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Chemistry and Characterization of Binary Organic Eutectics

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Phase diagrams of benzil with each of naphthalene, β-naphthol and *p*-chloronitrobenzene show the formation of simple eutectics. The growth velocity (v) data studied at different undercoolings (ΔT) by measuring the rate of movement of interface in a capillary obey the Hillig-Turnbull equation, $v = u(\Delta T)^n$, where u and n are constants depending on the nature of materials involved. Using enthalpy of fusion values, obtained by the DSC method, enthalpy of mixing, interfacial energy, entropy of fusion, excess thermodynamic functions and radius of the critical nucleus were calculated. Microstructural investigations give characteristic features of the eutectics.

INTRODUCTION

Chemistry and characterization of eutectics,[1] monotectics[2] and molecular complexes[3] have been a subject of potential investigation due to their unusual physical properties not normally shown by parent components. Metal[4, 5] eutectics and intermetallic[6] compounds constitute an interesting area of investigation in metallurgy and materials science. Due to low transformation temperature, ease in purification, transparency, wider choice of materials and minimized convection effects, organic systems are being used as model systems for unravelling the mysteries of solidification[7] which control the properties of materials. In addition, easy and convenient experimentation associated with organic systems has prompted a large number of research groups[8–13] to work on some physico-chemical aspects of organic eutectics, monotectics and molecular complexes. In the present investigation benzil (BEN), naphthalene (NAP), β-naphthol (BN) and *p*-chloronitrobenzene (CNB) have high enthalpy of fusion values and simulate nonmetallic solidification. As such systems of benzil with each of naphthalene, β-naphthol and *p*-chloronitrobenzene may be taken as organic analogs of nonmetal-nonmetal systems. In view of this phase diagram, growth kinetics, thermochemistry and microstructure of BEN-NAP, BEN-BN and BEN-CNB systems were studied in the present investigation.

EXPERIMENTAL

Materials and purification: While naphthalene obtained from Fluka was purified by sublimation followed by recrystallization from cyclohexane, β-naphthol (Fluka) was purified by repeated distillation under low pressure. *p*-Chloronitrobenzene (SD Lab. Chem. Industry, India) was purified by fractional crystallization with ethanol. Benzil (CDH, India) was purified by repeated crystallization from ethyl acetate. Purity of each compound was checked by comparing its melting point with the values reported in literature.

Phase diagram: The phase diagram of each system was determined by the thaw-melt method.[14] In this method mixtures of two components covering entire range of composition are prepared and they are homogenized by melting in silicone oil followed by chilling in ice-cold water. Thaw and melting temperature were determined and a plot between melting temperature and composition of a system gives its phase diagram.

Growith kinetics: The values of linear velocity of crystallization of pure components and eutectics at different undercoolings were determined by the capillary method.[15, 16]

Enthalpy of fusion: The values of enthalpy of fusion of pure components and eutectics were determined by the DSC method[17, 18] using a Mettler DSC-4000 system. The amount of sample and heating rate were about 5 mg and 10°C/min, respectively, for each estimation.

Microstructure: To study the microstructure[19] of the pure components and the eutectics, a small amount of sample was taken on a well washed and dried glass slide and placed in an oven maintained at a temperature slightly above the melting point of the sample. The supercooled melt was nucleated by the solid of the same composition and then it was unidirectionally solidified. The slide was placed on the plateform of a Leitz Laborlux D, optical microscope and different regions of the slide were observed. The microphotographs of suitable magnification were recorded with the help of a camera attached with the microscope.

RESULTS AND DISCUSSION

Phase diagram

Phase diagrams (Figs. 1–3) of BEN-NAP, BEN-BN and BEN-CNB systems show the formation of a simple eutectic in each case. Melting point of benzil is 96°C and it decreases with the addition of the second component and reaches a minimum value. This minimum temperature is the eutectic temperature of a

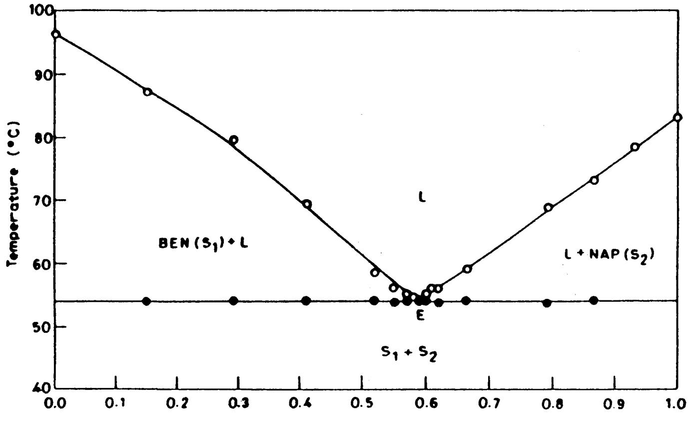

Fig. 1. Phase diagram of benzil-naphthalene: (1) • Thaw temperature, (ii) o Melting temperature

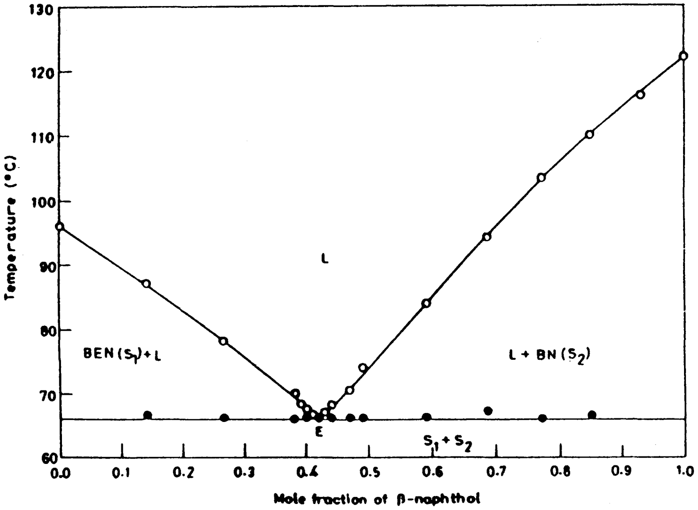

Fig. 2. Phase diagram of benzil-β-naphthol: (i) • Thaw temperature, (ii) o Melting temperature

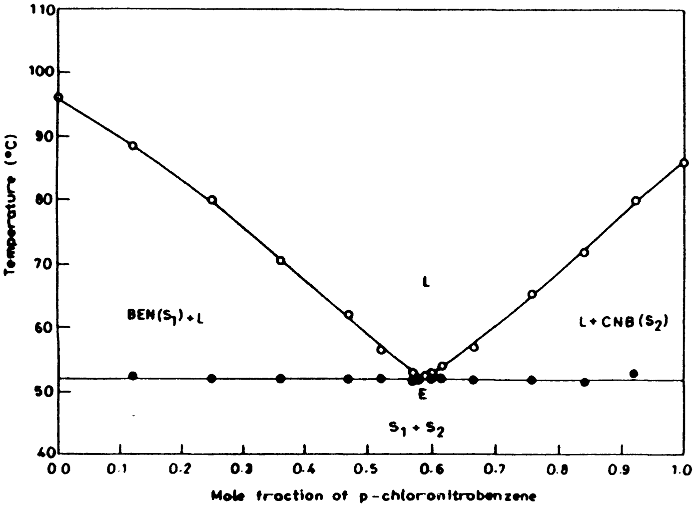

Fig. 3. Phase diagram of benzil-*p*-chloronitrobenzene: (i) • Thaw temperature, (ii) o Melting temperature

system and at this point the system is invariant. Above this temperature the system gives a homogeneous liquid and below this temperature it dissociates to give two solids according to the following equation:

$$L \rightarrow S_1 + S_2$$

When mole fraction of the second component increases beyond the eutectic composition, the melting point again rises till it reaches to the melting temperature of the pure component. At the eutectic temperature a liquid and two solid phases are in equilibrium. The phase diagram of BEN-NAP, BEN-BN and BEN-CNB systems are given in Figs 1–3 and the compositions and melting temperatures of the eutectics are reported in Table-1.

TABLE-1
MELTING POINT AND COMPOSITION OF PURE COMPONENTS AND THEIR EUTECTICS

System	Composition (mole fraction of benzil)	Melting point (°C)
Benzil-naphthalene:		
(i) Benzil	—	96.0
(ii) Naphthalene	—	83.0
(iii) Benzil-naphthalene eutectic	0.4075	54.0
Benzil-β-naphthol:		
(i) β-Naphthol	—	122.0
(ii) Benzil-β-Naphthol eutectic	0.5765	66.0
Benzil-*p*-chloronitrobenzene:		
(i) *p*-Chloronitrobenzene	—	86.0
(ii) Benzil-*p*-chloronitrobenzene eutectic	0.5862	52.0

Growth kinetics

The linear velocity of crystallization (v) of the pure components and the eutectics was determined at different undercoolings (ΔT) and the values are

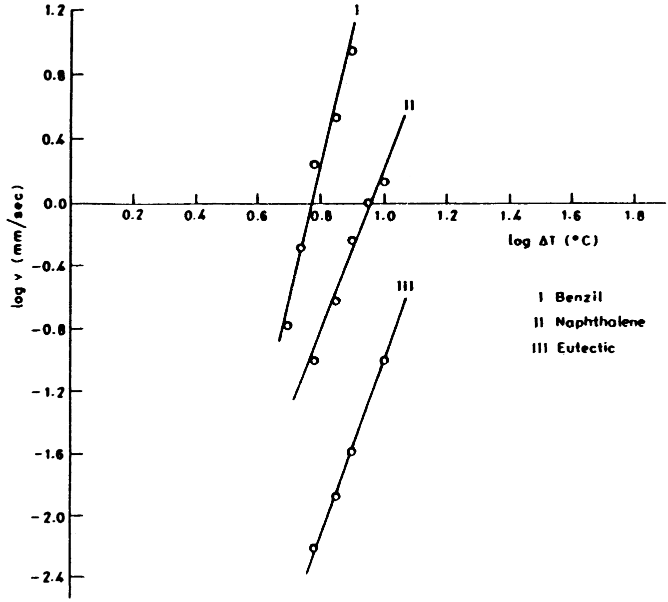

Fig. 4. Linear velocity of crystallization of benzil, naphthalene and their eutectic

reported in the form of linear plots in Figs. 4–6. The linear dependence of log v *vs* log (ΔT) plots suggests that the data obey the Hilling-Turnbull[20] equation given by

$$v = u(\Delta T)^n \tag{1}$$

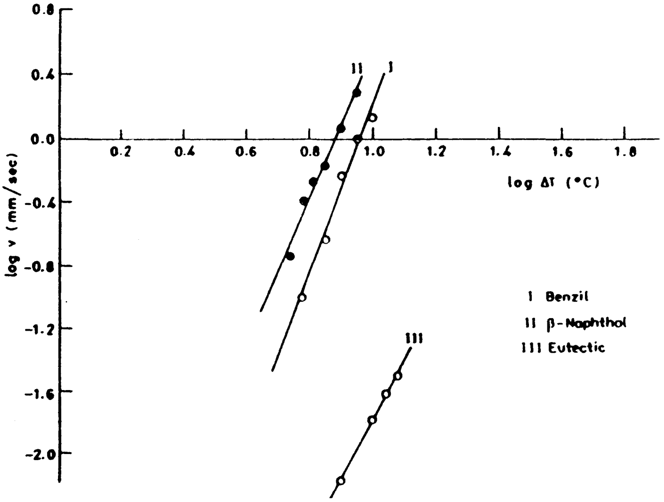

Fig. 5. Linear velocity of crystallization of benzil, β-naphthol and their eutectic

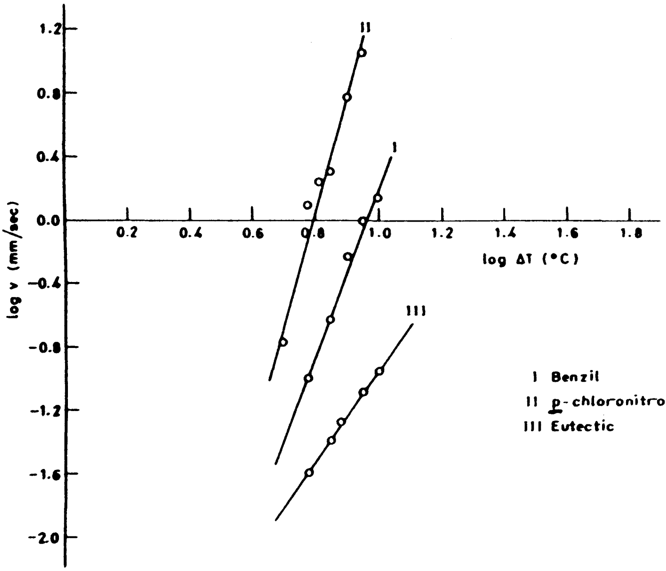

Fig. 6. Linear velocity of crystallization of benzil, *p*-chloronitrobenzene and their eutectic

where u and n are constants depending on the nature of solidification of the materials involved. Using linear plots the values of u and n were calculated and these values are given in Table-2. The basic criterion for the determination of growth mechanism[21] is the comparison of the temperature dependence of linear velocity of crystallization with the theoretically predicted equations. Normal growth generally occurs on the rough interface and for this there is direct proportionality between crystallization velocity and the undercooling. Lateral growth is facilitated by the presence of steps, jogs, bends etc. and under such condition the relationship for the spiral mechanism follows the parabolic law given by equation (1).

TABLE-2
VALUES OF u AND n

Materials	n	n
Benzil	5.3	8.3×10^{-6}
Naphthalene	7.5	4.0×10^{-7}
β-Naphthol	4.6	7.9×10^{-5}
p-chloronitrobenzene	7.0	2.8×10^{-6}
Benzil-naphthalene eutectic	5.7	2.8×10^{-7}
Benzil-β-naphthol eutectic	3.8	2.5×10^{-6}
Benzil-*p*-chloronitrobenzene	2.9	1.3×10^{-4}

The values of u give measure of growth rates. While in case of BEN-NAP and BEN-BN systems the value of u for the eutectc is less than that of the pure components, in case of BEN-CNB system the value of u for eutectic is more than that of either component. These results can be explained on the basis of the mechanism proposed by Winegard *et al.*[22] Eutectic solidification begins with the nucleation of one of the phases. When one phase nucleates, it rejects the other phase surrounding the nucleus and the other phase also nucleates. Now there are two possibilities. In the first possibility, the two nuclei may grow side-by-side if u for pure components is less than the value of u for the eutectic. On the other hand the eutectic may grow by alternate nucleation mechanism if u for the pure components is more than that of the eutectic. In the present article eutectics of BEN-NAP and BEN-BN systems grow by alternate nucleation mechanism while the eutectic of BEN-CNB system grows by the side-by-side growth of the two phases. In BEN-NAP and BEN-CNB systems, benzil with high melting point nucleates first followed by the nucleation of the second component. On the other hand, in BEN–NAP system β-naphthol nucleates first followed by the nucleation of benzil.

Thermochemistry

The phase transformation involves two steps, namely, nucleation and growth. The nucleation mechanism depends on the solid-liquid interfacial energy which can be calculated from the heats of fusion data. However, the growth step depends on the manner in which particles from the liquid phase are added at the solid-liquid interface, which is determined by its structure. The interface structure depends on the entropy of fusion of the material under investigation and also upon the thermal environment in which the crystal is growing. Thus, heats of fusion of pure components and eutectic are very important in understanding the mechanism of solidification. From the heats of fusion data, the entopy of fusion, interfacial energy, enthalpy of mixing, radius of critical nucleus and excess thermodynamic functions can be calculated.

Enthalpy of mixing and entropy of fusion

The enthalpy of fusion values of the pure components, and the eutectics determined experimentally, are repored in Table-3. If a eutectic is a simple mechanical mixture of two components involving neither heat of mixing nor any type of association in the melt, the heat of fusion may simply be given by the mixture law.[23]

$$(\Delta_f h)_e = x_1 \Delta_f h_1^o + x_2 \Delta_f h_2^o \qquad (2)$$

where x and $\Delta_f h$ are the mole fraction and heat of fusion, respectively, of the component indicated by the subscript. For the purpose of comparison the calculated values are also given in Table-3. When a solid eutectic melts, there is considerable possibility of association and heat mixing[24] ($\Delta_{mix}H$) which is the difference between the experimental and the calculated values of heat of fusion as also given in Table-3. Thermochemical studies[25] suggest that the structure of a binary eutectic melt depends on the sign and magnitude of the heat of mixing. As such, three types of structures are suggested; (i) quasi-eutectic for $\Delta_{mix}H > 0$, (ii) clustering of molecules for $\Delta_{mix}H < 0$, and (iii) molecular solution for $\Delta_{mix}H = 0$. The negative values of enthalpy of mixing in all the systems suggest clustering of molecules in the binary eutectic melts.

TABLE-3
HEAT OF FUSION, HEAT OF MIXING, ENTROPY OF FUSION, ROUGHNESS PARAMETER AND INTERFACIAL ENERGY

Materials	Heat of fusion ($kJ\ mol^{-1}$)	Heat of mixing ($kJ\ mol^{-1}$)	Entropy of fusion ($kJ\ mol^{-1}K^{-1}$)	Roughness parameter ($\Delta S_f/R$)	Interfacial energy ($ergs\ cm^{-2}$)
Benzil	23.8	—	64.5	7.8	33.7
Naphthalene	18.2	—	51.1	6.2	34.5
β-Naphthol	21.2	—	53.5	6.5	43.0
p-Chloronitrobenzene	18.5	—	51.5	6.2	35.7
Benzil-naphthalene euctectic	15.9	–4.6	48.6	5.9	34.1
Benzil-β-naphthol eutectic	15.2	–7.5	44.8	5.4	37.6
Benzil-*p*-chloronitrobenzene eutectic	18.2	–2.5	56.0	6.8	34.9

The entropy of fusion gives an idea about its role in melting of the pure components and the eutectics. It is calculated from the equation

$$\Delta_f S = \frac{\Delta_f H}{T} \tag{3}$$

where $\Delta_f H$ is the enthalpy of fusion and T is melting temperature. The values given in Table-3, being all positive, suggest that both factors, namely, energy and entropy, favour the melting process of the pure components and the eutectics.

Excess thermodynamic functions

The excess thermodynamic functions provide a quantitative measure of the deviation of the system from ideal behaviour. With a view to understanding the nature of interactions between the components forming the eutectic, some excess thermodynamic functions, such as free energy (g^E), enthalpy (h^E) and entropy (s^E) were calculated using the following equations:[26]

$$g^E = RT(x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l) \tag{4}$$

$$h^E = -RT\left(x_1 \frac{\delta \ln \gamma_1^l}{\delta T} + x_2 \frac{\delta \ln \gamma_2^l}{\delta T}\right) \tag{5}$$

$$s^E = -R\left(x_1 \ln \gamma_1^l + x_2 \ln \gamma_2^l + x_1 T \frac{\delta \ln \gamma_1^l}{\delta T} + x_2 \frac{\delta \ln \gamma_2^l}{\delta T}\right) \tag{6}$$

The activity coefficient, γ_i^l, of the component i in the eutectic melt was calculated using the relation

$$-\ln x_i^l \gamma_i^l = \frac{\Delta_f h_i^o}{R}(T^{-1} - T_i^{o\,-1}) \tag{7}$$

where x_i^l, $\Delta_f h_i^o$ and T_i^o are mole fraction, heat of fusion and melting temperatue of component i, respectively; R is the gas constant and T is the melting temperature of the eutectic. The values of excess thermodynamic functions are given in Table-4. The negative value of g^E suggests strong association between like molecules. While the positive values of g^E predicts[27] that molecular association between unlike molecules is stronger than that between like molecules. The values of h^E and s^E correspond to these g^E values and are a measure of excess enthalpy and excess entropy, respectively.

TABLE-4
EXCESS THERMODYNAMIC FUNCTIONS FOR EUTECTICS

Materials	g^E (J mol^{-1})	h^E (k J mol^{-1})	s^E (J mol^{-1} K^{-1})
Benzil-naphthalene eutectic	152.9	1.6	5.5
Benzil-β-naphthol eutectic	—473.6	—2.8	—6.9
Benzil-*p*-chloronitrobenzene eutectic	—377.1	—0.5	0.4

Interfacial energy and radius of critical nucleus

It is well known that the solid-liquid interfacial energy (σ) plays very important roles in the kinetics of nucleation process during phase transformaition. It is given by the expression,[28]

$$\sigma = \frac{C \cdot \Delta_f H}{(N)^{1/3} \cdot (V_m)^{2/3}} \tag{8}$$

where N is the Avogadro number, V_m is the molar volume and parameter C lies between 0.30 and 0.35. The calculated values of interfacial energy are given in Table-3. The melt contains a number of tiny particles, each containing a large number of molecules. If the size of a particle is smaller than the size of the critical nucleus, it is called embryo, and it does not give a stable nucleus for subsequent growth to take place. On the other hand, when the particle size corresponds to the size of the critical nucleus, it gives a stable nucleus for growth of a crystal. The radius of the critical nucleus (r*) is given[29] by

$$r^* = \frac{2\sigma T}{\Delta_f H \cdot \Delta T} \tag{9}$$

where T is the melting temperature, ΔT is the undercooling and $\Delta_f H$ is the enthalpy of fusion per unit volume. The radius of critical nucleus was calculated for pure components and the eutectics and the values are reported in Table-5. It can be inferred from the values given in the table that the radius of the critical nucleus decreases with the increase in the undercooling of melt. In fact there is a range of embryo sizes in the liquid at any temperature. Because of the increased amplitude of vibration at the higher temperature, the number of largest size embryo will be smaller.

Microstructure

The growth morphology[9, 30] developed by a eutectic system is governed by the growth characteristics of the individual constituent phases. They solidify with nonfaceted or faceted interfaces. This behaviour is related to the nature of the solid-liquid interface and can be predicted from their entropy of fusion data. Hunt

Fig. 7. Microstructure of eutectic of benzil-naphthalene × 600

and Jackson[31] predicted the structure of the solid-liquid interface of material in contact with its liquid using the α factor defined by the equation,

$$\alpha = \xi \frac{\Delta_f S}{R} \tag{10}$$

where ξ is crystallographic factor which is generally equal to or less than 1. If $\alpha > 2$, the solid-liquid interface is atomically smooth and the crystal develops a faceted morphology. If $\alpha < 2$, the solid-liquid interface is atomically rough and many sites are readily and continuously available to develop a non-faceted morphology. The values of α, given in Table-3, being more than, suggest faceted morphology.

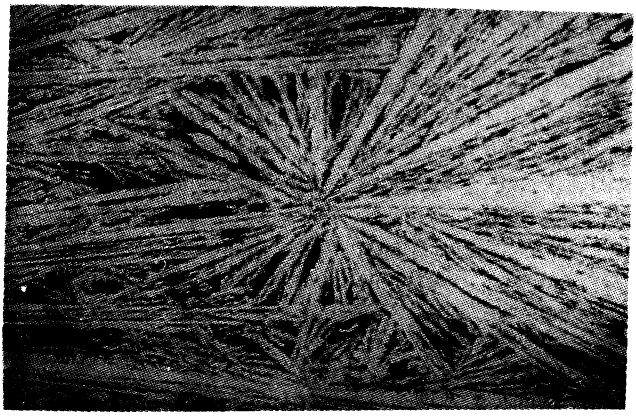

Fig. 8. Microstructure of eutectic of benzil-β-naphthol × 600

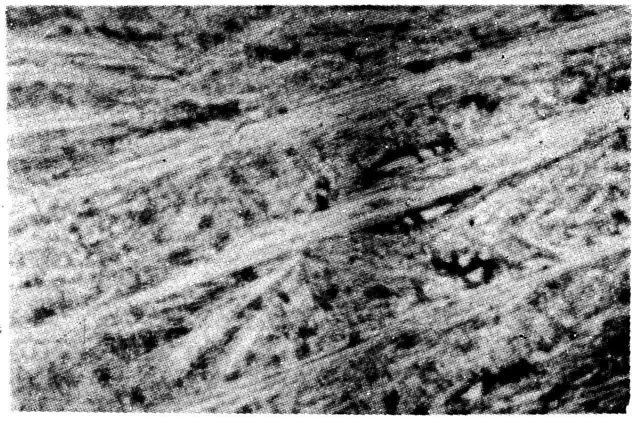

Fig. 9. Microstructure of eutectic of benzil-*p*-chloronitrobenzene × 600

Microstructures of eutectics BEN-NAP, BEN-BN and BEN-CNB systems are given in Figs. 7–9. Microstructure of eutectic of BEN-NAP system, given in

Fig. 7, shows feather type microstructure. This type of microstructure appears to grow by a screw dislocation but by a twin boundary. The micostructure of BEN-BN system (Fig. 8) shows a radial growth from the nucleation centre. The microstructure of BEN-CNB system is given in Fig. 9 where the second phase is embeded in the primary in the form of rod.

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REFERENCES

1. N.B. Singh and K.D. Dwivedi, *J. Sci. Ind. Res.*, **41**, 98 (1982).
2. W.F. Kaukler and D.O. Frazier, *J. Cryst. Growth*, **71**, 340 (1985).
3. U.S. Rai and K.D. Mandal, *Mol. Cryst. Liq. Cryst.*, **182**, 387 (1990).
4. R. Elliott, Cast Iron, Butterworths, London (1988).
5. J. Glazer, *Int. Mater. Rev.*, **40**, 65 (1995).
6. V.E. Kamper, *Russian Chem. Rev.*, **51**, 185 (1982).
7. D.M. Herlach, R.F. Cochrane, I. Egry, H.J. Fecht and A.L. Greer, *Int. Mater. Rev* , **38**, 273 (1993).
8. M.E. Glicksman, N.B. Singh and M. Chopra, *Manufacturing in Space*, **11**, 207 (1983).
9. V.V. Podolinsky, Y.N. Taran and V.G. Drykin, *J. Cryst. Growth*, **96**, 445 (1989).
10. R. Trivedi and W.Kurz, *Int. Mater. Rev.*, **39**, 49 (1994).
11. K.A. Jackson, *Materials Sci. Engg.*, **65**, 7 (1984).
12. R.P. Rastogi, D.P. Singh, N. Singh and N.B. Singh, *Mol. Cryst. Liq. Cryst.*, **73**, (1981).
13. H. Yasuda, I. Ohanaka, Y. Matsunga and Y. Shiohara, *J. Cryst. Growth*, **158**, 128 (1996).
14. U.S. Rai, O.P. Singh and N.B. Singh, *Can. J. Chem.*, **65**, 2639 (1987).
15. U.S. Rai and K.D. Mandal, *Bull. Chem. Soc. Jpn.*, **63**, 1496 (1990).
16. N.B. Singh and N.B. Singh, *Krist. Tech.*, **13**, 1175 (1978).
17. U.S. Rai and K.D. Mandal, *Thermochim. Acta*, **138**, 219 (1989).
18. J.W. Dodd and K.H. Tonge, in:B.T. Currel (Ed.), *Thermal Methods*, John Wiley and Sons (1987).
19. R.P. Rastogi and V.K. Rastogi, *J. Cryst. Growth*, **5**, 345 (1969).
20. W.B. Hilling and D. Turnbull, *J. Chem. Phys.*, **24**, 914 (1956).
21. D.A. Porter and K.E. Easterling, Phase Tansformation in Methods and Alloys, Van Nostrand Reinhold (U.K.) Co. Ltd. (1982).
22. W.C. Winegard, S. Mojka, B.M. Thall and B. Chalmers, *Can. J. Chem.*, **29**, 320 (1957).
23. U.S. Rai and Santhi George, *Thermochim. Acta*, **243**, 17 (1994).
24. U.S. Rai and H. Shekhar, *J. Thermal. Analy.*, **39**, 415 (1993).
25. Namwar Singh, N.B. Singh, U.S. Rai and O.P. Singh, *Thermochim. Acta*, **95**, 291 (1985).
26. U.S. Rai, O.P. Singh, N.P. Singh and N.B. Singh, *Thermochim. Acta*. **71**, 373 (1983).
27. J. Wisniak and A. Tamir, Mixing and Excess Thermodynamic Properties, Physical Science data, Elsevier Scientific Publishing Co., New York (1978).
28. U.S. Rai and H. Shekhar, *Cryst. Res. Technol.*, **29**, 551 (1994).
29. _________, *Mol. Cryst.. Liq. Cryst.*, **220**, 217 (1992).
30. U.S. Rai and Santhi George, *J. Mater. Sci.*, **27**, 721 (1992).
31. J.D. Hunt and K.A. Jackson, *Trans. Met. Soc. AMIE*, **236** (1966).

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