Temperature and Polarization Dependence of the Optical Absorption Edge of Gadolinium Molybdate

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The optical absorption spectrum of gadolinium molybdate (GMO) was measured as a function of photon energy and polarization between 40 and 205°C for absorption coefficients between 10 and 300 cm⁻¹. GMO undergoes a simultaneous ferroelectric-ferroelastic transition at 159°C; no discontinuity in the absorption spectrum was observed at this temperature. No differences were observed between spectra for light polarized along the a or b crystal axes, but the spectrum shifted to higher energy for light polarized along the c axis and shifted uniformly with temperature. Two absorption bands, each consisting of at least three separate lines, were superimposed on the optical absorption edge. The absorption coefficients were found to obey a modified form of Urbach's rule which, within experimental error, can be described equally well by either of two equations. The implications of these two equations are discussed.

I. INTRODUCTION

Gadolinium molybdate (GMO) has been the subject of considerable interest since the first report of its unusual properties in 1968. It exhibits a spontaneous strain and polarization that appear simultaneously at the ferroelectric transition temperature of 159°C. The directions of both spontaneous strain and polarization can be switched by either an applied field or a mechanical stress; consequently, GMO has been classified as a ferroelectric-ferroelastic material. In contrast with other ferroelectric materials, the ferroelectric rare-earth molybdates exhibit no change in the clamped dielectric constant at the transition. In GMO, the transition is driven by the condensation of two degenerate zone-boundary phonons at the transition temperature. The spontaneous strain and polarization are believed to result from anharmonic coupling of these condensed modes to zone-center modes. Because of this unusual behavior, GMO has several unique and potentially useful properties.

To date, most of the work on GMO has concentrated on an analysis of the lattice dynamics, the structural properties, and some of the macroscopic optical properties of the material; there is little information available on the electronic properties. We have studied the optical absorption spectrum of GMO near the fundamental absorption edge between 40 and 205°C for light polarized along the a and c axes of the paraelectric tetragonal phase and along the a, b, and c axes of the ferroelectric orthorhombic phase.

A further motivation for this work stems from the current interest in the shape of the optical absorption edge for nonmetallic crystals. The absorption coefficients of many of these materials have been found to vary exponentially with photon energy below the optical absorption edge. The behavior of the optical absorption edges of an important group of these materials is described by Urbach’s rule,

\[ \alpha = \alpha_0 e^{(E - E_0)/kT}, \]

where \( \alpha \) is the absorption coefficient, \( E \) is the photon energy, \( k \) is Boltzman’s constant, \( T \) is the crystal temperature, and \( \alpha_0, E_0, \) and \( \sigma \) are experimental constants. In many other materials, the edge is exponential but the temperature dependence is more complex than described by Eq. (1) and may depend on extrinsic as well as intrinsic factors. In doped semiconductors such as GaAs, the temperature dependence of the exponential absorption edge depends on the concentrations of impurities and for completely compensated samples, the absorption edge is independent of temperature. The ferroelectric materials BaTiO₃ and KTaO₃ have been found to obey a modified form of Urbach’s rule in which the temperature in Eq. (1) is replaced by an effective temperature,

\[ T^* = T + T_0, \]

where \( T_0 \) is an empirical constant. Frova suggests that this additional exponential broadening may be due to the presence of defect and impurity fields or to surface damage or both. Wemple, however, states that “there appears to be no reason to expect this effect to be simply describable in terms of an effective temperature \( T_0 \).” Furthermore, BaTiO₃ and KTaO₃ are chemically different and are grown at very different temperatures so
that it would be surprising if both materials displayed the same impurity-related tailing." Instead he suggests that the observed exponential absorption edge in these materials is produced by "phonon coupling to the valence-band p-like electrons."

Whether the exponentially broadened edges are produced by phonon coupling to the valence-band electrons or by any of the other coupling mechanisms that have been suggested, it is still difficult to justify the replacement of the crystal temperature in Eq. (1) by \( T^* \) as given by Eq. (2) if the optical absorption tails for \( \text{BaTiO}_3 \) and \( \text{KTaO}_3 \) are due to phonon-assisted processes alone. At present, it appears that the introduction of the effective temperature \( T^* \), as given by Eq. (2), in the modified Urbach's rule is justified on purely empirical grounds.

II. EXPERIMENTAL PROCEDURE

All the samples used in these measurements were cut from a single boule obtained from the Isomet Corp. and mechanically polished to the desired thickness. The measurements described here were made on six samples ranging in thickness from 0.215 to 1.140 mm. Although thinner samples were desired, the strong tendency of GMO to cleave or crack under stress prevented the polishing of samples to thicknesses less than about 0.2 mm without destroying them. The impurity content was quoted by Isomet to be less than one part per million. A microscopic analysis of the samples revealed a significant number of inclusions. Some of these inclusions were triangular and similar to those identified by Barkley et al. as platinum inclusions; other unidentified inclusions were also present.

Crystals were cut parallel to the \( a-c \) and \( b-c \) faces and their thickness determined with a calibrated E. Leitz-Wetzlar microscope. To minimize possible errors in the absorption spectra due to scattering losses and also to avoid the effects of the interchange of the \( a \) and \( b \) axes in adjacent domains, the measurements were made on single-domain samples. In GMO, domains can be formed easily by applied pressure or electric fields. Hence, it was necessary to maintain an external electric field of 5 kV/cm along the \( c \) axis of the crystal throughout these measurements to inhibit domain formation (the coercive field of GMO is approximately 5 kV/cm). The samples were electroded perpendicular to the \( c \) axis and were mounted on a boron nitride plate in a temperature cell which was heated by a cartridge heater. The temperature stability of the cell was better than \( \pm 0.5 \) °C. X-ray diffraction measurements have indicated that some ferroelectric domain structure persists into the high-temperature tetragonal phase to temperatures as high as 280 °C. To eliminate such residual domains, the crystals were annealed for several hours at 350 °C; measurements were then made as the crystals were slowly cooled in discrete steps from this temperature. Transmission spectra were measured at various temperatures in approximately 10 °C steps from 205 to 135 °C and 20 °C steps from 135 to 39 °C. A Beckman DK-1A double-beam spectrophotometer was used for these measurements. The sample-channel beam was polarized by a Glan polarizer which was placed in front of the sample.

Reflection measurements were made using a Spex model-1400 monochromator and an optical system which split the beam from the monochromator into a reference and sample beam which were chopped at different frequencies and measured using two PAR model-121 lock-in amplifiers.

III. DATA ANALYSIS

In these measurements, interference due to multiple reflections can be neglected, and if scattering can also be neglected, the normalized transmittance of a sample of thickness \( d \) and reflectance \( R \) is given by

\[
T = (1 - R)^2 \left[ 1 + \left( \frac{k}{n} \right)^2 \right] / (e^{ad} - R e^{-ad}),
\]

where \( k \) and \( n \) are the imaginary and real parts of the refractive index, respectively.

Transmission measurements were made for the six samples with thicknesses that ranged from 0.215 to 1.140 mm. The procedure for the calculation of the absorption coefficients is outlined below.

Transmission curves for the polarizer were obtained with the sample out. Since the light goes directly from the sample to the detector, no further corrections for the polarizing properties of the spectrometer are required. The sample areas were in general less than the beam area so it was necessary to multiply the sample-transmission data by an energy-independent constant to account for the geometric differences between the reference and sample beams. The appropriate normalization constant for each set of data was determined by dividing out the effects of the polarizer and plotting the sample transmission data at a given temperature and polarization for each sample. In the transmission base line region where \( \alpha = 0 \), Eq. (3) reduces to

\[
T = (1 - R)^2 / (1 - R^2),
\]

and the sample-transmission spectrum can be compared to the reflectance spectrum to normalize the data. \( \alpha \) can then be calculated from the normalized sample-transmission spectrum and the reflectance spectrum using Eq. (3), which in these measure-
ments can be simplified to

\[ T = (1 - R)^2 e^{-\alpha d}, \]  

since \( e^{2\alpha d} \gg R^2 \) and \( k \ll n \) over the spectral region of interest.

Analysis of the data indicates that \( \alpha \) is approximately zero at 4000 Å and the normalized sample transmission at a given energy is related to the measured transmission at that energy \( T^M \) by

\[ T = \frac{[(1 - R)^2/(1 - R_k^2)] T^M}{T^P}, \]  

where \( R_k \) is the reflectance at 4000 Å, \( T_k^M \) is the graphically determined sample transmission at 4000 Å, and \( T^P \) is the measured transmission of the polarizer at that energy. Equation (6a) can be reexpressed in terms of the normalization constant \( Y \) in Eq. (6b) which is constant for a given sample at a specific temperature and polarization. The absorption coefficient can then be calculated using Eqs. (5) and (6) if the reflectance \( R \) has been determined. This was accomplished with the aid of an IBM 360 computer and Cal Comp plotter. Since \( \alpha \) is independent of \( d \), the results obtained for each of the six samples were then averaged at each energy, temperature, and polarization.

The reflectance at normal incidence can be calculated from the refractive indices by the relation

\[ R = \frac{[(n - 1)^2 + k^2]/[(n + 1)^2 + k^2]]. \]  

\( k \) is related to the absorption coefficient by

\[ k = \alpha \lambda /4\pi, \]  

and thus for these wavelengths and for \( \alpha < 500 \text{ cm}^{-1} \),

\[ R \approx (n - 1)^2/(n + 1)^2. \]  

The known refractive indices of GMO can be extrapolated into the energy region of interest, and the reflectance spectrum can be calculated. Since the calculated reflectance neglects the contribution of surface blemishes and crystalline defects and inclusions, the reflectance was also measured at room temperature to determine the effect of these contributions. The transmission data indicated that no significant errors would be introduced in \( \alpha \) if the reflectance spectra were assumed to be independent of temperature.

IV. RESULTS

A. Absorption Coefficients

No differences in the absorption spectra were observed for light polarized along the \( a \) or \( b \) crystal axes but the spectra shifted to higher energies for light polarized along the \( c \) axis. Typical results for 39 and 190 °C are shown in Figs. 1 and 2. For \( \alpha > 30-40 \text{ cm}^{-1} \), the absorption coefficients vary exponentially with photon energy, but for \( \alpha < 30-40 \text{ cm}^{-1} \), the absorption curve deviates substantially from a pure exponential. This low-energy tail is similar to that observed in other materials and can result from several factors. Equation (3) assumes that there are no scattering losses from inclusions, defects, or persistent domains in regions of locally high stress. However, the measured reflectance spectra indicated that these effects are not negligible. Any transmission loss which is independent of energy is eliminated when the transmission data are normalized, but any dispersion in these nonabsorptive losses will result in errors in the calculated absorption coefficients. Such transmission losses have a significant effect on the calculated absorption coefficients in spectral regions where the percentage of crystal absorption is low but, for a constant nonabsorptive transmission loss, the error in \( \alpha \) decreases as the percent absorption increases. The magnitude of the error in \( \alpha \) produced by use of the calculated rather than the measured reflectance values was found to be less than 0.5% for \( \alpha > 50 \text{ cm}^{-1} \) but for \( \alpha = 10 \text{ cm}^{-1} \), the absorption coefficients

![Figure 1](#)

**FIG. 1.** Absorption spectrum of GMO at 39°C. (Δ) — Polarization perpendicular to the \( c \) axis. (O) — Polarization parallel to \( c \) axis. The lines were obtained by a least-squares fit to the data for \( \alpha > 35 \text{ cm}^{-1} \) excluding the two absorption bands of the Gd<sup>3+</sup> ion. The error bars indicate one standard deviation from the average value of \( \alpha \) obtained from the individual samples.
were approximately 10% higher if the calculated reflectance was used. The absorption tail for $\alpha < 30 \text{ cm}^{-1}$ is strongly influenced by these reflectance errors, by other scattering losses, and possibly by low-energy impurity absorption.

The values of $\ln \alpha$ as a function of energy were least-squares fitted to a straight line for values of $\alpha$ between 35 and 300 cm$^{-1}$ excluding those points containing the Gd$^{3+}$ absorption band (see Sec. C below). The slopes of the absorption curves thus obtained for the two polarizations at each temperatures agreed within an experimental error of about 4%. On extrapolating the curves to higher energy, two intersections were found corresponding to $E_0 = 4.80 \pm 0.15$ and $4.84 \pm 0.15$ eV for polarization perpendicular and parallel to the $c$ axis, respectively, independent of the temperature. This is in agreement with Eq. (1), i.e., $\alpha = \alpha_0$ for $E = E_0$.

The error in $\alpha_0$ is rather large in these measurements. It was found that $\alpha_0$ is between $10^3$ and $10^6$ cm$^{-1}$ for both polarizations.

In Fig. 3, the reciprocal slopes of the absorption curves are plotted against temperature. The best linear fit gives

$$T = \left(\frac{\alpha'}{k} \frac{dE}{d(\ln \alpha)}\right) = T_0,$$

where from a least-squares analysis, $\sigma' = 1.0$

$$T = \left(\frac{\alpha}{k} \frac{dE}{d(\ln \alpha)}\right) = T_0,$$

where $\sigma = 0.18 \pm 0.03$ and $C = 8.1 \pm 1.2$. Integrating this expression yields

$$\alpha = \alpha_0 e^{(\sigma/kT) + C E - E_0}.$$
FIG. 4. Variation in the slope of the absorption curves of GMO with reciprocal thermal energy. The line was obtained by a least-squares fit.

\[ \Delta (\ln \alpha) / \Delta E \ (eV)^{-1} \]

FIG. 5. Variation in the energy at which \( \alpha = 200 \text{ cm}^{-1} \) for GMO as a function of temperature. (\( \bigcirc \))—Polarization perpendicular to the \( c \) axis, (\( \bigtriangleup \))—Polarization parallel to the \( c \) axis. The lines were obtained by a least-squares fit.

FIG. 6. Absorption bands superimposed on the absorption edge of GMO: (a) full spectrum; (b) 3030–3100-Å band.

as \( E - E_{\alpha} \), \( \beta \) decreases as \( E - E_{\alpha} \). If instead, the energy at which \( \alpha = 200 \text{ cm}^{-1} \) is calculated and plotted as a function of temperature \( \beta \) decreases to \((-6.47 \pm 0.02) \times 10^{-4} \text{ eV}^{-1} \text{K}^{-1}\).

C. Absorption Bands

Figures 1 and 2 reveal a region of anomalously high absorption between 3.80 and 4.00 eV. This region is shown in detail in Fig. 6 and consists of two absorption bands, each of which is composed of three distinct absorption lines. The first has lines at 3129, 3124, and 3120 Å; the second at 3070, 3066, and 3062 Å. These lines were present for all three polarizations. No variation in the positions or relative magnitudes of these lines with temperature was observed, although the lines are more difficult to resolve at higher temperatures since they tend to be obscured by the shift of the absorption edge to lower energies with increasing temperatures.

These lines appear to be due to the internal transitions of the Gd\(^{+++}\) ion. Gadolinium has a partially filled \( f \) shell which is well shielded by the outer electronic shells. The lowest-energy transition is an \( ^{8}S_{7/2} \rightarrow ^{8}P_{7/2} \) which occurs in the 3111–3119-Å range in other host lattices such as GdCl\(_{3}\), Gd\(^{+++}\) in LaCl\(_{3}\), and other Gd salts.\(^23\) The second-lowest-energy transition is \( ^{8}S_{7/2} \rightarrow ^{8}S_{3/2} \) which occurs in the 3055–3062-Å range in those lattices.\(^20\) The positions of the observed lines in GMO can thus be correlated with the absorption spectrum of Gd\(^{+++}\) in other materials. Each transition is split into at least three components by the crystal field of the lattice.

V. CONCLUSIONS

The ferroelectric transition did not alter the slope or the energy separation of the optical absorption spectra for light polarized along the three crystal axes of GMO. In GMO, the spontaneous polarization in the ferroelectric phase is...
along the c axis and the symmetry change at the transition is accomplished by a rotation of the unit cell in the a-b plane accompanied by small changes in nearly all the atomic positions (the differences in the interatomic distances of nearest neighbors between the two phases are all less than 0.05 Å).18,24 This rotation of the unit cell will not affect the optical absorption spectrum along a given crystal axis. (The propagation directions of the light must be redefined to account for the rotation of the cell however.) The differences in interatomic distances in the a-b plane in the orthorhombic phase were apparently insufficient to induce significant differences in the optical absorption spectra along the a and b crystal axes. In other ferroelectrics, the temperature dependence of the energy separation between the absorption spectra measured along different polarization directions in the ferroelectric phase has been shown to be due entirely to the temperature dependence of the spontaneous polarization.25 In GMO, however, the spontaneous polarization is quite low (0.20 μC/cm² at room temperature) and apparently insufficient to induce observable temperature-dependent changes in the energy separation between the optical absorption spectra for light polarized parallel and perpendicular to the crystalline c axis.

These measurements reveal an exponential dependence of the optical absorption edge with photon energy. The absorption coefficients may be described equally well by either of two equations [Eqs. (11) or (13)]. We have discussed the interpretation of these results previously25,26 and have shown that the optical-absorption-edge data for BaTiO₃,18 and KTaO₃ are similarly ambiguous. To date, the data for GMO, BaTiO₃, and KTaO₃ are not sufficiently precise to distinguish between these two empirical descriptions.

Effective temperatures have been used successfully to describe exponential absorption edges at very low temperatures27,28 where zero-point vibrations introduce deviations from Urbach’s rule. Similarly, in acoustoelectric-modulation experiments29 where the phonon distribution deviates significantly from its equilibrium distribution, the propriety of an effective temperature is apparent. There is, however, no such apparent physical significance for the constant T₀ in Eq. (11).

Equation (12) can be interpreted as resulting from two independent interactions.25,26 In this case, the first exponential is identical to that given by Urbach’s rule [Eq. (1)] and thus associated with some type of phonon-assisted absorption; the second exponential is independent of temperature and could result, for example, from interactions with lattice impurities, from piezoelectric coupling to lattice strains,10 from surface or volume defects, or from a combination of these.

The linear temperature dependence over the full temperature range of the energy for a fixed absorption is surprising in view of the large nonlinear behavior of the lattice expansion near the transition temperature. However, if the absorption threshold is associated with an electronic transition within the molybdate ion, the linear temperature dependence of the expansion of the molybdate group would prevail, whereas the nonlinear temperature dependence of the translational symmetry of the molybdate groups would have little influence on the optical transition.

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