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OPTICAL PROPERTIES RELATED TO ELECTRICAL SWITCHING OF Li DOPED NiO CRYSTALS

Judith Bransky
Laser Hardened Materials Branch
Electromagnetic Materials Division

September 1982

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The optical absorption and electrical conductivity of single crystals of NiO and Li doped NiO crystals were studied. Changes in the electrical conductivity induced by an electrical field were measured. Charge transport mechanisms in NiO were extensively investigated. The optical spectrum of some samples displaying reversible and irreversible changes in resistivity before and after switching are given. The ratio of the resistivities between the "On" and "Off" states ranged between $10^6$ and $10^20$ for various samples. Differential dynamic measurements did not show any changes in optical transmission during.
switching, within the experimental accuracy stated. No transmission changes were detected over the whole spectral range (500 to 1100 nm) although the resistance switched by a factor of 30. The absence of such change in transmission indicates that the relation between the absorption coefficient and the conduction mechanism of the electrical switching is different from the one for increased defect concentration.
FOREWORD

This report was prepared by the Laser Hardened Materials Branch of the Electromagnetic Materials Division, Materials Laboratory, Air Force Wright Aeronautical Laboratories. Part of the described work was performed under Project 2422, Task 242204, WUD 24220401, under direction of Mr. Roger E. Rondeau, AFWAL/MLPJ. Dr. J. Bransky was a visiting scientist at AFWAL/MLPJ, under Contract F33615-79-C-5129, Universal Energy Systems, Dayton, Ohio during the period June - October 1981.

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SECTION I

INTRODUCTION

The present study was accomplished within the framework of screening materials having certain optical properties which are affected by externally stimulated transitions. Optical absorption in materials is related to the electrical conductivity, similar to the relation between the refractive index and the dielectric constant. Thus the large and abrupt changes of the electrical conductivity, induced by an electric field, reported in Li doped NiO (References 1, 2, and 3) are of particular interest. This effect is referred to as "switching".

The objectives of this work were:

(a) Synthesize single crystals of NiO and dope them with Li.

(b) Re-establish and study the conditions under which the switching occurs.

(c) Search for switching related optical changes.

The charge transport mechanism in NiO was extensively investigated and two models were suggested: Transport in a narrow 3d band model versus a localized charge hopping process model. The hopping model assumes conduction by transfer of a positive charge carrier from a Ni$^{+3}$ ion to any neighboring Ni$^{+2}$ ion. The Ni$^{+3}$ ions can be generated, in the material, by Ni vacancies in a nonstoichiometric crystal, or by Li$^+$ ions in doped crystals. The charge carriers are trapped by these negative centers. When thermally ionized, these centers provide the free charge carriers in the crystal. According to the hopping model, the free charge carrier is self-trapped at Ni$^{+2}$ sites, by the crystal polarization and conduction takes place through thermal activation of these states.
The electrical switching properties of pure NiO were first reported by Gibbons and Beadle in 1964 (Reference 1). These authors observed an "on-off" ratio of $10^5$ in the resistance, due to the application of a DC electric field. In the "on" state ($R=100\Omega$), the conductivity of NiO shows a negative temperature dependence and therefore was related, by these authors, to a metallic fiber clustering. The fibers were supposed to disrupt eventually by the joule heat of the current flowing through them and thus cause the sample to switch back to the "off" state. This crude model was refined later, by Fuschillo et al (Reference 2) process on an atomic scale. In any case, if the reversible switching effect occurring in highly doped crystals can be considered to be a result of an increase in the number of free charge carriers, induced by the electric field, a change in the optical absorption is expected.
SECTION II

EXPERIMENTAL

1. CRYSTAL GROWTH

It is always desirable to investigate the phenomena in pure single crystals. This eliminates possible contributions from grain boundaries and impurities. For this purpose, the well established technique of epitaxial growth developed by Cech and Allesandrini has been employed (References 4, 5, and 6).

NiO single crystals were grown epitaxially on MgO crystals* cleaved in the (100) direction. This growth proceeds according to the following reaction:

\[ \text{NiBr}_2 + \text{H}_2\text{O} + \text{NiO} + 2\text{HBr} \]

The reaction takes place at 650°C. The apparatus used is described in Figure 2. A movable furnace was used in order to achieve an instantaneous change in temperature. The water vapor was supplied by a distilled water container, maintained at 40°C to assure the necessary water vapor flow of 30 ml/min (Reference 4). The vapor was let into the system by means of a needle valve. A liquid nitrogen trap was used to condense the excess of H₂O and HBr vapors.

MgO substrates were etched in a 15% HBr solution for 10 minutes after cleavage, rinsed and arranged in their holders. The NiBr₂ was placed loosely on the bottom of an alumina crucible. A few grams were found to give films with a thickness range of 30-80 μm. The substrate holders made of alumina rings were placed on top of the bromide as shown in Figure 1. This arrangement maintains a constant distance between the substrates and the bromide during the reaction.

*MgO crystals were received from the Carborundum Company, Buffalo, New York.
The crucible was covered with a fitting lid in which four holes were drilled. The total area of the holes was 6 mm$^2$. The reaction tube was dried in 3000C for 30 minutes, then pumped down to about 1 mm Hg. The furnace was heated to 7000C, away from the crucible. When the temperature was attained, water vapor was let into the system and after the new pressure of 10 mm Hg was established, the furnace was rolled over the crucible and the reaction started. The time to complete the reaction was about two hours. The system was cooled with the furnace to room temperature (about two hours). The water vapor flow was shut off 10 minutes after the furnace was switched off.

To separate the NiO crystals, the edges of the substrates were exposed by polishing and the MgO was dissolved in a 15% H$_2$SO$_4$ solution at 600C for about 30 hours. The NiO layers were not affected by the acid at this concentration. In most cases, the separated NiO layers cleaved into small rectangles of few square millimeters. Similar breakage is reported elsewhere (Reference 5). Although, growth of larger crystals has been achieved, this breakage problem was not pursued further, as the size of the crystals was enough for the present work. The crystals, as grown, are green; spectrometric measurements of the crystals showed the typical absorption lines for NiO reported previously in the literature (Reference 7).

2. LI DOPING PROCEDURE

The NiO crystals were immersed in a 75% by weight (saturated) solution of LiNO$_3$. Care was taken to wet them on both sides (Reference 2). The crucible with the samples was slowly heated, to avoid intensive boiling of the solution, up to 6500C; at this temperature the nitrate decomposes and the lithium diffuses into the NiO. After being at 6500C for 15 minutes, the samples were cooled down, rinsed thoroughly, and annealed for an hour at 9000C to homogenize the Li distribution.

The doped crystals looked black. The amount of doping could be reduced by diluting the nitrate solution. Doping up to 0.4 atomic percent Li has been achieved. The amount of Li was determined from the initial resistivity using the data of Lalevic et al (Reference 3); this data is summarized in Figure 2.
3. ELECTRICAL MEASUREMENTS

Platinum contacts, 1.5 mm in diameter, were sputtered on one face of the doped crystals. The other face was cemented by conducting epoxy to a thin slab of copper. The samples were inserted into a spring loaded holder. The initial resistance of the samples was measured by a simple DC circuit applying low voltage to the sample (1-5 volts). Higher DC voltages were applied by the same circuit for switching effects.

Another circuit was used for pulsed resistance measurements. Voltage up to 300 V was applied to the sample through a diode switching circuit. The pulse duration was 2 μsec with a repetition rate of 50 pulses per second. The voltage and current were measured by a double beam oscilloscope. For combined electrical and optical measurements, a pair of strip platinum contacts were sputtered on one face of the crystal leaving a rectangular gap of 1 mm width. In this configuration, higher voltages for switching effects were necessary; therefore, the switching transistor was replaced by a high voltage triode. A 5 μsec pulse, with a repetition rate of 20 cyc/sec, activated the circuit and the tube. The sample was connected in series to the anode and to a 10k resistor R.

In order to avoid any possible changes due to the tube conductance, the voltage drop on the sample is recorded by subtracting $V_s = V_{t+s} - V_t$ and the current is calculated by

$$i = \frac{V_{DC} - V_{t+s}}{R}$$

where the various voltages are denoted according to the following diagram.
4. THE OPTICAL SYSTEM

In order to be able to take optical transmission data simultaneously with the electrical switching, a rectangular gap of \(0.1 \times 0.4\) cm was exposed for light transmission. The sample was mounted in a perforated holder with aluminum foil leads pressed on the contacts.

The holder was placed in the path of a chopped white light beam from a tungsten lamp source. The transmitted light was analyzed by a Perkin-Elmer manual spectrometer. A silicon diode was used as a detector with a wavelength range of 400-1100 nm. The dial reading of the spectrometer was calibrated by 10 narrow by-pass filters. Two types of measurements were taken:

a. The Transmission Spectrum

The transmittance of the sample was recorded point by point without applying an electric field. The actual spectral curve of the sample was calculated from the ratio of the transmitted light to the incident light at every measured wavelength, as analyzed by the detector.
The Differential Dynamic Measurements

These combined electric and optic measurements were intended to detect any change in the optical transmission upon application of a pulsed electric field and switching. The output signal of the detector was amplified by a fast response amplifier and displayed on one beam of the oscilloscope. The pulsed voltage drop on the sample, indicating the resistivity switching, was displayed on the second beam. The simultaneous display enables correlation of the resistivity switching with any changes of the optical absorption. Both signals are synchronized by the pulse triggering of the switching tube. The mechanical chopper was omitted in this type of measurement, the pulsed transmission changes serving in its place. The rise time of the diode and the amplifier were small compared to the pulse width. The "signal to noise" ratio of this differential-dynamic set-up enabled us to detect 2% change of the optical signal, at maximum transmission and 10% at maximum absorption.

The spectrum of some samples displaying irreversible changes in resistivity were measured on a commercial Cary Model 14 spectrometer before and after the switching.
SECTION III

RESULTS

1. SWITCHING CHARACTERISTICS

A typical DC current-voltage characteristic for a Li doped NiO single crystal (70 $\mu$m thick) is given in Figure 3. The initial slope of the curve can be considered ohmic, while at a certain field

$$\varepsilon_s = 2 \cdot 10^4 \text{ V/cm}$$

an abrupt increase in conductivity causes a X10 increase in current. This behavior seems to be related to a temperature effect. According to Fuschillo et al. (Reference 2) the temperature dependence of the conductivity is

$$\sigma = \sigma_0 e^{-\frac{E_a}{kT}}$$

with an activation energy of $E_a = 0.22$ e.v. It is obvious that the conductivity is very sensitive to temperature changes, and for any reliable measurements, of field induced switching, care must be taken to avoid heating of the sample. Usually when high voltage was applied to the samples, for a few seconds, they displayed unstable resistance and switched to an irreversible low resistivity state.

To eliminate the joule heating contribution to the switching effect, the pulsed measuring system described in Section II was used. Curve 2 in Figure 3 displays the current voltage characteristic of pulsed voltage measurements. It can be seen that due to minimization of the joule heating, the switching is more gradual in the pulsed voltage measurements. Typical resistance versus voltage curve is given in Figure 4. Curve 1 is the DC resistance as measured initially on a virgin crystal. Curve 2 is the pulsed voltage resistance of the same sample. As can be seen, the initial value of the resistance is 500 k$\Omega$.
SAMPLE No 314
(0.26 % at. Li)

CURRENT/VOLTAGE CHARACTERISTIC

Figure 3. D.C. Characteristics of a Lithium Doped NiO Crystal
SAMPLE N° 616
(0.4% at Ll)
THICKNESS: 35μ

RESISTANCE VERSUS VOLTAGE
GEOMETRIC RATIO 1.14

- D.C.
- PULSED
1 INITIAL CURVE (SEE SCALE ON RIGHT)
2 REVERSIBLE
3 IRREVERSIBLE SWITCHING

Figure 4. Resistance Versus Voltage Curves Displaying the Reversible and Irreversible Switching
and drops by a factor of 6 for a relatively low electric field: $0.21 \times 10^4$ V/cm. Exceeding this DC field threshold caused the samples to switch irreversibly to lower resistivity values. This type of irreversible switching occurred only in samples that were exposed to a DC field. The samples intended for combined optical and electrical measurements that were not exposed to DC fields did not undergo this type of initial irreversible switching.

Curve 2 displaying the pulsed voltage measurements shows a gradual drop from a much lower initial value of 47-48 k$. The effect of the temperature is eliminated and the switching from high to low resistivity is reversible up to $E_S = 10^4$ V/cm ($V_S = 50$V). The interesting feature of this switching effect is the leveling of the curve at voltages about 25% of the magnitude of $V_S$, the voltage for the irreversible switching. As long as the sample was not exposed to voltages above $V_S$ the behavior displayed in curve 2 is repeatable. After exceeding $V_S$, the resistance drops irreversibly. The low resistance voltage dependence is displayed in curve 3. This is an almost Ohmic relation.

Most of the samples displayed the same resistivity behavior, including the ones that were optically investigated. For these, the switching voltages were 30 times higher, and could not be attained in the present experimental set up. The ratio of the resistivities between the "ON" and "OFF" states ranged between $X6$ and $X20$, in the various samples.

2. OPTICAL MEASUREMENT

Typical spectral curves run by the optical system for different NiO samples are given in Figure 5. An undoped NiO crystal, a virgin Li doped crystal and a Li doped, previously switched, samples are displayed in curves a, b, and c respectively.

A notable absorption band is detected at $\lambda = 700$ nm for the doped samples, and so are two transmission peaks at $\lambda = 900$ nm and $\lambda = 560$ nm; in complete accordance with previous works (Reference 7). There is a notable change in the shape of the spectra as a result of the lithium doping, which seems to enhance the absorption at $\lambda = 700$ nm.
Figure 5. Spectrum of an Undoped, Doped, and Previously Switched Samples
The addition of defects by excess oxygen ions has the same effect on the spectrum as the lithium doping, as can be seen in Figure 6. The optical density of this sample was measured by the Cary 14 spectrometer, before and after annealing it in oxygen at 950°C for 60 minutes. As is to be expected, the previously switched and the unswitched samples display a similar spectrum (Figure 5), as the electrical resistance of the switched sample had been restored prior to the optical measurement.

The important result is the one resulting from the combined optical and electrical measurement. The differential dynamic measurement did not show any change in optical transmission during switching, within the experimental accuracy stated in Section IIb. No transmission changes were detected over the whole spectral range although the resistance switched by a factor of 30.
Figure 6. Optical Density Spectrum of a Stoichiometric NiO Crystal and Nonstoichiometric NiO$_{1+x}$ Crystal
SECTION IV

DISCUSSION

Newman and Cherenko (Reference 7) showed that the changes of the background absorption of nonstoichiometric and lithium doped NiO crystals, due to different defect concentration is correlated with their electrical resistivity. The higher the concentration of defects (Li or vacancies), the higher is the conductivity and the higher is the absorption coefficient. The phenomenological relation between the resistivity and the background absorption coefficient, for various concentrations of defects in NiO, is presented in Figure 7. The data is recorded for the transmission peak at $\lambda=700\text{nm}$. As can be seen, our results are in accordance with Newman and Cherenko's (Reference 7).

From the data in Figure 7, it can be seen that if the increase in conductivity, upon reversible switching, should affect the absorption in the same way, a change in transmission of about 25% is expected. This is the value estimated from Figure 7 when the resistivity changes from 2000 $\Omega\text{cm}$ to 200 $\Omega\text{cm}$; these were the measured values during the differential dynamic measurements.

The absence of such change in transmission, as was found in the present study, indicates, however, that the relation between the absorption coefficient and the conduction mechanism of the electrical switching is different from the one for increased defect concentration.

The electrical conductivity is given by

$$\sigma = p e \mu$$

where $p$ is the concentration of free charge carriers, $e$ is the electron charge, and $\mu$ is the charge carrier mobility. The concentration of free charge carriers at a temperature $T$ is:

$$p = p_0 e^{-E_1/kT}$$

where $p_0$ is the defect concentration and $E_1$ is the ionization energy.
Figure 7. Absorption Coefficient Versus Resistivity In Various Defect Concentrations in NiO
Two mechanisms can be invoked to account for the background absorption in heavily doped NiO crystals. The first is an absorption of photons by charge carriers trapped at a Li$^+$ site; i.e., photoionization. The second is a free charge carrier absorption. If the band model prevails, or, if the hopping process is assumed, the absorption is attributed to an optical activation of a hole out of a self-trapped position.

In the first case, the absorption coefficient $\alpha$ depends on the unionized defect concentration $p_0 - p$, in the second case $\alpha$ depends on $p$, the free carrier concentration.

In the case of a change in the electrical conductivity that is due to variation in the Li ion concentration,

$$\frac{\Delta \sigma}{\sigma_{\text{def.}}} = \frac{\Delta p_0}{p_0}. \quad (3)$$

Whereas in the case of a change in electrical conductivity that is due to a release of trapped charge carriers, as is assumed in the switching process:

$$\frac{\Delta \sigma}{\sigma_{\text{switch}}} = \frac{\Delta p}{p}. \quad (4)$$

Since $p_0$ is constant in this case, as stated above for photoionization, the absorption coefficient is assumed to be dependent on the concentration of the residual trapped charge carriers. Thus, for a change in the doping concentration

$$\frac{\Delta \alpha}{\alpha_{\text{dop}}} = \frac{\Delta (p_0 - p)}{p - p} = \frac{\Delta p_0 (1 - e^{-E_f/kT})}{p_0 (1 - e^{-E_f/kT})} = \frac{\Delta p_0}{p_0} = \frac{\Delta \sigma}{\sigma_{\text{dop}}}. \quad (5)$$
which is the case studied by Newman and Cherenko. For the switching case, when $P_0 = \text{constant}$:

$$\frac{\Delta a}{a_{\text{switch}}} = \frac{\Delta(P_0 - p)}{P_0 - p} = -\frac{\Delta p}{P_0 - p} = -\frac{\Delta a}{\sigma_{\text{switch}}} \times \frac{1}{\frac{P_0}{p} - 1}.$$ (6)

In this case $p = P_0 e^{-E_i' / kT}$, where $E_i'$ contains the electrical field energy.

Thus, for photoionization absorption

$$\frac{\Delta a}{a_{\text{switch}}} = \frac{\Delta a}{\sigma_{\text{switch}}} \times F$$ (7)

where $F = \frac{1}{e^{E_i' / kT} - 1}$

$E_i' = E_i - E_{\text{field}}$

$E_{\text{field}}$ is the atomic switching field energy.

According to Fuschillo et al. (Reference 2) $E_i = 0.22$ e.v.

$E_{\text{field}}$ is estimated to be 0.075 e.v. from the resistivity ratio upon switching:

$$E_{\text{field}} = kT \ln \frac{R_{\text{unswitched}}}{R_{\text{switched}}}$$

thus

$$F = \frac{1}{270}.$$  

Therefore the absorption variation due to photoionization, during the switching process, is negligible and could not have been detected in the experimental precision.
On the other hand, the absorption due to the free charge carrier is:

\[
\frac{\Delta a}{\alpha_{\text{switch}}} = \frac{\Delta P}{P} = \frac{\Delta \sigma}{\sigma_{\text{switch}}}
\]  

(8)

and should be as large as predicted by Figure 7.

The absence of observable changes in absorption, as found in this study, is a confirmation of the fact that the observed change in resistance upon switching is not due to an overall change in conductivity, but is restricted to a filamentary transport of charges along definite paths from one Li ion to the next. These changes of conductivity occur through very small regions of the material and thus do not affect the total absorption cross area.
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