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Structural evolution, dielectric and electro-optic properties of sol-gel derived potassium titanyl phosphate thin films

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Transparent potassium titanyl phosphate ($KTiOPO_4$) thin films were prepared by a sol-gel coating technique. The structural evolution of the KTP thin films was examined by means of DTA/TGA, FT-IR, XRD and SEM. The effect of UV irradiation on the crystallization behavior was investigated and it was found that the UV irradiation decreases the crystallization temperature of the KTP thin films and dried gels. The dielectric and electro-optic properties were evaluated. The dielectric measurement results show that the KTP thin films have a low dielectric constant of ∼12 in the temperature range of 25–100 °C and frequency range of 1–1000 kHz. The electro-optic results indicate that the KTP thin films exhibit a quadratic electro-optic effect and may have potential applications for electro-optic devices. *© 2000 Kluwer Academic Publishers*

1. Introduction

Potassium titanyl phosphate ($KTiOPO_4$ or KTP) single crystal is currently used for frequency doubling of Nd : YAG laser because of its high nonlinear-optical coefficient, high optical damage threshold, wide acceptance angles and thermally stable phase-matching properties [1]. Its large linear electro-optic coefficient and low dielectric constant also make it promising for some electro-optic applications such as modulators and Q switches [1]. However, these potential applications such as frequency modulators, Q-switches, and electro-optic waveguide modulators are limited by KTP's several drawbacks such as high cost, inclusion of impurities, and the difficulty for patterning and shaping.

Sol-gel derived KTP thin films appear to be an alternative choice because sol-gel processing can offer high purity and easy control of stoichiometry of the resulting thin films. The simplicity of the patterning and shaping of sol-gel thin film deposition makes KTP thin film possible for integrated-optic fabrication.

Barbe *et al.* [2] reported a sol-gel process and microstructure of KTP thin films. Hirano *et al.* [3] also investigated the relationship between the preferred orientation of KTP grains on single crystal substrates and obtained a weak second harmonic generation signal from the KTP thin film on a glass substrate. However, no electro-optic properties were reported. The present paper reports the preparation of sol-gel derived KTP thin films, the structure evolution, the dielectric and electro-optic properties.

2. Experimental procedure

2.1. Synthesis of KTP precursor solution

Potassium ethoxide (Aldrich Chemical Co., Milwaukee, WI) and titanium isopropoxide (Alfa Co., Ward Hill, MA) were used as starting precursors for K and Ti. Phosphate precursor was synthesized by dissolving 1.42 grams of phosphorus pentoxide (P_2O_5) (Aldrich Chemical Co., Milwaukee, WI) in 10.0 ml absolute ethanol (C_2H_5OH) (Aldrich Chemical Co., Milwaukee, WI) [4, 5]. The stoichiometric amount of 1.68 grams of potassium ethoxide (KOC_2H_5) was dissolved in 6.0 ml of titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$) and then the solution was mixed with the above ethyl phosphate precursor. The final KTP sol was refluxed at 80 °C for 6 hours. A clear light brown sol was obtained for thin film deposition.

2.2. KTP thin film deposition

A spin coater (Specialty Coating Co., Indianapolis, IN, Model P60204-A) was used to prepare KTP thin films. Soda-lime glass and ITO (In_2O_3-SnO_2) coated glass slides were used as the substrates. The KTP stock sol was diluted to 50% before dropping onto the substrates fixed on the spin coater for coating at 4000 rpm for 30 seconds. The above procedure was repeated five times to achieve a thickness of ∼0.5 μm. The final KTP thin films were dried at room temperature for 0.5 hour before a heat treatment. The entire preparation flow chart of KTP thin films is shown in Fig. 1.

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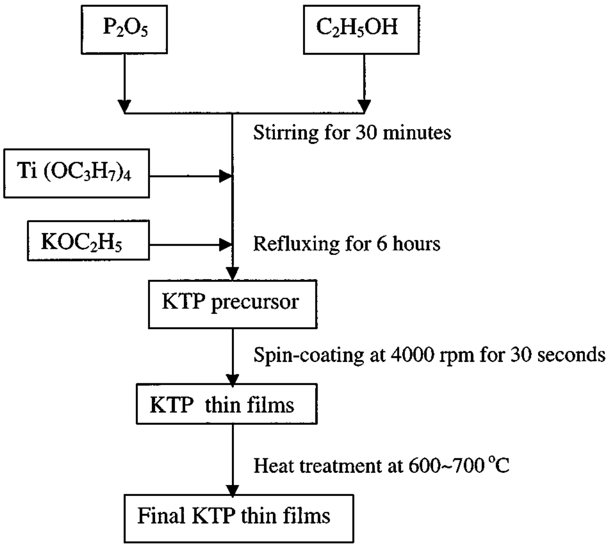


Figure 1 Preparation flow chart of the KTP thin films by sol-gel process.

2.3. Heat treatment of KTP thin films

In order to evaluate the effect of ultraviolet (UV) irradiation on the crystallization, the as-deposited KTP thin film samples of about 0.4 μm and KTP dried powder samples were placed under a UV light (100 W) irradiation for 13 hours. The irradiated powder samples were used to examine the crystallization temperature. The irradiated KTP thin film samples were placed on a hot stage for 15 minutes at 200 °C for organic decomposition. Another set of KTP thin film samples were placed on the hot plate without any UV irradiation. At this stage, the KTP thin films began to nucleate but the crystallites were still immature. Hence a high temperature crystallization stage was still needed to promote the existing nuclei and small crystallites to grow into a fully crystallized $KTiOPO_4$ polycrystalline structure. This stage could be achieved by firing the thin films at higher temperatures.

2.4. Characterization of KTP gels and thin films

The crystallization behavior of the KTP powders was analyzed by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and x-ray diffractometry (XRD). The FT-IR spectra of the KTP dried gel and fired powder were obtained by a Mattson Infinity FT-IR spectrophotometer with a diffuse reflectance technique. The KTP thin film samples on ITO coated glass substrates were fired at 650 °C for 2 hours for dielectric and electro-optic measurement. The top electrodes in 1 mm diameter were deposited on the films with a mask via sputtering. The dielectric constant and dissipation factor were measured by a HP 4194A Impedance/Gain-Phase Analyzer [5]. The refractive indices and electro-optic coefficients were measured by the differential ellipsometry measurements as shown by Wang *et al.* [6, 7].

3. Results and discussion

3.1. Gel structure and phase formation

When phosphorus pentoxide (P_2O_5) reacts with absolute ethanol, the phosphorus precursor, a mixture of diethyl phosphate ($(OEt)_2P(O)(OH)$) and mono ethyl phosphate ($(OEt)P(O)(OH)_2$) [3, 4] was produced. A clear, light brown KTP sol was obtained by mixing potassium ethoxide (KOC_2H_5), titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$) and the ethyl phosphate precursor. The KTP dried gel and fired powder were used to examine the gel structure and phase formation.

Fig. 2 shows TGA and DTA of the dried KTP gels. The TGA shows two decomposition steps during the pyrolysis. The first weight loss at 250–300 °C corresponds to the oxidation reaction of the adsorbed alcohol and alkyl groups in the KTP gels. The second weight loss at 600–700 °C is an exothermic reaction attributed to the removal of the residual carbonaceous material and accompanied by crystallization. This reaction is confirmed by the DTA which shows an exothermic peak at 600–700 °C.

Fig. 3 is the FT-IR spectra of the KTP gel dried at 100 °C for 4 hours and fired at 800 °C for 2 hours. The absorption peaks at $\sim$2987 cm^{-1} in Fig. 3 (a) is due to $-CH_3$ and C-H groups. It is obvious that this peak disappears at the higher temperature because of the removal of these groups during the high temperature firing. The prominent peaks at 2000 cm^{-1} after firing at 800 °C must be associated with the KTP crystal structure. The $-OH$ absorption at $\sim$3400 cm^{-1}, 2170 cm^{-1}, 1628 cm^{-1} [2, 3, 8] in Fig. 3 (a) and Fig. 3 (b) indicates that R-OH group and P-OH group exist in the sample (a) and P-OH group in sample (b) even after firing at

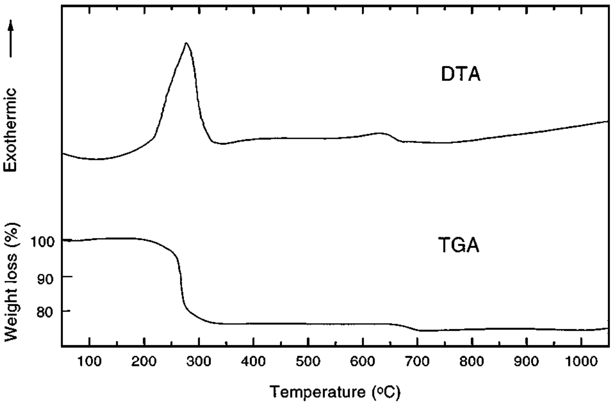


Figure 2 Thermal analysis of the KTP dried gels.

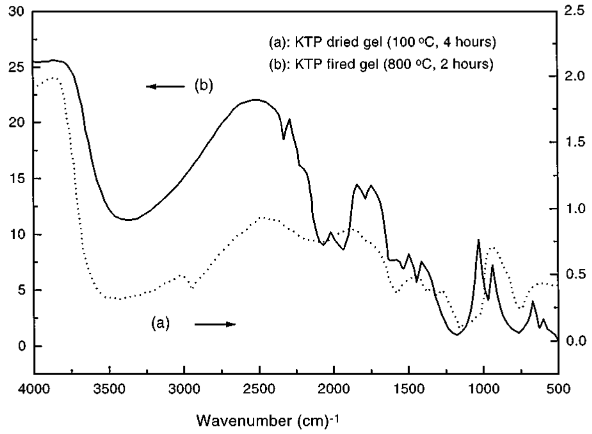


Figure 3 FT-IR spectra of the KTP dried gel and fired powder: (a) KTP dried gel and (b) KTP fired powder.

800 °C. The peak at 1237 cm^{-1} corresponds to P=O stretching vibrations [2]. The peak at 600–700 cm^{-1} is due to Ti-O vibrations [2].

3.2. Crystallization behavior vs. UV irradiation

KTP single crystal belongs to the orthorhombic crystal system and the acentric point group mm (space group $Pna2_1$) [1]. The lattice parameters are: $a = 12.814$ angstrom, $b = 6.404$ angstrom, and $c = 10.616$ angstrom. Its structure consists of chains of TiO_6 octahedra and the chains are linked at two corners and separated by PO_4 tetrahedra [1].

In order to have electro-optic properties, which the KTP single crystal possesses, the KTP thin films must fully crystallize to a polycrystalline structure. A heat treatment is needed to promote the growth of the KTP crystallites in the films. The crystallization behavior of the KTP gel dried at 100 °C for 4 hours was examined after a UV irradiation for 13 hours. It must be noted that the penetration depth of UV is about 1 μm, so a regular stirring of the dried KTP gel samples for more even UV exposure was used. Fig. 4 shows XRD powder patterns of the KTP samples fired at different temperatures without UV irradiation. The samples were prepared by firing the dried KTP gels at various temperatures in air for 2 hours. The XRD patterns show that the KTP gels began crystallizing at a temperature above 600 °C. When fired at 650 °C, the samples have become fully crystallized. It is noted that all the peaks are attributed to the $KTiOPO_4$ single phase [2]. Fig. 5 is the XRD powder patterns for the KTP gels after a UV irradiation of 13 hours followed by a 2-hour firing at different temperatures. Fig. 5 shows that the KTP samples can be fully crystallized at 550 °C, which is about 100 degree lower than the crystallization temperature of the non-UV irradiated KTP samples. This is known as the photo-induced crystallization. It is believed that the UV energy breaks down the organics and induce the structure evolution from amorphous to polycrystalline [9]. The further reduction of the crystallization temperature using higher power UV light and thinner films may make it possible to integrate KTP thin film directly onto the integrated optics system without firing at high temperatures [10].

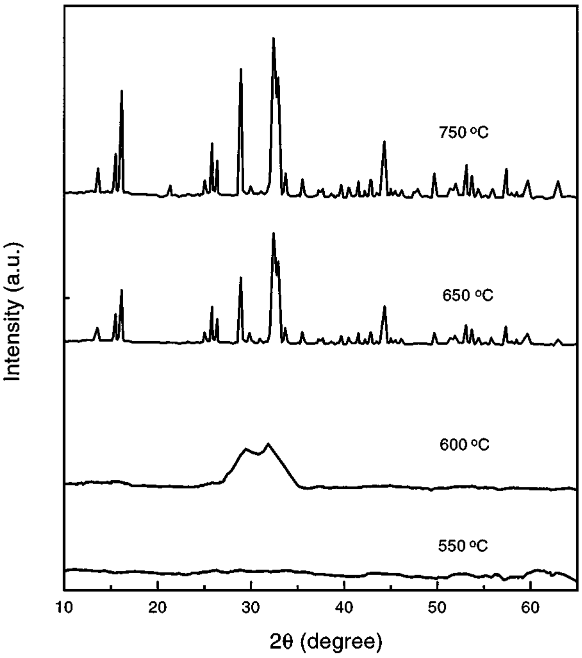


Figure 4 XRD powder patterns of the fired KTP powders without UV irradiation.

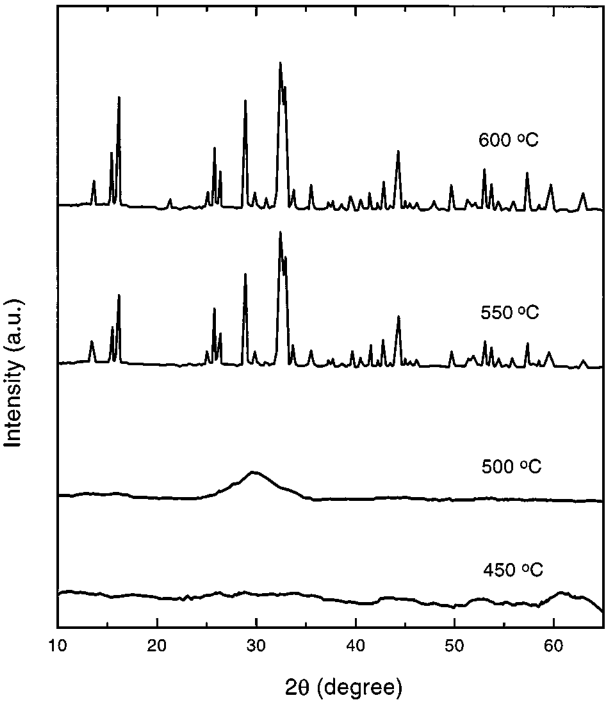


Figure 5 XRD powder patterns of the fired KTP powders with UV irradiation.

The KTP thin film samples were also used to examine the grain morphology of the KTP thin films with and without UV irradiation. Fig. 6 shows the SEM top surface micrograph of the KTP thin films fired at 650 °C without UV irradiation. The grain size is about 100 nm. However, after applying UV to the as-deposited KTP thin films, the nucleation, an initial crystallization stage

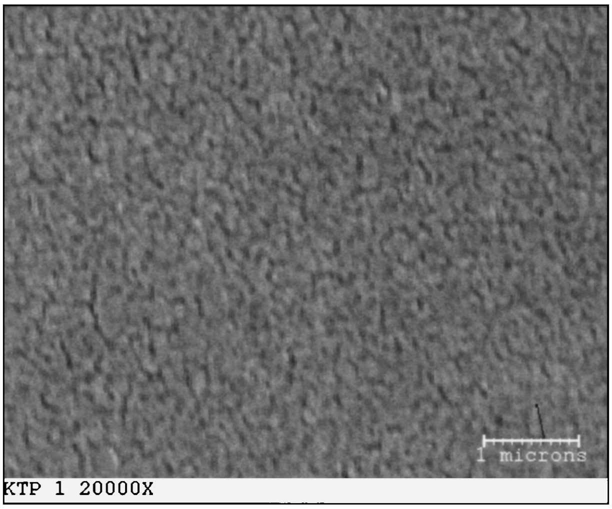
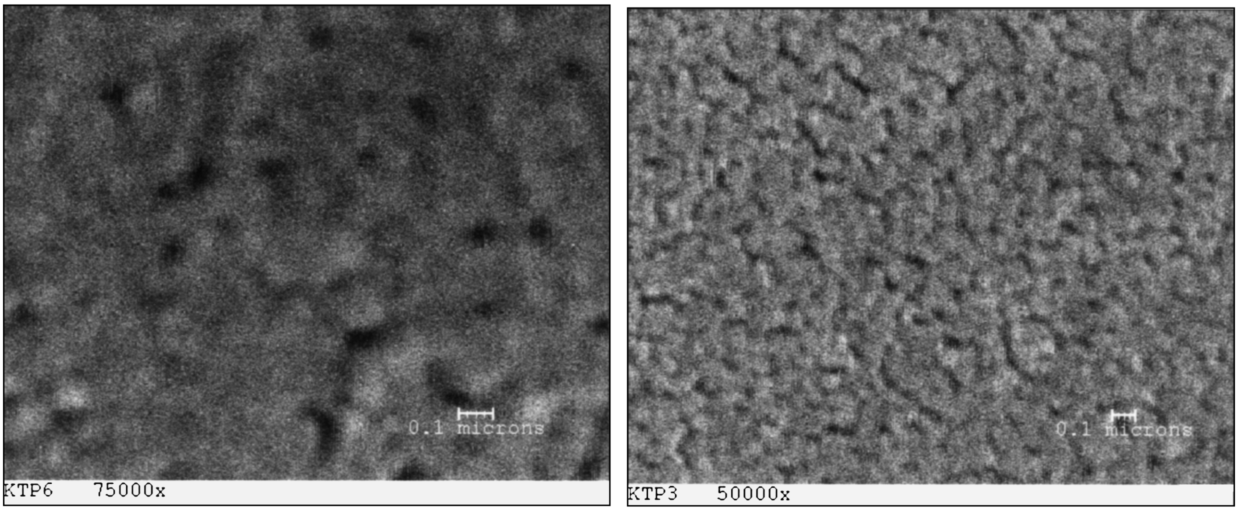


Figure 6 SEM micrograph of the KTP thin film fired at 650 °C for 2 hours without UV irradiation.



(a) (b)

Figure 7 SEM micrographs of the KTP thin films with UV irradiation: (a) 13-hour UV irradiation, (b) 13-hour UV irradiation and 2-hour firing at 600 °C.

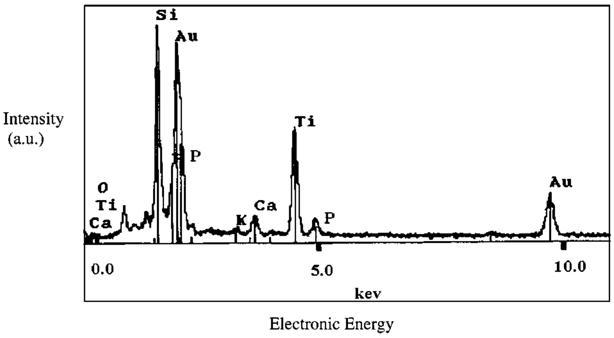


Figure 8 EDAX spectrum of a 0.5 μm KTP thin film fired at 600 °C.

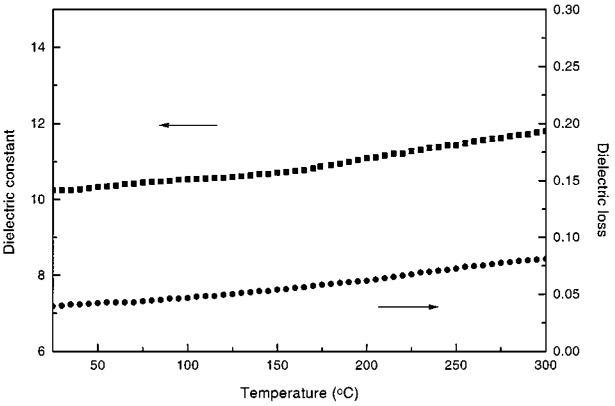


Figure 9 Temperature dependence of dielectric constant and dielectric loss at 1 kHz for the KTP thin film fired at 650 °C for 2 hours.

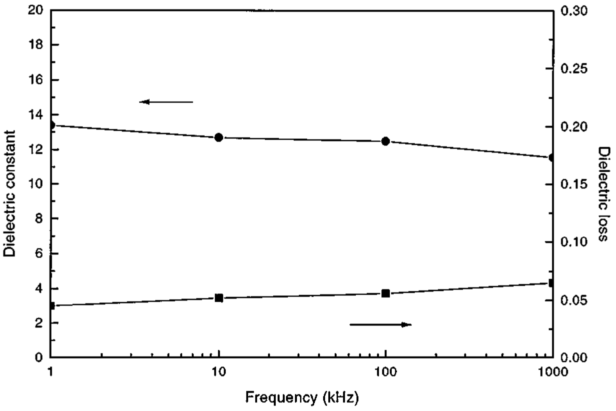


Figure 10 Frequency dependence of the dielectric constant and dielectric loss at room temperature for the KTP thin film fired at 650 °C for 2 hours.

shown in Fig. 7a, can be observed in the sample even before any heat treatment. This result, along with XRD data, indicates that UV can induce the nucleation and growth of the KTP crystallites and decrease the crystallization temperature. Fig. 7b shows a fully crystallized polycrystalline structure with a gain size of 100 nm when the UV-irradiated KTP thin film was fired at 600 °C for 2 hours.

The composition profile of the KTP crystallites is shown by the EDAX spectrum in Fig. 8. It was found that the crystallites in the KTP thin film samples conform to stoichiometric composition of $KTiOPO_4$ phase in which potassium, titanium and phosphorus are in a 1 : 1 : 1 ratio according to ZAF method calculated from EDAX spectrum. The Si and Ca in the spectrum came from the glass substrate and the gold came from the sputtered surface coating for SEM measurement.

3.3. Dielectric properties

The effect of temperature and frequency on the dielectric constant and dielectric loss at 1 kHz was obtained for the fired KTP thin films on ITO coated glass substrates as shown in Figs 9 and 10. It was found that the KTP thin films have low dielectric constant of ∼10.3 at room temperature and are almost independent of temperature ranging from 25–100 °C. No obvious dielectric peak was observed in this temperature range. These results reveal that the KTP thin films have a stable structure and no phase transition occurs in this temperature range. This is very important for KTP thin films to maintain the electro-optic properties of $KTiOPO_4$ orthorhombic structure. On the other hand, it is also shown in Fig. 9 that the dielectric loss is around 0.04

at room temperature, but increases slightly with the increase of temperature from 25 to 300 °C.

Fig. 10 shows the frequency dependence of the dielectric constant and dielectric loss at room temperature. The dielectric constant decreases slightly with the increase of frequency although the dielectric loss increases slightly, but no significant changes over the frequency range (1–1000 kHz) were observed. This result makes it possible for high frequency application because of the small energy dissipation at high frequency [11].

3.4. Electro-optic properties

The field-induced birefringence in the KTP films was measured by means of the differential ellipsometry in a transverse mode [6, 7]. Co-planar electrodes with 40 micron gap width were fabricated on the film surface to facilitate the application of the external electric field. A He-Ne laser of wavelength at 632.8 nm was utilized during the measurements. The relative phase shift between the light polarized parallel to the DC field and the orthogonal light component was measured as a function of the applied DC voltage. The measured phase shift, Γ, is related to the field-induced birefringence, Δn, in the KTP films through the equation [11]: $\Gamma = \Delta n \times t$, where t is the thickness of the film being measured.

Because of the polycrystalline nature, KTP thin films, in contrast to KTP single crystal material, lack linear electro-optic coefficients due to their macroscopic isotropy. As shown in Fig. 11, the measured birefringence exhibits a quadratic dependence on the applied DC field. At a DC field strength of 2.6 volts per micron, a relative phase shift ($\Delta\Gamma$) of approximately 0.0217 and a field-induced birefringence (Δn) of 0.0049 were measured from a KTP film of 0.45 μm and it was noted that a portion of the measured birefringence responded rather slowly to the applied DC field, along with a faster responding portion. The curve in Fig. 11 indicates that KTP thin films demonstrate a quadratic electro-optic characteristic and may have potential application for electro-optic devices. Further research work is needed to develop this material for practical applications.

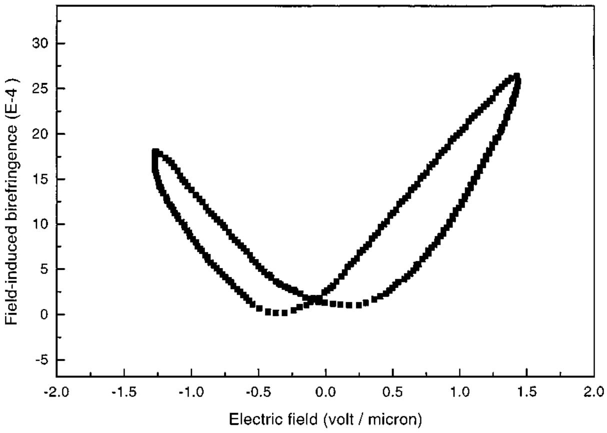


Figure 11 Electro-optic loop of transverse-mode birefringence vs electric field of the KTP thin film of 0.46 μm.

4. Conclusions

The KTP thin films were prepared by a sol-gel coating process from phosphorus pentoxide, potassium ethoxide and titanium isopropoxide. The polycrystalline structural evolution of the KTP thin films and dry gels has been examined by DTA/TGA, FT-IR, XRD and SEM. It is found that the crystallization temperature of the KTP gels can be reduced about 100 °C after UV irradiation. The dielectric measurement results show that the KTP thin films have a stable dielectric constant of ∼12 in the temperature range of 25–300 °C and frequency range of 1–1000 kHz. The electro-optic results indicate that the KTP thin films exhibit a quadratic electro-optic effect and have potential applications for electro-optic devices.

Acknowledgements

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