Thermochimica Acta, 165 (1990) 297–299
Elsevier Science Publishers B.V., Amsterdam

Note

GROWTH CONDITIONS OF ORGANIC NON-LINEAR OPTICAL CRYSTALS

R.N. SINGH, J.P. GUPTA, NAMWAR SINGH, N.P. SINGH and O.P. SINGH *

T.D. Post-Graduate College, Jaunpur (U.P.) (India)

N.B. SINGH, R.H. HOPKINS and R. MAZELSKY

Westinghouse Science and Technology Center, Pittsburgh, PA 15235 (U.S.A.)

(Received 22 January 1990)

m-Nitroaniline (*m*-NA) and *m*-hydroxyaniline (*m*-HA) samples were prepared by repeated distillation followed by directional freezing. Heats of fusion measurements were made and growth conditions were determined from the calculations using simple treatment of heat transfer during crystal growth.

Substituted anilines have been recognised as a very important class of non-linear optical materials for frequency conversion applications in the 0.4–2.0 μm wavelength range. While these materials have attracted attention as potentially important and useful media for non-linear optical and electro-optical applications, their use is very limited due to the unavailability of optical quality single-crystal thin films. This article is an attempt to present an approximate condition for the melt growth of two non-linear organic compounds, *m*-nitroaniline and *m*-hydroxyaniline.

m-Nitroaniline and *m*-hydroxyaniline crystals can be grown by the Bridgman technique if the purity of the source material is high [1]. Impurities are not only responsible for the breakdown of the solid–liquid interface during freezing but they also enhance the decomposition of the anilines. The prediction of the optimum growth rates and temperature gradients for simple crystal growth by a trial-and-error method is a very lengthy and time-consuming process. Some simple calculations can aid in defining the conditions. The heat transfer conditions for the directional solidification can be given as

$$Q = K_s G_s + K_l G_l \quad (1)$$

also

$$Q = Vd\,\Delta H_f \quad (2)$$

* Present address: Chemistry Department, K.N. Government Post-Graduate College, Gyanpur, Varanasi (U.P.), India.

TABLE 1

Properties of *m*-nitroaniline and *m*-hydroxyaniline

Property	*m*-NA	*m*-HA
Molecular formula	$C_6H_6N_2O_2$	C_6H_7NO
Molecular weight (g)	138.13	109.13
Melting temperature (°C)	114.0	123.0
Density (g cm^3)	1.175	1.233
Heat of fusion (cal g^{-1})	40.99	50.30
Thermal conductivity in solid (cal cm^{-1} K^{-1} s^{-1})	4.23×10^{-4}	4.11×10^{-4}
Roughness parameter ($\Delta H_f / T_m$)	7.3	5.7

where K is the thermal conductivity, G is the thermal gradient and s and l denote the solid and liquid phases. Q, V, d and H_f denote the amount of heat content, growth velocity, density and heat of fusion. For the case of zero supercooling solid–liquid interface, $G_l = 0$. By substituting the value of Q from eqn. (2) into eqn. (1), we get the relation between the growth velocity and temperature gradient

$$V = \frac{K_s G_s}{d \, \Delta H_f} \tag{3}$$

Heats of fusion were measured using a Perkin–Elmer DSC-2 with computer-aided data acquisition and analysis systems [2]. The heats of fusion are listed in Table 1 along with the densities and thermal conductivities of both anilines. By substituting the values of the parameters of eqn. (3), a relation is obtained between growth rate and temperature gradients; the results are plotted in Fig. 1. As the heat released during solidification must dissipate to the surroundings, the appropriate growth conditions for *m*-nitroaniline and *m*-hydroxyaniline are to the right of the straight lines in Fig. 1. The present conditions are for very slow growth rates. The heat transfer problems with

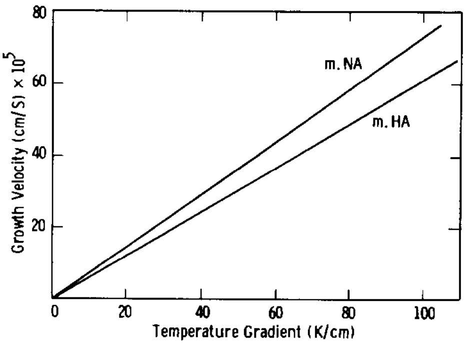

Fig. 1. Growth velocity–temperature gradient relationship for the growth of *m*-NA and *m*-HA crystals.

the moving boundary conditions are discussed in ref. 3. Also eqn. (3) does not account for the heat flow problems in the melt. It is therefore clear that the growth conditions calculated here occur in a much smaller region and the present findings are relevant only to the actual growth conditions. Experiments to verify these conditions and to grow optical quality crystals are under way.

REFERENCES

1 N.B. Singh, T. Henningsen, R. Hopkins and R. Mazelsky, ICCG-9, Sendai, Japan, 23 Aug. 1989.
2 O.P. Singh, Some Studies on Organic Eutectics and Monotectics, Ph.D. Thesis, Banaras Hindu University, Varanasi, India, 1986.
3 H.S. Carlslaw and J.C. Jeager, Conduction of Heat in Solids, Oxford University Press, Oxford, 1959.