POTASSIUM TITANYL PHOSPHATE

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Abstract

The Potassium titanyl phosphate(KTP) is a non-linear optical material which is widely used in laser technology and micro- and opto-electronics. In this write-up, I review the structure, some optical , thermal and dielectic properties of KTP. A Peak-shaped anomaly in specific heat indicating a phase transition has been revealed in the $C_p(T)$ curve at T≅279 K.

1 Introduction

Potassium titanyl phosphate($KTiOPO_4$ or KTP) single crystal is currently used for frequancy doubling of Nd:YAG laser because of its high nonlinear-optical coefficient, high optical damage threshold and thermally stable phase-matching properties.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.A very considerable commercial and fundamental research effort has been expanded on a search for improved Second Harmonic Generation(SHG) perfomance, by varying composition. And this has led to the poduction of whole family of structural analogues where K is substituted Rb or Tl and P by As. The structure and properties of all of these anologue materials have been reviewed in great detail. Some other highly efficient SHG matrials have been found,but the chemical variations make it difficult to isolate the principal structure deteminants of the SHG power.

2 Structure of $KTiOPO_4$

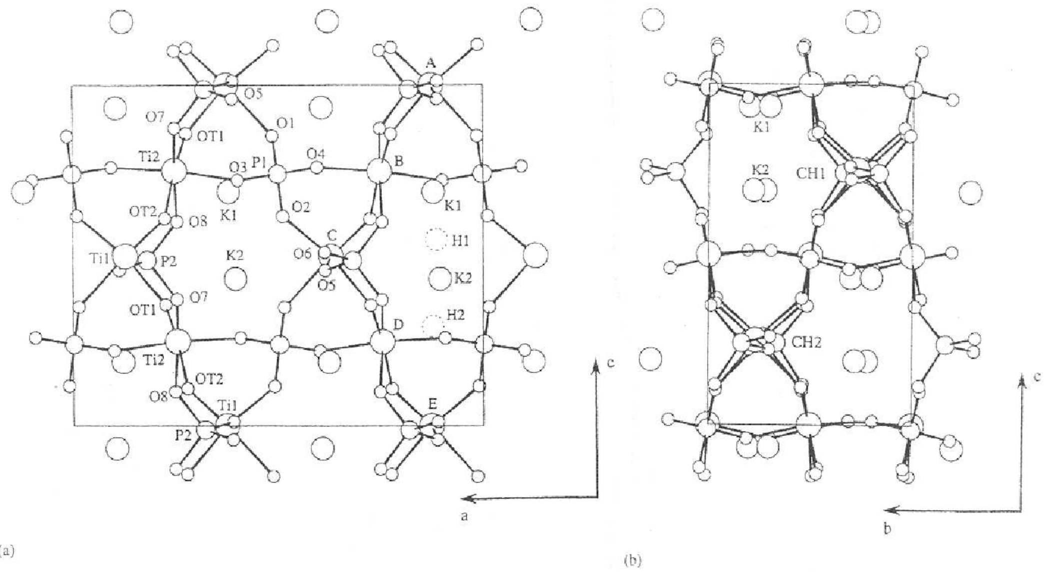

Figure 1: *The views of KTP structure (a) along the b-axis and (b) along the a-axis. The atoms labelled A, B, C, D, E are titanium atoms forming a chain linked by alternately long and short Ti-O bonds.[1]*

At ambient temperature and pressure, the parameters of the structure of KTP are follows; $a = 12.819A, b = 6.399A, c = 10.584A, V = 868.1A^3$ and characterized by cross-linking chains of alternating TiO_6 Octahedra and PO_4 tetrahedra, directed parrallel to the a and b axes, which form a framework surrounding the K atoms. It is the highly distorted TiO_6 octahedra that have been associated with the non-linear optical properties and they form additional helical chains, the direction of which alternates between [0 1 1] and [0 $\bar{1}$ 1], linked by alternately long and short Ti-O bonds (as indicated in figure 1).[1]

3 Some optical properties of $KTiOPO_4$

3.1 Non-Linear Optical Properties of KTP

If a Non-Linear Optical material is exposed to light with electric field components $E(\omega)$, the induced second harmonic polarization P_i is given by

$$P_x = 2d_{15}E_xE_z$$
$$P_y = 2d_{24}E_yE_z$$
$$P_z = d_{31}E_x^2 + d_{32}E_y^2 + d_{33}E_z^2$$

where d_{ij} is the nonlinear optical coefficient given the usual reduced subscript notation. The second harmonic generation has been of practical interest ever since it was demonstrated that efficient conversion from fundarmental to second harmonic frequancies could obtained at resonable fundamental power level.

The Non Linear optical coefficients of $KTiOPO_4$ are

$$d_{15} = 6.1 \times 10^{-12} mV^{-1}$$
$$d_{24} = 7.6 \times 10^{-12} mV^{-1}$$
$$d_{31} = 6.5 \times 10^{-12} mV^{-1}$$
$$d_{32} = 5.0 \times 10^{-12} mV^{-1}$$
$$d_{33} = 13.7 \times 10^{-12} mV^{-1}$$

3.2 Optical damage of NLO marerials

Many non linear materials are limited in their applications by damage caused by large-amplitude electric fields needed in non optical applications. For an example, $Ba_2NaNb_5O_{15}$ has been reported to become damaged at power densities of $3MW/cm^2$. The damage is not only structural but in some instances can also be seen as changes in the index of refraction.

No optical damage to $KTiOPO_4$ has been detected either after several hours exposure to the highly focused output of a 5-W cw Nd-YAG laser or with repeated pulses of $150MW/cm^2$ from a Q-switched Nd-YAG laser. The lack of damage was ascertained by examining interferograms of the crytals before and after exposure.[2]

3.3 Refractive index of $KTiOPO_4$

For a material to be useful as a nonlinear optical material, it must be possible to have the fundamental radiation stay in phase with that genarated at the second harmonic, i.e, the phase velocity must be the same for both the second harmonics and the fundamental waves. Thus if $n_1(\theta, \phi, \omega)$ and $n_2(\theta, \phi, \omega)$ are the two refractive indices associated with a particular frequancy, ω, and propagation direction, the phase matching occurs when

Type I

$$n_1(\theta, \phi, 2\omega) = n_2(\theta, \phi, \omega)$$

Type II

$$n_1(\theta, \phi, 2\omega) = \frac{1}{2}[n_1(\theta, \phi, \omega) + n_2(\theta, \phi, \omega)].$$

While the phase matching conditions are an intrinsic property of any given material, it is possible to alter them by changing the temperature or by varying the composition of $K_xRb_{1-x}TiOPO_4 (0 \le x \le 1)$. The refractive index measurements were made as a function of temperature, wavelength and composition using the the method of minimum deviation. Values of $n_x$and n_z were determined using the prism fromed by the intersection of natural(110) crytal faces, while n_y and n_z were determined using the (201) surfaces. [2]

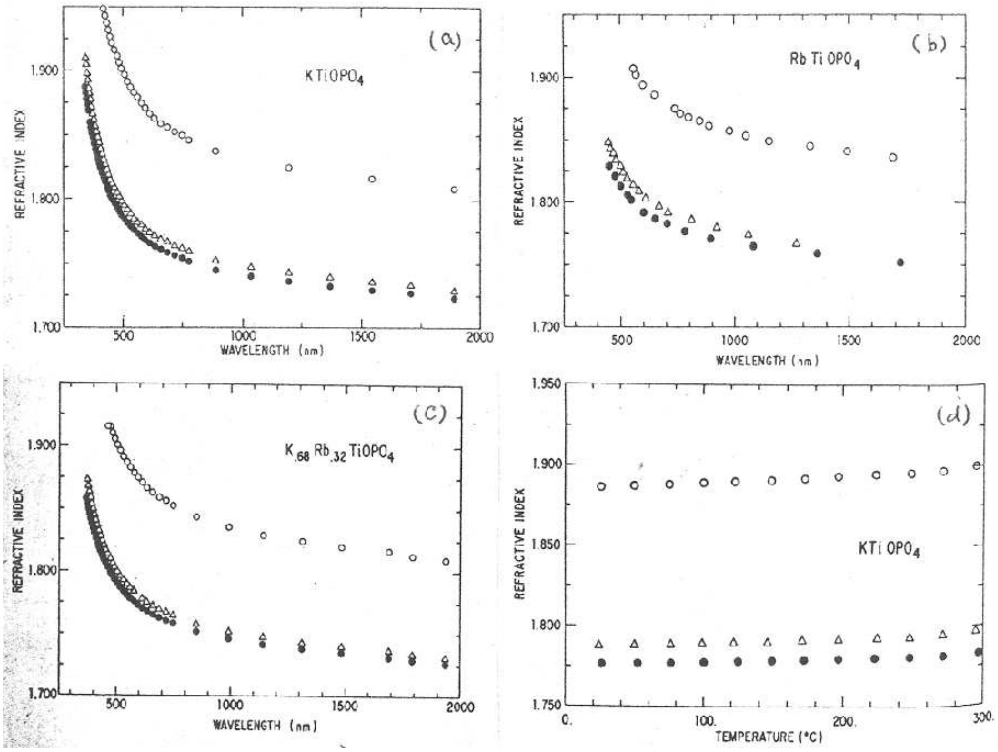

Figure 2: *Refractive index versus wave length of (a) KTP, (b) RbTiOPO*$_4$*, (c)* $K_{0.68}Rb_{0.32}TiOPO_4$ *and (d) Temperature dependance of the refractive indices of* $KTIOPO_4$*,[2]* $\bullet \rightarrow n_x$ $\triangle \rightarrow n_y$ $\circ \rightarrow n_z$

4 Thermal properties of $KTiOPO_4$

4.1 Temperature dependance on volume of the unit cell $KTiOPO_4$

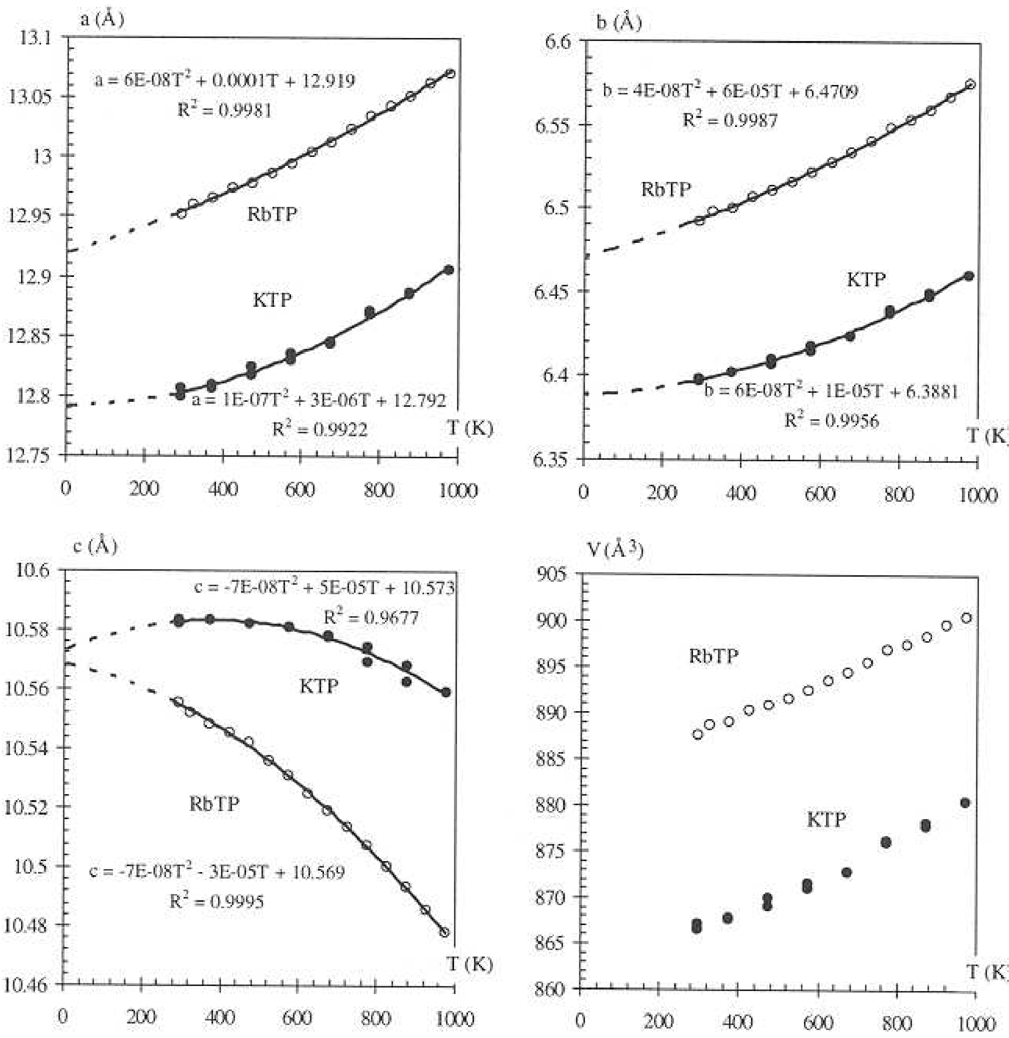

Figure 3: *the evolution of the volume and those of the cell parameter a,b,c vs temperature.[3]*

The changes in the cell parameters and in the unit cell volume vs temperature are shown in the figure 3. Compared to those obtained for $RbTiOPO_4$. These measurments have been made by increasing and decreasing the temperatures. We can see clearly that there is no hysteresis.

4.2 Specfic Heat of $KTiPO_4$

Figure 4 shows the specific heat of KTP against temperature. The specific heat of the KTP crystal is seen to grow monotonically with temperature, but at T≅279 K there is a clearly pronounced peak-shaped anomaly in the $C_p(T)$ curve. The presence of an anomaly in specific heat implies a structural transformation in the KTP crystal at the temperature of 279 K.[4] A dielectric study of KTP revealed breaks in the temperature dependences of ϵ at T≅280 K .[5] It was concluded that the crystal undergoes a structural rearrangment at this temperature.

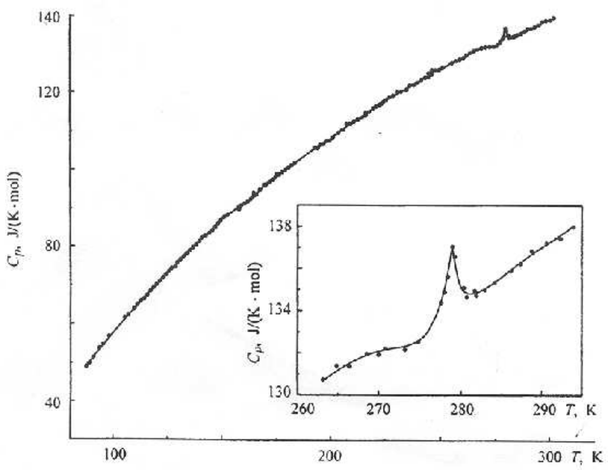

Figure 4: *Temperature dependance of the specific heat KTP.[4]*

5 Dielectric properties of KTP

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 5 and 6. It was found that the KTP thin films have low dielectric constant of $\sim$ 10.3 at room temperature and are almost independent of temperature ranging from 25-100 C^0. 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 $KTiOPO_4$ structure. On the other hand, it is also shown in Fig. 5 that the dielectric loss is around 0.04 at room temperature, but increases slightly with the increase of temperature from 25 to 300 C^0. Fig. 6 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 .[6].

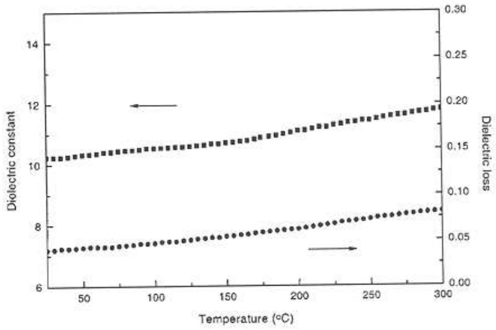

Figure 5: *Temperature dependance of the dielectric constant for the KTP thin film.[6]*

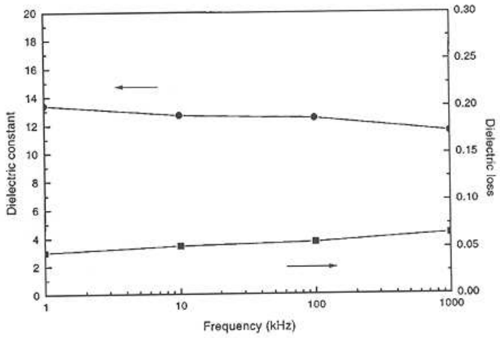

Figure 6: *Frequancy dependance of the dielectric constant for the KTP thin film.[6]*

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