²⁺Y³⁺O₄²⁻-type compounds where X and Y are cations (at least one of which belongs to the transition element group) and O is oxygen [2]. For the so-called normal spinels the cation X is bivalent (Mg²⁺, Mn²⁺, Fe²⁺, Ni²⁺, Zn²⁺), while cation Y is trivalent (Al³⁺, V³⁺, Cr³⁺, Fe³⁺, Mn³⁺). The crystal has a face-centered cubic (FCC) lattice. The anions (located at vertexes) form the closest cubic three-layer package. One may recognize the following two cation sublattices in the spinel structure: tetrahedral (A-sublattice) and octahedral (B-sublattice). Chemical bonding in the spinel structure is of mixed ionic-covalent type. In normal spinels the cations X²⁺ occupy the tetrahedral (A) interstitials, while the cations Y³⁺...
occupy the octahedral (B) ones. In this case the chemical formula \(X^{2+}Y^{3+}O_4^{2-}\) is valid. The MgAl\(_2\)O\(_4\) spinel belongs to normal, while MgFe\(_2\)O\(_4\), Fe\(_2\)O\(_3\) belong to inverse spinels. The spinel structure is like to that of the Fe\(_2\)O\(_3\) magnetite: the Mg\(^{2+}\) ions occupy the tetrahedral interstitials and the Al\(^{3+}\) ions are located at the octahedral sites.

Highly symmetric (Fd\(_{3}mn\)) structure of cubic spinelides results in a rather simple form of IR absorption spectrum in the 200-1000 cm\(^{-1}\) region. Depending on the compound studied and sample origin, this spectrum usually involves from two to four intense bands and a variable number of weaker bands that manifest themselves as “shoulders” at the intense band slopes.

After 1955, interpretation of the IR spectra in compounds of spinel structure is based on a theory that has been initially advanced by Waldron [3]. In his model the crystal structure considered has a rhombohedral primitive cell. In the case of normal spinel this cell contains two AO\(_2\) tetrahedrons (each having four oxygen ions and a tetrahedral cation A at its center) and a tetrahedron B (that involves four octahedral cations). The vibrations of each of the above groups of ions have been classified according to the features of the point group \(T_d\) (which is believed to correspond to vibrations of the crystal as a whole). As a result, Waldron has concluded that only four crystal vibrational modes are IR-active. Two of them (having the highest frequencies \(\nu_1\) and \(\nu_2\)) stem from oxygen ion motion, while the other two modes are related to motion of metal cations.

Comprehensive experimental studies of spinel IR spectra have been performed after the paper [3] by Waldron has appeared. Their results have been in favor of existence of four fundamental absorption bands in the cubic spinel-type compounds. Indeed, four bands were observed. They were accompanied by weaker bands and inflections (“shoulders”) [3]. In two or three cases it was possible to relate some of these weaker bands and “shoulders” to presence of structural imperfections in the crystals studied, but generally their nature remained unclear.

An alternative approach to the problem of spectra interpretation has been advanced in [3]. The experimentally observed spectral features have been explained in terms of vibrations of crystal as a whole. It was shown that IR absorption in MgAl\(_2\)O\(_4\) could be rather adequately described with a spectrum whose peaks were related to the critical points in the Brillouin zone.

Three intense bands (at frequencies of 692, 526 and 307 cm\(^{-1}\)) are observed in the IR absorption spectrum of synthetic MgAl\(_2\)O\(_4\) spinel, along with a weaker peak or “shoulder” at a frequency of 720 cm\(^{-1}\) (see Table 1). The experiments for a set of spinels where Mg\(_2\)O\(_4\) is a principal component showed that two other important frequencies also lie near 570 and 455 cm\(^{-1}\). The observed spectrum features might depend on the preparation technique and material stoichiometry.

The absorption spectrum of the natural spinel is known to slightly differ from that of the synthetic material [3]. A comparison between the data for synthetic and natural spinels published by different authors is given in Table 1. The features of reflection spectrum for the natural MgAl\(_2\)O\(_4\) single crystal published in 1964 by Slack [4] are also of interest; they are given in Table 2.

<table>
<thead>
<tr>
<th>Spectral feature</th>
<th>Frequency, cm(^{-1}) (a)</th>
<th>Frequency, cm(^{-1}) (b)</th>
<th>Frequency, cm(^{-1}) (c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic spinel</td>
<td>Synthetic spinel</td>
<td>Natural spinel</td>
<td>Natural spinel</td>
</tr>
<tr>
<td>“Shoulder”</td>
<td>720</td>
<td>750</td>
<td>752</td>
</tr>
<tr>
<td>Peak</td>
<td>692</td>
<td>690</td>
<td>685</td>
</tr>
<tr>
<td>“Shoulder”</td>
<td>570</td>
<td>-</td>
<td>578</td>
</tr>
<tr>
<td>Peak</td>
<td>526</td>
<td>538</td>
<td>521</td>
</tr>
<tr>
<td>“Shoulder”</td>
<td>455</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak</td>
<td>307</td>
<td></td>
<td>309</td>
</tr>
</tbody>
</table>

For spinel whose primitive unit cell contains 14 ions 42 branches are to exist for the phonon dispersion. Thus, the problem of adequate interpretation of IR spectra is rather complicated due to the lack of additional information concerning the phonon dispersion curves. Since the ordinary unit cell of spinel belongs to the cubic (FCC) lattice, the Brillouin zone for spinel is similar to that of sphalerite (zinc blende) [4]. Therefore the phonon wave vectors at critical points are known.

The author of [4] has measured optical reflection from Mg\(_2\)O\(_3\) and FeAl\(_2\)O\(_4\) in the 0.03 up to 2.0 eV range to determine the strong lattice absorption region and obtain reflection coefficient \(R\). The measurements have been performed at a temperature of 300 K and almost normal incidence of light beam. Intense peaks of lattice absorption have been found in the photon energy range from 0.03 to 0.11 eV. The MgAl\(_2\)O\(_4\) sample used was a natural spinel crystal from Burma; it was pale-rose colored. The synthetic FeAl\(_2\)O\(_4\) crystal has been grown without additional annealing. The crystal surfaces were polished in such a way as to be optically flat for reflection measurements.

The results of MgAl\(_2\)O\(_4\) reflection spectrum recording are shown in Fig. 1. The principal lattice absorption peaks lie at 0.066 and 0.091 eV (533 and 735 cm\(^{-1}\)).

Table 1. IR absorption spectra of MgAl\(_2\)O\(_4\) spinel [3].

<table>
<thead>
<tr>
<th>Spectral features</th>
<th>Energy, eV</th>
<th>Frequency, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak “shoulder”</td>
<td>0.104</td>
<td>840</td>
</tr>
<tr>
<td>Sharp peak</td>
<td>0.091</td>
<td>735</td>
</tr>
<tr>
<td>“Shoulder”</td>
<td>0.072</td>
<td>582</td>
</tr>
<tr>
<td>Broad peak</td>
<td>0.066</td>
<td>533</td>
</tr>
<tr>
<td>“Shoulder”</td>
<td>0.059</td>
<td>477</td>
</tr>
<tr>
<td>Sharp peak</td>
<td>0.0375</td>
<td>304</td>
</tr>
</tbody>
</table>

The data on other (less intense) peaks obtained are given in Table 3. The values of $R$ at normal incidence of light beam onto the sample (Table 3) are believed to be rather accurate [4]. The values of $R$ for FeAl$_2$O$_4$ recorded at angle of incidence equal to 30° are approximate, but they still give relative intensities of different peaks.

The intense reflection peaks are related to strong absorption. There is close similarity between these lattice vibrational peaks for MgAl$_2$O$_4$ and FeAl$_2$O$_4$ because both crystals belong to the spinel structure and their lattice parameters are almost the same. A Fe atom is heavier than a Mg one; the FeAl$_2$O$_4$ reflection peaks lie at energies that are below those in MgAl$_2$O$_4$ by about 5%. The reflection coefficient $R$ for MgAl$_2$O$_4$ is very low (from 2 to 8%) in the energy range from 0.12 to 3.0 eV (actually up to 4 eV). The overall situation for FeAl$_2$O$_4$ is similar.

Optical properties of spinel that served as substrate when growing silicon layers were studied in [5]. The MgAl$_2$O$_4$ substrate was Czochralski-grown; it had the structure of normal cubic spinel. Two principal MgAl$_2$O$_4$ absorption bands (lying at 688 and 522 cm$^{-1}$) have been identified. They are related to the O-Al complex in the octahedron.

Table 3. Reflection spectrum of MgAl$_2$O$_4$ spinel natural single crystal [4]. (Greek letters are used for absorption bands labeling.)

<table>
<thead>
<tr>
<th>Band label</th>
<th>Energy, eV</th>
<th>Frequency, cm$^{-1}$</th>
<th>Reflection coefficient $R$, %</th>
<th>Spectral features</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.0375</td>
<td>303</td>
<td>36</td>
<td>Broad peak</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.059</td>
<td>476</td>
<td>89</td>
<td>Sharp peak</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.066</td>
<td>533</td>
<td>100</td>
<td>Broad peak</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.072</td>
<td>581</td>
<td>75</td>
<td>&quot;Shoulder&quot;</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>0.091</td>
<td>735</td>
<td>100</td>
<td>Sharp peak</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>0.104</td>
<td>840</td>
<td>50</td>
<td>Slightly pronounced &quot;shoulder&quot;</td>
</tr>
<tr>
<td>$\theta$</td>
<td>0.176</td>
<td>Low</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2. Reflection spectra of MgAl$_2$O$_4$ spinel synthetic single crystals: 1, 2 – experimental spectra for two samples; 3 – spectrum taken from [5]; 4 – calculated spectrum with parameters $R(\nu)$ given in Table 4.

2. Results and discussion

Here we present some results of our experiments dealing with the optical properties of Czochralski-grown synthetic MgAl$_2$O$_4$ spinel. We used IR reflectance spectroscopy and surface polariton spectroscopy in the reststrahlen region. The IR reflection spectra in the 400-1400 cm$^{-1}$ range were taken with spectrometer IKS-29 (equipped with attachment IPO-22) using polarized radiation. These spectra (Fig. 2, curves 1, 2) somewhat differ from those given in [5]. The reflection peaks taken in [5] (see Fig. 2, curve 3) lie at frequencies of 745 and 545 cm$^{-1}$. They refer to the same lattice vibrations as the absorption peaks. The reflection peaks are shifted toward higher frequencies as compared to the absorption peaks. This is characteristic of strong absorption bands. The reflection coefficient $R = 0.13$ in the 0.3-3 µm wavelength range leads to the refraction index value $n = 1.7$. This value agrees with those (1.7-1.72) obtained in a number of papers at a wavelength of 0.6 µm. From the interference fringes observed in experiments with spinel transparency it follows that the refraction index value is close to 3; at low (near 1 kHz) frequencies the spinel permittivity is 8.4.

A comparison between the MgAl$_2$O$_4$ reflection spectra obtained in [4] and [5] evidences that they differ substantially. In [4] it was stated that the reflection spectrum has two peaks corresponding to total (100%) reflection. Contrary to this, the reflection peaks at frequencies of 745 and 545 cm$^{-1}$ obtained in [5] corresponded to reflection coefficient of about 80% and 65%, respectively. No model has been advanced in either [4] or [5] that could give a quantitative description for the spinel reststrahlen region.
A computer analysis of variance made for the spectra obtained enabled us to advance a mathematical model for spinel reflection spectra. In our calculations we used the consistent data on the optical parameters of spinel single crystals that were obtained by comparing the experimental and calculated spectra.

When calculating the reflection coefficient, we used the following well-known expression [6]:

\[
R(\nu) = \left( \frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} - \sqrt{2 \left( \sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1} \right) + 1}}{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \sqrt{2 \left( \sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_1} \right) + 1}} \right)^2
\]

Here \( \varepsilon_1 \) and \( \varepsilon_2 \) are, respectively, the real and imaginary parts of the crystal permittivity that was taken in the following form:

\[
e(\nu) = \varepsilon_1 + i\varepsilon_2 = \varepsilon_\infty + \sum_{i=1}^{3} \frac{S_i \nu_{Ti}^2}{\nu_{Ti}^2 - \nu^2 - i\gamma_{Ti}\nu}
\]

where \( \varepsilon_\infty \) is the high-frequency permittivity; \( S_i \) is the \( i \)-th oscillator strength; \( \nu_{Ti} \) (\( \gamma_{Ti} \)) is the frequency (damping coefficient) of the \( i \)-th oscillator, i.e., transverse optical phonon. The summation is made for the case of a multiphonon vibrational system of the crystal lattice. A root-mean-square deviation \( d \) of the experimental parameter value from the calculated one is determined from the formula:

\[
d = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (R_{Ei} - R_{Ti})^2}
\]

and angle \( \alpha \) (angle of incidence for an ATR unit).

Table 4. Optical parameters of the reflection spectra model \( R(\nu) \) and ATR for spinel.

<table>
<thead>
<tr>
<th>( R(\nu) )</th>
<th>( \varepsilon_0 )</th>
<th>( \varepsilon_\infty )</th>
<th>( \nu_{T1} )</th>
<th>( \nu_{T2} )</th>
<th>( \nu_{T3} )</th>
<th>( \gamma_{T1} )</th>
<th>( \gamma_{T2} )</th>
<th>( \gamma_{T3} )</th>
<th>( b_1 )</th>
<th>( b_2 )</th>
<th>( b_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu, \alpha )</td>
<td>7.4</td>
<td>2.89</td>
<td>510</td>
<td>680</td>
<td>795</td>
<td>5</td>
<td>1.4</td>
<td>16</td>
<td>3.58</td>
<td>0.73</td>
<td>0.2</td>
</tr>
<tr>
<td>ATR</td>
<td>7.4</td>
<td>2.89</td>
<td>502</td>
<td>650</td>
<td>830</td>
<td>65</td>
<td>20</td>
<td>136</td>
<td>3.58</td>
<td>0.73</td>
<td>0.2</td>
</tr>
</tbody>
</table>

At the moment there are a number of papers dealing with investigation of surface polaritons (SP) in such compounds as silicon carbide, aluminum oxide, etc. For spinels, however, the characteristics of SP in the IR region practically have not been studied yet [7, 8]. Here we present, for the first time, results of our investigations of surface phonon polaritons in MgAl\(_2\)O\(_4\) spinel.

One of the experimental techniques used when studying SP is attenuated total reflectance (ATR). We took the ATR spectra of SP for Czochralski-grown synthetic MgAl\(_2\)O\(_4\) spinel in the 400-1100 cm\(^{-1}\) frequency range. In our experiments we used polarized radiation and spectrometer IKS-29 equipped with attachment NPVO-1. Shown in Fig. 3 is the so-called SP reflection surface, \( R(\nu, \alpha) \). It is a set of eight experimental SP ATR spectra taken at angles from 30 up to 39°. A reflection surface \( R(\nu, \alpha) \) is a three-dimensional presentation of the system transmission that depends on the radiation frequency \( \nu \) and angle \( \alpha \) (angle of incidence for an ATR unit).

If there are SP damping and dissipation of the electromagnetic wave energy, then the surface \( R(\nu, \alpha) = I(\nu, \alpha)/I_0(\nu, \alpha) \) has two “canyons” connected with a “pass”.

Fig. 3. Experimental SP ATR spectra of MgAl\(_2\)O\(_4\) spinel synthetic single crystal (curves 1, ..., 8 have been taken at reflection angles of 30.3, ..., 39.3°).
(Here \( I(\nu, \alpha) \) is the intensity of radiation passing through the “ATR unit (semicylinder)-gap-sample” system; \( I_0(\nu, \alpha) \) is the intensity of radiation incident onto the ATR unit.) The “canyon” depth depends on the system parameters: gap \( d \) between the ATR semicylinder and sample, radiation frequency \( \nu \), complex permittivity \( \varepsilon(\nu, \kappa) \) of the sample, permittivities of the ATR unit and gap. The SP dispersion curves \( \nu, (k) \) correspond to the “canyons”, i.e., to the set of ATR spectra minima. (Here \( \nu_s \) is the SP frequency and \( k \) is the SP wave vector.) The frequencies at which the minima of the experimentally determined surface \( R(\nu, \kappa) \) lie, as a rule, agree with those of the calculated dispersion curve \( \nu, (k) \) at the phonon damping coefficient \( \gamma_T = 0 \).

The relation between the ATR spectrum minima and SP dispersion curve is given by the following equation:

\[
k = (2\pi\nu/c)\sin\alpha
\]

(3)

Here \( \nu \) is the frequency of the ATR spectrum minimum; \( c \) is the speed of light in a vacuum; \( n \) is the refractive index of material of the ATR semicylinder. (We used the material KRS-5 with \( n = 2.37 \).) If the optical phonon damping is taken into account, then one more “canyon” appears at the reflection surface \( R(\nu, \kappa) \), with a “pass” to the first “canyon” in the frequency region \( \nu > \nu_s \). This can be detected by recording the SP ATR spectra at \( \nu = \) const and scanning over the angle \( \alpha \) values.

Three experimental ATR spectra (curves 1-3) taken at angles \( \alpha = 29.3, 31.3 \) and \( 33.3^\circ \) are shown in Fig. 4. Curves 4 and 5 are the theoretical ATR spectra calculated at \( \alpha = 31.3 \) and \( 33.3^\circ \); the oscillation frequencies were 502, 650 and 830 cm\(^{-1}\), while the damping coefficients were 65, 20 and 136 cm\(^{-1}\).

Figure 5 presents the calculated (full curves) and experimental (dots) SP dispersion curves in spinel. The feature of dispersion curves in MgAl\(_2\)O\(_4\) spinel is presence of three branches. This fact agrees with the developed mathematical model for spinel that takes into account contributions from three oscillators (phonons) to the permittivity. The obtained consistent data concerning the optical parameters (zero- and high-frequency permittivities, transverse optical phonon frequencies and corresponding damping coefficients) of spinel single crystals are presented in Table 4.

The \( R(\nu) \) row in Table 4 has been obtained from comparison between the experimental and calculated spectra. The ATR row gives the parameter values used when trying to simulate the calculated ATR spectra at \( \alpha = 31.3 \) and \( 33.3^\circ \). One can see from Fig. 4 that only qualitative agreement exists between the spectra 2, 3 and 4, 5. When comparing the data obtained from the \( R(\nu) \) and ATR spectra, one can see that to get better agreement one should take essentially different frequencies of three oscillators, as well as the corresponding damping coefficients. In particular, the oscillator frequencies differ by 10-30 cm\(^{-1}\) and the damping coefficients differ by a factor of 10-15. This indicates at the effect of a near-surface layer on the properties of phonon SP in spinel. We propose to obtain the data concerning optical properties of near-surface regions in materials from quantitative comparison between the experimental and theoretical reflection surfaces made using PC. This will make it possible to get more detailed information on the system studied.

3. Conclusion

Using IR reflectance spectroscopy and surface polariton spectroscopy in the reststrahlen region, we investigated Czochralski-grown MgAl\(_2\)O\(_4\) spinel. The computer analysis of variance made for spectra enabled us to get a mathematical model for reflection spectra of spinel. In our calculations we used consistent data for optical parameters (zero- and high-frequency permittivities, transverse optical phonon frequencies and corresponding damping coefficients) of spinel single crystals that have been obtained from comparison between the measured and calculated spectra. These data were used when studying ATR spectra and dispersion curves for surface polaritons in MgAl\(_2\)O\(_4\) spinel.
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