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An Investigation of the Chemical and Physical Properties of Pristine, Electrochromically Damaged, and Photochromically Damaged $KTiOPO_4$ (KTP) using Surface Analytical and Optical Spectroscopic Techniques.

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Abstract

A variety of experimental techniques were employed to study the properties of electrochromically (EC) damaged, photochromically (PC) damaged, and pristine $KTiOPO_4$ (KTP). Additionally, nonlinear optical calculations were performed to complement the experimental work in an effort to elucidate the respective mechanisms operative in producing EC and PC damage to KTP. Several independent experiments indicate that there is Ti deficiency in the EC damaged material, which is due to migration of these ions to the electrode surface. The laser experiments indicate that UV radiation can produce reversible PC damage. UV-producing SFG processes accidentally occurring in SHG cut KTP may lead to macroscopic damage. It must be emphasized that a fundamentally different mechanism is responsible for EC damaged versus PC damaged KTP.

Background

Single crystal $KTiOPO_4$ (KTP) is one of the most widely used and versatile nonlinear optical materials in the field of optics and laser sciences[1]. KTP's excellent overall chemical and physical properties enable it to be the material of choice in applications that include second harmonic frequency generation of 1 μm lasers[2], production of tunable NIR and IR wavelengths in optical parametric oscillators[3] (OPO), fast electro-optical Q-switching[4] of polarized laser output, and development as a substrate in optical waveguide[5] devices. Despite KTP's exceptional properties, however, some commercial applications have been limited by the fact that this material can suffer irreversible damage due to high intensity electrical and electromagnetic fields[6,7].

The presence of impurities, defects, vacancies, and electron or hole transfers is most likely related to the damage susceptibility. Most studies on KTP have focused on bulk measurements of optical and electrical properties. However, Scripsick and Halliburton[8], and Roelefs[9] have reported important results focused on the behavior of KTP at a microscopic level using EPR as a probe of defect and impurity local structure. In this report, we will show

the results of alternative but equally valuable surface and near-surface ("bulk") techniques based on mass detection (Secondary ion mass spectrometry [SIMS]), particle beam/matter interactions (Rutherford Backscattering [RBS], particle induced X-ray emission [PIXE], channeling). Additionally, the results of optical experiments on pristine and damaged KTP are reported. These results give valuable information needed to understand the damage mechanism and the nature of the defect site. All samples used in this study were grown at Philips Components using a high temperature solution (flux) method.

Experimental Techniques

Experiments were performed to study both the electrochromically (EC) and the photochromically (PC) damaged KTP material. Electrochromic damage was induced by a device that applies variable but steady DC voltage across silver coated faces normal to the c-axis of XYZ cut samples. Optical absorption scans were acquired in real time simultaneously with the damage. EC damage thresholds ranged from 2750 V/cm to 4250 V/cm. Damage (dark green streaks) commenced at the cathode. A thick white residue formed at the cathode at applied voltages well below the damage threshold. Photochromic damage was produced by pulsed 355 nm UV radiation from a Quanta-Ray DCR-IIA Nd:YAG laser operating at 10 Hz with energies of 1.5 mJ/pulse and pulse widths of about 10 ns for at least 15 minutes. The beam was focused on the polished crystal surface. Fundamental and second harmonic light was blocked by a UV pass/Vis-NIR absorbing glass filter. "Hot spots" in the beam profile were reduced by first scattering off of a ground glass plate, with subsequent refocusing onto the KTP sample.

Material Analysis

Figure 1 shows the overlaid spectra of two Rutherford Backscattering (RBS) measurements. Although the RBS results do not show any differences in oxygen concentrations (at the 2% detection level) between pristine, EC, and PC damaged samples, it is noteworthy that the EC damaged regions of the KTP crystal have approximately 10% less Ti ions than the pristine areas of KTP. Channeling is a term used to denote the penetrability of the ion beam in the solid; generally, the better the penetration ability, the higher the degree of crystallinity. The EC damaged material channels better than the pristine area, probably because there are (10%) fewer titanium ions to back scatter the alpha particles; otherwise, the pristine region, being more regular, should channel better. Examination of the RBS and PIXE spectra reveal the presence of Nb (282 ppm ± 10%), Zr (189 ppm ± 10%), and Sb (150 ppm ± 10%) impurities. The presence of the three measurable impurities appears to be uniform throughout the sample because no intensity differences are observed in both the RBS and PIXE spectra between pristine and EC damaged regions.

Secondary ion mass spectroscopy was performed with a Leybold SSM 200 module mounted on a MAX100 ultra-high vacuum chamber (base pressure 5×10^{-11} Torr). A 5 keV argon ion electron impact source was utilized, rastering over a 4 mm by 4 mm surface area. Both static (surface) and dynamic (200 Å depth) SIMS experiments were conducted for both the positive and negative secondary ions in the range of 1-150 mass-to-charge (m/z). The SIMS technique is sensitive to the presence of Ag^+ ions; however, none were detected in our experiments. Absolute quantitative calibration of the signals in SIMS is difficult because ion intensities are heavily host dependent; therefore, we relied on the PIXE measurements for those determinations.

SIMS data indicates the presence of the following nine impurities in both pristine and EC damaged KTP: Na, Mg, Al, Si, Ca, Fe, Sr, Sb, Ba. Silver ions (Ag^+), suspected contaminants from the silver paint often used at the electrode surfaces, are not detected by

SIMS. The lack of silver ions is confirmed by RBS and PIXE. SIMS spectra do not indicate any O deficiencies. Comparative SIMS spectra between EC damaged and pristine KTP clearly indicate the deficiency of Ti ions in the sample in such a way as to strongly suggest their migration to the electrode. We found a significant reduction in Ti signal when the center of the EC damaged material was cut away to expose it as a surface for the SIMS measurement (relative to the pristine material in the bulk). At the true surface of the material (the face in contact with the electrode), the opposite result (Ti signal enhancement) was observed.

Optical Properties

Absorption spectra spanning wavelengths from 300 to 850 nm on EC damaged and pristine KTP were acquired at temperatures from 10 K to 300 K. At all temperatures, a weak peak centered at about 410 nm grows in strength upon EC damage (see Figure 2). Additionally, an extremely broad band ranging from 500-700 nm is observed for EC damaged KTP, but not for pristine KTP.

Upon exposure to 355 nm laser radiation, second harmonic generation (SHG) cut KTP was observed to have light brown discoloration, the "gray track" often cited in the literature[10]. Most experiments were performed at room temperature and the damage fully reversed in about 15 hours at room temperature. The gray track was actually a "gray spot" because it only penetrated about 1 mm into the bulk of the KTP crystal. This is consistent with KTP's large absorption cross section for 355 nm light. Identical damage conditions applied to KTP crystals held under vacuum produced the same damage and reversibility results, and we discount the role of the presence of oxygen (or lack of) in the atmosphere around the crystal as a factor in the damage mechanism.

Recently, it has been suggested that sum frequency mixing of either the fundamental or Raman shifted fundamental with either the second harmonic or Raman shifted second harmonic could produce UV photons [10]. These photons would have energies higher than the absorption band edge of KTP and could initiate charge transfer processes creating Ti^{3+}. In order to investigate this possibility, phase matching calculations for the various processes must be performed. Since Type I and Type II phase matching require initial components with different polarization properties, knowledge of the polarization dependent Raman spectra for KTP in the SHG orientation is needed to determine whether the Raman shifted components will have the proper polarization to participate in efficient sum freuquency mixing.

We obtained Raman spectra of KTP in the 40 cm^{-1}-1200 cm^{-1} spectral region using a Jobin Yvon Model U1000 Raman Spectroscopy system. Spectra were obtained for the incident light polarized parallel to the z-axis and propagating in the direction typical for second harmonic generation (theta=90, phi=23.3). Although the spectra were significantly polarized in the z-direction (>20/1), they also indicated significant Raman scattering in the plane perpindicular to z. These results indicate that Raman shifted components of either the fundamental or second harmonic with the required polarization for either Type I or Type II phase matching are present.

The main results from a series of nonlinear optical calculations to determine the appropriate phasematching curves in theta, phi (θ, ϕ) space for SHG of 1.064 μm laser radiation and Raman assisted SFG of fundamental and 532 nm radiation to produce UV are presented. There are many Raman lines that could have been used for the shifting of the laser, but we concentrated only on the strongest of these at 729 cm^{-1}. The 729 cm^{-1} was measured at variable temperatures after incident 532 nm light was shifted from an SHG cut KTP crystal. The energy of this line is about 30 cm^{-1} higher in energy than the strongest peak in this spectral region observed in the Raman experiments; however, this 5% difference does not change the final phasematching curves significantly.

The phasematching calculations show that several Type I UV curves lie close to the Type II SHG curve. Although the value of d_{eff} needs to be considered for each unique θ, ϕ pair, the zeroth order choice of crystal cut would be one which is maximally distant from any angles that phasematch for UV radiation, which is strongly absorbed by KTP and could be potentially damaging. Indeed, Philips Components cut their KTP at about theta=90° and phi=23.3°for 1.064 μm at 25 C, and this is precisely the point on the SHG curve that is farthest from any of the SFG curves.

Summary

These results suggest mechanisms for the formation of EC and PC damaged KTP. The EC damage may occur upon reduction of Ti^{4+} to Ti^{3+} by trapping electrons passing through the ion channels present in KTP. Another possibility is Ag^{+} ion migration through the ion channels under an applied voltage, with subsequent macroscopic damage. We heavily discount this latter possibility based on the RBS and SIMS data. The RBS and SIMS data both clearly indicate Ti ion migration based on bulk deficiency of Ti ions in the EC damaged regions; this is can be rationalized based on the established practice of diffusion of titanium ions into lithium niobate for waveguide fabrication. Ti^{3+} optical absorption could produce the observed dark macroscopic damage. It has been calculated that SHG cut KTP could sum frequency mix 1.06 μm and 532 nm wavelength radiation to produce 355 nm UV radiation. There are also indications that sum frequency mixing the Raman shifted fundamental and second harmonic could produce 364 or 374 nm radiation in this region[11]. These UV wavelengths can be absorbed into the UV band edge to initiate a photochemical process such as charge transfer from the oxide ligand to Ti^{4+} to create Ti^{3+} and an oxygen trapped hole[12]. These defect sites may be stabilized by one of the impurity metal ions.

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Figure 1. RBS spectra of EC damaged KTP (solid line) and pristine KTP (dashed line). Note the lower abundance of Ti in the EC damaged sample. The inlay enlarges the Ti signal.

Figure 2. Unpolarized room temperature optical absorption spectra of $KTiOPO_4$. Note the peak at 410 nm and the broad band from 500-700 nm in the EC damaged sample.

Figure 3. Phasematched loci for NdYAG laser radiation in KTP. The solid lines are curves for second harmonic generation. The dashed lines depict angles for sum frequency generated UV radiation. The 364 nm curves closest to the Type II SHG is for Raman shifted fundamental; the other 364 curve is for Raman shifted 532 nm. The 374 curve represents Raman shifted fundamental and 532 nm.

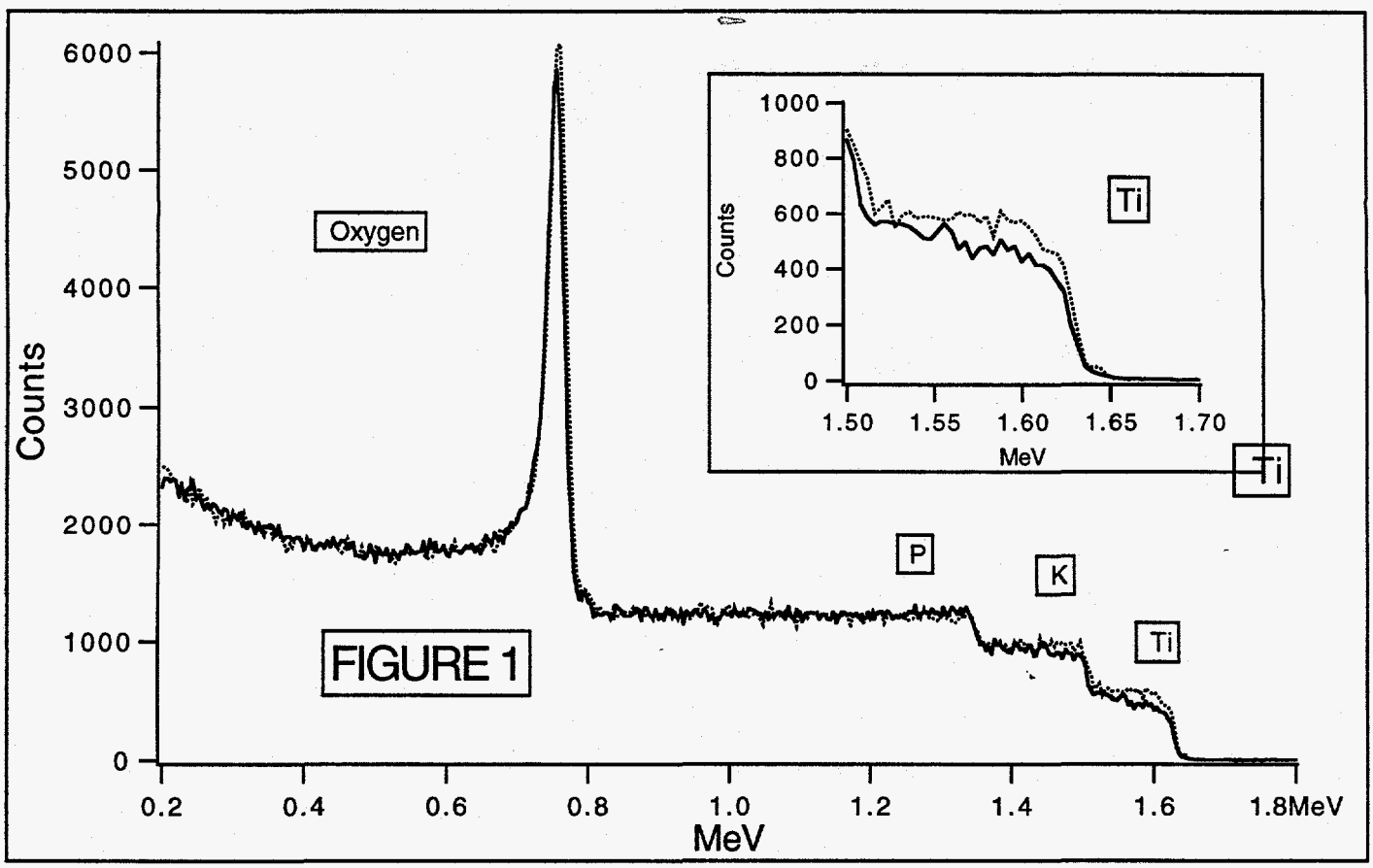
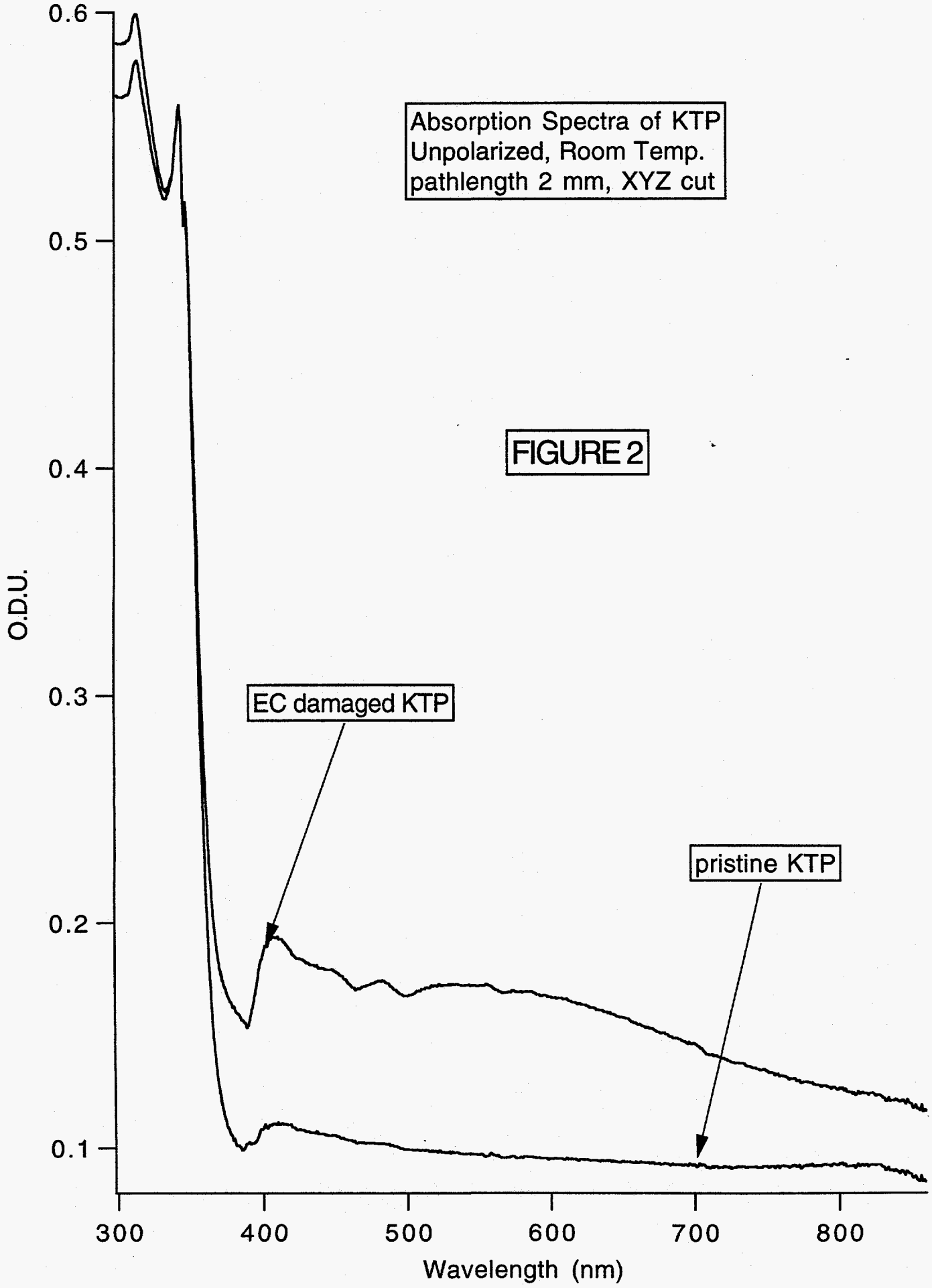

6000
5000
4000
3000
2000
1000
0
Counts
Oxygen
P
K
Ti
Ti
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8MeV
MeV
1000
800
600
400
200
0
Counts
Ti
1.50
1.55
1.60
1.65
1.70
MeV
Ti

FIGURE 1


Absorption Spectra of KTP
Unpolarized, Room Temp.
pathlength 2 mm, XYZ cut
FIGURE 2
EC damaged KTP
pristine KTP
O.D.U.
0.6
0.5
0.4
0.3
0.2
0.1
300
400
500
600
700
800
Wavelength (nm)

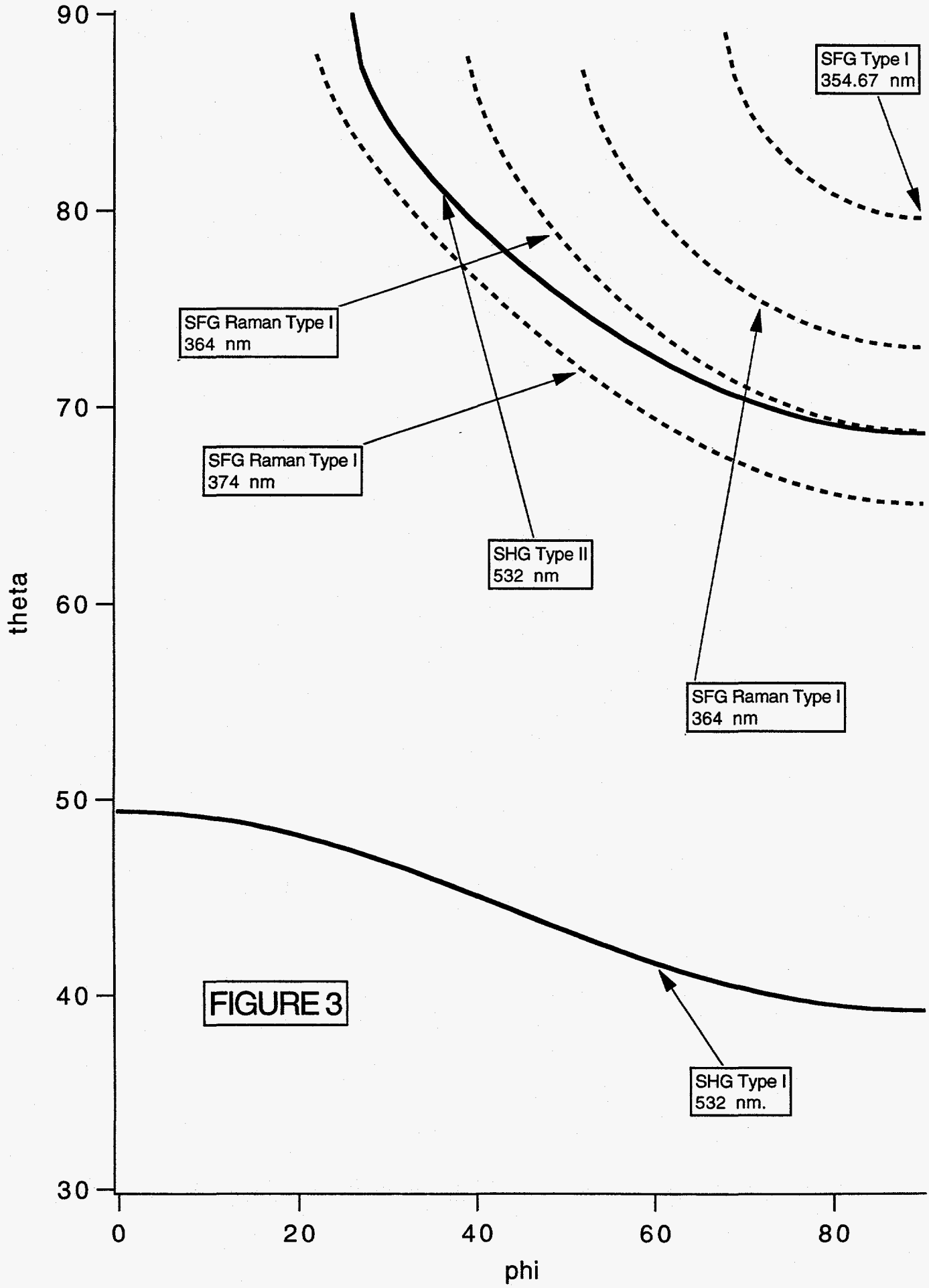

90
80
70
60
50
40
30
theta
0
20
40
60
80
phi
SFG Type I
354.67 nm
SFG Raman Type I
364 nm
SFG Raman Type I
374 nm
SHG Type II
532 nm
SFG Raman Type I
364 nm
SHG Type I
532 nm.

FIGURE 3