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STUDY OF THE EFFECTIVE PHASE TRANSITION ACTIVATION ENERGY IN K_2SeO_4 CRYSTALS

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The high-temperature phase transition of K_2SeO_4 was studied by using differential thermal analysis. The Kissinger equation and the Mahadevan approximation were applied to evaluate the effective phase transition activation energy (E). The average value of E was 12.85 ±0.04 eV.

The thermal analysis of phase transitions has been of great interest in many publications in the past few years. Kissinger [1] demonstrated that the variation in peak temperature with the change of heating rate could be used to determine the activation energy E.

Since the discovery of an incommensurate phase in K_2SeO_4, increasing interest has arisen in this compound as well as in other members of the family A_2BX_4 [2]. At room temperature, the K_2SeO_4 crystal belongs in the Pmcn spatial group with a strong pseudohexagonal structure. Below 93 K (T_c), it exhibits a spontaneous polarization along the orthorombic a_o axis [3]. Between 129 K and 93 K, an incommensurate phase [4] has been observed. Above 129 K, the crystal displays paraelectric behaviour and it undergoes an orthorombic - hexagonal phase transition at 745 K.

Most of the work to date has been concerned with microscopic measurements. From a macroscopic point of view, a precise knowledge of the effect of the heating rate on the high-temperature phase is of considerable interest as a source of information about the energetic balance between the orthorombic – hexagonal phase transitions.

The aim of the present work was to determine the phase transition activation energy (E) of the high-temperature phase transition of K_2SeO_4 by using the continuous heating method of differential thermal analysis (DTA).

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Experimental

Single-crystals of K_2SeO_4 were grown from the saturated aqueous solution by slow evaporation at 50°. The crystals obtained were of a good quality, but were small ($1 \cdot 2 \cdot 2$ cm^3).

The thermal behaviour was investigated with a Du Pont 1090 differential thermal analyser. The temperature calibration of the instrument was performed via the well-known melting temperature of the high-purity indium supplied with the instrument. The measured temperature accuracy was ±0.1 deg.

The phase transition thermoanalytical curves were recorded as the temperatures of the samples were increased at a uniform rate. Tipically, 20 mg of sample in powdered form (average particle size = 54 μm) was taken in standard glass tube and scanned over the temperature range from room temperature to about 500° at uniform heating rates (α) ranging from 3.0 to 70 deg/min in static air.

X-ray investigation of powder K_2SeO_4 (average particle size = 54 μm), was performed with a Philips 1710 diffractometer. The patterns were run with Cu as target and Ni as filter (λ = 1.54178 Å), at 40 kV and 30 mA, with a scanning speed of 3.6 deg/min.

The best fit for the results was calculated by the least square method. The arithmetic mean and the standard deviation were calculated for the activation energy.

Results and discussion

A typical DTA curve of powder K_2SeO_4 (average particle size = 54 μm), obtained at a heating rate of 10 deg/min, is shown in Fig. 1. The DTA curve from room temperature up to 500° shows only one endothermic peak (T_p), at 471.4°, corresponding to the phase transition from the orthorombic to the hexagonal phase [4]. X-ray diffraction was used to control both the purity and the crystal structure (Fig. 2). The obtained pattern was in good agreement with the ASTM card [no. 22-853] as concerns the peak positions. The high-temperature phase transition observed by means of DTA is in good agreement with that reported by Topez Echarri [5].

Figure 3 shows DTA curves of powder K_2SeO_4 at different heating rates. The phase transition peak temperature (T_p) varies by 4.6 deg as the heating rate (α) is varied from 3.0 to 70 deg/min.

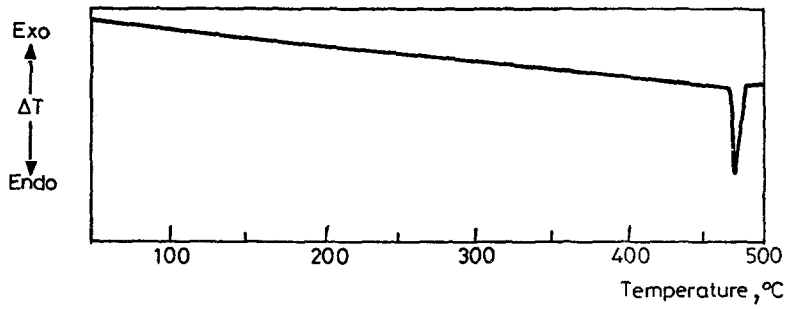

Fig. 1 Typical DTA curve of powder K_2SeO_4 at heating rate 10 deg/min

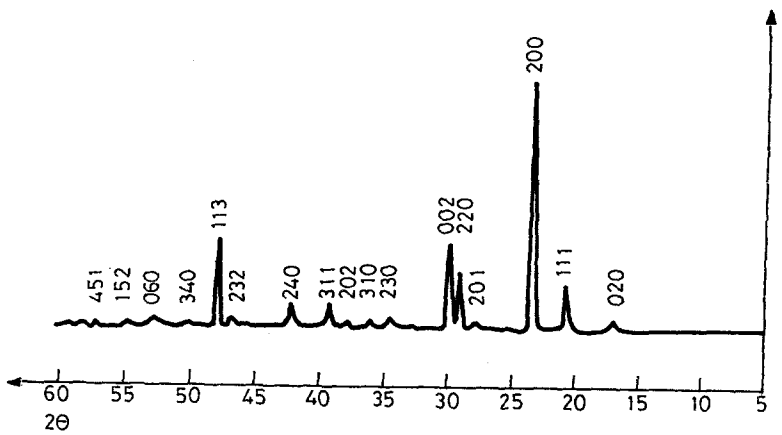

Fig. 2 The X-Ray diffractogram of K_2SeO_4 powder

For evaluation of the crystallization activation energy (E) from the variation in T_p with α, Kissinger's equation [1] can be used. During the past few years, the Kissinger equation has been developed and applied in many types of studies [6-9].

In phase transition studies, this equation can be written in the form [1, 6, 9]:

$$\ln (\alpha / T_p^2) = \text{const.} - (E / KT_p) \quad (1)$$

where E is the effective activation energy of the phase transition and K is the Boltzmann constant.

Plots of $\ln(\alpha / T_p^2)$ *vs.* $1/T_p$ for powder K_2SeO_4 were linear, as shown in Fig. 4. E was found to have a value of 12.81 eV.

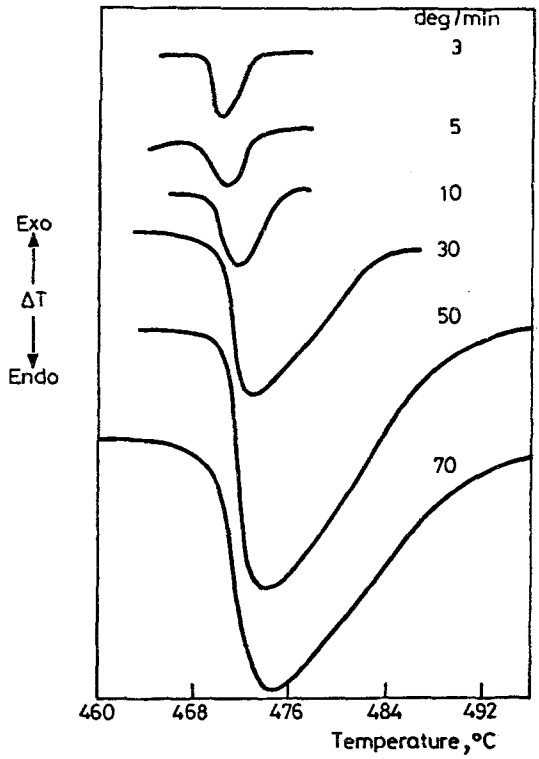

Fig. 3 Typical DTA curves of powder K_2SeO_4 at different heating rates

The phase transition activation energy (E) was also calculated by using the approximation of Mahadevan *et al.* [6].

The Mahadevan approximation reveals that the variation in $\ln(1/T_p^2)$ with $\ln(\alpha)$ is much slower than that in $(1/T_p)$ with $\ln(\alpha)$ [6].

Therefore, the Kissinger equation can be approximated in the form:

$$\ln(\alpha) = -E/KT_p + \text{constant} \tag{2}$$

Figure 5 shows the relation between $\ln(\alpha)$ and $1/T_p$. The value of E deduced from this relation was 12.89 eV.

The difference between the two E values deduced from the Kissinger equation and the approximate Kissinger equation is about 0.7%. Therefore,

the two forms of Kissinger's equation can be used to determine the effective phase transition activation energy (E).

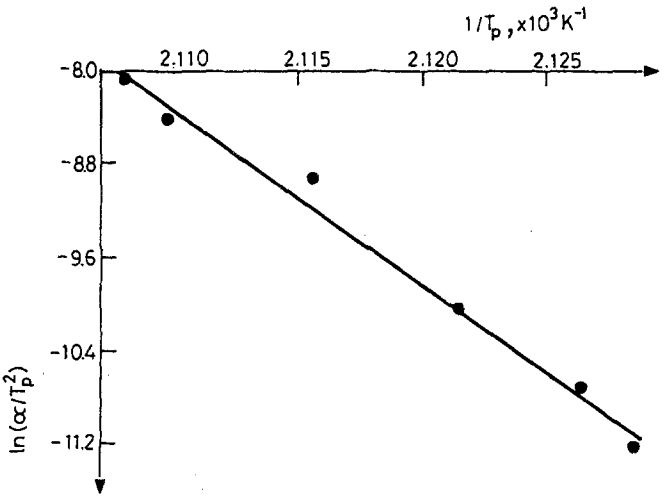

Fig. 4 $\ln(\alpha/T_p^2)$ *vs.* $1000/T_p$ of powder K_2SeO_4

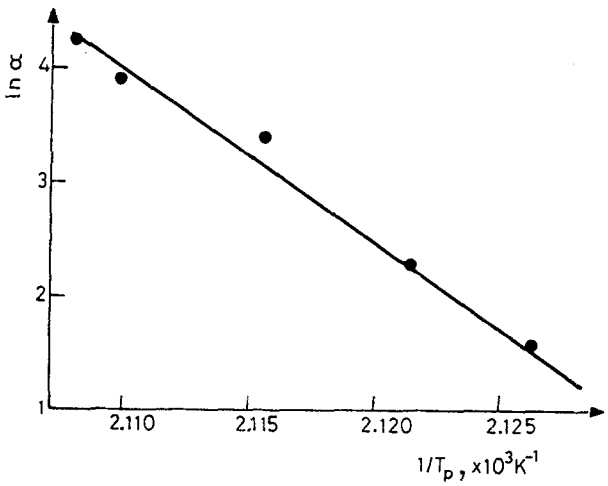

Fig. 5 $\ln(\alpha)$ *vs.* $1000/T_p$ of powder K_2SeO_4

From the experimental results, the Kissinger equation for powder K_2SeO_4 takes the form:

$$\ln(\alpha / T_p^2) = (-148604.2) / T_p + 305.225 \quad (3)$$

and after the Mahadevan approximation [6], this equation can be written as:

$$\ln(\alpha) = (-149572.9) / T_p + 319.591 \quad (4)$$

Thus, the average value of the phase transition activation energy of powder K_2SeO_4 is 12.85 ±0.04 eV.

Conclusions

The effective phase transition activation energy (E) of K_2SeO_4 was calculated by using the Kissinger equation and the Mahadevan approximation. The average value of E for K_2SeO_4 was 12.85 ±0.04 eV. One result of this study is that the Kissinger equation and the Mahadevan approximation can be used to evaluate the effective phase transition activation energy of K_2SeO_4.

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References

1 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
2 M. Wada, A, Sawada, Y. Ishibashi and Y. Takagi, J. Phys. Soc. Japan, 42 (1977) 1229.
3 K. Aiki, K. Hukuda, H. Koga and T. Kobayashi, J. Phys. Soc. Japan, 28 (1970) 389.
4 M. Iizumi, J. D. Axe, G. Shirane and K. Shimaoka, Phys. Rev., B15 (1977) 4392.
5 A. Topez Echarri, M. J. Tello and P. Gill., Solid. State Commun., 36 (1980) 1021.
6 S. Mahadevan, A. Giridhar and A. K. Singh, J. Non-Cryst. Solids, 88 (1986) 11.
7 K. Matusita, T. Konatsu and R. Yorota, J. Mat. Sci., 19 (1984) 291.
8 D. R. MacFarlane, M. Matecki and M. Poulain, J. Non-Cryst. Solids, 64 (1984) 351.
9 H. E. Kissinger, J. Res. Nat. Bur. Stand., 57 (1956) 217.

Zusammenfassung — Mittels DTA wurde die Hochtemperatur-Phasenumwandlung von K_2SeO_4 untersucht. Für die Ermittlung der effektiven Aktivierungsenergie der Phasenumwandlung (E) wurde die Kissinger-Gleichung und die Mahadevan-Näherung angewendet. Der mittlere Wert für E betrug 12.85±0.04 eV.