THERMAL DIFFUSIVITY OF $LiTaO_3$, RELATED TO ITS PHASE TRANSITION AND CRYSTAL ORIENTATION

XI TONGGENG (XI TUNGGEN 奚同庚), WANG BENMIN (王本民),
NI HELIN (倪鹤林) AND YIN ZHIWEN (YIN CHIH-WEN 殷之文)

(Shanghai Institute of Ceramics, Academia Sinica)

Received November 12, 1980.

Lithium tantalate ($LiTaO_3$) single crystal is one of the most important ferroelectric crystals for its excellent piezoelectric, pyroelectric and photoelectric properties. Many of its physical properties have been widely studied[1-6]. However, due to experimental difficulties, the thermal conductivity, which is very important in many applications, has scarecely been measured. Studies of its thermal diffusivities at high temperatures and at different crystal orientations, as well as the influence of its phase transition, have not yet been seen reported. Our research work is carried out by means of computerized laser thermal diffusivity measurement apparatus[7]. Experimental results show the high degree of anisotropy of thermal diffusivity for $LiTaO_3$. Besides, when the thermal diffusivity of $LiTaO_3$ is plotted against temperature, there is a sudden change at about 600°C on the curve. This point is shown to be the Curie temperature, and it is coincident with the result determined by the electric method. Finally, the mean free path of phonons for $LiTaO_3$ can be calculated from the data of thermal diffusivity.

$LiTaO_3$ single crystal samples, prepared by the crystal growth research group of our Institute, was grown by pulling method, with highly pure Li_2CO_3 and Ta_2O_5 as raw materials. The mole ratio of Li_2O and Ta_2O_5 is 0.95. Samples were polarized along the z-axis, and cut along the x, y and z planes respectively. The testing samples are machined into small disks 10 mm in diameter and about 1 mm in thickness. The computerized laser thermal diffusivity measurement apparatus is used for determining thermal conductivity (λ) by the nonsteady-state method. Its physical model can be expressed in this manner: when a laser impulse irradiates perpendicularly the surface of the circular disk sample, which is thermally insulated from its surroundings, the temperature distribution $T(x, \tau)$ at any point and at any instant, due to the heat propagation only in one direction, can be expressed by the following equation[8]:

$$T(x,\tau) = \frac{1}{L}\int_0^L T(x,0)dx + \frac{2}{L}\sum_{n=1}^{\infty}\exp\left(\frac{-n^2\cdot\pi^2\cdot a\tau}{L^2}\right)\cos\frac{n\pi x}{L} \cdot \int_0^L T(x,0)\cdot\cos\frac{n\pi x}{L}dx. \quad (1)$$

If the back surface of the sample is taken into consideration, with the corresponding boundary conditions, and there are two dimensionless parameters reasonably defined, from Eq. (1), it can be deduced that,

$$\alpha = 0.138L^2/\tau_{1/2}. \tag{2}$$

In the experiments, the sample thickness L can be measured, and the half time $\tau_{1/2}$ required for reaching the highest temperature can be determined, so the thermal diffusivity can be calculated. From the experimental data we obtained the velocity of temperature propagation in the sample, known as thermal diffusivity (α). α is a physical parameter, including thermal conductivity λ, specific heat c_p, and density ρ, that is

$$\alpha = \lambda/c_p \cdot \rho. \tag{3}$$

In order to keep the laser light (1.06 μ) from entering the sample, the surface of the samples are covered with a special film.

Fig. 1 shows the effect of temperature on the thermal diffusivity of samples along the x, y and z axes. Some of the data corresponding to these curves are listed in Table 1.

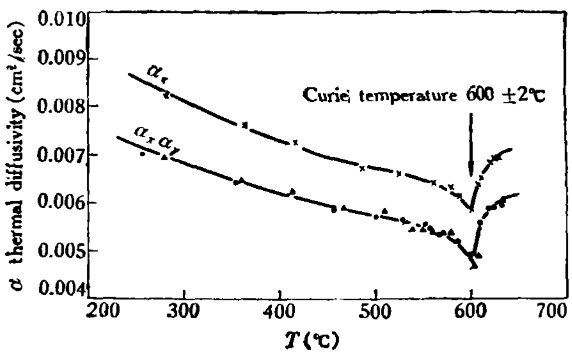

Fig. 1. Thermal diffusivity of $LiTaO_3$ single crystals along different axes. ×—α_z, parallel to z-axis; ●—α_x; △—α_y, perpendicular to z-axis.

Table 1

Thermal Diffusivity α of $LiTaO_3$ Single Crystals Along Different Axes

T(°C) / α(cm²/sec)	250	300	400	500	600±2 Curie Temp.	630
α_x	0.0072	0.0068	0.0062	0.0057	0.0047	0.0060
α_z	0.0086	0.0081	0.0073	0.0067	0.0059	0.0070

The results from Fig. 1 and Table 1 show:

(1) The thermal diffusivities of $LiTaO_3$ along x and y axes are similar, but much lower than those along z axis. Since $\lambda = \alpha \cdot \rho \cdot c_p$, evidently the difference in values along different axes of the same sample just gives their difference in the thermal conductivity λ. α is determined by the mean free path l of the phonons and phonon

velocity V (nearly equal to the velocity of acoustic wave in the samples)[9], that is,

$$\alpha = \frac{1}{3} V \cdot \bar{l} = \sqrt{\frac{E}{\rho}} \cdot \bar{l}/3 \tag{4}$$

The velocity of acoustic wave of polarized $LiTaO_3$ single crystals along x and z axes determined by Smith and Welsh[5] was $V_x = 4.22 \times 10^5$ cm/sec and $V_z = 6.16 \times 10^5$ cm/sec respectivety. From Eq. (4) as we already know V_x, V_z and α_x, α_z, we can obtain the mean free path $\bar{l}_x$ and $\bar{l}_z$ along x and z axes, listed in Table 2.

Table 2

Mean Free Path of Phonons in $LiTaO_3$ Single Crystal Along x and z Axes

$\bar{l}$(Å) \ T(°C)	250	300	400	500	600±2 Curie Temp.	630
$\bar{l}_x$	5.12	4.83	4.41	4.05	3.34	4.27
$\bar{l}_z$	4.19	3.94	3.56	3.26	2.87	3.40

Obviously, the anisotropy of $LiTaO_3$ thermal conductivity is due to the different values of V and $\bar{l}$ along x and z axes. $\bar{l}_z < \bar{l}_x$, this means that the probability of phonon collisions along z axis is larger than that along x axis.

(2) On the thermal diffusivity-temperature curve of $LiTaO_3$, there is a sudden change at 600°C ± 2°C. This temperature is coincident with the Curie temperature measured by Y. Fujino[10], and it is also coincident with the data determined by the Crystal Physics Group of our Institute using electric method. At the Curie point, the polarized $LiTaO_3$ crystal changes from the ferroelectric state into the paraelectric state. Correspondingly, its point group changes from $C_{3v}(3m)$ without center of symmetry to $D_{3d}(\bar{3}m)$ with center of symmetry[11]. The development in the symmetrical structure increases the thermal diffusivity, the presence of sudden change on the thermal diffusivity, curve at the Curie point shows that the thermal diffusivity measurement can be used as a new method for the study of ferroelectric phase transition and Curie point determination.

(3) The sudden change of thermal diffusivity at Curie temperature includes two factors, both the sudden change of specific heat and that of thermal conductivity. These two changes at Curie point were already confirmed experimentally by different authors[12,13]. As to $LiTaO_3$ crystals, it is still not quite clear as to, which of the two plays a more important role, the specific heat or the thermal conductivity, in the sudden change of thermal diffusivity. This is another problem that should be further studied.

(4) Above the Curie temperature $LiTaO_3$ crystal belongs to the paraelectric phase, and the average difference in the α values along x- and z-axes is 13.5 ~ 15%. Of course, this is entirely due to the structural anisotropy of $LiTaO_3$ crystals. Below Curie temperature, $LiTaO_3$ crystal belongs to the ferroelectric phase. In this case, the difference in the α-values along x- and z-axes reaches 17.5 ~ 19.4% on the average. This

shows that the thermal diffusivity behavior of the $LiTaO_3$ crystal in the ferroelectric phase is more anisotropic than that in the paraelectric phase.

References

[1] Ballman, A. A., *J. Am. Ceram. Soc.*, **48**(1965), 112.
[2] Lenzo, P. V. et al., *Appl. Phys. Letters*, 8(1966), 81.
[3] Kim, Y. S. & Smith, R. T., *J. Appl. Phys.*, **40**(1969), 4637.
[4] Miller, R. C. & Savage, A., *Appl. Phys. Letters*, **9**(1966), 169.
[5] Smith, R. T. & Welsh, F. S., *J. Appl. Phys.*, **42**(1971), 2219.
[6] Yamada, T. et al., *J. Appl. Phys. Japan*, 8(1969), 1127.
[7] 奚同庚,周新宇,李宗杰,倪鹤林,顾宗义,工程热物理学报, **2**(1980), 147.
[8] Parker, W. J. et al., *J. Appl. Phys.*, **32**(1961), 1679.
[9] 奚同庚,无机材料热物性学,上海科技出版社, 1982.
[10] Fujino, Y. et al., *Ferroelectrics*, **2**(1971), 113.
[11] 郭常霖,硅酸盐学报, **9**(1981), 384.
[12] Glass, A. M., *Phys. Rev.*, **172**(1968), 564.
[13] Mante, A. J. H. & Volger, *J. Phys. Letters*, **24A**(1967), 139.