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ROOM-TEMPERATURE, NEAR IR FLUORESCENCE OF HIGH OPTICAL QUALITY KTP (POSTPRINT)

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14. ABSTRACT

We investigated room temperature fluorescence in the 500-900nm spectral region from high optical quality, polished and uncoated KTP crystals from three different commercial vendors. The crystals were all cut into 5x5x5 mm3 cubes with their dielectric axes along the cube edges. The pump source was a tripled Nd:YAG laser operating at 355nm and 7mJ energy having 3ns pulse width and 100Hz pulse repetition rate. Samples from two vendors showed low fluorescence of similar magnitude while samples from the third vendor showed nearly two orders of magnitude higher value in the peak fluorescence near 800nm. In addition, all samples showed a weaker secondary fluorescence band peaking near 600nm. A low fluorescence sample from one of the vendors also showed typical "gray tracking" at these pump radiation conditions. We have also measured lifetimes of 2.9 ± 0.7 μs and 4.9 ±0.1 μs for the centers responsible for fluorescence near 845nm and 595nm respectively in the KTP sample showing highest fluorescence and "gray tracking" in this group of samples. The manufacturing processes used to produce high optical quality and low fluorescence KTP materials are proprietary to the commercial vendors and were not provided. Possible sources of fluorescence in these materials are discussed.

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Room-temperature, near IR fluorescence of high optical quality KTP

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ABSTRACT

We have investigated room temperature fluorescence in the 500-900nm spectral region from high optical quality, polished and uncoated KTP crystals from three different commercial vendors. The crystals were all cut into 5mm x 5mm x 5mm cubes with their dielectric axes along the cube edges. The pump source was a tripled Nd:YAG laser operating at 355nm and 7mJ energy having 3ns pulse width and 100Hz pulse repetition rate. Samples from two vendors showed low fluorescence of similar magnitude while samples from the third vendor showed nearly two orders of magnitude higher value in the peak fluorescence near 800nm. In addition, all samples showed a weaker secondary fluorescence band peaking near 600nm. A low fluorescence sample from one of the vendors also showed typical "gray tracking" at these pump radiation conditions. We have also measured lifetimes of 2.9±0.7 μs and 4.9±0.1 μs for the centers responsible for fluorescence near 845nm and 595nm respectively in the KTP sample showing highest fluorescence and "gray tracking" in this group of samples. The manufacturing processes used to produce high optical quality and low fluorescence KTP materials are proprietary to the commercial vendors and were not provided. Possible origin and sources of fluorescence in these materials are discussed consistent with those published in the literature.

Keywords: KTP, Spectroscopy, Fluorescence

1. Introduction

Potassium titanyl phosphate ($KTiOPO_4$ or KTP) with its high transmission covering the 350-3500nm wavelength regions is a widely used nonlinear optical material in such applications as second harmonic frequency generation (SHG) of the fundamental output of Nd:YAG and Nd:YLF lasers, as a source for nonlinear optical conversion in optical parametric oscillator systems, for entangled photon generation and as a choice material for electro-optic Q-switches. The high power requirement for these devices calls for excellent optical quality KTP material with low absorption and fluorescence both at the pump and the operating region wavelength. The presence of intrinsic defects such as point defects and vacancies resulting from the growth process and extrinsic impurities in the form of both intentional and unintentional residual impurities used in the source material for crystal growth give rise to unwanted absorption and fluorescence which can lead to catastrophic failure in the device performance and operation. Also, entangled photon generation applications require low levels of background fluorescence since entangled photon detection rates are typically quite low. In this study, we have investigated room temperature fluorescence properties in the visible and near IR wavelength region (500nm-900nm) and the lifetime of centers giving rise to this fluorescence from high optical quality KTP crystals from three vendors when pumped at 355nm by a tripled, Q-switched, Nd:YAG laser.

2. Samples

Uncoated, optically polished on all sides, KTP cubes with dimensions of 5mm x 5mm x 5mm, were purchased from three commercial vendors. The crystals were cut with their crystallographic axes along the cube edges. There were six samples from vendor A, consisting of two samples each from three growth conditions and two samples each from single growth processes from vendors B and C. All of the samples from vendor A and Vendor C were flux grown.

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Samples from vendor B were hydrothermally grown. Further details of the growth processes were proprietary to the vendors and were unavailable to us. The sample characteristics are described in Table-1.

Table-1 KTP Sample Parameters

Vendor	Dimensions (mm)	Growth Type	Comments
A, Sample#1, #2	5 x 5 x 5	Flux	Beveled cube edges. All faces optically polished. High gray track resistant. Lower fluorescence and no "gray tracking."
A, Sample #3, #4	5 x 5 x 5	Flux	Beveled cube edges. All faces optically polished. High fluorescence and "gray tracking."
A, Sample #5, #6	5 x 5 x 5	Flux	Beveled cube edges. All faces optically polished. Highest fluorescence and "gray tracking."
B, Sample #1, #2	5 x 5 x 5	Hydrothermal	Index arrow, All faces optically polished. Lowest fluorescence. No "gray tracking."
C, Sample #1, #2	5 x 5 x 5	Flux	No identification markings. All faces optically polished. Ultra gray track resistant. Low fluorescence and "gray tracking."

3. Experiment

3.1. Fluorescence

Unpolarized, room temperature fluorescence in KTP samples was excited by frequency tripled, Q-switched, Nd:YAG laser pulses at 355nm with ~700mw average power (~7mJ/pulse, 100Hz rep rate, ~3ns pulse width). The ~3mm diameter laser beam was unfocused on the samples. The resulting fluorescence, in the 500-900nm region, was collected at 90^0 relative to the incident beam by a scanning spectrometer (0.33m focal length, f/3.9) fitted with a 750nm blazed grating and a GaAs photocathode photomultiplier (PMT) used in a photon counting mode as a detector. A sharp cut-on, long wavepass filter in-front of the spectrometer entrance slit helped reduce the intensity of pump radiation and fluorescence wavelengths less than 500nm entering the spectrometer. A schematic of our experimental setup is shown in Figure 1. The spectra shown as a function of wavelength are corrected for spectrometer response. This was accomplished in the usual way by using a standard blackbody source at 1000^0C for calibration. The end points of the spectral curves in the display of Figure 6 (a, b) are only shown up to 850nm instead of 900nm because of the sharp drop in the responsivity of the GaAs PMT beyond this wavelength.

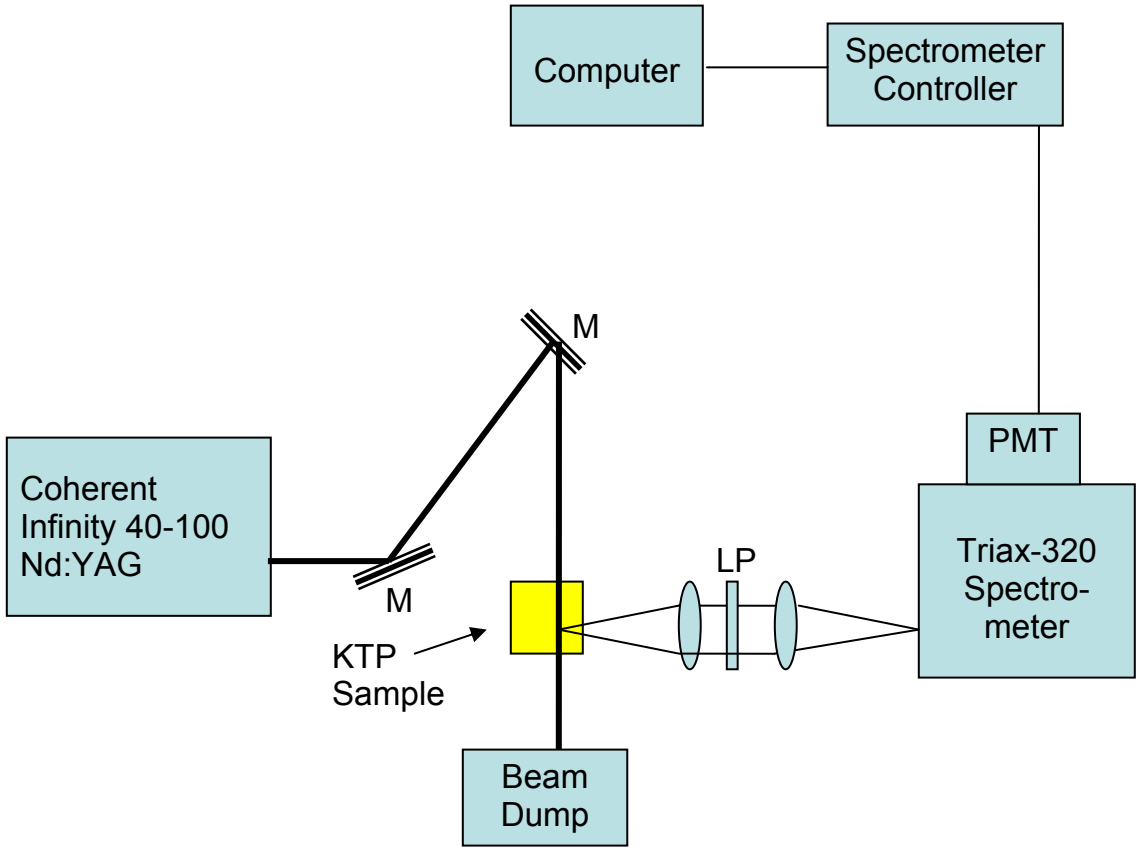
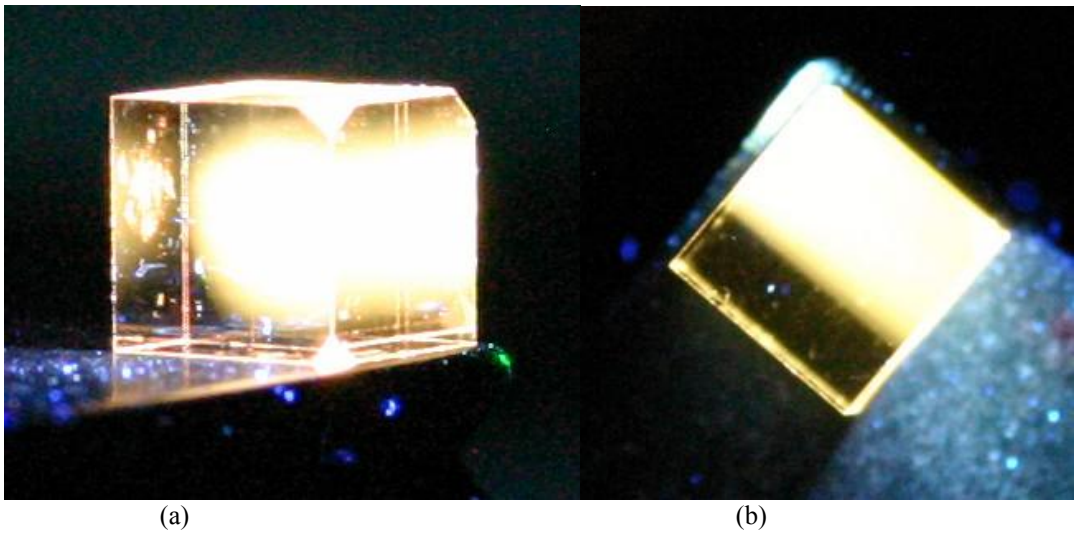


Figure 1. Experimental layout. LP=long pass filter, M=mirror and PMT=photomultiplier tube.



(a) (b)

Figure 2. (a) Side view photograph of KTP sample #5 from Vendor A, excited with 7mJ, ~3mm diameter laser beam at 355 nm. Excitation along Y direction, fluorescence along Z direction (Y (x, x) Z). (b) Top view.

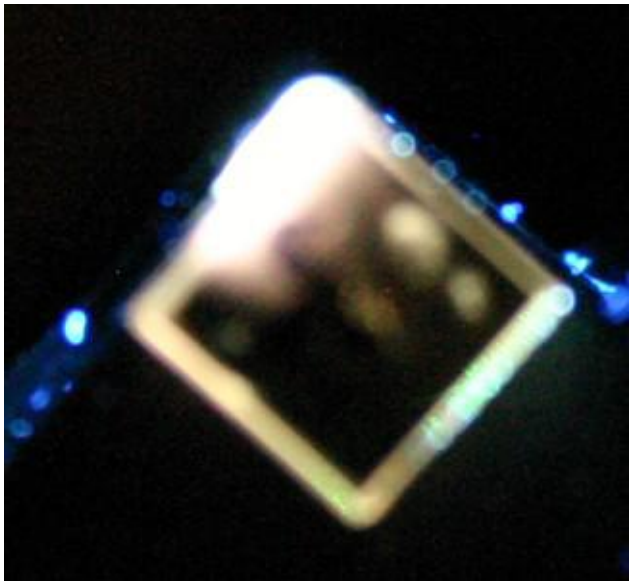


Figure 3. Top view photograph of KTP sample #1 from Vendor #2, excited with 7mJ, ~3mm diameter laser beam at 355 nm. Excitation along Y direction, fluorescence along Z direction (Y (x, x) Z). Note that there is negligible internal fluorescence; the light observed is mostly surface scattering.

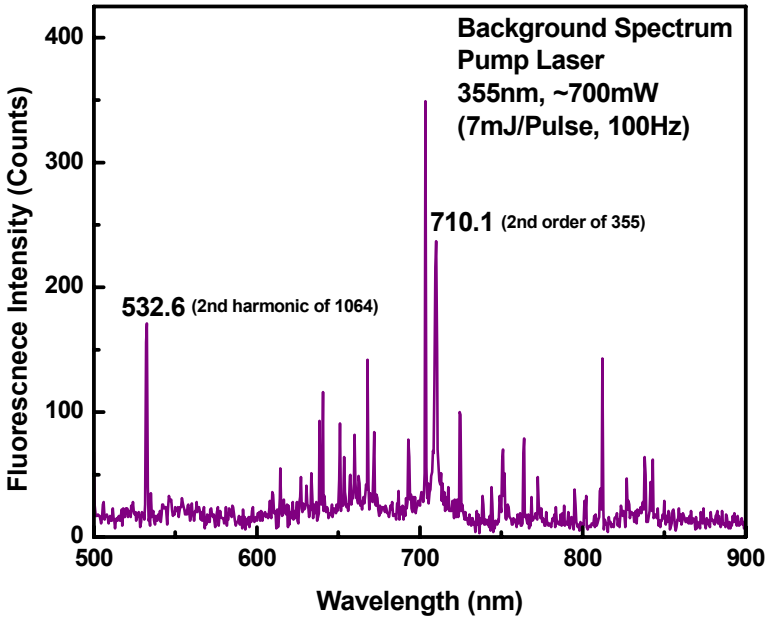


Figure 4. Background Spectrum (No sample) from 355nm, ~700mW (7mJ, 100Hz) laser line. 2nd harmonic of fundamental is seen at 532.6 nm. The line at 710.1 nm is the 2nd order line of the excitation source at 355 nm.

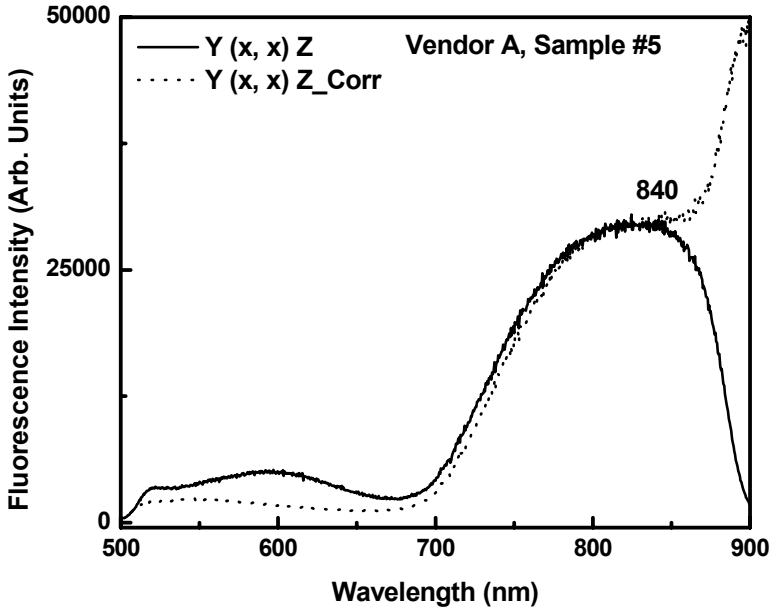
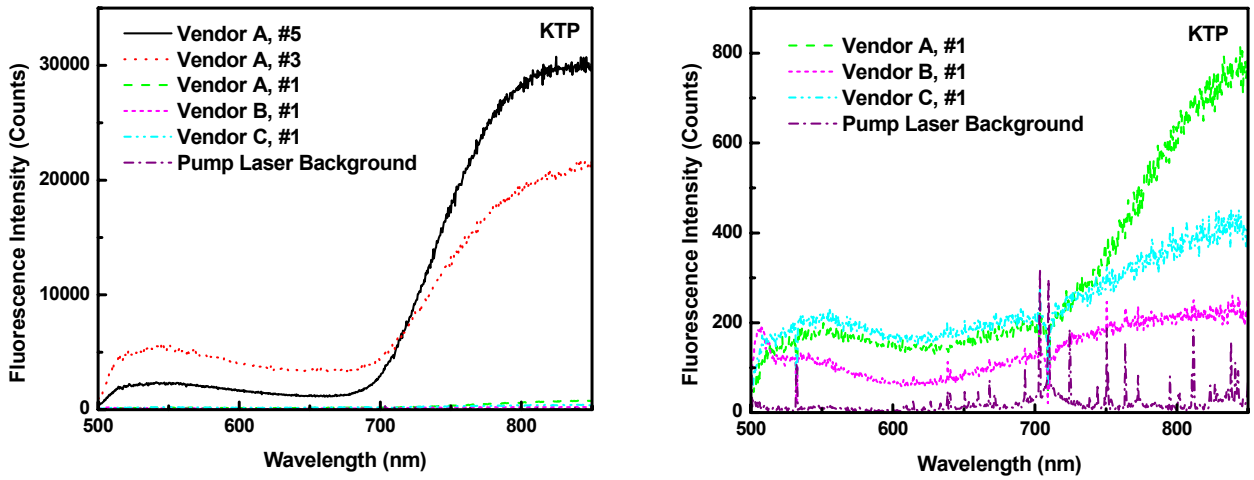


Figure 5. Uncorrected and spectrometer response corrected, room temperature fluorescence from KTP sample #5 of Vendor A for the Y(x, x)Z orientation.



(a) (b)

Figure 6. (a) Background subtracted and spectrometer response corrected, room temperature fluorescence from all the KTP samples showing strong broadband fluorescence in two of the Vendor A samples. (b) Much weaker fluorescence (note change in the ordinate scale) from other KTP samples.

3.2. Lifetime Measurements

Fluorescence lifetime measurements were carried out using a fast digital oscilloscope (1 GHz BW). The decay from the broad fluorescence peaks centered at 845nm and 595nm for sample #3 and #5 from vendor A, were collected on the oscilloscope as a function of time. The lifetime results measured at these peaks are tabulated in Table-2. Typical fluorescence intensity vs. time plots used to measure the lifetime values and their fits are displayed in Figure 7.

Table 2. Comparison of averaged fluorescence lifetimes for peaks observed in KTP samples #3 and #5 from Vendor A.

KTP Sample ID	845nm Peak (Lifetime τ μsec)	595nm Peak (Lifetime τ μsec)
Vendor A, #3	2.9±0.7	4.9 ±0.10
Vendor A, #5	1.5±0.1	6.6 ±0.03

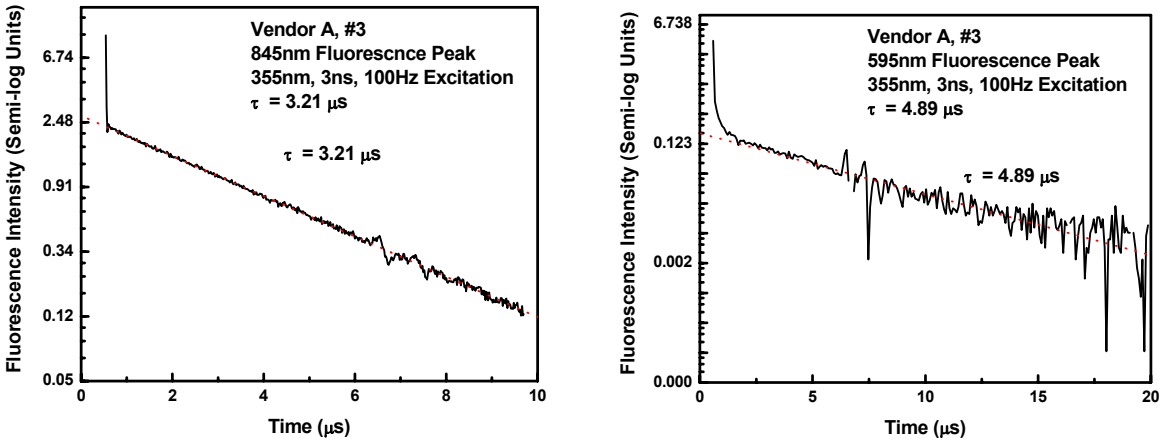


Figure 7. Linear fit examples for fluorescence lifetime of 845nm and 595nm peaks in KTP sample #3 from Vendor A.

4. Discussion

Initial fluorescence data from KTP samples, showed sharp features at 545nm and 613nm. We tentatively attributed these lines to the flashlamp source in the pump laser. However, a careful study identified the source as coming from the LCD monitors used in the experimental data collection and the control of the pump laser. The fluorescence data shown in this report were collected by turning off these LCD monitors and room lights and they are free of the sharp features at 545nm and 613nm seen in the initial data. Immediately after the experiment, a streak of laser damage, brownish red in color (gray track?), similar in dimensions to the pump laser beam, could be seen along the excitation direction in the materials from samples #3, #4 and #5, #6 from vendor A. How long this effect lasted after shutting off the laser excitation was not investigated but the discoloration has since disappeared from the samples. This is similar to the classic gray tracking observed in many commercial KTP samples.

Figures 2-3 show photographs of KTP sample #5 from Vendor A and sample #1 from Vendor B when excited by 7mJ/pulse at 100Hz with a 355nm laser beam. The excitation propagates along the Y direction and the fluorescence was collected along the Z direction (Y (x, x) Z) for both samples. No polarizers were used. The notation merely indicates plane of excitation and the plane of fluorescence collected. This is the orientation of maximum fluorescence

for sample #5 from Vendor A. The background spectrum, without the sample and just the excitation laser beam is shown in Figure 4. The low count rate of < 400 photons/s is nearly two orders of magnitude lower than the fluorescence signal displayed in Figure 5 from KTP sample #5 from Vendor A. This sample showed maximum fluorescence compared to all the samples investigated in this study.

The spectral plots of the data from these samples are shown in Figures 5 and 6. Figure 5 shows both uncorrected raw data and the spectrometer response corrected data for the Y(x, x)Z orientation for KTP sample #5 from vendor A; Figure 6 displays only the spectrometer response corrected spectra plotted from 500 to 850nm for the samples investigated in this study. The intensity axis is scaled by the spectrometer response function. This same response function was applied to all of the measured spectra.

The following conclusions are drawn from the room temperature fluorescence from this group of KTP samples. The hydrothermally grown KTP samples from vendor B had the lowest fluorescence in the 500-850 nm region and showed no gray tracking. The material from vendor C had low fluorescence, similar to that from vendor B but suffered from possible "gray tracking" and excessive pump beam scattering. The flux-grown material from Vendor A varied considerably in the amount of fluorescence and gray tracking from sample to sample.

The origin of gray tracking in KTP material has been observed and explained by several groups in the literature[1, 2]. One explanation is the nonlinear optical process of two photon absorption of two 532-nm SHG photons to reach the strongly absorbing band edge. This excitation into the band edge would trigger a reduction of normal state Ti^{+4} to Ti^{3+} via charge transfer from a neighboring oxygen ion. This [Ti^{3+}-O^-] electron-hole pair in most instances should revert back to the ground state on a time scale much faster than the laser pulse width and therefore not absorb any SHG photon. Impurities or vacancies, however, may stabilize these electron-hole pairs long enough to allow absorption of the SHG frequency, resulting in discoloration or localized heating that leads to gray tracking and catastrophic damage, respectively. The lower wavelength band in the 500-600nm and peaking at ~590nm, seen in the room temperature fluorescence spectra from sample #3 and #5 from vendor A, we believe is from gray tracking.

Fluorescence in the 700-850nm region in KTP has also been investigated by several groups in the literature.[1-3] It is believed that the center involving [Ti^{3+}-O^-], and occupying the normal Ti^{4+} sites is responsible for the fluorescence band in KTP in this region. In hydrothermally grown KTP material, the source of the O^- is believed to be an OH^- ion and in flux grown material it is possibly an O^- vacancy from a neighboring O atom. Another possibility is a self trapped electron in the normal Ti site.

The measured fluorescence lifetimes of several microseconds are similar to those measured for Ti^{3+} ions in various oxide host lattices. Thus the lifetime measurements confirm the identification of the fluorescence as originating from Ti^{3+} complexes. A similar value of 4.7 μs at room temperature was observed[4] for a KTP sample of unknown growth condition and was attributed to a [Ti^{3+}-O^-] center.[2] . The fact that the 845nm peak and the 595nm peak have significantly different lifetimes indicates that they originate from different Ti^{3+} complexes. The different wavelengths may be related to differences in crystal field strength. The sample-to-sample variations of lifetime for the same emission peak in samples grown by Vendor A may indicate some variation in growth procedure between samples. That would also explain the large variations in fluorescence intensity from sample to sample in Vendor A samples.

5. Conclusions

The presence of Ti^{3+} complexes at the normal Ti^{4+} sites in KTP is thus responsible for both gray tracking and the strong fluorescence bands in the near IR region observed in this study. Hydrothermally grown material has low fluorescence and is gray track resistant. Flux grown material varies greatly in its gray tracking and fluorescence properties. Apparently, details of the flux growth process can make a major difference in the optical properties.

It is also important to know the presence and concentration of hole traps arising from residual impurities such as silicon, platinum, iron, chromium, etc. in the source material used in the growth of a particular KTP crystal since these may significantly contribute to this effect. Various processes used by commercial crystal vendors to reduce this fluorescence and gray tracking are proprietary and are not disclosed to customers. Therefore it is difficult to attribute

the source of gray tracking and large fluorescence observed in KTP samples #3 and #5 from vendor A and low fluorescence and no gray tracking seen in samples from Vendor B. The low fluorescence observed in flux grown samples from Vendor C was similar in magnitude to that seen in hydrothermally grown samples from Vendor B but they showed "gray tacking" which was unusual and is unexplained at this time.

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