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Spherulitic growth of single (Gd & Pr) and mixed (Di) rare earth heptamolybdates in silica gels

V. HANGLOO, S. PANDITA, K. K. BAMZAI, P. N. KOTRU*
CGMR-Lab., Department of Physics & Electronics, University of Jammu, Jammu - 180 006, India
E-mail: pn_kotru@yahoo.com

N. SAHNI
Department of Geology, Panjab University, Chandigarh - 160 014, India

Single (Gd and Pr) and mixed rare earth (Di—a mixture of four rare earths La, Pr, Nd & Sm) heptamolybdates grow as platelet, multifacetted crystals and spherulites when corresponding rare earth chloride ions are made to react with ammonium paramolybdate. Various spherulitic formations are illustrated. It is shown that the spherulitic formations may be due to either fibres radially diverging from multiple nuclei or agglomeration of tiny crystallites orienting and accommodating themselves in a spherical space or intergrowth of multiple crystals which may include multiple twinning of interpenetrating type.

1. Introduction

Spherulites are polycrystalline aggregates. Their crystallization is one of the most interesting, exceptional and anomalous problems in the well-known theories of crystal growth. Comprehensive theory which can offer satisfactory explanation of the mechanism of formation of spherulites from different environments is still not formulated. High polymers [1, 2] are usually spherulitic. Gel growth leads to spherulitic crystallization in number of cases [3–9], because of which this technique of growth offers means of understanding spherulitic crystallization. The problems posed by crystallization leading to spherulitic morphology have excited renewed interest and are gaining some technological importance also. Inspite of several attempts having been made over the years to resolve these problems, the development of the subject has been fragmentary. As a consequence of this, it has been rendered impossible for the researchers of various periods to formulate a comprehensive theory which can explain the mechanism of crystallization on a unified basis, and in terms sufficiently general as to be applicable to spherulitic morphology and spherulite forming systems of all types known till date.

Spherulitic crystallization of various compounds have been reported by several workers; the spherulitic formation having been defined as the growth of radiating crystal fibres [10, 11]. Spherulitic formation is also reported in various glass systems [12–18], organic as well as inorganic compounds [19–30]. Spherulitic morphology is also assumed by several varieties of tungstates, phosphates & carbonates [11]. Crystallization of spherulitic formations have also been reported in a number of rare earth containing materials [31–34]. Formation of monodispersed Y-Ba-Cu-O superconductor spherulitic particles via sol-gel methods have also been reported [35]. The spherulitic morphology is also reported by Matsuno and Koishi [36] in the case of materials named as 3DSA and 3DSB. Based on the experimental results, several authors have tried to explain the phenomenon of spherulitic crystallization. Keith and Padden [37] have provided a phenomenological theory of spherulitic crystallization. According to them, high viscosity and presence of impurities are basic requirements for spherulitic crystal growth. According to Bolotov and Muravev [38] a spherulite grows from a single crystal nucleus, drawn out in a direction perpendicular to C-axis lying in the plane of the crystal, the circular shape arising due to surface tension forces acting on different faces. Spherulitic crystallization has also been explained to be as a result of lamellas or crystalline fibres growing and diverging radially from a common centre or a nucleus [39]. That the spherulitic morphology is due to fibres radially diverging from multiple nuclei and not from a centrally located common nucleus has been explained by Kotru *et al.* [40] and Anima Jain *et al.* [34].

Experiments leading to crystal growth of praseodymium, gadolinium and didymium molybdates, employing gel encapsulation method, using the system RCl_3-$(NH_4)_6Mo_7O_{24}$-NH_4NO_3-HNO_3-Na_2SiO_3 (where R = Pr, Gd & Di) are already reported [41–44]. In this paper, the results of spherulitic morphologies of single rare earth (Pr & Gd) and mixed (Di—a combination of four rare earths viz., La, Nd, Pr

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*Author to whom all correspondence should be addressed.

& Sm) rare earth heptamolybdates offering different modes of formations, are reported.

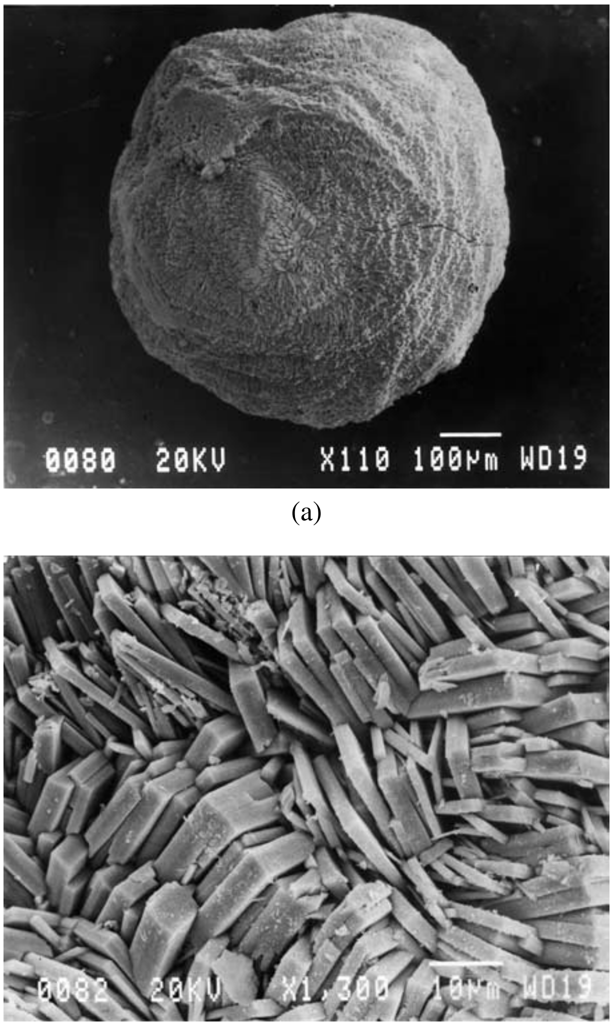
2. Experimental

Experiments on crystal growth of pure and mixed rare earth heptamolybdates are performed using the procedure as reported in the literature [41–43]. Table I is a summary of the crystallization conditions used in the growth of various spherulitic formations under discussion in this paper. Optical microscope (Neophot-2, Carl Zeiss, Germany) and Scanning electron microscope SEM (Jeol JMS-25 S and 6100 Japan made) are used to examine the outer and sectioned surfaces of the spherulites thus obtained. In order to look into the internal structure of spherulitic formation, the spherulites are cleaved with the help of a sharp glass knife. Prior to the SEM examination, the crystals are gold plated under vacuum, using ion sputter coating model JFC-1100.

3. Results and discussion

3.1. Gadolinium heptamolybdate spherulitic crystals

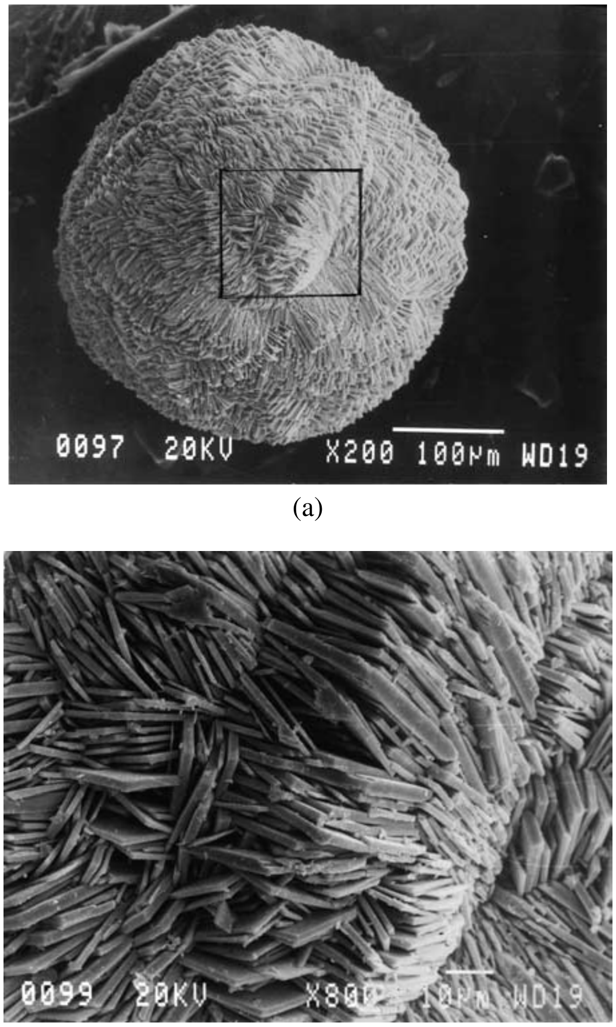
Layered type spherulitic formation of Gadolinium heptamolybdate is shown in Fig. 1a. The layers are clearly circular in shape when examined under a higher magnification. A small region of the surface of this spherulite, when examined under a higher magnification is as shown in Fig. 1b. It reveals that the circular layered structure is actually clustering of small crystallites in spherical envelope. Each tiny crystallite has well defined habit faces and is either a platelet like or a prismatic rod formation. An aggregate of crystallites spread all over the surface of a spherulitic formation is shown in Fig. 2a. That these crystallites collectively tend to orient themselves as to be in a spherical formation is revealed by Fig. 2b which shows a region somewhere within the inset of Fig. 2a at a higher magnification. Thus, the surface of each isolated spherulite is composed of tiny crystallites aggregated in a spherical formation. There are examples of clustering of such spherulites such as to stimulate a twinning process of interpenetrating type. Fig. 3 illustrates an agglomeration of several spherulites interpenetrating into each others formation. Fig. 4a offers an example of three spherulitic formations interpenetrating into each other. Their boundaries of interpenetration simulate the grain boundaries between three single crystals. That each individual spherulitic formation maintains its growth seems to be clear from



(a)

(b)

Figure 1 (a) Layered spherulitic formation of gadolinium heptamolybdate. (b) A region of Fig. 1a, at a higher magnification, reveals circular layered structures.



(a)

(b)

Figure 2 (a) Aggregate of gadolinium heptamolybdate crystallites spread over the surface of a spherulitic formation. (b) A region within the inset of Fig. (a) at a higher magnification showing crystallites collectively orienting themselves in a spherical formation.

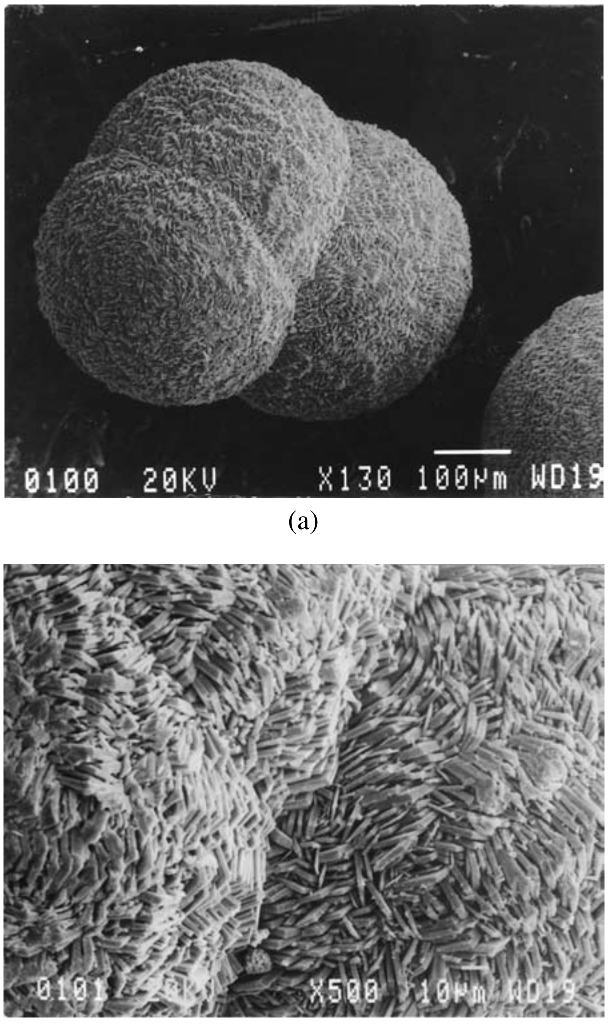
TABLE I Crystallization conditions of various forms of spherulites

Crystal type	Stoichiometric composition of crystals	Type of spherulitic structure	Growth medium	Crystal growth system	Gel content		Gel pH	Gel age (in hrs)	Gel molarity	Temp. (°C)	Growth time (in days)	Remarks
					UR*	LR*						
Type A. Whole spherulites												
GdHM	$Gd_2Mo_7O_{24}\cdot XH_2O$	Layered type spherulite (Fig. 1)	Silica gel	Single tube	1.0 M	0.03 M	4.5	72	0.5 M	35–40	45	Size of spherulite is 650 μm dia.
		Bunching of prismatic rod like tiny crystallites (Fig. 2)	Silica gel	Single tube	1.0 M	0.03 M	4.5	72	0.5 M	35–40	45	Spherulite size: 363.5 μm dia. Initially radiating fibers diverging from multiple nuclei lead to spherulitic formation (See under cleaved surface Part B). Subsequently, tiny crystallites spread all over and cover spherical surface.
		Intergrown spherulites (Figs 3 and 4)	Silica gel	Single tube	1.0 M	0.03 M	4.5	72	0.5 M	35–40	45	Twinning in spherulites. Size of the Intergrown spherulitic matter is ~669 μm.
PrHM	$Pr_2Mo_7O_{24}\cdot 40H_2O$	Intergrown multiple crystallites in a spherical envelope (Type A Figs 6 and 7)	Silica gel	Single tube	0.5 M	0.03 M	4.5	72	0.5 M	25–35	45	Size of spherulite of type A is 397.2 μm. Formation as a result of intergrowth of multiple crystals.
		Aggregate of crystallites oriented and accommodated in a spherical envelope (Type B Fig. 6)	Silica gel	Single tube	0.5 M	0.03 M	4.5	72	0.5 M	25–35	45	Size of spherulite of type B is 461 μm. Formation as a result of an aggregate of crystallites. Unlike, spherulite of Fig. 2, the aggregation of crystallites starts from the very beginning.
DiHM	$Di_2Mo_7O_{24}\cdot 40H_2O$	Multiple twinned structure (Fig. 9)	Silica gel	Single tube	0.5 M	0.03 M	4.5	72	0.5 M	25–35	45	Size of whole twinned structure is 158 μm.
Type B. Cleaved (sectioned) spherulitic surfaces												
GdHM	$Gd_2Mo_7O_{24}\cdot XH_2O$	Fibrous cleaved surface (Fig. 5)	Silica gel	Single tube	1.0 M	0.03 M	4. 5	72	0.5 M	35–40	45	Fibres diverging out radially from multiple nuclei dispersed within a small hollow space at the centre of the spherulitic formation. Spherulite size before sectioning is 594 μm dia.
PrHM	$Pr_2Mo_7O_{24}\cdot 40H_2O$	Crystal aggregates in a spherical envelope (Fig. 8)	Silica gel	Single tube	0.5 M	0.03 M	4. 5	72	0.5 M	25–35	45	Aggregate of crystallites (platelets with sharp corners and facets) bunched together to form a spherulite. Spherulite size before sectioning is 400 μm dia.
DiHM	$Di_2Mo_7O_{24}\cdot 40H_2O$	Crystal aggregates in a spherical envelope (Fig. 10)	Silica gel	Single tube	0.5 M	0.03 M	4. 5	72	0.5 M	25–35	45	Aggregate of crystallites (platelets with sharp corners and plane facets) bunched together resulting into spherulitic formation. Spherulite size before sectioning is 317 μm dia.

UR*: RCl_3 (R = Gd, Pr, Di); LR*: $(NH_4)_6Mo_7O_{24}$ with addition of $NH_4NO_3 + HNO_3$.

Figure 3 Agglomeration of spherulites of gadolinium heptamolybdate interpenetrating into each others formation.

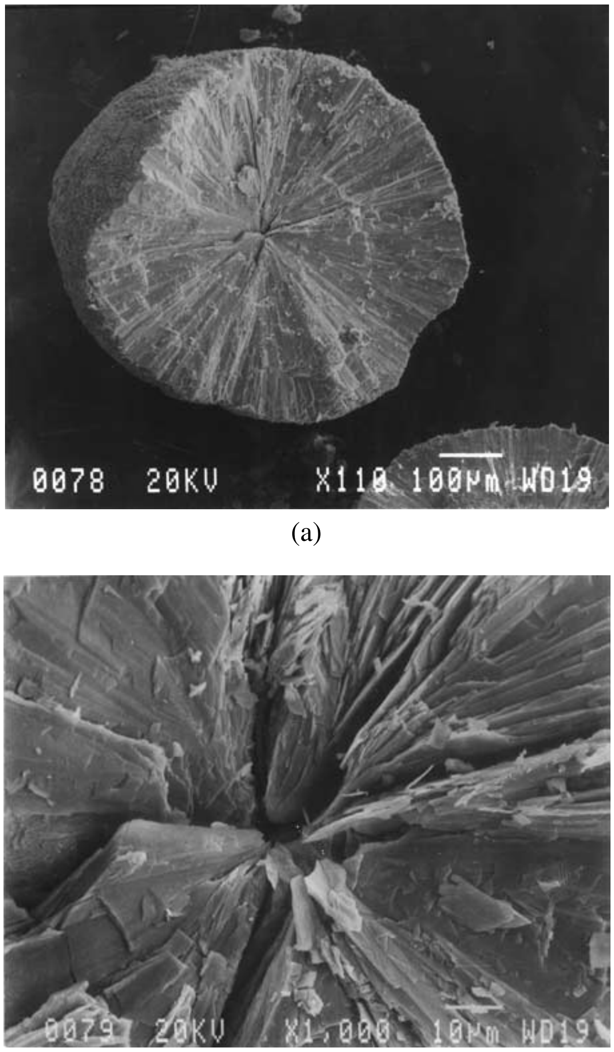
the trisection of the boundaries of Fig. 4a as shown at a higher magnification in Fig. 4b. The maintenance of orientation of crystallites in such a way as to maintain their belongingness to their own spherulitic formation is very apparent from this figure. The spherulitic formations reported here resemble with some of those reported earlier by Kotru *et al.* [40] and Jain *et al.* [34] for rare earth tartrates.



(a)

(b)

Figure 4 (a) Three spherulitic formations interpenetrating into each other. (b) The trisection of the boundaries of the three spherulites of Fig. 4(a) shown at a higher magnification.



(a)

(b)

Figure 5 (a) A cleaved section of gadolinium heptamolybdate spherulite showing crystal fibres diverging radially from the centre. (b) Central portion of Fig. (a) at a higher magnification revealing multiple nuclei generating radiating crystal fibres.

The internal structure of the spherulitic formation is different from what is reflected by its surface. Fig. 5a is a cleaved section of gadolinium heptamolybdate spherulite. The crystal fibres appear to be radially diverging from the centre. Fig. 5b shows the centre of the sectioned spherulite of Fig. 5a at a higher magnification. It clearly shows that the nucleus of radially diverging fibres is not common to all. The space at the centre is hollow. These are multiple nuclei dispersed within the central region wherefrom the crystal fibres originate and diverge radially, resulting into spherulitic formation. What is seen at the later stages of its development is the clustering of crystallites all over the surface of spherulitic formation which initially had resulted from diverging crystal fibres from multiple nuclei dispersed in a centrally located space. The tiny crystallites get nucleated all over the surface of the spherulitic formation covering its entire surface, giving to its outer surface a look of randomly oriented crystallites aggregated in a spherical envelope. The concept of splitting

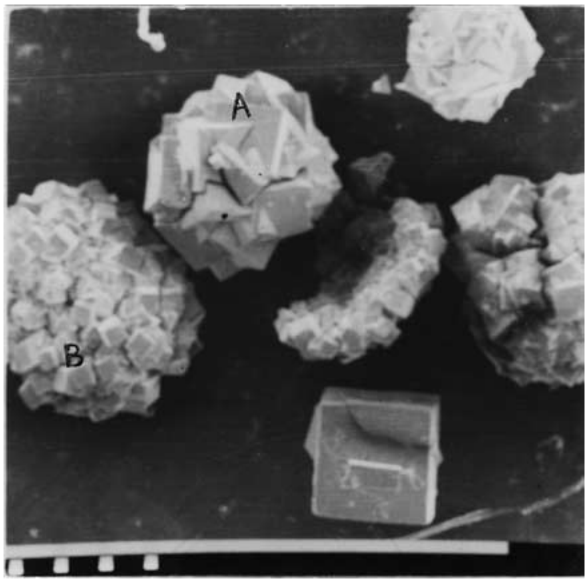


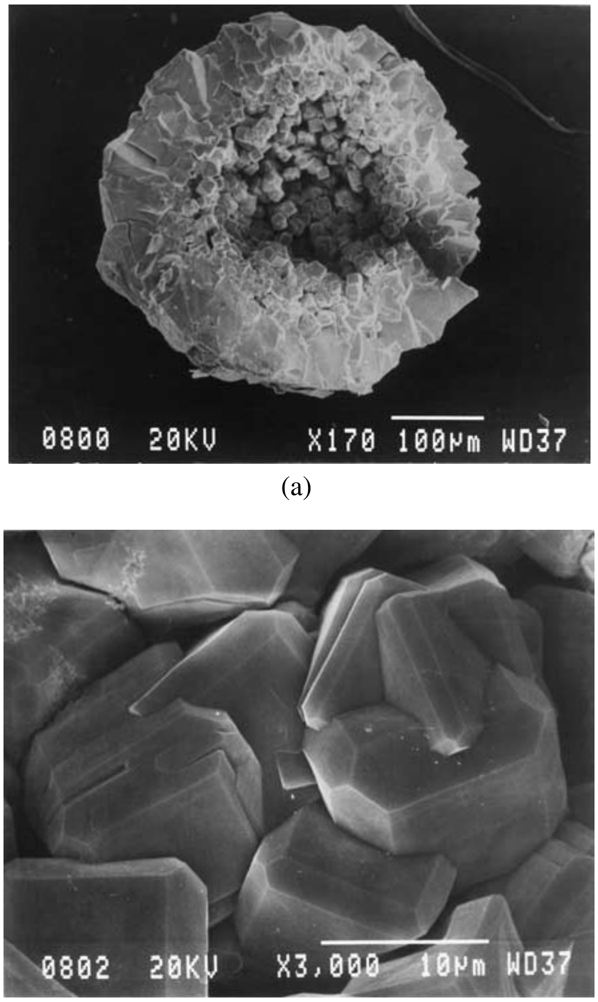
Figure 6 Crystals of praseodymium heptamolybdate revealing different morphologies. Notice two distinct spherulitic formations A & B.

of a single crystal nucleus [41] under the influence of stresses arising on crystallization, as a means of explaining the growth mechanism of a spherulitic formations, cannot be ruled out here as is also supported from what follows.

3.2. Praseodymium heptamolybdate spherulitic crystals

Praseodymium heptamolybdate grows both as a single crystal as well as a spherulite. The spherulitic formations in this case are different from what is reported in the case of Gadolinium heptamolybdate crystals as discussed above. Fig. 6 shows morphologies assumed by Praseodymium heptamolybdate crystals grown by gel technique. It includes distinctly different spherulitic formations (say type A and type B) and single crystals. One type of spherulitic formation owes its origin to multiple twinning (see A). A large number of crystals interpenetrate resulting into twinning, leading to what appears to be a spherulitic formation of the type A as shown in Fig. 7. Twinned structures giving the appearance of a spherulitic formation is observed in the case of fluorite [10]. So, one can attribute the spherulitic formation of the type A of Fig. 6 to crystal intergrowths. The second type of spherulite of Praseodymium heptamolybdate owes its origin to different mechanism of formation. Fig. 8a illustrates a cleaved section of the second type of spherulite (marked as B in Fig. 6). Unlike gadolinium heptamolybdate spherulites (Fig. 5a) here the spherulitic formation is not due to radially diverging crystal fibres from a centrally located nuclei, but is, in fact, an agglomeration of tiny crystallites accommodating themselves in a spherical envelope. This spherulitic formation is just a collection of randomly oriented crystallites arranging themselves in a spherical space, probably due to requirement of minimum volume. Each crystallite is a platelet with well defined faces as is shown, on a higher magnification, in Fig. 8b. It is a small region of the central portion in Fig. 8a shown at a higher magnification.

Figure 7 Interpenetrating multiple praseodymium heptamolybdate crystals leading to complex twinning and giving the appearance of spherulitic formation.



(a)

(b)

Figure 8 (a) Cleaved section of praseodymium heptamolybdate crystal of the type B of Fig. 6, showing randomly arranged separately nucleated crystallites within a spherical envelope. (b) A small region of Fig. (a), at a higher magnification, revealing that each separately nucleated crystallite is a platelet with well defined faces.

3.3. Mixed rare earths (Di) heptamolybdate crystals

Didymium is a mixture of La, Nd, Pr & Sm. Its crystal when grown in silica gel assume morphologies

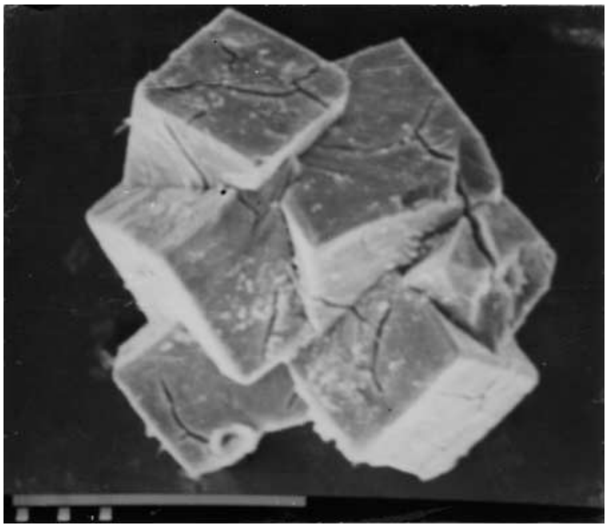
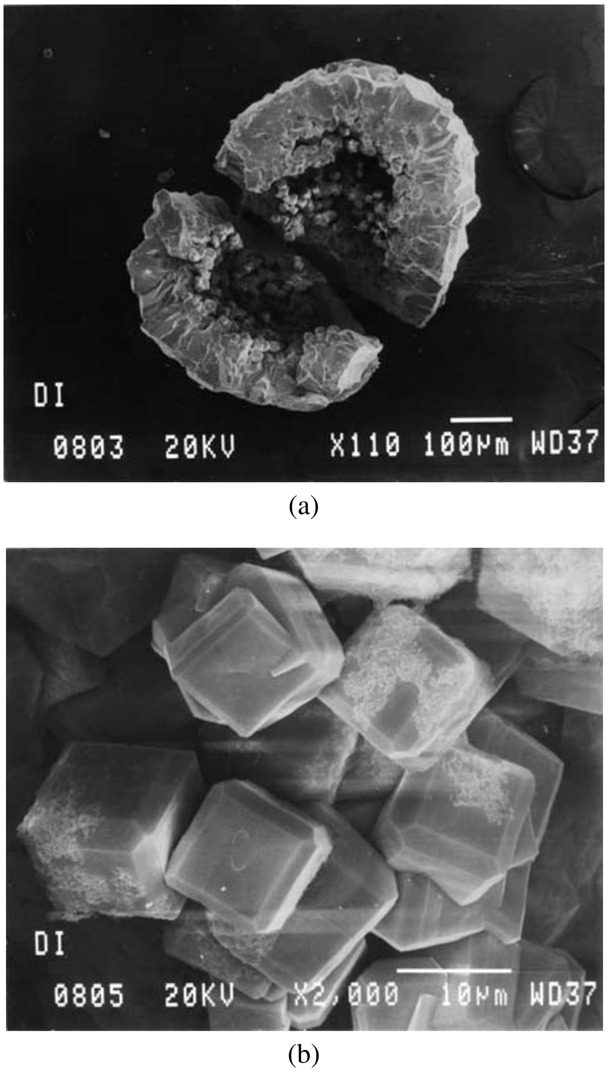


Figure 9 Intergrowth of several crystallites of didymium heptamolybdate—A case of multiple twinned structure.

that include platelets, cuboids, multifacetted crystals and spherulites. Twinned structures are not uncommon. Fig. 9 shows intergrowth of several crystals of Didymium heptamolybdate. Fig. 10a is a cleaved section of a spherulite. This spherulitic formation is very similar to what is exhibited by single rare earth (Praseodymium) heptamolybdate as described above and owes its origin to a mechanism similar to that. Unlike gadolinium heptamolybdate spherulites as discussed in Section 3.1, the origin of didymium heptamolybdate spherulites is not due to radially diverging crystal fibres from centrally nucleated multiple nuclei. The central portion of the cleaved section of Fig. 10 a is shown at a higher magnification in Fig. 10b. The crystallites are randomly oriented and each one of these is a platelet with well defined faces. So here too, the spherulites are a result of agglomeration of tiny crystallites orienting and accommodating themselves in a spherical envelope.



(a)

(b)

Figure 10 (a) Cleaved section of a didymium heptamolybdate spherulite revealing its internal structure. (b) Central portion of Fig. (a) at a higher magnification, showing that each crystallite platelet has well defined faces.

4. Conclusions

The observations made on as—grown surfaces and the cleaved sections of the spherulites of single rare earth (Gadolinium and Praseodymium) and mixed rare earths (Di—a mixture of La, Nd, Pr & Sm) heptamolybdates, as explained above, suggest that the spherulitic formations of crystalline materials may be due to variety of causes which could include the following:

1. Initially, the spherulitic formations may result due to crystal fibres radially diverging from multiple nuclei dispersed within the central region of the spherulite. Subsequently, it may be followed by nucleation and clustering of crystallites all over the surface of the spherulitic formation at a later stage of its growth and development. Example of this type is offered by Gadolinium heptamolybdates.
2. The spherulitic formation may also arise due to agglomeration of tiny crystallites orienting and accommodating themselves in a spherical space. The same process may continue till the cessation of crystal growth process. This process of spherulitic formation is suggested by single rare earth (Praseodymium) as well as mixed rare earth (Didymium) heptamolybdate spherulites.
3. The spherulitic formation may also owe its origin to multiple twinning/intergrowths of multiple crystallites. The evidence to this effect is offered by examples of Praseodymium heptamolybdate spherulites.

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References

1. C. W. BUNN and T. C. ALCOCK, *Trans. Faraday Sci.* **41** (1945) 317.
2. A. KELLER, *Polym. J. Sci.* **17** (1955) 291.
3. S. BHAT, P. N. KOTRU and M. L. KOUL, *Mater. Sci. Engg.* B **34** (1995) 138.
4. P. N. KOTRU and K. K. RAINA, *J. Mater. Sci. Lett.* **5** (1986) 760.
5. S. BHAT, P. N. KOTRU and M. L. KOUL, *J. Mater. Sci. Engg.* B **23** (1994) 73.

6. V. MANSOTRA, K. K. RAINA and P. N. KOTRU, *J. Mater. Sci.* **26** (1991) 3780.
7. A. JAIN, P. N. KOTRU and M. L. KOUL, *Mater. Chem. Phys.* **38** (1994) 332.
8. P. N. KOTRU, N. K. GUPTA, K. K. RAINA and I. B. SHARMA, *J. Mater. Sci.* **21** (1986) 83.
9. A. JAIN, P. N. KOTRU and M. L. KOUL, *J. Mater. Sci. Technol.* **12** (1996) 81.
10. E. S. DANA, "A Text Book of Mineralogy," 4th ed., Revised & Enlarged by W. E. Ford (Asia Publishing House, Calcutta, India, 1962) pp. 180, 329, 538.
11. J. W. MACAULEY and R. ROY, *Amer. Mineralogist* **59** (1974) 947.
12. M. H. LEWIS, J. METCHALF-JOHANSEN and P.S. BELL *J. Amer. Ceram. Soc.* **62** (1979) 278.
13. S. W. FRIEMAN, G. Y. ONODA and A. G. PINCUS, *ibid.* **55** (1972) 354.
14. M. H. LEWIS and G. SMITH, *J. Mater. Sci.* **11** (1976) 2015.
15. A. EISENBERG and A. TOBOLSKY, *J. Polymer. Sci.* **46** (1960) 19.
16. *Idem.*, *Ibid.* **61** (1962) 483.
17. R. C. KEEZER and M. W. BAILY *Mater. Res. Bull.* **2** (1967) 185.
18. M. S. CARR and K. N. SUBRAMANIAN, *J. Cryst. Growth* **60** (1982) 307.
19. S. L. SAMUELS and G. L. WIKES, *Amer. Chem. Soc. Div. Polymer. Chem.* **12** (1971) 694.
20. E. M. MACCHI, *J. Polym. Sci.* A **10** (1972) 45.
21. J. F. JACKSON, T. S. HSU and J.W. BRASCH, *ibid.* B **10** (1972) 207.
22. A. EWART *Mineral. Mag.* **38** (1971) 424.
23. P. J. BLAU, H. J. AXON and GOLDSTEIN, *J. Geophys. Res.* **67** (1973) 363.
24. R. C. EWING, *Science* **184** (1974) 561.
25. O. SOHNEL and J. W. MULLIN, *J. Cryst. Growth* **60** (1982) 239.
26. A. R. PATEL and S. K. ARORA, *ibid.* **18** (1973) 199.
27. Z. BLANK and W. BRENNER, *ibid.* **11** (1971) 255.
28. H. W. MORSE, C. H. WARREN and J. D. H. DONNEY, *Amer. J. Sci.* **23** (1932) 421.
29. H. W. MORSE and J. D. H. DONNEY, *Amer. Mineralogist* **21** (1932) 391.
30. K. NASSAU, A. S. COOPER, J. W. SCHIEVER and B. E. PRESCOTT, *J. Solid State Chem.* **8** (1973) 260.
31. P. N. KOTRU, N. K. GUPTA and K. K. RAINA, *J. Mater Sci.* **21** (1986) 90.
32. *Idem.*, *Cryst. Res. Technol.* **21** (1986) 15.
33. P. N. KOTRU, K. K. RAINA and N. K. GUPTA, *ibid.* **22** (1987) 177.
34. A. JAIN, A. K. RAZDAN and P. N. KOTRU, *Mater. Chem. Phys.* **45** (1996) 180.
35. R. SANJINES, R. K. THAMPI and J. KIWI, *J. Amer. Ceram. Soc.* **71** (1988) 512.
36. T. MATSUNO and M. KOSIHI, *J. Cryst. Growth* **71** (1985) 263.
37. H. D. KEITH and F. J. PADDAN, *J. Appl. Phys.* **34** (1953) 2409.
38. I. E. BOLOTOV and E. W. MURAVEV, "Growth and Imperfections of Metallic Crystals," edited by Orsienko D. E. (Consultants Bureau, New York, 1968) p. 76.
39. B. FELTON and C. A. GRIFFITHS, *J. Appl. Phys.* **39** (1968) 3663.
40. P. N. KOTRU and K. K. RAINA, *J. Cryst. Growth Lett.* **91** (1988) 221.
41. S. PANDITA, V. HANGLOO, K. K. BAMZAI, P. N. KOTRU and N. SAHNI, *Int. J. Inorg. Mater.* **3** (2001) 675.
42. V. HANGLOO, S. PANDITA, K. K. BAMZAI, P. N. KOTRU and N. SAHNI, *Cryst. Growth & Design* **3** (2003) 753.
43. S. PANDITA, R. TICKOO, K. K. BAMZAI, P. N. KOTRU and N. SAHNI, *Bull. Mater. Sci.* **24** (2001) 435.
44. L. S. PALATNIK and M. V. KOSOVICH, in "Rost Kristallov", Vol. 3 (Izd Akaf Nauk, SSSR, Moscow, 1961) [English Transl Growth of Cryst. Vol. 3 (Consultants Bureau, New York, 1962)].

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