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Infrared optical properties of Mn$_{1.56}$Co$_{0.96}$Ni$_{0.48}$O$_4$ spinel films sputter deposited in an oxygen partial pressure series

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Mn$_{1.56}$Co$_{0.96}$Ni$_{0.48}$O$_4$ spinel films were sputter deposited onto silicon substrates using a series of oxygen partial pressures. Fourier transform infrared transmission and reflectance, and Raman scattering measurements were made. The 1–25 µm wavelength range was examined using these optical techniques. The complex index of refraction was calculated for this entire wavelength range. Infrared active vibrations were analyzed using multiple oscillator analysis, Kramers–Kronig analysis, and derivative reflectance spectroscopy. The Raman and infrared active lattice vibrations were observed to shift with increasing oxygen partial pressure during film deposition, and were consistent with the earlier published shift in Debye frequency calculated from resistivity data. The films were shown to have an optically transparent window from 6 to 14 µm wavelength, with the multiphonon cutoff occurring at 14 µm. The frequency of the multiphonon cutoff was also observed to shift to higher frequency with the oxygen partial pressure during sputtering. These studies, and the earlier work on the variation of the thermopower and resistivity with oxygen partial pressure and film temperature, are consistent with a change in the ratio of Mn$^{3+}$ to Mn$^{4+}$ cations with oxygen, with small polaron hopping as the charge transport mechanism. © 1999 American Institute of Physics. [S0021-8979(99)01417-6]

I. INTRODUCTION

Mn–Co–Ni–O spinel, owing to its large temperature-dependent resistivity, is an attractive ternary system for thermistor applications, and for infrared detecting bolometers. The materials resistivity can be changed by altering the relative contents of the metallic species, producing a range of spinel structured solid solutions. Mn$_{1.56}$Co$_{0.96}$Ni$_{0.48}$O$_4$ is a composition of some specific importance because it is very near the resistivity minimum for the ternary oxide. Though the traditional approach to make thermistor sensors and infrared bolometers has been to use sintered ceramics, in the last decade thin films of the ternary oxide have been fabricated successfully by rf magnetron sputtering with electrical properties approaching the sintered material. Applications of these films in infrared detecting bolometers and in uncooled focal plane arrays have been described in conference proceedings. However, to our knowledge there have been no systematic and complete studies of the optical properties of the Mn–Co–Ni–O thin films prior to this work.

The objectives of this study were as follows: (1) characterize the optical transmittance, reflectance, and absorption of the films from near to far infrared; (2) calculate the complex refractive index of the films over the entire wavelength range of study; (3) use multiple oscillator analysis and also Kramers–Kronig analysis to analyze the IR active vibrations; (4) observe and understand the changes to the above optical and electronic properties as the oxygen content in the films is varied, and relate these changes to stoichiometry. In the opinion of the authors, such a study combined with the earlier studies on thermopower and electrical resistivity of these films, results in a fairly complete understanding of their electronic and optical properties. The properties of the films in the ultraviolet and visible will be published separately, along with a detailed analysis of the electronic absorption mechanism.

The optical properties of oxides such as spinel may be understood as follows. In the infrared region, radiation stimulates vibrations of the atoms of the solid at the characteristic reststrahlen frequencies. In the ultraviolet region, radiation promotes electrons from filled bands to higher energy unfilled bands. Between these two strong absorption regions is a window in which the material is transparent and known as the optical window region. For MgAl$_2$O$_4$ spinel, the optical window is from 0.2 to 6 µm. The infrared edge of the window is known as the Urbach edge. In the transparent win-
dow region, absorption is low and due to impurities. Transmission losses are mainly due to scattering by imperfections from the single-crystal structure; in the case of the sputter deposited films the films are polycrystalline.\textsuperscript{2,3} An interesting aspect of the Mn–Co–Ni–O thin films is that the long-wave cutoff occurs around 14 \(\mu\)m, which is a very long cutoff wavelength for an oxide and may have some practical applications. In comparison, MgO has a long-wave cutoff at 8.5 \(\mu\)m and MgAl\(_2\)O\(_4\) spinel a cutoff at 6 \(\mu\)m.\textsuperscript{9}

II. FILM PREPARATION AND COMPOSITION

The deposition of the films, along with preparation of the ceramic oxide target, and the technique of rf magnetron sputtering of the oxide material has been detailed in earlier publications.\textsuperscript{2,3} Briefly, a total Ar+O\(_2\) pressure of 40 mTorr was used with rf power of 350 W, using a sputtered oxide target of the composition Mn\(_{0.56}\)Co\(_{0.90}\)Ni\(_{0.48}\)O\(_{4}\). This is also the desired composition of the deposited films, and the historical composition used in the fabrication of the sintered ceramic flakes for infrared bolometers. X-ray diffraction showed the target material to be single-phase cubic spinel with 56% Mn, 32% Co, and 16% Ni. The deposited films were also observed to be a single phase and spinel-like, with some variation of the peak intensities. X-ray energy dispersive spectroscopy showed, for all films, that the metallic composition varied by less than 2% from the target for each species.

Films were deposited using a series of oxygen partial pressures 0, 0.16, 0.8, 1.6, and 4 mTorr out of the total of 40 mTorr of Ar+O\(_2\). 4 mTorr thus corresponding to a percent diatomic oxygen of 10%. These partial pressures were selected based on the studies described in Ref. 3, where oxygen partial pressures were varied to minimize electrical resistivity so as to approach the ceramic film resistivities. The film resistivity is in the range 250–500 \(\Omega\) cm for the thicker films (3–8 \(\mu\)m). For the infrared and Raman studies, both sides polished, undoped silicon wafers 225 \(\mu\)m thick were used as substrates. The thickness of these specimens was 3–8 \(\mu\)m depending on the oxygen partial pressure, since the deposition time was kept constant at 8 h. Film thickness decreased as the oxygen partial pressure increased. Scanning electron microscopy (SEM) showed that the morphology was a dense, columnar, late zone 1 to early zone 2 structure with a cap agglomerate size about 0.5–0.7 \(\mu\)m in diameter. For all films, transmission electron microscope (TEM) images and electron diffraction ring patterns showed the films to be polycrystalline with agglomerates composed of crystallites on the order of 25–50 nm in diameter. There were no amorphous rings in the TEM diffraction patterns and no large low angle intensity on the x-ray diffractograms to suggest the presence of any amorphous phase.

Various attempts were made to deduce the cation distribution of the oxides in the partial pressure series, using both electron energy loss spectroscopy and electron spectroscopy for chemical analysis (ESCA). Due to the lack of good standard materials (and the surface sensitivity of ESCA), we do not believe the results obtained were reliable. However, based on our transport study (Ref. 7), we believe the oxygen stoichiometric cation distribution to be

\[
[\text{Co}^{2+}_{0.55}\text{Mn}^{2+}_{0.443}]_7[\text{Ni}^{2+}_{0.48}\text{Co}^{3+}_{0.403}\text{Mn}^{4+}_{0.48}\text{Mn}^{3+}_{0.637}]_6\text{O}_{4}^{2-}
\]

Note that the only multivalent cation on a single type of polaron hopping site (\(O\) for octahedral, \(T\) for tetrahedral) are Mn\(^{3+}\) and Mn\(^{4+}\) on octahedral sites. Based on our work in Ref. 7, we believe this remains the most important hopping site for other oxygen stoichiometries.

III. OPTICAL PROPERTIES IN THE INFRARED

A. Theoretical introduction

IR radiation interacts with the optical modes of a crystal. The photon–phonon interaction in an ionic crystal originates from the forced, damped motion of oppositely charged ions both parallel and perpendicular to the direction of the electric field vector of the incident radiation.

Using a dipole model, the equation of motion of displacement \(u\) for a pair of equal and oppositely charged ions of charge \(\pm e\), subject to a forced, damped vibration with damping constant \(\gamma\), where the forcing function is a frequency dependent electric field \(E\), is

\[
(d^2u/dt^2) + \gamma (du/dt) + \omega_0^2 u = e^*E/m.
\]

Here \(\omega_0 = f/m\) is the natural frequency of the ionic vibration, \(m^{-1} = M^{-1}_\parallel + M^{-1}_\perp\), which is the reciprocal of the reduced mass of the positive and negative ions, and \(f\) is the force constant characterizing the stiffness of the lattice, or bonding between the ions. Assuming that \(u = u_0 \exp(-i\omega t)\) and \(E = E_0 \exp(-i\omega t)\), that the volume polarizability of \(N\) equal oscillators is \(\chi = (N/V)e^*u\), and that \(D = eE = E + 4\pi\mathbf{P}\) from the definition of the displacement field, the dispersion relation may be solved for \(\epsilon(\omega)\) with the result\textsuperscript{10}

\[
\epsilon(\omega) = 1 + 4\pi VNe^*/m(\omega_0^2 - \omega^2 + i\gamma \omega).
\]

This expression gives purely the ionic contribution to the dielectric constant. We must add to Eq. (2) the electronic contribution from the electrons orbiting the ion cores, \(\epsilon_{\text{elec}}\), which is a constant in the infrared. In Eq. (2), this amounts to a replacement of 1 by \(\epsilon(\infty) = \epsilon_{\text{elec}} + 1\). If there was no damping, this expression could be rewritten as

\[
\epsilon(\omega) = [\epsilon(\infty) - \epsilon(0)]/[(\omega^2/\omega_0^2 - 1)] + \epsilon(\infty),
\]

where \(\epsilon(\infty)\) and \(\epsilon(0)\) are the high and low frequency limits of Eq. (2), termed the dynamic and static dielectric constants. The frequencies, which lead to roots and divergence in this equation, can be related to the type of mode of the vibration by considering Maxwell’s equations. Let all field terms \(D, E, P\) have a spatial variation \(\sim X_0 \exp[i(\mathbf{k} \cdot \mathbf{r})]\) where \(X_0\) stands for any of the fields, and \(\mathbf{k}\) is the propagation vector of the radiation. Maxwell’s equations demand that with no free charge \(\text{div}(D) = 0\) and \(\text{curl}(E) = 0\), and the conditions that satisfy this are

\[
\mathbf{k} \cdot D_0 = 0\text{ requiring } \mathbf{X} \text{ perpendicular to } \mathbf{k},
\]

or requiring \(D = 0\). (4)
\[ \mathbf{k} \times \mathbf{E}_0 = 0 \] requiring \( \mathbf{X} \) parallel to \( \mathbf{k} \),
or requiring \( \mathbf{E} = 0 \).

When the mode is transverse, atoms move parallel to the electric field vector of the radiation, or, perpendicular to \( \mathbf{k} \). Therefore, the polarization field \( \mathbf{P} \) generated must be perpendicular to \( \mathbf{k} \) so the consistent solution is \( \mathbf{E} = 0 \) of Eq. (5). From the definition of displacement, \( \mathbf{E} = 0 \) only if \( \epsilon = \infty \). \( \epsilon = \infty \) when \( \omega = \omega_0 \). The transverse optical (TO) frequency is identified with \( \omega_0 \).

When the mode is longitudinal, atoms move perpendicular to the electric field vector of the radiation, or, parallel to \( \mathbf{k} \). Therefore, the polarization field \( \mathbf{P} \) generated must be parallel to \( \mathbf{k} \) so the consistent solution is \( \mathbf{D} = 0 \) of Eq. (4). \( \mathbf{D} = 0 \) only if \( \epsilon = 0 \). \( \epsilon = 0 \) when \( \omega^2 = \omega_0^2 \epsilon(0)/\epsilon(\infty) \). The longitudinal optical (LO) frequency is identified with the root of \( \epsilon \) just after the divergence at the TO frequency.

This model assumes one oscillator. In a crystal, there are many optical modes. With \( p \) atoms per primitive cell, there are \( 3p-3 \) optical modes. A general expression which is frequently used to fit a smooth curve through reflectance data when more than one mode is observable whose constants may be related to physical parameters is \( 10,11 \)

\[
\epsilon_1 = \epsilon(\infty) + \sum_i 4 \pi \rho_i \omega_i^2 (\omega_i^2 - \omega^2)\left[ (\omega_i^2 - \omega^2)^2 + (\gamma_i \omega_i)^2 \right],
\]

\[
\epsilon_2 = \sum_i 4 \pi \rho_i (\gamma_i \omega_i^2 / (\omega_i^2 - \omega^2)^2 + (\gamma_i \omega_i)^2),
\]

\[
n^2 = (1/2)[\epsilon_1 + (\epsilon_2^2 + \epsilon_1^2)^{1/2}],
\]

\[
\epsilon_2 = 2n \kappa,
\]

\[
R = [(n - 1)^2 + \kappa^2]/[(n + 1)^2 + \kappa^2],
\]

where \( R \) is reflectance, \( \rho_i \) is an oscillator strength, \( \epsilon_1 \) and \( \epsilon_2 \) are the real and imaginary parts of the dielectric constant, \( \epsilon(\infty) \) is the high frequency limit of \( \epsilon \), and \( n \) and \( \kappa \) are the real and imaginary parts of the index of refraction.

These expressions are used to fit reflectance data, and then generate the dispersion relation. The \( \omega \) parameters are interpreted as the TO frequencies which are the maxima of \( \epsilon_2 \) and are also near to reflectance peaks. The LO frequencies are not measurable directly, unless thin film specimens are used at grazing incidence using polarized light.\( ^{12} \) The LO frequencies, though not directly observable, are given by the root of \( \epsilon_1 \) which occurs immediately after the \( \epsilon_2 \) maxima, in analogy with the simpler model.

This model will be used to compute optical constants and vibration frequencies from the reflectance data of the films prepared in the oxygen partial pressure series. The clarification provided by this theoretical model is considered necessary, since many publications list IR absorption bands by the minima in reflection for fingerprinting, without analyzing the data with a dispersion model to resolve the oscillator positions.

In MgAl\(_2\)O\(_4\) there is continued debate over whether there are 4 or 6 IR active oscillators,\( ^{11,13} \) i.e., whether the space group is \( Fd3m \) or \( F43m \). The fundamental vibration frequencies are normally associated with peaks in the reflectance or by shoulderlike features in the reflectance which indicate a nearby oscillator. The published results for Raman and IR active frequencies for MgAl\(_2\)O\(_4\) are shown in Table I. These were used as starting points for the multiple oscillator analysis of the Mn–Co–Ni–O films, but there is no reason to expect these frequencies to be the same as the material under study, since the masses of the ions are not the same.

### B. Infrared spectra

Infrared transmittance and reflectance measurements were made using a Nicolet Magna 550 Fourier transform infrared (FTIR) spectrometer with a KBr beam splitter and a DTGS detector to cover the infrared region from 11,000 to 400 cm\(^{-1}\). Reflectance was done using an attachment for an angle of incidence of 30\(^\circ\). All the FTIR data shown were collected with a resolution of 2 cm\(^{-1}\) with 512 sample scans. Figure 1(a) shows the reflection spectra of the thin films and also that of the bare silicon substrate. Reststrahlen bands are visible at wave numbers less than 700 cm\(^{-1}\). A reflection spectrum of the sputtering target material was also taken and is shown in Fig. 1(b). The reststrahlen peaks are also evident in the target reflectance and indicate that the peaks in film reflectance are not due to thickness fringes. Thickness fringes are evident in the film reflectance [Fig. 1(a)] for wavenumbers greater than 700 cm\(^{-1}\), and in the transmission spectra (Fig. 2) due to the transparency of the films in this wavelength region. The reflectance data of Fig. 1(a) are shown in Fig. 3 expanded for 400 to 900 cm\(^{-1}\). There is a consistent shift to higher wave number with oxygen partial pressure of the reflection minima in this region (Fig. 4). These minima occur in the sintered target material [Fig. 1(b)] at about 550 and 690 cm\(^{-1}\), respectively, and are labeled V2 and V1, respectively; hence, the minima are not artifacts of sputtering or interference from the substrate. Also, the reflectance of the films increases the most after 0.16 mTorr, which is the partial pressure where the carrier type changes from \( p \) to \( n \) and where the polaron activation energy drops by the largest interval.\( ^{3,7} \) The progression near V2 is \( [R \text{ of } 0 \text{ mTorr} < R \text{ of } 0.16 \text{ mTorr} < R \text{ of } 0.8 \text{ mTorr} < R \text{ of } 1.6 \text{ mTorr}] \), where \( \approx \) indicates the largest increase with oxygen lies between the bracketed sets. From Fig. 2 it is observed that the 4 mTorr film has some transmission in this wavelength region; this is ascribed to the film being the thin-

**TABLE I. Raman and IR active frequencies (in cm\(^{-1}\)) for MgAl\(_2\)O\(_4\) from Streiffer and Boldish and O’Horo et al. (Refs. 11–13).**

<table>
<thead>
<tr>
<th>Raman Active</th>
<th>IR-TO (Fd3m)</th>
<th>IR-TO (F43m)</th>
<th>IR-LO (F43m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>772</td>
<td>...</td>
<td>812</td>
<td>864</td>
</tr>
<tr>
<td>671</td>
<td>670</td>
<td>674</td>
<td>806</td>
</tr>
<tr>
<td>492</td>
<td>485</td>
<td>581</td>
<td>609</td>
</tr>
<tr>
<td>...</td>
<td>428</td>
<td>491</td>
<td>580</td>
</tr>
<tr>
<td>410</td>
<td>...</td>
<td>363</td>
<td>365</td>
</tr>
<tr>
<td>311</td>
<td>...</td>
<td>306</td>
<td>310</td>
</tr>
<tr>
<td>...</td>
<td>305</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
nest in the series, and is discussed further in Sec. II H. The minima and maxima positions for V1 and V2 are recorded in Table II.

These reflectance minima are also similar in position to the reflection minima observed in Co$_3$O$_4$, at 650–660 cm$^{-1}$ and 550–560 cm$^{-1}$ (Ref. 14), and LiMn$_2$O$_4$ at 619 and 526 cm$^{-1}$ (Ref. 15).

The minima shift with increasing oxygen is an indication that the oscillator frequencies are shifting. If the reflectance peaks are well resolved, they should also shift, but, if they are comprised of more than one overlapping oscillator where the features of the individual oscillators are obscured, then the peaks are not a good indication of the actual IR active vibration frequencies. The peak minima and maxima both shift in this case.

This is because multiple peaks may broaden due to disorder and meld into one another forming what appears to be a single broad peak whose maxima may behave strangely. This may be happening in the ternary material in this study, since MgAl$_2$O$_4$ has been fit with a six oscillator model$^{11}$ and four oscillators are found in the region between 400 and 700 cm$^{-1}$ in MgAl$_2$O$_4$, whereas only two features (peaks) are visible in the ternary in the same range.

An attempt was made to resolve the oscillator frequencies from the reflection data by three different methods: (1) multiple oscillator modeling and (2) Kramers–Kronig Analysis using GRAMS$^\text{TM}$ 5.0 software by Galactic, a fast Fourier transform routine; (3) derivative reflectance spectroscopy. Analysis of combined transmission and reflection data in the far infrared will not be attempted since the films do not transmit in the oscillator region. Since only two features appear in the reflection, we cannot hope that the oscillator model treatment will generate more features. The optical constants determined by this method depend more on getting the oscillator frequencies correct than Kramers–Kronig analysis. The Kramers–Kronig analysis does not depend at all on the ability to resolve features in the reflection. However, the integrals demand knowledge of the reflection data.
between 0.16 and 0.8 mTorr at the sputtering of films and of the target. Note that the target V1-min falls between 0.16 and 0.8 mTorr at the p–n transition, but the rest of the features do not.

C. Raman spectra

The Raman spectra were collected using a Nicolet 960 FT-Raman spectrometer under the following conditions: (1) 1.4 W laser power at the sample, (2) 512 sample scans, (3) 4 cm⁻¹ resolution, (4) Ge detector. The collection time was 13 min/sample using a backscatter geometry.

Shown in Fig. 5 are the Raman spectra of the films in the oxygen partial pressure series. The peaks in the Raman spectra are from single-phonon processes, resulting from a decrease in the photon energy from incident to scattered photons in the scattering process. Raman is a form of energy loss spectroscopy, and a peak in the Raman spectra gives the intensity of the light that has lost an amount of energy relative to the energy of the monochromatic incident radiation. The photon may also be able to increase in frequency on scattering; that process is known as anti-Stokes in contrast to Stokes, which is energy loss. The Raman shift is then a measure of the energy change of the light, due to the generation of an optical phonon of frequency \( \nu_p = \nu_0 - \nu_f \), or, wave number change measured, \( \Delta k = k_0 - k_f = \text{Raman shift} \). In FTIR infrared absorption, the light of wave number \( k \) will stimulate an ionic vibration of frequency \( ck \), and if that same mode is also Raman active, the frequency is \( c \Delta k \). Therefore, \( k_{\text{FTIR}} = \Delta k_{\text{Raman}} \) if the mode is both IR and Raman active. The Raman active vibrations can be taken directly from the spectra.

![Raman Spectra](image_url)

**FIG. 5.** Raman spectra of the oxygen partial pressure series 0, 0.16, 0.8, 1.6, 4 mTorr shown in descending order. Note the shift of the peaks to higher wave number from top to bottom with increasing oxygen. Data are spaced along the vertical axis for clarity.

The Raman active modes and IR active modes generally do not coincide, the type of vibrations that are active in each process being dependent on the crystal structure. Shown in Table III are the positions of the four observed Raman peaks, and here, the two strongest vibrations also show an increase in the frequencies with oxygen partial pressure. The observed Raman intensities are more difficult to interpret in general, more so in this case since the films have different thicknesses.

That this shift occurs in the Raman active vibrations, a completely different mechanism than reststrahlen reflection, is further evidence that the shift observed in FTIR reflectance measurements is not an artifact of the film geometry.

**D. Multiple oscillator analysis**

With the film thickness known from SEM measurements, \( n(\infty) = e(\infty)^{1/2} \) may be estimated from the thickness fringes in the transparent region between 1000 and 4000 cm⁻¹ from the reflection data using the expression for refractive index,

\[
\begin{align*}
\frac{1}{n^2} & = 1 + \left(1 - \frac{4\sin^2(\theta/2)(\Delta k)^2}{8\hbar(\Delta k)^2} \right)^{1/2}, \\
& = 1 + \left(1 - \frac{4\sin^2(\theta)}{8\hbar(\Delta k)^2} \right)^{1/2},
\end{align*}
\]

where \( \theta \) is the angle of incidence measured from the sample normal, \( \Delta k \) is the wave number spacing between reflectance thickness fringes, and \( \hbar \) is the film thickness. Note that this expression reduces to \( 2\sin^2(\theta) = 1/\Delta k^2 \) for normal incidence. Spectra were collected at 50° angle of incidence from normal. Use of \( \theta = 30° \) showed negligible difference from \( \theta = 0° \) in Eq. (11). This wave number region gives the best estimate of the dynamic dielectric constant \( e(\infty) \) used in the multiple oscillator analysis, essentially, the average over the dispersion of the \( e_1 \) in the transparent region. There is a change in the index of refraction from 1.73 at 0 mTorr of oxygen to 2.6 at 4 mTorr. This is a fairly large change, and is reflective of the large stoichiometry variation that is supported by the spinel lattice, and the effect on the atomic polarizability of the cations with increasing oxidation state. As the oxygen/cation ratio is increased, the cations must assume higher oxidation states to retain charge balance. The spinel structure is retained by the robust fcc oxygen lattice, with the generation

<table>
<thead>
<tr>
<th>( \text{O}_2 ) partial pressure (mTorr)</th>
<th>V1-min</th>
<th>V1-peak</th>
<th>V2-min</th>
<th>V2-peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>676</td>
<td>613</td>
<td>560</td>
<td>469</td>
</tr>
<tr>
<td>0.16</td>
<td>681</td>
<td>616</td>
<td>563</td>
<td>476</td>
</tr>
<tr>
<td>0.8</td>
<td>692</td>
<td>620</td>
<td>585</td>
<td>476</td>
</tr>
<tr>
<td>1.6</td>
<td>695</td>
<td>623</td>
<td>584</td>
<td>482</td>
</tr>
<tr>
<td>4</td>
<td>702</td>
<td>623</td>
<td>590</td>
<td>491</td>
</tr>
<tr>
<td>Target</td>
<td>687</td>
<td>603</td>
<td>551</td>
<td>442</td>
</tr>
</tbody>
</table>

**TABLE III.** Raman active vibrations (in cm⁻¹) for Mn₁.5₅Co₀.₉₆Ni₀.₄₈O₄ spinel films.
The results of this two oscillator dominated model are shown in Figs. 8(a)–8(e), the peak near 600 cm\(^{-1}\) is too weak to cause \(\varepsilon_1\) to pass through zero in the 0.8 and 1.6 mTorr specimens, so the LO component of the V2 vibration cannot be determined by this method. The LO component can be roughly estimated with the use of the Lyddane–Sachs–Teller relation.

The generalized Lyddane–Sachs–Teller (LST) relation for two oscillators is

\[
\frac{\varepsilon(0)}{\varepsilon(\infty)} = \Pi(\omega_{\text{LO}}/\omega_{\text{TO}})^2, \tag{12}
\]

where the product is over each oscillator. \(\varepsilon(0) = \varepsilon(\infty) + \sum 4\pi\rho_1\) and for our case, this result is only approximate since only two TO modes are discernable in the range of wavelengths studied and we cannot carry out the sum over all oscillators. However, for MgAl\(_2\)O\(_4\) spinel, the sum is dominated by a single peak. The result of this calculation along with the parameters of each oscillator is shown in Table IV. Comparison of the last two columns of Table IV shows that the LST relationship is obeyed quite well for the 0, 0.16, and 4 mTorr specimens, since the difference is only in the first decimal place. In Table IV for these specimens, the right-hand side of Eq. (12) is slightly smaller than the left-hand side and this is to be expected since there may be lower frequency oscillations missing from the product which could not be observed in this study. The V2-LO frequency was adjusted until the LST relationship was satisfied for the 0.8 and 1.6 mTorr specimens. This is compared with another estimation (Refs. 18 and 19, and references therein) of the V2-LO frequencies which is from the peaks in a plot (not shown) of \(-\text{Im}(1/(\varepsilon_1 + i\varepsilon_2))\) for the 0.8 and 1.6 mTorr specimens. Table V shows the data, demonstrating there is little difference in both approximations to LO frequency, when there is no root, as the frequencies given by \(-\text{Im}(1/\varepsilon)\) also obey LST.

As can be seen in Table IV, the static and dynamic dielectric constants both increase with oxygen partial pressure, as does the strength of the V2 vibration. Table V shows the results of the fitting of the oscillator model to determine the actual vibrations. From this can be seen several reversals in the trend with increasing oxygen partial pressure, which was more consistent in the minima and maxima in the reflection. Though noisy, there is still a trend of increasing frequency with increasing oxygen partial pressures. The LO and TO components are similar to those reported for cobaltite spinels\(^{14}\) of Zn, Mn, Fe, Cu, and Ni, with V1-LO \(\sim 685\) cm\(^{-1}\), V1-T0 \(\sim 640\) cm\(^{-1}\), V2-LO \(\sim 590\) cm\(^{-1}\), and V2-TO \(\sim 540\) cm\(^{-1}\), but the TO components are about 100 cm\(^{-1}\) lower than the LO in our material.

### E. Derivative reflectance spectroscopy

Reference 19 discusses a heuristic approach in which the TO and LO vibrations can be taken directly from the reflectance spectra with the following: \(\lambda_{\text{T0}}\) is found at \(\lambda\) where \(dR/d\lambda < 0\) and \(d^2R/d\lambda^2 = 0\); \(\lambda_{\text{LO}}\) is found at \(\lambda\) where \(dR/d\lambda > 0\) and \(d^2R/d\lambda^2 = 0\) in a plot of reflectance \(R\) versus wavelength \(\lambda\). These results are shown in Table VI, and the trend is again consistent with the multiple oscillator method.
The V2-TO vibration was difficult to find in this manner due to the noisy derivatives and the broadness of that reflectance peak. The wave numbers calculated fall near the turning points of the reflectance curve, that is, TO vibrations are near the peaks and LO vibrations are near the minima.

F. Comparison of Raman active and IR active vibrations

Table VII compares the IR active vibrations to the Raman active vibrations. Although the R-1 and V1-LO vibra-

![Example oscillator model fit](dotted line) for the 4 mTorr specimen. (b)–(c) Optical constant dispersion calculated from the two oscillator model. It was found for the partial pressure series that $[\varepsilon_1$ of 0 mTorr $< \varepsilon_1$ of 0.16 mTorr] $\ll [\varepsilon_1$ of 4 mTorr $< \varepsilon_1$ of 0.8 mTorr $< \varepsilon_1$ of 1.6 mTorr], where the $\ll$ indicates the largest increase with oxygen lies between the bracketed sets, the largest increase occurs after 0.16 mTorr oxygen partial pressure, where the $p-n$ transition occurs, and where $W_p$ decreases by the largest interval.

![Optical constant dispersion calculated from the two oscillator model.](image)

**TABLE IV.** Oscillator parameters, dielectric constant limiting values, and check of LST relation.

<table>
<thead>
<tr>
<th>$O_2$ partial pressure (mTorr)</th>
<th>$4\pi\rho$</th>
<th>$\gamma$</th>
<th>$4\pi\rho$</th>
<th>$\gamma$</th>
<th>$\varepsilon(\infty)$</th>
<th>$\varepsilon(0)$</th>
<th>$\varepsilon(0)/\varepsilon(\infty)$</th>
<th>LST</th>
<th>LST$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.26</td>
<td>0.09</td>
<td>3.1</td>
<td>0.28</td>
<td>2.87</td>
<td>6.23</td>
<td>2.171</td>
<td>1.96</td>
<td>...</td>
</tr>
<tr>
<td>0.16</td>
<td>0.34</td>
<td>0.085</td>
<td>4.0</td>
<td>0.28</td>
<td>3.67</td>
<td>8.01</td>
<td>2.183</td>
<td>1.985</td>
<td>...</td>
</tr>
<tr>
<td>0.8</td>
<td>0.21</td>
<td>0.1</td>
<td>5.8</td>
<td>0.25</td>
<td>4.17</td>
<td>10.18</td>
<td>2.441</td>
<td>2.441</td>
<td>2.35</td>
</tr>
<tr>
<td>1.6</td>
<td>0.24</td>
<td>0.09</td>
<td>6.4</td>
<td>0.23</td>
<td>4.74</td>
<td>11.38</td>
<td>2.401</td>
<td>2.403</td>
<td>2.33</td>
</tr>
<tr>
<td>4</td>
<td>0.27</td>
<td>0.08</td>
<td>6.4</td>
<td>0.29</td>
<td>6.1</td>
<td>12.77</td>
<td>2.083</td>
<td>1.917</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$The V2-LO frequency was adjusted to satisfy the LST relationship, since there was no root.

$^b$Calculated with $-\text{Im}(1/\varepsilon)$ since there was no root.
TABLE V. TO and LO components of the V1 and V2 vibrations as determined by the two oscillator model.

<table>
<thead>
<tr>
<th>O2 partial pressure (mTorr)</th>
<th>V1-TO</th>
<th>V1-LO</th>
<th>V2-TO</th>
<th>V2-LO (LST)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>591</td>
<td>673</td>
<td>440</td>
<td>541</td>
</tr>
<tr>
<td>0.16</td>
<td>593</td>
<td>681</td>
<td>445</td>
<td>546</td>
</tr>
<tr>
<td>0.8</td>
<td>600</td>
<td>690</td>
<td>435</td>
<td>581</td>
</tr>
<tr>
<td>1.6</td>
<td>601</td>
<td>688</td>
<td>435</td>
<td>580</td>
</tr>
<tr>
<td>4</td>
<td>611</td>
<td>671</td>
<td>460</td>
<td>580</td>
</tr>
</tbody>
</table>

*Estimated with LST relation.

TABLE VI. Vibrations from derivative reflectance spectroscopy.

<table>
<thead>
<tr>
<th>O2 partial pressure (mTorr)</th>
<th>Peak reflectance V1</th>
<th>V1-TO</th>
<th>V1-LO</th>
<th>V2-TO</th>
<th>V2-LO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>613</td>
<td>594</td>
<td>652</td>
<td>466</td>
<td>452</td>
</tr>
<tr>
<td>0.4</td>
<td>616</td>
<td>597</td>
<td>658</td>
<td>470</td>
<td>?</td>
</tr>
<tr>
<td>2</td>
<td>620</td>
<td>603</td>
<td>660</td>
<td>477</td>
<td>?</td>
</tr>
<tr>
<td>4</td>
<td>623</td>
<td>605</td>
<td>661</td>
<td>480</td>
<td>?</td>
</tr>
<tr>
<td>10</td>
<td>623</td>
<td>606</td>
<td>661</td>
<td>480</td>
<td>?</td>
</tr>
</tbody>
</table>

TABLE VII. Comparison of Raman and multiple oscillator IR active vibrations (cm⁻¹).

<table>
<thead>
<tr>
<th>O2 partial pressure (mTorr)</th>
<th>R-1</th>
<th>R-2</th>
<th>V1-TO</th>
<th>V1-LO</th>
<th>V2-TO</th>
<th>V2-LO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>641.7</td>
<td>517.3</td>
<td>591</td>
<td>673</td>
<td>440</td>
<td>541</td>
</tr>
<tr>
<td>0.16</td>
<td>643.7</td>
<td>520.5</td>
<td>593</td>
<td>681</td>
<td>445</td>
<td>546</td>
</tr>
<tr>
<td>0.8</td>
<td>651.1</td>
<td>~533</td>
<td>600</td>
<td>690</td>
<td>435</td>
<td>581</td>
</tr>
<tr>
<td>1.6</td>
<td>652.8</td>
<td>533.6</td>
<td>601</td>
<td>688</td>
<td>435</td>
<td>580</td>
</tr>
<tr>
<td>4</td>
<td>653</td>
<td>533–540</td>
<td>611</td>
<td>671</td>
<td>460</td>
<td>580</td>
</tr>
</tbody>
</table>

*Estimated with peak of − Im(1/ε) since the curve did not have a root.

G. Kramers–Kronig analysis

Figures 9(a)–9(d) show the optical constants computed with Kramers–Kronig analysis from reflectance between 400 and 700 cm⁻¹, using the GRAMS™ 5.0 fft software. The software assumes normal incidence in its calculations. Input reflectance spectra were collected at 30° angle of incidence from the composite of the films of the oxygen partial pressure series deposited on doubly polished silicon. Greater than 700 cm⁻¹ the material is transparent as evidenced by the composite transmission being essentially equal to that of the bare substrate. The low absorption region between 1000 and 3500 cm⁻¹, where κ~0, was used to determine the dynamic dielectric constant using the reflectance data (Fig. 6). Above 3000 cm⁻¹ there is a drop in transmission as well as in specular reflection [Fig. 1(a)] for all the films. This may be due to: (1) increased scattering at shorter wavelengths due to the granularity of the films, resulting in a greater percentage of diffused reflection and diffused transmission not captured

H. Multiphonon edge

Shown in Fig. 10 are the transmission spectra for the composite of the films of the oxygen partial pressure series deposited on doubly polished silicon. Greater than 700 cm⁻¹ the material is transparent as evidenced by the composite transmission being essentially equal to that of the bare substrate. The low absorption region between 1000 and 3500 cm⁻¹, where κ~0, was used to determine the dynamic dielectric constant using the reflectance data (Fig. 6). Above 3000 cm⁻¹ there is a drop in transmission as well as in specular reflection [Fig. 1(a)] for all the films. This may be due to: (1) increased scattering at shorter wavelengths due to the granularity of the films, resulting in a greater percentage of diffused reflection and diffused transmission not captured...
in the specular FTIR measurements; (2) the onset of polaron absorption with peak absorption occurring at \(4W_H \sim 1.2\,\text{eV}\) or \(\sim 10^3\,\text{cm}^{-1}\) (see the discussion for \(W_H\)); (3) the onset of absorption from localized gap states from structural disorder. Features like this will be discussed in a forthcoming paper on the behavior of this oxide in the UV visible.

At less than 650 cm\(^{-1}\) the material becomes highly reflective and the absorption increases as a result of the multiphonon edge, and/or the ionic vibrations between 400 and 700 cm\(^{-1}\). As can be seen, the transmission drops to less than 4% throughout that range for even the thinnest film, the 4 mTorr specimen, so the substrate features are unlikely to be influencing the reflectance measurements in that region.

Figure 10 shows that with the exception of the 4 mTorr specimen, the edge shifts to higher wave number. Putting aside the behavior of the 4 mTorr specimen, the edge shift of the remaining films is in agreement: since the edge occurs due to multiphonon processes, e.g., the combined vibrations 3LO, 2TO+LO, 2TO+LA, etc., if the individual vibrations are shifting to higher wave number, then the combined vibration must also shift to higher wave number. For the vibrations which we have been able to measure, no combination of three of them adds to 650 cm\(^{-1}\), implying that there are weaker vibrations which we cannot detect, lower frequency IR active vibrations at less than 400 cm\(^{-1}\), or acoustic modes which we cannot measure acting at the multiphonon edge. It is traditional to describe the multiphonon edge as a three-phonon edge. However, this nomenclature and much of the analysis comes from studies of optical windows of thicknesses in the millimeters to a centimeter.\(^{9,22,23}\)

---

**TABLE VIII.** Estimation of TO and LO components from Kramers–Kronig \(\varepsilon_2\) maxima and \(-\text{Im}(1/\varepsilon)\) maxima, and check of the LST relation against the static and dynamic dielectric constant ratio from the oscillator model.

<table>
<thead>
<tr>
<th>(O_2) partial pressure (mTorr)</th>
<th>V1-TO</th>
<th>V1-LO</th>
<th>V2-TO</th>
<th>V2-LO</th>
<th>(\varepsilon(0)/\varepsilon(\infty))</th>
<th>LST</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>614</td>
<td>664</td>
<td>490</td>
<td>542</td>
<td>2.171</td>
<td>1.43</td>
</tr>
<tr>
<td>0.16</td>
<td>613</td>
<td>667</td>
<td>496</td>
<td>545</td>
<td>2.183</td>
<td>1.43</td>
</tr>
<tr>
<td>0.8</td>
<td>611</td>
<td>670</td>
<td>481</td>
<td>570</td>
<td>2.441</td>
<td>1.68</td>
</tr>
<tr>
<td>1.6</td>
<td>612</td>
<td>672</td>
<td>481</td>
<td>572</td>
<td>2.401</td>
<td>1.70</td>
</tr>
<tr>
<td>4</td>
<td>620</td>
<td>672</td>
<td>501</td>
<td>572</td>
<td>2.083</td>
<td>1.53</td>
</tr>
</tbody>
</table>

---

*FIG. 9.* (a)–(d) Optical constants dispersion computed using Kramers–Kronig analysis of films on Si.
For thin films with thicknesses of order of microns, stronger transitions such as two-phonon absorptions may lead to the observed infrared absorption edge. The absorption strength of three-phonon transitions is typically in the range \(10^0-10^{-2}\) cm\(^{-1}\); this would provide noticeable absorption only if the material were several millimeters thick. Until detailed analysis of the long-wave absorption edge is done to identify the responsible transitions, it is not clear why the region of transparency goes out to 14 \(\mu\)m or 700 cm\(^{-1}\), which is a long cutoff wavelength for an oxide and is the start of the one-phonon region in this material.

The deviation of the 4 mTorr specimen from the trend is likely due to the reduced film thickness which leads to less linear absorption with an increase in transmission at the edge. This would cause the edge to appear to shift to lower wave number.

**IV. DISCUSSION**

The shift in position of the infrared reflectance maxima and minima with increasing oxygen partial pressure can be understood by analyzing the changes occurring in the Debye frequency and Debye temperature, and small polaron conduction activation energy, which have been calculated independent of optical measurements. The Debye temperature for the films has been studied in detail in an earlier publication,\(^7\) based on measurements of thermopower and resistivity, and then applying relations for small polarons derived by Mott\(^2\) and Schnakenberg.\(^2\) The Debye temperature is observed to increase monotonically with oxygen partial pressure and is listed in Table IX and plotted in Fig. 11 as Debye wave number (compare to Fig. 4). The increase of the Debye frequency/temperature/wave number with an increase in wave number positions of the oscillators using multiple oscillator, Kramers–Kronig, and Raman can be understood as follows: Debye temperature is a measure of the stiffness of the lattice, the shifts in the oscillator positions also point to a stiffening of the lattice. It has been shown that the lattice constant, and therefore, the bond lengths are decreasing functions of the oxygen partial pressure,\(^1\) resulting in the stiffening of the bonds since the bulk modulus varies inversely with bond length\(^0\) (\(B \sim d^3\), where \(n = 3\) for alkali halides and 5 for homopolar, covalently bonded tetrahedral solids).

**TABLE IX.** Variation of lattice parameter, small polaron conduction activation energy \(W_H\), Debye temperature and wave number, and \(\kappa_p\) as a function of oxygen partial pressure, from Refs. 7 and 16. (Note: The 0.4 mTorr specimen has not been optically analyzed.) Note the electrically determined Debye wave number is smaller than the optically measured vibration wave numbers, and the magnitude of the size of the frequency increase is larger.

<table>
<thead>
<tr>
<th>Oxygen partial pressure (mTorr)</th>
<th>(a(t)) (10^{-10}) m</th>
<th>(W_H) (eV)</th>
<th>(\theta_D) (K)</th>
<th>(k_D) (l/cm)</th>
<th>(1/\kappa_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.355</td>
<td>0.372</td>
<td>552</td>
<td>383</td>
<td>0.188</td>
</tr>
<tr>
<td>0.16</td>
<td>8.34</td>
<td>0.372</td>
<td>619</td>
<td>430</td>
<td>0.148</td>
</tr>
<tr>
<td>0.4</td>
<td>...</td>
<td>0.362</td>
<td>625</td>
<td>439</td>
<td>...</td>
</tr>
<tr>
<td>0.8</td>
<td>...</td>
<td>0.292</td>
<td>635</td>
<td>441</td>
<td>0.142</td>
</tr>
<tr>
<td>1.6</td>
<td>8.326</td>
<td>0.282</td>
<td>681</td>
<td>473</td>
<td>0.123</td>
</tr>
<tr>
<td>4</td>
<td>...</td>
<td>0.256</td>
<td>741</td>
<td>515</td>
<td>0.086</td>
</tr>
</tbody>
</table>

Debye temperature with increasing oxygen partial pressure. The decreasing lattice constant with oxygen partial pressure is a sensible result since as the oxygen content of the lattice increases, the average oxidation states of the cations should increase to conserve charge balance, leading to smaller ionic radii, and therefore smaller bond lengths. This is provided that \(O^2-\) atoms and cations surrounding the vacancies being generated are not relaxing into vacant sites. This effect is difficult to verify.

The results of the Debye frequency increase can also be related to the measured trend in the static and high frequency dielectric constants in the context of a very simple model.\(^10\) In an ionic crystal with only two ions per primitive cell, accounting for both ionic polarizability and atomic polarizability, the relationship between the static and dynamic dielectric constants is

\[
\frac{\epsilon(0) - 1}{\epsilon(0) + 2} = \frac{\epsilon(\infty) - 1}{\epsilon(\infty) + 2} - \frac{\epsilon_{\text{dip}}^2}{\hbar \omega_{\text{dip}}}.
\]

where \(\omega_{\text{dip}}^2 = k/M\) is the characteristic frequency of the dipole of oppositely charged ions, \(k\) is a force constant, and \(M^{-1} = M_1^{-1} + M_2^{-1}\) the reciprocal of the reduced mass. The second term is related to atomic polarizability as \((a_+ + a_-)\), the sum of the atomic polarizabilities of the ions involved. If the second term increases more quickly than the first in response to some alteration of the system (in our case, the stoichiometry), the implication is that the characteristic frequency is increasing, and in a lattice, this corresponds to a frequency on the order of the Debye frequency. In Fig. 12, the left-hand
FIG. 12. Plot of the left-hand side of Eq. (13). In the context of the model used this would imply an increase in the vibration frequency, and by extension the force constants and Debye frequency.

side of Eq. (13) is plotted against oxygen partial pressure. Although very nonrigorous, it allows the intuitive conclusion that the frequencies of all modes and the Debye frequency increase, because the bonding force constants between transition metals and oxygen atoms are increasing as the oxygen content increases; the lattice becomes stiffer.

It has been shown that the small polaron hopping conduction activation energy \( W_H = W_p / 2 \), where \( W_p \) is the formation energy of a polaron (or, the depth of the self-trapping potential well). \( W_p \) follows a relation like \(^{25}\)

\[
W_p = \frac{Ze^2}{2r_p} \left( \frac{1}{e(\infty)} - \frac{1}{e(0)} \right)
\]

where \( e \) is the electronic charge, \( Z \) is the charge of the trap, \( r_p \) is the polaron radius, or hopping distance, which may be as large as the lattice constant. The bracketed terms are sometimes referred to as \( 1/\kappa_p \). From the multiple oscillator model,

\[
e(0) = e(\infty) + \sum_i 4\pi\rho_i,
\]

where the sum is over the oscillator strengths of the infrared active vibrations, \( \rho_i \). \(^{27}\) For MgAl\(_2\)O\(_4\), it has been shown,\(^1\) using a six-oscillator model, that the sum equals approximately 5, and the sum is dominated by a single oscillator. Again, in the present case, we have only two oscillators to sum, and so \( e(0) \) may be an underestimate. It can be seen from Fig. 13 that \( W_H \) and therefore \( W_p \) are decreasing functions of the oxygen partial pressure. \( e(\infty) \) and \( e(0) \) were shown to be increasing functions of oxygen partial pressure, consistent with the trend in \( W_H \).

Note that Fig. 14 shows an increasing \( W_p \) with increasing \( 1/\kappa_p \). The slope of the dotted line, a linear least-squares fit, is 2.48 eV and the energy intercept is 0.289 eV. We investigate whether the slope yields a reasonable estimate of the polaron radius, which is computed to be 2.9Z Å using the dotted line. This value is about right, if \( Z = 3 \) to 4 for the Mn\(^{3+}\) and Mn\(^{4+}\) ions involved, with a measured lattice constant of about 8.4 Å. Therefore, we have the qualitative result that \( W_p \) should increase with \( 1/\kappa_p \), and the quantitative return of physically reasonable values for the polaron radius.

V. CONCLUSIONS

Thin films of Mn\(_{1.56}\)Co\(_{0.96}\)Ni\(_{0.48}\)O\(_4\) spinel were sputter deposited using a series of oxygen partial pressures. The 1 to 25 \( \mu \)m wavelength range was examined using FTIR transmission and reflectance, and Raman scattering optical techniques. The complex index of refraction was calculated for the entire wavelength range. Raman and IR active vibrations were analyzed using multiple oscillator analysis, and also Kramers–Kronig analysis using GRAMS software.

The positions of the Raman and IR active lattice vibrations were observed to shift with increasing oxygen partial pressure during deposition, along with an increase in the dynamic and static dielectric constants calculated from the reflectance data. These shifts were consistent with the shift in Debye frequency calculated from earlier thermopower and resistivity data, and related to a stiffening of the lattice via reduction in bond lengths. The films were shown to have an optically transparent window from 6 to 14 \( \mu \)m wavelength. The multiphonon cutoff occurred at 14 \( \mu \)m, which is a long wavelength cutoff for an oxide material and is possibly due to two-rather than three-phonon transitions. The frequency of the multiphonon cutoff was also observed to shift to higher frequency with the oxygen partial pressure used during sputtering. These studies, and the earlier work on the variation of the thermopower and resistivity with oxygen partial pressure and film temperature, are consistent with a change in the ratio of Mn\(^{3+}\) to Mn\(^{4+}\) cations with oxygen, with small polaron hopping as the charge transport mechanism.

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19 GRAMS software, Galactic Industries Corporation, Salem, NH.