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Low Temperature Thermal Diffusivity of LiKSO₄ Obtained Using the Photoacoustic Phase Lag Method

*M.P.P.M. Jorge^a, M.M.F. Vieira^b, J. Mendes Filho^c, A.C. Oliveira^d,
N.D. Vieira Jr.^b, S.P. Morato^b*

^a*Instituto Nacional de Pesquisas Espaciais – INPE
Avenida dos Astronautas - 1758, C.P. 515, 12.201-970
São José dos Campos - SP, Brazil
e-mail: paulete@met.inpe.br*

^b*Instituto de Pesquisas Energéticas e Nucleares - IPEN/CNEN
Travessa R - 400, 05422-970 São Paulo - SP, Brazil
e-mail: mmvieira@net.ipen.br*

^c*Universidade Federal do Ceará,
Bloco 913, 60000 Fortaleza - CE, Brazil
e-mail: josue@fisica.ufc.br*

^d*Departamento de Física,
Universidade de Brasília,
70910-900 Brasília - DF, Brazil
e-mail: aderbal@guarany.cpd.unb.br*

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This paper describes the determination of the thermal diffusivity of LiKSO₄ crystals using the photoacoustic phase lag method, in the 77 K to 300 K temperature interval. This method is quite simple and fast and when it is coupled to a specially designed apparatus, that includes a resonant photoacoustic cell, allows for the determination of the thermal diffusivity at low temperatures. The thermal diffusivity is an important parameter that depends on the temperature, and no values of this parameter for LiKSO₄, at low temperature, have yet been reported. The LiKSO₄ is a crystal with many phase transitions which can be detected via the anomalies in the variation of the thermal diffusivity as a function of the temperature.

Keywords: *phase transitions, thermal diffusivity, photoacoustic*

1. Introduction

At room temperature, LiKSO₄ is a pyroelectric, hexagonal crystal that presents several phase transitions in the temperature range from 20 K to its fusion temperature, at 998 K. This crystal can be grown from an aqueous solution of Li₂SO₄·H₂O and K₂SO₄, in stoichiometric proportions, through slow evaporation, under controlled conditions at 303 K¹.

Since the LiKSO₄ is an insulator, heat transport is caused by fonons and there is an interest in investigating its changes in thermal properties during the phase transitions. The thermal diffusivity is a very important parameter to completely characterize this crystal, whose thermal conductivity² and specific heat are known³.

The phase transitions were described by several authors, using different experimental techniques, with emphasis on the

physical mechanisms of the transitions⁴. The scheme below shows all phase transitions observed up to now.

FUSION - 998 K - PHASE I - 948 K - PHASE II - 711 K - PHASE III - 245 K - PHASE IV - 190 K - PHASE V - 83 K - PHASE VI - 65 K - PHASE VII - 38 K - PHASE VIII - 20 K

Some of these phase transitions can be observed by measuring the thermal diffusivity temperature dependence using the photoacoustic phase lag method, which is presented in the next section.

2. Photoacoustic Phase Lag Method

The photoacoustic effect consists basically in the conversion of light into sound. This conversion occurs as the following sequence of events: first, a beam of periodically modulated light reaches the sample surface (the sample is kept inside an hermetic gas filled cell). The sample absorbs the light and releases heat, which after propagating through the sample causes the heating of the surrounding gas. The periodic heating of the gas produces pressure waves that are detected by a microphone coupled to the cell.

The photoacoustic phase lag method was proposed by Pessoa Jr. *et al.*⁵ as an alternative to that of Yasa and Amer⁶. It consists in non simultaneous illumination of the front and back sides of the sample, and the measurement of the relative phase lag between the generated photoacoustic signals, for a single chopping frequency. This method can be applied to optically opaque samples (all incident light is absorbed at the sample surface) and it is independent of the surface and the power calibration conditions.

The method is based on the theoretical model of Rosencwaig and Gersho⁷ (RG model), which assumes that the source of the photoacoustic signal is the heat diffusion through the sample. The method is valid only when the x dimension of the sample is much smaller than the y and z dimensions. Other assumptions are: the cell dimensions must be small enough to prevent convection in the gas; the thermal expansion⁸ and thermoelastic bending⁹ of the sample should be negligible; and the gas and the cell material should not contribute to the photoacoustic signal.

The intensity of the photoacoustic signal depends on the amount of heat generated in the sample, which, in turn, depends on the light intensity, optical absorption coefficient and the light-into-heat conversion efficiency of the sample, and on the thermal diffusivity.

According to the RG model, the photoacoustic signal intensity is described by the expression (1):

$$I = \frac{I_0 \beta \gamma P_0}{2 \sqrt{2} \kappa_s l_g a_g T_0 (\beta^2 - \sigma_s^2)} \frac{[(r-1)(b+1)e^{\sigma_s l_s} - (r+1)(b-1)e^{-\sigma_s l_s} + 2(b-r)e^{-\beta l_s}]}{[(g+1)(b+1)e^{\sigma_s l_s} - (g-1)(b-1)e^{-\sigma_s l_s}]} \quad (1)$$

where I_0 is the light intensity reaching the sample, β is the optical absorption coefficient of the sample for the wavelength of the light,

$\gamma = C_p / C_v$ is the Poisson constant,

P_0 is the atmospheric pressure,

T_0 is the room temperature,

κ_s is the sample thermal conductivity,

$\sigma_s = (1 + i)(\omega / 2\alpha_s)^{1/2}$, where ω is the modulation frequency of the light and α_s is the sample thermal diffusivity,

l_s is the sample thickness,

l_g is the gas column thickness,

$a_g = (\omega / 2\alpha_g)^{1/2}$, where α_g is the gas thermal diffusivity,

$r = (1 - i) \beta (\alpha_s / 2\omega)$,

$b = \kappa_b \alpha_s^{1/2} / \kappa_s \alpha_b^{1/2}$, where κ_b is the backing material thermal conductivity and α_b is the backing material thermal diffusivity,

$g = \kappa_g \alpha_s^{1/2} / \kappa_s \alpha_g^{1/2}$, where κ_g is the gas thermal conductivity and α_g is the gas thermal diffusivity.

The thermal diffusivity α is the quantity which measures the rate of heat diffusion through the sample, that is

$$\alpha = \frac{\kappa}{\rho c} \quad (2)$$

where κ is the thermal conductivity, ρ is the density and c is the specific heat at constant pressure. In addition to its relation with the thermal conductivity, density and specific heat, the thermal diffusivity provides information on the heat diffusion under non-stationary conditions¹⁰.

The thermal diffusivity of the sample is determined by recording the photoacoustic signal as a function of the frequency, and considering the special cases of the RG model, for optically opaque samples⁷. These cases depend on the thermal, optical and geometrical properties of the sample, on the gas and backing material, in particular when comparing the thermal diffusion length of the sample, and on the sample thickness. In general, the backing material is the cell material, but in the phase lag method, it is a gas. In this experiment, the LiKSO_4 works as a thermally thick solid, that is, the thermal diffusion length of the sample is smaller than the sample thickness.

However, this procedure is not necessary in the phase lag method, since the thermal diffusivity can be directly obtained for a single frequency, by inverting the expression of the phase lag $\Delta\phi$, between the front and back illumination signals¹¹:

$$\Delta\phi = \arctan \left[\tan \left[\frac{l_s}{\left(\frac{2\alpha_s}{\omega} \right)^{1/2}} \right] \tanh \left[\frac{l_s}{\left(\frac{2\alpha_s}{\omega} \right)^{1/2}} \right] \right] \quad (3)$$

3. Experimental

The experimental arrangement used in the thermal diffusivity measurements by the photoacoustic phase lag method consists of the resonant photoacoustic cell, the excitation system, the detection and the temperature control systems. Figure 1 shows this arrangement.

The experiment consists in illuminating the front and the back surface of the crystal sample, not simultaneously, using optical fibers, for each value of the temperature in the 77 K - 300 K range. The photoacoustic cell is immersed in a liquid nitrogen bath, in order to be cooled to 77 K. The intermediate temperatures are obtained using a furnace which surrounds the sample holder.

Helium is used to improve the thermal coupling between the liquid nitrogen, the furnace and the sample, and also to compensate for the internal pressure changes with the temperature and to avoid water condensation. Figure 2 shows the resonant photoacoustic cell details.

The source of the photoacoustic signal is an Argon ion laser, continuous and mechanically modulated by a chopper. The photoacoustic signal is detected by a commercial microphone, and its amplitude and phase are measured by a lock-in amplifier.

The samples were cut in pieces of 1 cm², 0.03 cm thick, with the crystal c-axis parallel to the sample faces, so the thermal diffusivity measurements were made with the heat flux perpendicular to the c-axis.

To satisfy the method requirement of optically opaque samples, an aluminum film of approximately 1 μm thick, was deposited on both sides of the crystal sample. As the thermal diffusivity of the aluminum is four orders of mag-

nitude greater than that of the crystal¹², the aluminum film does not invalidate the thermal diffusivity measurements for the LiKSO₄ crystals¹³.

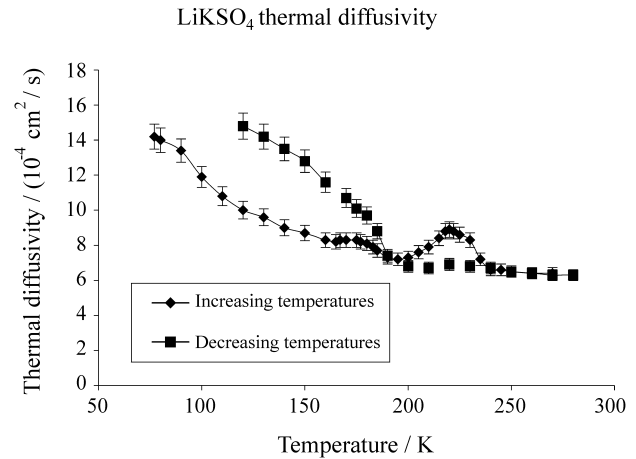


Figure 3. LiKSO₄ thermal diffusivity values for increasing and decreasing temperatures.

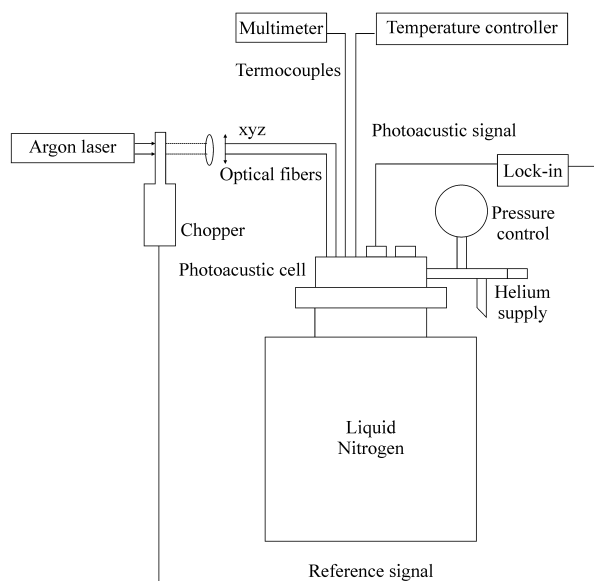


Figure 1. Schematic representation of the experimental arrangement.

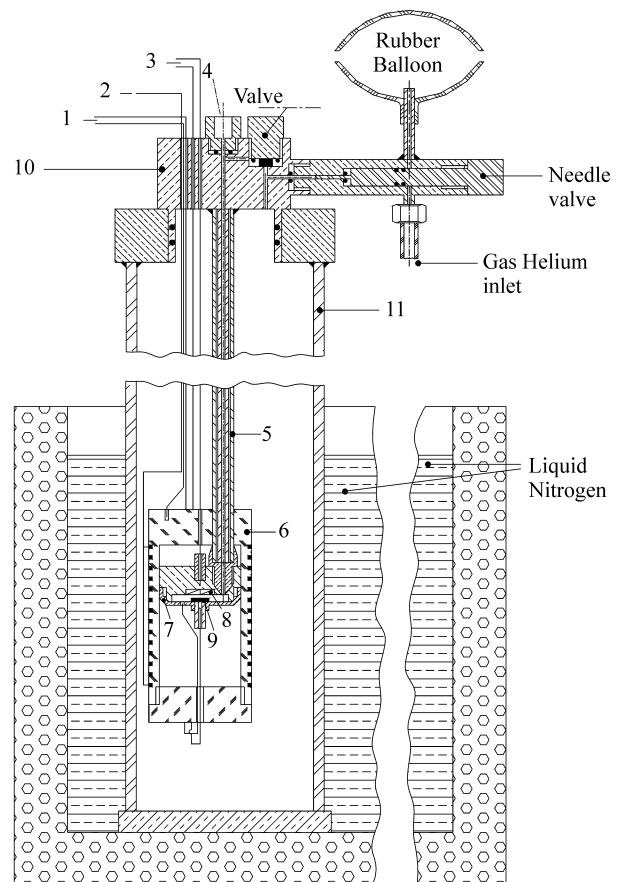


Figure 2. Schematic representation of the resonant photoacoustic cell. 1: thermocouples; 2: resistance; 3: optical fibres; 4: microphone; 5: resonance tube; 6: furnace; 7: sample holder; 8: optical window; 9: sample; 10: brass cylindrical part; 11: stainless steel cylinder.

4. Results

The thermal diffusivity values for LiKSO_4 crystals as a function of the temperature are shown in Fig. 3.

As it can be seen in Fig. 3, for increasing temperatures, there is an anomaly in the thermal diffusivity around 240 K, that corresponds to the transition from phase IV to phase III. This transition is also observed at the same temperature for the case of decreasing temperatures, although less pronounced.

For the increasing temperature curve, there is another anomaly in the thermal diffusivity around 190 K. This anomaly corresponds to the transition from phase V to phase IV, and it is also observed around 190 K, for decreasing temperatures.

The transition from phase VI to phase V, at 83 K, was not observed in this experiment, neither when the temperature was increasing nor decreasing, a fact also observed when using other techniques.

Bansal *et al.*¹⁴ were the first to observe the transition from phase IV to phase III by Raman scattering and to consider it as a first order transition. The transition temperature was 242 K during the sample heating and at 201 K during the sample cooling, with 41 K of hysteresis.

Bansal suggested that this phase transition is due to the SO_4^{2-} ions rotation of 60° around the crystal c axis, without any alteration of the other ions positions. In this regard, the LiKSO_4 change the C_{3v}^4 symmetry of phase IV into the C_6^6 symmetry of phase III.

Tomaszewski *et al.*¹⁵ using X-ray diffraction and thermal expansion measurements proposed the C_{6v}^4 symmetry for phase IV, in contradiction to the Bansal suggestion. According to them, during the transition into phase III, the SO_4^{2-} ions rotate 27° around the crystal c axis and the top oxygen atom oscillates between three random positions.

The transition from phase V into phase IV was first observed by thermal expansion coefficient measurements¹⁶, at the crystal c axis direction. This transition is related to the top oxygen atom that freezes at one of the three random positions, assuming one inclination with respect to the 6_3 axis and the C_{mc21} orthorhombic symmetry.

The transition from phase VI into phase V was observed at 83 K by EPR¹⁷ and considered incommensurate. The C_3^1 group was suggested as one possible symmetry for phase VI.

5. Conclusion

The photoacoustic phase lag method is, probably, the simplest method for the measurement the thermal diffusivity of many materials. The experimental arrangement makes possible to obtain the LiKSO_4 thermal diffusivity from 77 K to 300 K, and therefore the observation of its phase transitions.

The investigation of phase-transitions is a well established application of the photoacoustic technique, but gen-

erally in a small range of high temperatures¹⁹. In this regard, this paper presents a new contribution for the LiKSO_4 characterization, allowing for the measurement of the thermal diffusivity in a wide range of low temperatures, and it presents the photoacoustic phase lag method as a practical technique to observe phase transitions in this material.

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