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A NON-ISOTHERMAL TECHNIQUE USING THERMAL OPTICAL ANALYSIS TO FOLLOW THE KINETICS OF POLYMER CRYSTALLIZATION AND SOLID STATE PHASE TRANSFORMATION AND THE DETERMINATION OF THE LENGTH OF THE CRYSTALLINE SEGMENT*

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ABSTRACT

A non-isothermal technique was developed to study the kinetics of solid transformations using thermal optical analysis (TOA). Similar to the methods using TGA and TXA we previously reported, an expression was derived that utilizes integral and differential curves. TOA involves the measurement of transmitted light intensities of a material examined between cross polars and does not require a weight change or an extractable crystalline peak. For quantitative data, it is necessary to have instrumentation in which the photometer optics and temperature state are integrated to optimize the light intensities and to record them quantitatively. In addition, circular polarized light was used to eliminate sample orientation. In order to confirm its applicability and for comparison, the technique was applied to the low density crosslinked polyethylene polymer previously studied using TGA and TXA. The enthalpy for the transformation was found to be 13.2 kcal/equiv. which was in agreement with TXA results. TOA also showed, however, a second transformation at higher temperatures and low % crystallinities, with a 67.2 kcal/equiv. enthalpy.

INTRODUCTION

In previous communications, we have introduced a non-isothermal method using the thermogravimetric technique[1] in which we were able to extract the kinetic parameters of drug desolvation and degradation[2,3,10] as well as the enthalpy of

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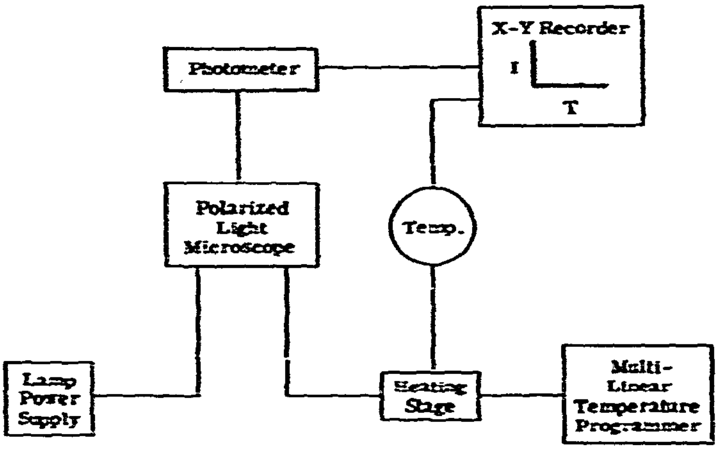

Fig. 1. Block diagram of thermal optical analysis system.

sublimation and vaporization[4]. Also, the thermal X-ray was used to follow phase transformation of both single crystal and powder[5].

In this paper, we wish to demonstrate the use of thermal optical analysis to follow the kinetics of phase transformation and compare it with the previously described technique using thermal X-ray diffraction.

INSTRUMENTATION AND CALIBRATION

Thermal optical analysis involves the measurement of transmitted light intensities of a material examined between cross polars. Figure 1 shows a block diagram of a thermal optical analysis system. A high quality optical microscope with polarized light attachment (or circular polarized light), a heating stage controlled by a multi-linear temperature programmer, and photometer attached to the eyepiece. As the sample is heated, the transmitted circular polarized light will be measured by the photometer as a function of temperature. Both the transmitted light and the temperature of the sample are recorded by a X–Y recorder.

In order to obtain quantitative data from the thermal optical analyser, it is necessary that both the instrumental and specimen-related conditions required for quantitative interpretation of the intensity of transmitted polarized light should be controlled. The instrumental requirements dictate that the photometer must be linear in percent transmission, of high sensitivity, stable, measure integrated intensity and be linearly proportional to the area fraction of the measuring field. The optical system for depolarized light intensity measurements must require an objective aperture slightly greater (10°) than the aperture of incident light. This minimizes scattering losses. Moreover, the larger the collecting objective aperture, the lower the scattering loss. Crossed circular polarized light eliminates the dependence of transmitted light intensity on sample orientation[6]. It is also preferred to the conventional crossed plane polars in photometry because the signal-to-noise levels are optimized. The

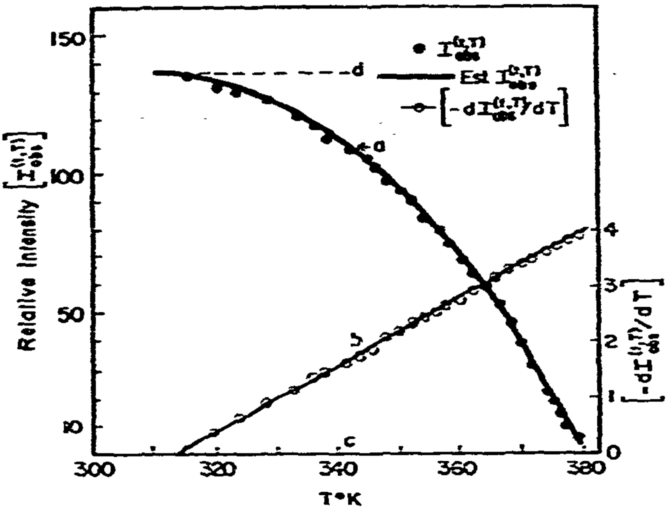

Fig. 2. Thermal optical data for crosslinked polyethylene (XLPE) phase transformation with its first derivative curve.

heating stage, programmer and temperature monitoring system must be accurate and controllable. Heating and cooling rates must be reproducible.

On the other hand, specimen requirements dictate that transparent, colorless and low light scattering samples must be required to reduce or eliminate factors which result in competitive causes for changes in transmitted light intensity. Thin films of uniform thickness and with an area equal to or greater than the measured area are optimal. Samples with fixed geometry which occupy only a fraction of the measured field are acceptable alternatives. The intensity of transmitted polarized light is proportional to retardation only in the 0–275 nm range. Samples with retardations greater than 275 nm are more complex in their intensity–retardation relationship and should, when possible, be avoided. Uniform retardation is optimal for exact measurements as integrated intensity measurements will average intensity and retardation values. Residual mechanical stresses must be removed by annealing if crystalline birefringence is to be observed free of other factors.

The total intensity of polarized light transmitted by a thin section of materials results from the sum of the intensity due to the crystalline birefringence of the solid plus the intensity due to the stress birefringence less the intensity loss due to scatter. In order to obtain quantitative data, circular polarized light was used to eliminate the sample orientation parameter, role of light scattering and loss of intensity by small nuclei and other scattering interfaces. In addition, the sample was annealed to minimize the mechanical stress. The data output is the relative intensity as a function of temperature. Figure 2 illustrates the nature of information determined by TOA.

To correlate the relative intensity on the TOA tracing, it was decided to take a sample as a function of temperature in order to determine the percent crystallinity of each sample. The percent crystallinity was determined by X-ray crystallography with a Philips X-ray diffractometer and copper radiation. The 110 and 200

TABLE 1

COMPARISON OF X-RAY CRYSTALLINITY AND INTENSITY

Temperature (°C)	*Crystallinity* (*fc*)	*Intensity* (*I*)	*I/fc*	*Δ*
35	0.420	136	323	+6
55	0.390	126	323	+6
65	0.360	114	316	−1
75	0.315	97.6	309	−6
95	0.145	45.6	314	−3
		Average	317±6	
		Average deviation 1.5%		

crystalline reflections and amorphous scatter were recorded. The reflections were resolved into Gaussian peaks and converted to intensities. A comparison of X-ray crystallinity to TOA intensity is listed in Table 1. The percent crystallinity was found to be directly proportional to the relative intensity with a proportionality constant given in eqn. (1).

$$I = Cf_c \tag{1}$$

Figure 3 shows a plot of percent crystallinity as a function of temperature in relationship to the data obtained from TOA after dividing the relative intensity by the proportionality, *C*. The density measurement also agrees with both X-ray and TOA measurements. Therefore, the total intensity of transmitted light can be considered equal to the intensity due to crystalline birefringences.

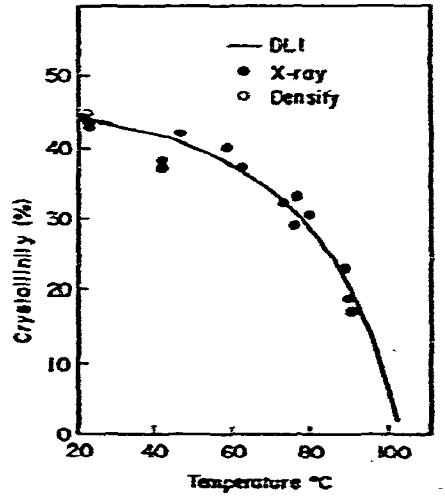

Fig. 3. X-ray crystallinity and scaled TOA data for crosslinked polyethylene (XLPE).

MATHEMATICAL APPROACH

In this study, the intensity of the light transmitted by the material was plotted as a function of temperature, (TOA). The integral curves were differentiated to give the differential thermal optical analysis. Therefore, we have the following data.

(1) The relative intensity observed at a particular temperature, $(I_{obs}^{t,T})$.

(2) The relative intensity changes as a function of temperature $(\mathrm{d}I_{obs}^{t,T}/\mathrm{d}T)$.

By taking this available data into consideration, the phase transformation kinetics of any solid compound or solid polymer, which does not show any weight change can be studied.

$$\text{Phase}_1 \xrightarrow{\Delta} \text{Phase}_2$$

If the phase transformation can be followed by measuring the intensity of transmitted light, as a function of temperature, then, the rate of phase disappearance can be written as

$$\frac{\mathrm{d}I^{t,T}}{\mathrm{d}t} = -k(I^{t,T}) \tag{2}$$

where k is the specific rate constant, $I^{t,T}$ is the relative intensity of the transmitted light through phase$_1$ at time t and temperature T K. A more useful version of this equation for the studies reported in this communication can be obtained by converting the time derivative of the observed change in phase$_1$ to a temperature derivative of the observed change in the phase. The results are shown in the equation

$$-\frac{\mathrm{d}I^{t,T}}{\mathrm{d}T} = \frac{k}{a}(I^{t,T})$$

where a is the heating rate given by $\mathrm{d}T/\mathrm{d}t$.

Let us consider the process to be continuous with the intensity of the transmitted light traced as a function of temperature and its first derivative being simultaneously traced on the same recorder. Therefore, the traced intensity, $I^{t,T}$, is also equal to the observed intensity, $I_{obs}^{t,T}$, at time t and temperature T K. Therefore the resulting equation is given by

$$-\frac{\mathrm{d}I_{obs}^{t,T}}{\mathrm{d}T} = \frac{k}{a}(I_{obs}^{t,T}) \tag{3}$$

For non-isothermal conditions, the dependence of the specific rate constant on temperature must be considered. Therefore, from eqn. (3) and the Arrhenius expression, $k = Z\exp[-\Delta H^*/RT]$, we may write

$$-\frac{\mathrm{d}I_{obs}^{t,T}}{\mathrm{d}T} = \frac{Z}{a}\mathrm{e}^{-\Delta H^*/RT}(I_{obs}^{t,T}) \tag{4}$$

Taking the logarithm of eqn. (4)

$$\log\left[\frac{-\,\mathrm{d}I_{\mathrm{obs}}^{t,T}/\mathrm{d}T}{I_{\mathrm{obs}}^{t,T}}\right] = \log\frac{Z}{a} - \frac{\Delta H^*}{2.303RT} \tag{5}$$

A plot of $\log\,[(-\,\mathrm{d}I_{\mathrm{obs}}^{t,T}/\mathrm{d}T)/I_{\mathrm{obs}}^{t,T}]$ versus $1/T$ K will yield a linear function, for a single process, of slope $-\,\Delta H^*/2.303R$ and an intercept of $\log(Z/a)$.

For the isothermal condition, integration of eqn. (1) gives

$$\int_{I_{\mathrm{obs}}^{t=0}}^{I_{\mathrm{obs}}^{t=t}} \frac{\mathrm{d}I_{\mathrm{obs}}^{t}}{I_{\mathrm{obs}}^{t}} = -\,k\int_{0}^{t}\mathrm{d}t \tag{6}$$

where $I_{\mathrm{obs}}^{t=0}$ is the initial transmitted light intensity.

Therefore

$$\ln\,(I_{\mathrm{obs}}^{t}) = -\,kt + \ln\,(I_{\mathrm{obs}}^{t=0}) \tag{7}$$

According to eqn. (7), a plot of $\ln(I_{\mathrm{obs}}^{t})$ versus time t will produce a straight line of slope $-\,k$.

Equation (5) requires that both the integral curve of the light intensity as a function of temperature, and the instantaneous first derivative are available. The integral curve could be obtained either by a continuous tracing of the light intensity transmitted through the phase at a particular heating rate as a function of temperature, or by measuring the relative light intensity transmitted through the phase at a particular percentage crystallinity at a constant temperature and then plotted to give the integral curve. The integral curve is then differentiated to give its simultaneous derivative. The differentiation could be done simultaneously, by specific instrumentation as we measure the relative intensity as a function of temperature, by computer fitting, or by a glass rod technique. Care should be taken in the case of computer fitting, as a slight deviation could lead into a significant effect on the calculated differential curve. In the case of the construction of the integral curve, the heating rate, a, is a constant value which does not affect the calculated enthalpy, but affects the intercept of the obtained non-isothermal plot.

RESULTS AND DISCUSSION

Kinetics of polymer crystallization

Low density chemically crosslinked polyethylene (XLPE) was used as model compound to study this system using a thermal optical analyser and to compare it with the previously described quantititive X-ray approach[5].

The thermal optical analyser measures the transmitted light continuously as a function of temperature. Figure 4 shows a plot of relative light intensity as a function of temperature and the first derivative of the produced curve. The first derivative was obtained by computer fitting the integral data according to *n*th polynomial regression

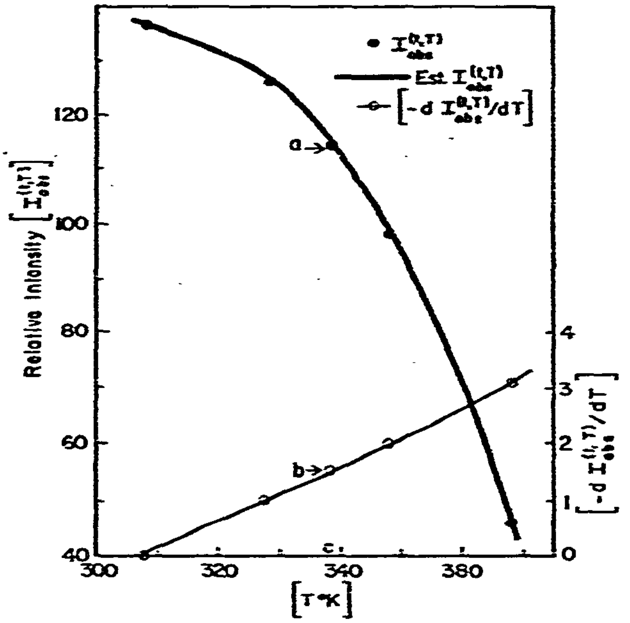

Fig. 4. Thermal optical data for crosslinked polyethylene (XLPE) phase transformation with its first derivative curve (data obtained from Table 1).

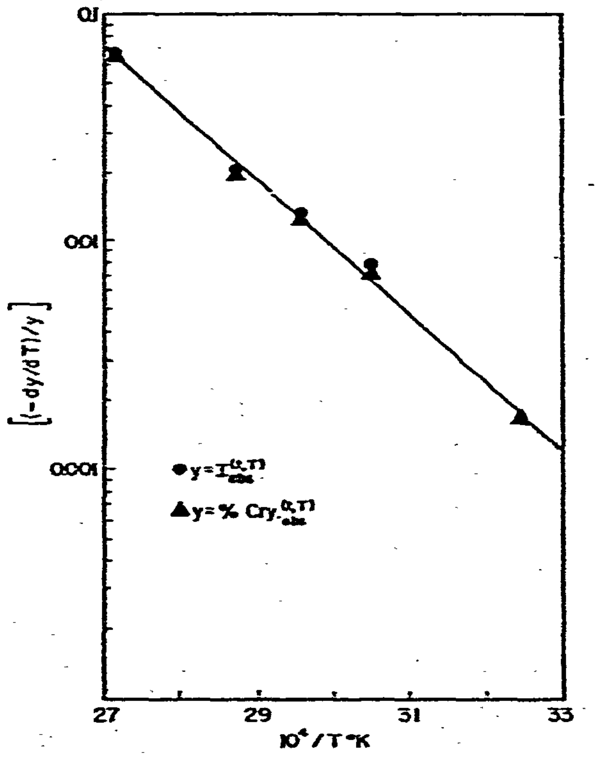

Fig. 5. Non-isothermal plots of low density crosslinked polyethylene phase transformation (of crystalline phase to amorphous phase using both thermal X-ray and thermal optical data.

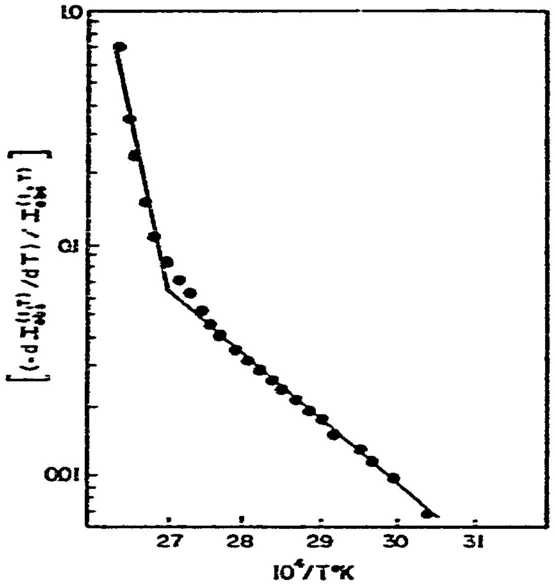

Fig. 6. Non-isothermal plot of low density crosslinked polyethylene (XLPE) of crystalline phase to amorphous phase.

program. From Fig. 4, the relative intensity at point a is $(I_{\mathrm{obs}}^{t;T})$, and its first derivative at point b is given by $[\mathrm{d}(I_{\mathrm{obs}}^{t;T})/\mathrm{d}T]$. This process is repeated across the graph, and the value of $\{[-\mathrm{d}(I_{\mathrm{obs}}^{t;T})/\mathrm{d}T]/I_{\mathrm{obs}}^{t;T}\}$ is plotted on semilogarithmic paper versus $10^4/T$. The resulting non-isothermal plot of crosslinked, low density, semicrystalline polythylene is shown in Fig. 5, which gives a straight line with a heat of activation equal to 13.2 kcal/cryst. equiv. Figure 5 also shows that the calculated heats of activation from thermal X-ray analysis[5] and thermal optical analysis are equal and the points superimposable. This indicates the validity of our mathematical approach as well as its wide application and the independence of the calculated parameters from the method of analysis.

Since the TOA is a continuous tracing and able to trace the intensity of transmitted light at low percentage crystallinity, which the X-ray method can not provide, it could reveal more than one phase transformation. Figure 6 shows a non-isothermal plot of the chemically crosslinked polyethylene obtained from the complete analysis of the entire trace given in Fig. 2. Figure 6 shows two phases of transformation, each with a characteristic heat of activation. The first stage has a heat of activation of 13.2 kcal/cryst. equiv. and the second phase transformation, which occurs at low percentage crystallinity, has a heat of activation equal to 67.2 kcal/cryst. equiv. It is thought that the second stage is responsible for the breakage of the crosslinked bonds.

This discussion leads to the conclusion that the instrument build by Reffner and Johnson[6] has an accuracy comparable with that of the X-ray method of analysis[5] and that the thermal optical analyser has advantages over the X-ray method in detecting phase transformation at low percentage crystallinity.

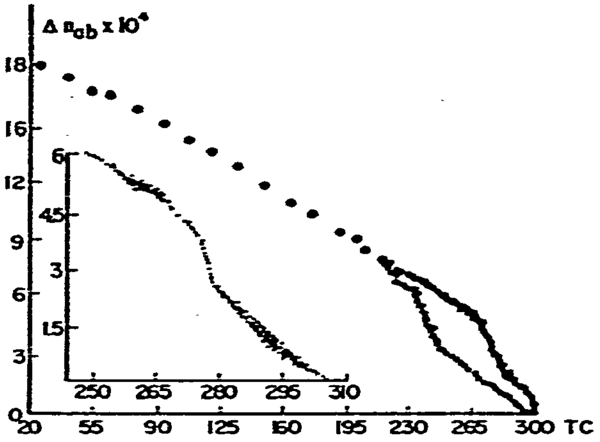

Fig. 7. Birefringence Δn_{ab} in the (001) plane of $Ba_2NaNb_5O_{15}$, as a function of temperature. The inner curve corresponds to a scale expansion of the heating run in the vicinity of the transition. Measurements are performed near 300°C at intervals of approximately 0.3 degree. The absolute accuracy on Δn_{ab} is $\pm 5 \times 10^{-4}$.

Determination of the length of the crystalline segment

In a previous communication[5], a model for measuring the length of the crystalline segment was established. The model depends on the crystalline equivalent enthalpy, ΔH (obtained from the kinetic method) and the specific enthalpy, ΔH_2 (obtained from adiabatic calorimetry) relationship in the equation

$$\text{length of crystalline segment} = \frac{(\Delta H_1/\Delta H_2)d}{\text{equiv. wt.}} \tag{8}$$

where d is the distance between each alternate carbon atom in the fully extended, planar, zigzag conformation of the polymer.

The application of this model to the calculation of the length of the crystalline segment of XLPE gave a value equal to 65 Å which agrees with the previous findings[5] using X-ray diffraction technique.

The kinetics of the ferroelastic transformation of barium sodium niobate from single crystals using the temperature dependence of the birefringence data

Toledano and Schneck[7] followed the birefringence, Δn_{ab} in the (001) plane of barium sodium niobate (BSN), as a function of temperature. Measurements of Δn_{ab} were performed at $\lambda = 546$ nm by Senarmont compensation method[8] on a Zeiss universal-model polarizing microscope provided with a mica quarter-wave plate. The sample was a plate cut from a single crystal and was sandwiched between two silver discs pierced with 1 mm apertures, in close contact with the heating element of a modified leitz hot stage. The temperature was probed with a calibrated platinum resistor inserted in a copper cylinder located in the vicinity of the sample. Figure 7 shows the resulting change of birefringence of BSN for both the heating and cooling systems. A large thermal hysteresis is shown by the fact that heating and cooling

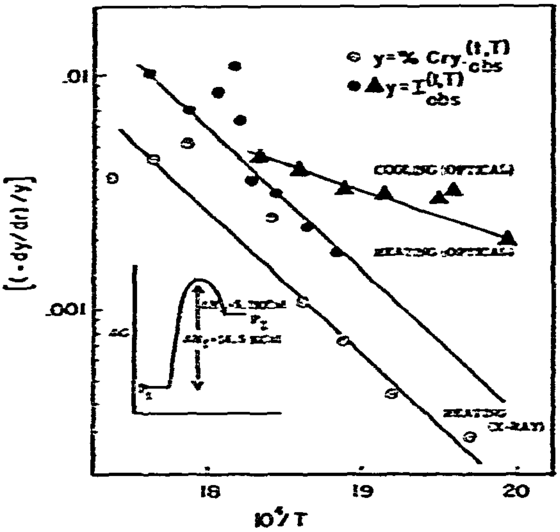

Fig. 8. Non-isothermal plot of ferroelastic transition of sodium barium niobate from single crystals using both thermal X-ray and thermal optical data. The inner curve corresponds to the free diagram of the ferroelastic transition. ⊖, Obtained from X-ray data (heating mode); ●, obtained from thermal optical data (heating mode); ▲, obtained from thermal optical data (cooling mode).

curves are distinct above 215°C. Data from this graph was magnified and the instantaneous first derivative of both integral curves (i.e. heating and cooling curves) were calculated using the glass rod diffraction technique. The resulting non-isothermal plot, plotted according eqn. (5), is given in Fig. 8. Figure 8 shows that both heating and cooling curves are linear but with different heats of transformation. The heating curve gives heat of transformation for the orthorhombic to tetragonal transformation with symmetric change from 4mm → mm2 equal to 14.5 kcal/mole while the cooling curve yields heat of transformation (for tetragonal to orthorhombic transformation with symmetry change from mm2 → 4mm) equal to 5.2 kcal/mole.

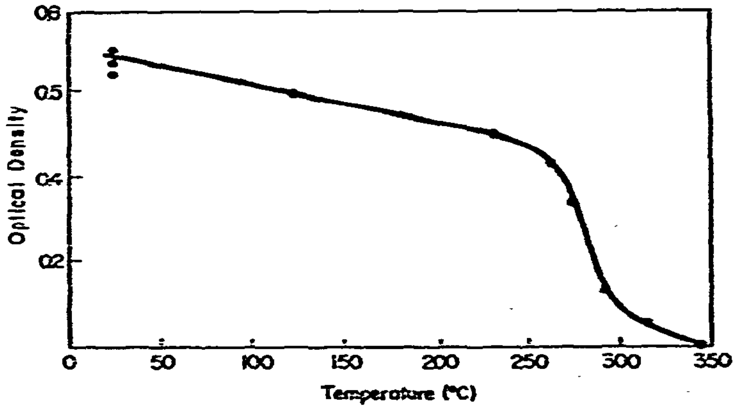

Fig. 9. Reflection intensity of the layer line (*hkl*) vs. temperature in a single crystal of barium sodium niobate. The disappearance above 300°C shows the change in translational symmetry which occurs along (001) at the ferroelastic transition.

Burgent and Toledano[9] studied the ferroelastic transformation of BSN from a single crystal, mounted in a goneometer parallel to the (001) plane, using a Weissenberg camera, as a function of temperature. The sample was heated by dry nitrogen gas and the temperature was probed by a copper–constant an thermocouple positioned about 1 mm from the crystal. The ferroelastic transformation of BSN from orthorhombic to tetragonal involving the symmetry change 4mm → mm2 is given in Fig. 9. The data in Fig. 9 was analysed by an equation[5] hybrid to eqn. (5) and the resulting non-isothermal plot from X-ray data (heating process) was found to be parallel to that obtained from optical data (heating process), with heat of transformation equal to 14.5 kcal/mole. This indicates that both X-ray technique[5] and thermal optical technique were comparable. It should be noted that a hybrid[4] of eqn. (5) was also used to calculate the enthalpy of sublimation and vaporization from thermogravimetric curves and found that the data agrees with Knudsen effusion technique. This indicates that the calculated kinetic data from the above technique is not only comparable using different techniques but accurate.

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REFERENCES

1 R. R. A. Abou-Shaaban and A. P. Simonelli, *Thermochim. Acta*, 26 (1978) 89.
2 R. R. A. Abou-Shaaban and A. P. Simonelli, *Thermochim. Acta*, 26 (1978) 111.
3 R. R. A. Abou-Shaaban, T. L. Haberfield, E. M. Barell, J. F. Johnson and A. P. Simonelli, *Polym. Eng. Sci.*, 16 (1976) 544.
4 R. R. A. Abou-Shaaban and A. P. Simonelli, to be submitted to *J. Phys. Chem.*
5 R. R. A. Abou-Shaaban, J. A. Reffner and A. P. Simonelli, *Thermochim. Acta*, 26 (1978) 125.
6 J. A. Reffner and J. F. Johnson, *7th North East Regional Meeting of Am. Chem. Soc., Aug. 8–11, 1976*, Paper 320.
7 J. C. Toledano and J. Schneck, *Solid State Commun.*, 16 (1975) 1101.
8 H. G. Jerranrd, *J. Opt. Soc. Am.*, 38 (1948) 35.
9 J. Burgent and J. C. Toledano, *Solid State Commun.*, 20 (1976) 281.
10 R. R. A. Abou-Shaaban and A. P. Simonelli, to be submitted to *J. Pharm. Sci.*