

CURIE TEMPERATURE MEASUREMENTS ON KTiOPO₄ SINGLE CRYSTALS GROWN BY FLUX AND HYDROTHERMAL TECHNIQUES

P. F. BORDUI and R. G. NORWOOD

Crystal Technology, Inc. 1051 E. Meadow Circle, Palo Alto, CA 94303 USA

and

M. M. FEJER

Department of Applied Physics, Stanford University, Stanford, CA 94305 USA

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Curie temperatures of a variety of KTiOPO₄ crystals were measured to range from 947 to 960°C. T_c was generally higher for hydrothermal than for flux-grown crystals. With continued measurement, T_c decreased for hydrothermal samples and increased for flux-grown samples. For both types of samples, after 24 hours of continuous Curie measurement an additional polarization-sensitive line appeared in the absorption spectrum at 2.814 μm . T_c in KTiOPO₄ was found to be a sensitive function of measurement parameters including time at temperature, sample thickness, applied electric field, and surrounding atmosphere.

Keywords: KTiOPO₄, KTP, Curie temperature.

KTiOPO₄ (potassium titanyl phosphate; KTP) is a nonlinear optical material of much current interest. Single crystals can be grown using either hydrothermal or flux methods. Some of the physical properties of KTiOPO₄ crystals, including most notably low-frequency dielectric constants and high-power optical damage characteristics, have been reported to vary widely depending on the growth process.¹ KTiOPO₄ has previously been reported to be ferroelectric with a Curie temperature (T_c) of roughly 935°C.²⁻³ This paper presents Curie temperature characterization performed on a variety of KTiOPO₄ crystals, including both flux-grown and hydrothermally-grown specimens. An attempt to correlate the measured T_c data with IR absorption spectra is also presented.

Flux-grown specimens were prepared at Crystal Technology, Inc. (CTI) and also supplied by Philips Laboratories-Briarcliff (PL-B). These crystals were grown over the temperature range of 970 to 930°C by a seeded method using a heat pipe based furnace system previously described.⁴ The solvent applied was of the composition K₆P₄O₁₃. Hydrothermally-grown specimens were prepared by Airtron. These were grown using the 600°C 25kpsi process described previously.⁵

Samples were prepared for T_c measurement by saw-cutting to size, then painting the z-faces with a thin coat of platinum paste. Samples from hydrothermally-grown crystals measured 5 mm(x) by 5 mm(y) by 1 mm(z). Samples from flux-grown crystals measured 5 mm(x) by 5 mm(y) by 0.5 mm, 1 mm, and 2 mm(z).

T_c measurements were performed by a standard dielectric technique. On cycling the temperature of a sample, a dielectric anomaly such as a ferroelectric phase transition was indicated by a sharp peak in the phase difference between sample and reference arms of an AC impedance bridge circuit. Measured T_c values were determined to be independent of AC frequency over a range from less than 10 kHz to greater than 2 MHz. Most of the T_c measurements were performed using a 1 Volt peak-to-peak signal at 1 MHz, as this frequency yielded the sharpest phase difference peaks. The phase difference peaking effect was strong enough to enable a furnace ramp rate during cycling of 1°C/minute. Following an initial 90 minute furnace ramp from room temperature to a temperature near T_c , thermal cycles spanned roughly 10°C peak-to-peak and were each carried out in roughly 20 minutes. Temperature cycling was carried out automatically by a programmed computer. Similar phase difference peaks were detected on heating and cooling. No thermal hysteresis was observed.

The use of multiple measurement thermocouples positioned against either face of a sample and an adjustable sample holder allowed tuning the system for a given sample size to achieve sample placement in the thermal center of the furnace, thereby minimizing thermal gradient effects and maximizing temperature measurement accuracy. The absolute accuracy of a T_c measurement was determined to be $\pm 0.4^\circ\text{C}$. The reproducibility of a given measurement was $\pm 0.3^\circ\text{C}$. Two identical apparatus were employed in the work, both yielding equivalent measurements.

Measured T_c values ranged from roughly 947 to 960°C and were found to depend on a variety of factors. Samples of the same origin and size and subjected to the same measurement conditions displayed identical T_c behavior, within measurement error.

Samples from hydrothermally-grown crystals exhibited an initial T_c of 958.9°C. This measured T_c was found to decrease with time if a sample was maintained in the measurement furnace at high temperature. As shown in Figure 1, T_c of a 1 mm thick sample decreased roughly 1.1°C over 24 hours of continuous measurement for the condition of flowing dry oxygen through the furnace at a rate of 60 l/hour.

Samples from flux-grown crystals exhibited initial T_c values ranging from 946.8 to 950.9°C. Initial T_c values for CTI-grown material averaged roughly 1.5°C lower than those for material obtained from PL-B. In contrast to the behavior of hydrothermally-grown samples, the measured T_c of all flux-grown samples was found to increase with time for samples maintained in the furnace at high temperature. As shown in Figure 1, for the case of a 1 mm thick flux-grown sample with a 60 l/hour flow rate of dry oxygen through the furnace, T_c started at 947.3°C, then increased roughly 2.5°C over 24 hours of continuous measurement.

We examined the influence of a variety of measurement conditions on the time dependence of measured T_c values for flux-grown KTiOPO_4 . Conditions examined were specimen thickness, oxygen flow rate through the furnace, moisture content of the flowing oxygen, and the duty cycle of the applied AC field.

The rate of T_c variation was found to decrease with increasing sample thickness. As illustrated in Figure 2, for the case of a 60 l/hour flow rate of dry oxygen through the furnace during continuous measurement over a 24 hour period, samples 0.5, 1, and 2 mm in thickness exhibited T_c increases of roughly 4.2, 2.5, and 0.4°C, respectively. Note that this last value approaches the precision of the measurement.

CURIE TEMPERATURE OF $KTiOPO_4$

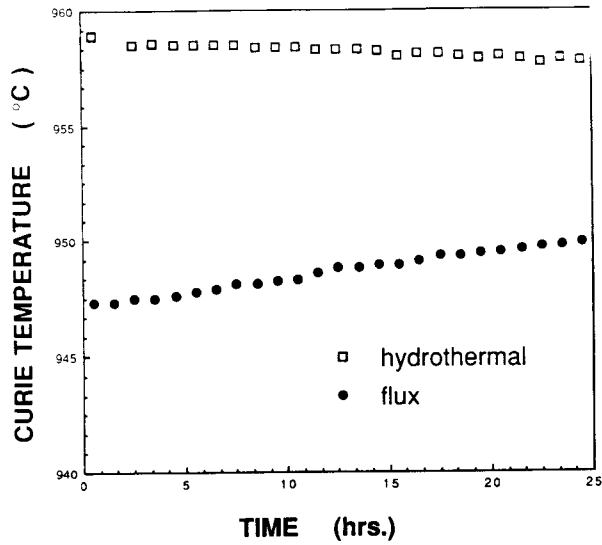


FIGURE 1 T_c vs. time for hydrothermal and flux-grown KTP. 1 mm sample thickness. 60 l/hour dry oxygen flow. Flux-grown sample from CTI.

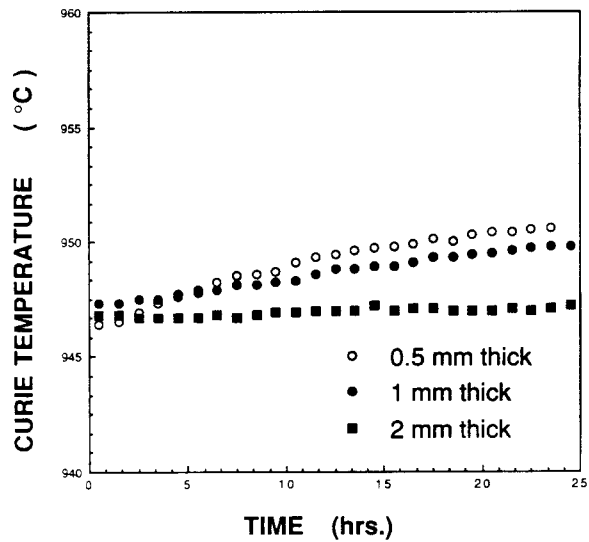


FIGURE 2 T_c vs. time for flux-grown KTP of varying thickness. 60 l/hour dry oxygen flow. Samples from CTI.

The rate of T_c variation was found to also decrease with reduced duty cycle of the applied AC measurement signal. Figure 3 shows that for the case of a 0.5 mm thick sample with a 60 l/hour flow rate of dry oxygen through the furnace, T_c increased roughly 0.18°C/hour over 24 hours with the AC measurement signal being continuously applied. On repeating the experiment, restricting the application of

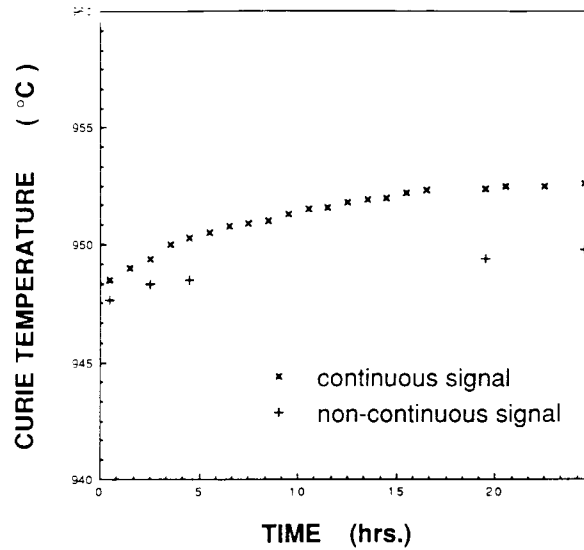


FIGURE 3. T_c vs. time for flux-grown KTP with and without continuous AC measurement signal applied. 0.5 mm sample thickness. 60 l/hour dry oxygen flow. Samples from PL-B.

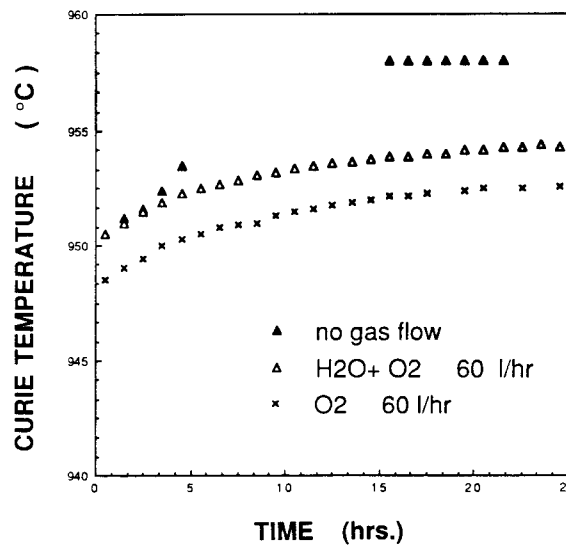


FIGURE 4. T_c vs. time for flux-grown KTP under different gas-flow conditions. 0.5 mm sample thickness. Samples from PL-B.

the AC signal to 5 measurement segments of 20 minutes each over the 24 hour duration yielded a T_c increase of only $0.09^\circ\text{C}/\text{hour}$. Care was taken to verify that the measurement signal contained no DC component.

Gas flow through the measurement furnace was found to have a significant effect on the time dependence of T_c . Figure 4 illustrates our findings. For the case of 0.5 mm thick samples during continuous measurement over 24 hours, a 60 l/hour flow

rate of dry oxygen yielded an initial T_c of 948.5°C followed by a steady $0.18^\circ\text{C}/\text{hour}$ increase. Repeating the experiment with the oxygen bubbling through water at room temperature yielded an initial T_c of 950.5°C followed by a $0.16^\circ\text{C}/\text{hour}$ increase. Repeating the experiment with no gas flow yielded an initial T_c of 950.9°C followed by a $0.56^\circ\text{C}/\text{hour}$ increase to an apparent steady-state T_c value of 958.7°C .

IR absorption spectra of some of the samples were measured using a Perkin-Elmer Lambda 9 Spectrophotometer. Absorption spectra of as-grown samples of hydrothermal and flux material both exhibited the largest OH- peaks at $2.804\ \mu\text{m}$, similar to previous descriptions.⁶ Secondary peaks in the vicinity of $2.8\ \mu\text{m}$ were significantly different between the two spectra. Spectra of both hydrothermal and flux-grown samples that had been subjected to 24 hours of continuous T_c measurement exhibited OH- absorption peaks at $2.814\ \mu\text{m}$ not present in the spectra of as-grown samples of either origin. These $2.814\ \mu\text{m}$ peaks were observed for input radiation polarized in the crystallographic y -direction and not observed with x -polarized radiation. We found that a flux-grown sample annealed at 950°C for 100 hours in 60 1 hour of oxygen bubbled through water exhibited a spectrum with a similar $2.814\ \mu\text{m}$ absorption peak.

Overall, the data gathered suggest no obvious explanatory mechanisms. We speculate that the difference in initial T_c values between flux-grown and hydrothermally-grown KTP is likely due to differences in potassium ion or OH- species concentration or OH- species site distribution. Similar considerations apply to the smaller observed differences in initial T_c values between CTI and PL-B flux-grown material. The IR spectroscopy results suggest that the difference in the time variation of T_c between flux-grown and hydrothermally-grown KTP involves at least the OH- species site distribution. The data on T_c versus time for different thicknesses of flux-grown samples suggest that the time variation of T_c involves a mechanism that does not occur simultaneously throughout a sample, such as, for example, one involving diffusive transport to or from surfaces. Further experiments on these issues are in progress.

In interpreting any of the data reported here, it should be noted that multiple mechanisms may be simultaneous and that the kinetics of simultaneous mechanisms may be coupled. Further, spurious electrode effects may be present including Pt impurity incorporation or mass transport restriction across the z -faces of the samples.

In summary, the Curie temperatures of KTiOPO_4 crystals were measured to range from 947 to 960°C . T_c was generally higher for hydrothermal than for flux-grown crystals. With continued measurement, T_c decreased for hydrothermal samples and increased for flux-grown samples. For both types of samples, after 24 hours of continuous Curie measurement an additional polarization-sensitive line appeared in the absorption spectrum at $2.814\ \mu\text{m}$. T_c in KTiOPO_4 was found to be a sensitive function of measurement parameters including time at temperature, sample thickness, applied electric field, and surrounding atmosphere.

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