# Efficient second harmonic generation in $\gamma$-TeO$_2$ phase

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Tellurium dioxide-based glasses and crystalline phases are very promising for use in the technology of non-linear optical materials. The origin of their exceptional non-linearity can be clearly attributed to the hyperpolarizability of the Te$^{IV}$ atom electronic lone pairs [1]. In recent years our group has developed expertise in both experimental and fundamental research on TeO$_2$-based materials. One of the most significant results was the discovery and the structural characterization of two metastable crystalline polymorphs of TeO$_2$, which we have called $\delta$ and $\gamma$ [2, 3]. These two phases have been found during the crystallization of rich-TeO$_2$ compositional glasses [4–6]. The $\gamma$-TeO$_2$ variety crystallizes with orthorhombic symmetry (space group P2$_1$2$_1$2$_1$) and unit cell parameters a = 4.898(3) Å, b = 8.576(4) Å and c = 4.351(2) Å. The $\delta$-TeO$_2$ form is related to the face centred cubic (fcc) fluorite type structure (space group Fm3 m, unit cell parameter a = 5.691(1) Å) and exhibits a fcc cationic long range order but a very disordered oxygen sublattice. These two metastable phases transform into the stable paratellurite form $\alpha$-TeO$_2$ (space group P4$_1$2$_1$2 and the unit cell parameters a = 4.8082(3) Å and c = 7.612(1) Å) at temperature above 400 °C [4, 5]. Among these three polymorphs, the $\alpha$ and $\gamma$-TeO$_2$ phases are particularly interesting as they both present a non-centrosymmetric structural character. This character is necessary for the existence of a second order non-linearity. Second harmonic generation (SHG) has recently been demonstrated in the stable $\alpha$-TeO$_2$ phase [7]. In this paper, we report the characterization of SHG in a powder $\gamma$-TeO$_2$ compound. The $\gamma$-TeO$_2$ SHG signal intensity is then compared to those measured for $\alpha$-TeO$_2$, LiNbO$_3$ and $\alpha$-SiO$_2$ powders.

$\alpha$-TeO$_2$ powder was prepared by decomposition at 550 °C of commercial H$_6$TeO$_6$ (Aldrich 99.9%). $\gamma$-TeO$_2$ samples were obtained by crystallization for 24 h, either at 320 °C for a 95 mol% TeO$_2$–5 mol% PbO compositional glass or at 390 °C for a 85 mol% TeO$_2$–15 mol% WO$_3$ compositional glass. The lead and tungsten tellurites glasses were previously prepared by first melting at 800 °C for 30 min appropriate quantities of reagent grade $\alpha$-TeO$_2$ and PbO (Aldrich 99.5%) or WO$_3$ (Aldrich 99%) in a platinum crucible and then air-quenching the melts. All samples were then milled in an agate mortar. As measured using scanning electron microscopy, the average grain size of the powders was about 40 $\mu$m. The crystallization of the phases was checked using X-ray diffraction. Both $\alpha$-quartz SiO$_2$ (National Institute of Standards and Technology) and LiNbO$_3$ (Alfa Aesar 99.9995%), were used as references to estimate the relative SHG efficiency of our samples.

Since the synthesis of $\gamma$-TeO$_2$ single crystal was impossible because of the metastable nature of this phase, a powder technique was used to measure the second order non-linearity [8].

The experimental set up, shown in Fig. 1 and based on the work of Kurtz and Perry, was used to evaluate the non-linearity of the powder samples [9].

The laser source was a diode pumped Nd/YAG laser with a vertically polarized output wavelength of 1064 nm. It was operating at a repetition rate of 5.4 kHz and had a pulse width of 600 ps with an average power of 87 mW. The fundamental light was focused (L$_1$) in order to irradiate the sample with a beam diameter of 1 mm, which encompassed enough particles to account for their random orientation. The signal generated at the sample was then collected with a lens of great numerical aperture (L$_2$, NA = 0.7) and its image was formed at the detector surface. Monochromatic light was obtained with the use of two BG-18 colored glass filters (F$_1$) which absorbed the fundamental light and a band pass interference filter centered

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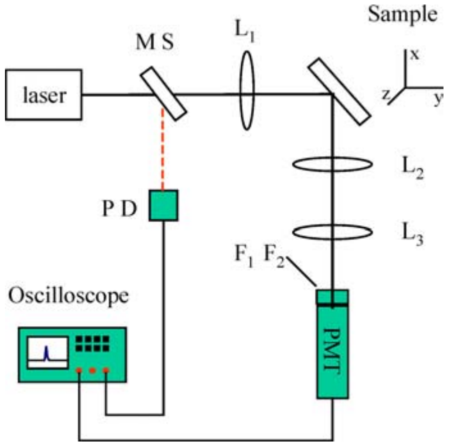

*Figure 1* Schematic of the experimental set up: MS: Microscope Slide, L: Lens, $F_1$: BG-18 colored glass filter (IR absorber), $F_2$: Band pass interference filter centered at 532 nm (FWHM of 10 nm), PD: Photodiode, PMT: Photomultiplier Tube.

at 532 nm ($F_2$) with a full width at half maximum of 10 nm. The signal intensity was subsequently detected by a photomultiplier tube module (P25 A, Electron tubes Ltd., UK) with high quantum efficiency in the green region of the spectrum. The signal was measured on an oscilloscope triggered by a photodiode. The sample holder cell was made of a cardboard strip sandwiched between two strips of double-sided tape perforated with a hole of 1 cm in diameter. Once stuck on a clean microscope glass slide, the 1 cm diameter cell was filled up with the powdered sample and a second clean microscope glass slide was stuck on the top. The cell thickness was less than 0.3 mm.

In a dark room and upon laser irradiation, a diffused bright green light emanating from the $\gamma$-$TeO_2$ sample was observed by the naked eye whereas nothing was seen for the $\alpha$-$TeO_2$ one. This already strongly suggests that the $\gamma$-$TeO_2$ compound presents a strong second order non-linearity. Both samples of $\gamma$-$TeO_2$, prepared by crystallization of either lead or tungsten tellurite glass, present strictly similar SHG characteristics, so that no distinction is made between these two compositions in this communication.

Theoretically, the SH generation is synchronized with the laser pulse, and its width is reduced by a factor of $\sqrt{2}$ with respect to the fundamental one. As the pulse width of the laser was shorter (600 ps) than the response time of our detection system (few ns), we compared oscillograms of the different samples under laser irradiation to the one from a know crystal doubler. Both $LiNbO_3$ and $\alpha$-$SiO_2$ have identical oscillograms, excepted from their intensities, and can therefore be used without distinction as reference signal. Here we present a comparison to the $LiNbO_3$. This enabled us to differentiate SHG from other phenomena. Signals due to other phenomena, like fluorescence, last longer than the laser pulse width and decay with time. Typical oscillograms of the signal emanating from $LiNbO_3$, $\gamma$-$TeO_2$ and $\alpha$-$TeO_2$ compounds and that of the infra-red viewer card are shown in Fig. 2.

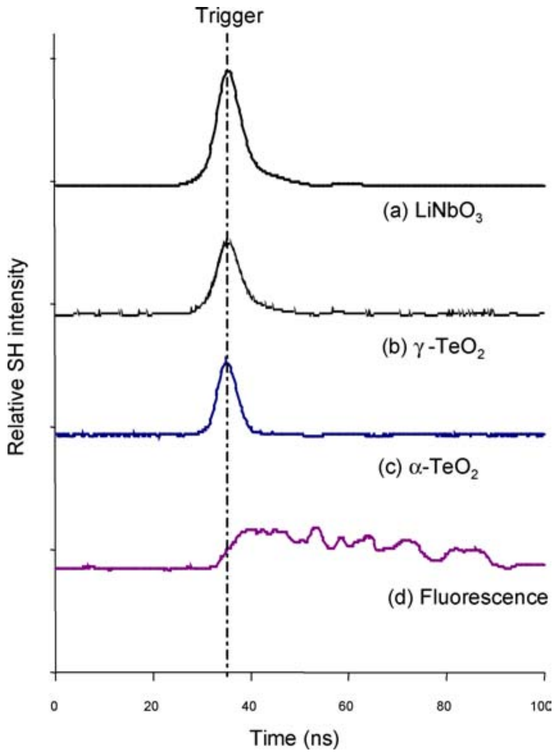

*Figure 2* Oscillograms of the different powder samples: (a) $LiNbO_3$ (attenuation factor of 100), (b) $\gamma$-$TeO_2$ (attenuation factor of 100), (c) $\alpha$-$TeO_2$ and (d) the infra-red viewer card (fluorescence).

For clarity, both signals measured with $LiNbO_3$ and $\gamma$-$TeO_2$ samples are attenuated by a factor of 100. The signals measured with $\gamma$ and $\alpha$-$TeO_2$ phases are similar in shape to that obtained with the $LiNbO_3$ powder suggesting these samples exhibit SHG and not fluorescence. The signal observed for the infrared viewer card, which is fluorescence, lasted longer than the one observed for $LiNbO_3$ and decayed with time. This reinforces the fact that the two $TeO_2$ crystalline phases are frequency doubling crystals. It is also known that in SHG, the signal intensity is proportional to the square of the fundamental power [10] whereas this is not verified for other phenomena. This square law between signal intensity and fundamental beam power was checked for both $\alpha$ and $\gamma$-$TeO_2$ polymorphs (as an example Fig. 3 shows the curve measured for the $\gamma$-$TeO_2$ compound).

This confirms that both $\gamma$ and $\alpha$-$TeO_2$ phases exhibit second order non-linearity. Under our experimental conditions, the SH signal intensity and therefore second order non-linearity of $\gamma$-$TeO_2$ crystalline powder is about 100 times higher than that of $\alpha$-$TeO_2$ phase. Moreover the SH signal intensity measured for $\alpha$-$TeO_2$ compound is relatively weak and of the same order of magnitude to that measured previously by Porter *et al.* ($I_{SH}(\text{quartz}) \approx 1.7 \times I_{SH}(\alpha\text{-}TeO_2)$) [7].

The SH signal of $\gamma$-$TeO_2$ compound is around 70 times higher than that of quartz and about 6 per cent of that of powder $LiNbO_3$.

In summary, efficient second harmonic generation has been demonstrated in $\gamma$-$TeO_2$ crystalline powder which

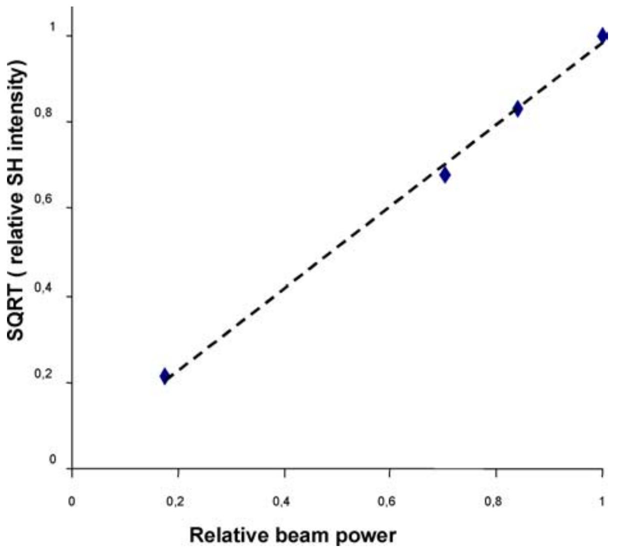

*Figure 3* Square root of the relative SH intensity versus relative beam power for $\gamma$-$TeO_2$ compound.

indicates this phase is a promising material for frequency doubling applications. Further studies are now under investigation in order to: (i) Determine whether $\gamma$-$TeO_2$ is phase matchable and estimate its nonlinear optical susceptibility ($d_{\mathrm{ijk}}^{2\omega}$). (ii) Correlate the crystal structure (Te—O bond lengths and polyhedra linking) with the second order non-linearity property of tellurium dioxides and tellurium dioxide-rich compounds.

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