Barium oxalate single crystals' cultivation and examinatio

.Dr.ARVIND PRASAD
[1] Resarch Scholar in Sage University, Indore 452020,
[2]Department of Physics, Shri. V. S. Naik, Arts, Commerce and Science College, Raver, Jalgaon 425508, (M.S.) India,
[3] Department of physics Sage University, Indore 452020
Email- bharatrraval93@gmail.com

Abstract :

The exploration of barium oxalate single crystal growth and analysis within agar gel has garnered considerable interest owing to their distinct characteristics and potential utility across diverse domains. This study endeavors to delve into the growth dynamics and crystal structure of barium oxalate crystals cultivated within agar gel. Agar gel provides an ideal substrate for crystal growth experimentation, facilitating a regulated milieu for crystal nucleation and expansion. Through modulation of barium and oxalate ion concentrations within the gel matrix, alongside variables like temperature and pH, precise and high-quality single crystals can be attained.

The experimental protocol entails the formulation of agar gel mediums with defined concentrations of barium and oxalate ions. Subsequently, controlled cooling or evaporation techniques are employed to prompt crystal formation. The resultant crystals undergo comprehensive characterization employing an array of analytical methods, including optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR). These methodologies enable examination of crystal morphology, size, and structural intricacies, as well as identification of functional groups within the crystals.

The acquired findings furnish insights into the growth mechanisms and crystallographic attributes of barium oxalate single crystals within agar gel. Furthermore, the impact of various growth parameters on crystal properties is scrutinized, facilitating optimization of growth conditions tailored to specific applications. Barium oxalate crystals hold promise in realms such as optoelectronics, catalysis, and sensing technologies, and comprehending their growth dynamics within agar gel paves the way for innovative crystal growth methodologies and applications.

Introduction :

Barium oxalate crystals have attracted considerable attention due to their unique properties and potential applications in various scientific and technological fields. These crystals exhibit excellent optical, electrical, and mechanical properties, making them suitable for use in optoelectronic devices, catalysis, and sensors. The growth of high-quality single crystals is essential for exploring and harnessing these properties effectively.

Various methods have been employed for the growth of barium oxalate crystals, including solution-based techniques such as slow evaporation, cooling crystallization, and gel-based methods. Among these, the use of agar gel as a growth medium offers distinct advantages. Agar gel, derived from seaweed, is a versatile material commonly used in biological and chemical research due to its unique physical and chemical properties.

Agar gel provides a stable and controlled environment for crystal growth experiments. Its porous structure allows for the diffusion of ions and molecules, facilitating the nucleation and growth of crystals. The gel medium also provides mechanical support, minimizing crystal damage during the growth process. Additionally, the ability to tune the gel composition and growth parameters enables control over crystal size, shape, and quality.

ISSN NO: 2249-3034

In this study, we focus on the growth of barium oxalate single crysta
characterization of their morphology and structure. By manipulating the c
and oxalate ions in the gel, along with other growth parameters such as temperature and pH, we aim to optimize the crystal growth conditions for obtaining high-quality single crystals.

Characterization of the grown crystals is performed using various analytical techniques. Optical microscopy allows for the observation of crystal morphology and size, providing initial insights into the growth behavior. Scanning electron microscopy (SEM) provides detailed information about the crystal surface topography. X-ray diffraction (XRD) analysis is employed to determine the crystal structure and orientation. Fourier-transform infrared spectroscopy (FTIR) is used to identify the presence of functional groups within the crystals, aiding in understanding their chemical composition.

The results obtained from this study will contribute to a deeper understanding of the growth mechanism and crystallographic aspects of barium oxalate single crystals in agar gel.

Experimental:

The growth of barium oxalate crystals in agar gel was conducted using high-quality chemicals, including acetic acid, barium chloride, oxalic acid, and agar-agar, all of which were of analytical grade.

Agar-agar gel, a widely used growth medium for crystal formation (Brezina and Harvan-kova 1991; Agrawal et al., 1999), was specifically employed in this study for both single and double diffusion techniques.

For the single diffusion method, a test tube measuring 25 cm in length and 2×5 cm in diameter was utilized. Initially, a hot aqueous agar gel solution was thoroughly mixed with oxalic acid solution and allowed to set in the test tube. Following the setting and aging of the gel, barium chloride solution was added to the prepared gel.

In the reverse scenario, the reactants were interchanged. Hot aqueous agar gel was mixed with barium chloride solution, and the resulting mixture was set in the test tube. After aging, the gel was supplemented with oxalic acid solution.

In the double diffusion technique, a U-shaped tube was filled to appropriate levels with hot agar-agar solution and left to set and age. One limb of the U tube was filled with oxalic acid solution, while the other limb was filled with barium chloride solution.

The chemical reaction responsible for crystal growth can be expressed as follows:

$$BaCl2 + H2C2O4 = BaC2O4 + 2HCl.$$

Result and discussion :

The optimal growth conditions for barium oxalate crystals are provided in Table 1, outlining the key parameters for successful crystal formation.

ISSN NO: 2249-3034

In the single diffusion method, dendritic and spherulitic growth patter
a few days. **Figure 1** illustrates the conical growth of barium oxalate c
showcases prismatic platy-shaped transparent crystals formed at the interstitial regions and spherulitic growth within the gel when the reactants were reversed in the single diffusion process. Additionally, **Figure 3** exhibits high-quality transparent crystals alongside spherulite crystals.

Several factors, such as reactant concentration, gel pH, solvent impurities, and gel setting time, significantly influence the growth rate. In the presence of a steady concentration gradient, the growth rate stabilizes, promoting the growth of spherulite crystals. However, when growth occurs slowly along one direction, plate-like crystals are formed. Conversely, rapid growth in a specific direction leads to the development of elongated crystals, such as conical crystals.

Table 1. Optimal Growth Conditions for Barium Oxalate Crystals.

Conditions	Single diffusion	
% of gel	1.5	
Concentration of barium chloride	1 M	
Concentration of oxalic acid	1 M	
Gel setting period	3 days	
Gel aging	40 h	
Period of growth	30 days	
Temperature	Room temp.	
Quality	Transparent	Size
17 ′4 ′2, 4 ′3 ′2 and 4 mm diameter		

ISSN NO: 2249-3034

Figure 1. Conical shaped barium crystals

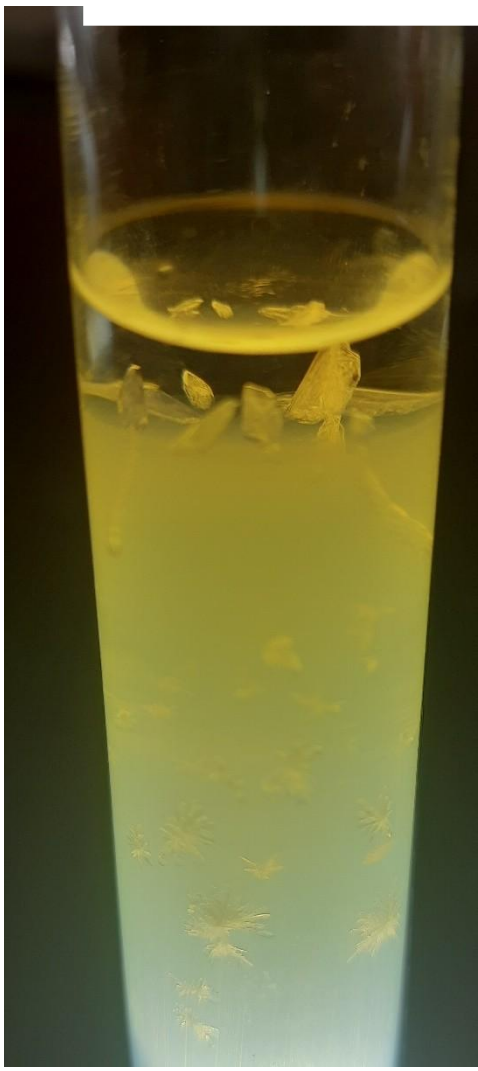
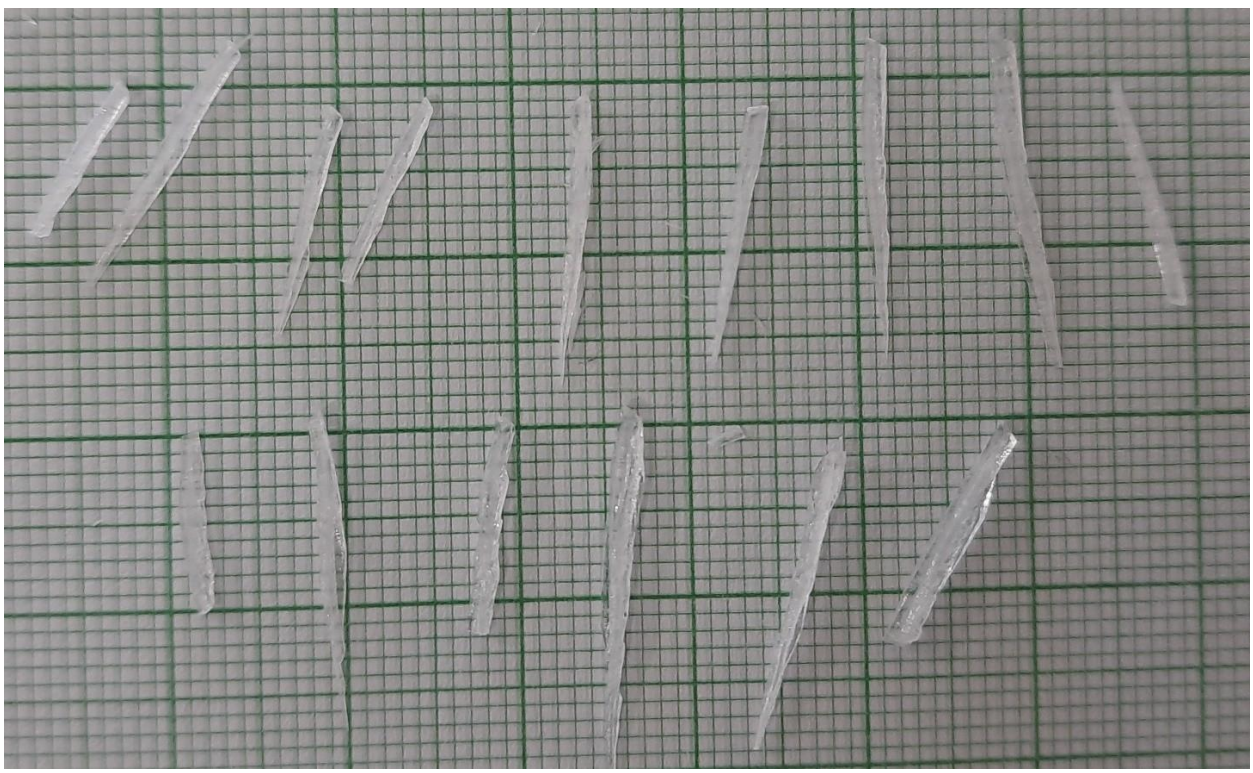


Figure 2. Prismatic platy shaped transparent crystals at the interstitial and spherulites inside the gel.



ISSN NO: 2249-3034

Figure 3. - Some good quality transparent as well as spherulite crystals.

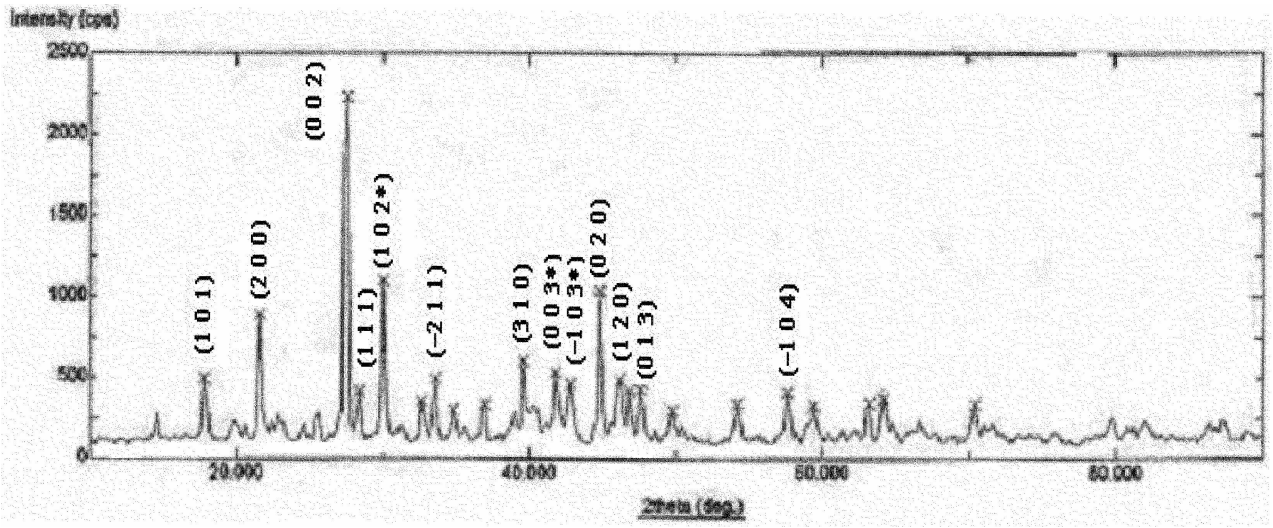


Figure 4. X-ray diffractogram of barium oxalate

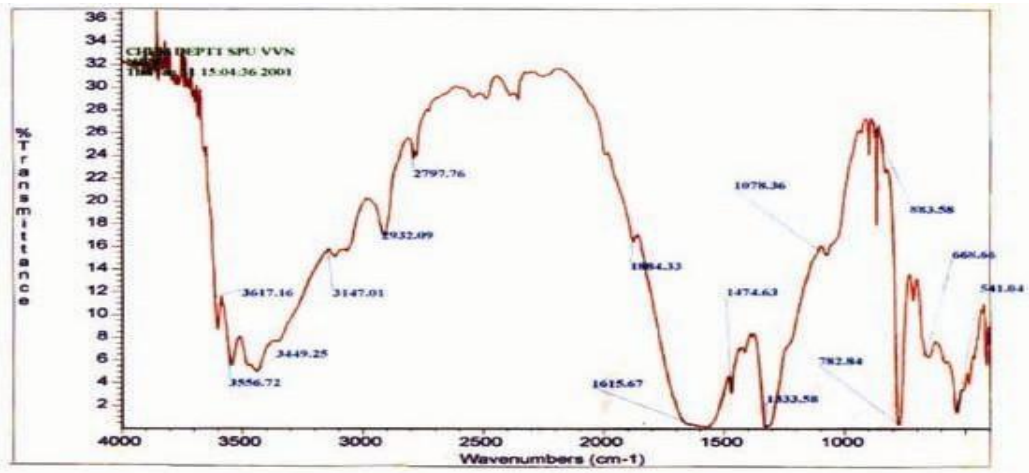


Figure 5. Infrared spectra (IR) of barium oxalate.

The growth mechanism of spherulites:

They are observed in the crystallization process of various substances, particularly those composed of large molecules such as polymers. Spherulites possess a distinctive characteristic where one of the crystallographic axes does not align with the direction of the molecule chains present along the radius of the spherulite (Sheftal, 1968).

The formation of spherulite shapes can be effectively explained using a model that visualizes a sheet of paper crumpled into folds, with the edges being compressed toward the center. This compression results in the crystal adopting a spherical shape (Sheftal, 1968). This model provides a satisfactory explanation for the observed morphology of spherulites.

Characterization :

X-ray Diffraction :

X-ray powder diffractograms of barium oxalate were obtained using a Miniflex model, Rigaku, with CuKa radiation and a scanning speed of 10°/min. The diffractograms were recorded, and Figure 4 displays the X-ray diffractogram of barium oxalate.

To determine the d-values for different *h k l* planes, a computer program called POWD (Interactive Powder Diffraction Data Interpretation and Indexing Program, Version 2.2) was utilized. The program calculated the corresponding 'd' values, which were then compared to the reported values. It was found that the calculated 'd' values matched the reported values, indicating agreement between the experimental and theoretical data. The calculated unit cell parameters are presented in Table 2.

Table 2. Calculated unit cell parameters

Parameters	**Barium oxalates**
System	*Monoclinic (P)*
a	8.2326 Å
b	4.0358 Å
c	6.4606 Å
β	92.329 Å
V	215.70 Å^3

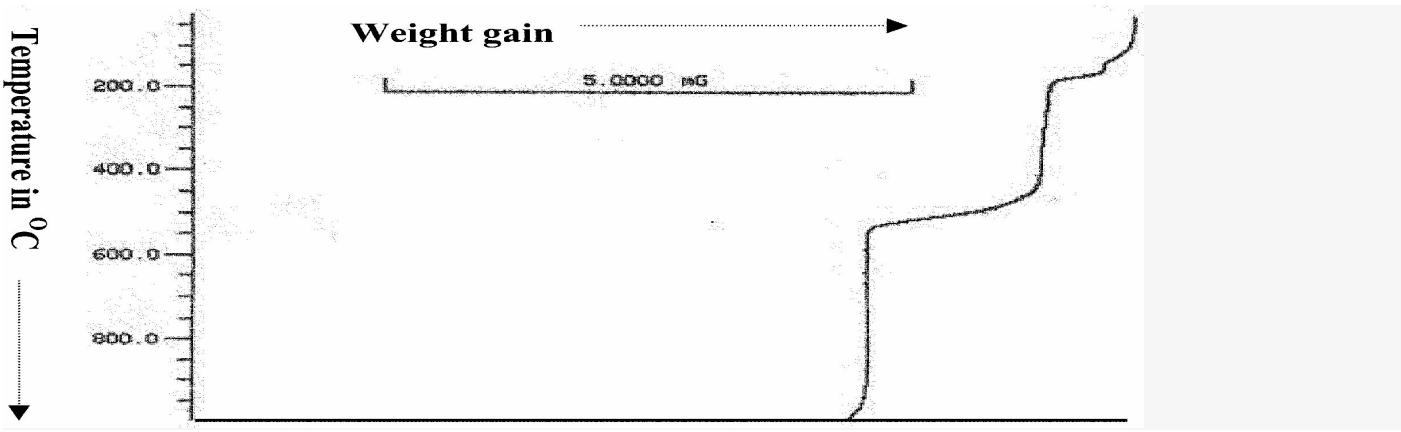


Figure 6. Thermogravimetric analysis (TGA) of barium oxalate.

Infrared spectra :

The infrared (IR) absorption spectrum of barium oxalate crystals **(Figure 5)** reveals distinct features. A prominent broad and intense peak is observed at 3556.72 cm^{-1}, which can be

ISSN NO: 2249-3034

attributed to the asymmetric and symmetric stretching vibrations Additionally, a peak at 1615.67 cm^{-1} corresponds to the bending vit indicating the presence of water molecules within the crystal lattice, indicating the presence of water of crystallization.

Another sharp peak at 782.84 cm^{-1} can be attributed to the metal-oxygen bond. This peak signifies the interaction between the barium ions and oxygen atoms in the crystal structure of barium oxalate.

Thermal analysis:

The TGA (Thermogravimetric Analysis) and DTA (Differential Thermal Analysis) of the grown barium oxalate crystals were performed using the Mettler TA4000 system at the National Chemical Laboratory in Pune.

The TGA curves **(Figure 6)** indicate that the compound remains stable up to a temperature of 55°C. Between 54°C and 141°C, there is a 2.1% weight loss, which is likely attributed to the loss of moisture. In the temperature range of 142.5°C to 217.1°C, a 3.77% weight loss occurs, which can be attributed to the dehydration of 0.5 water molecules present in the crystal structure. No further weight loss is observed up to 408.5°C, indicating complete dehydration of barium oxalate.

From 408.5°C to 556°C, an 11.601% weight loss is observed, suggesting the loss of CO (carbon monoxide). The compound remains stable up to 991°C and then starts to decompose. This decomposition may be due to the loss of CO2 (carbon dioxide). The thermal behavior of barium oxalate can be explained using the following scheme (Raju et al., 1998):

$BaC_2O_4 \cdot 0.5H_2O \quad BaC_2O_4 + 0.5H_2O$

$BaC_2O_4 \quad BaCO_3 + CO$

$BaCO_3 \quad BaO + CO_2$

The weight loss observed in the grown sample is further supported by DTA analysis **(Figure 7)** conducted at the respective temperatures.

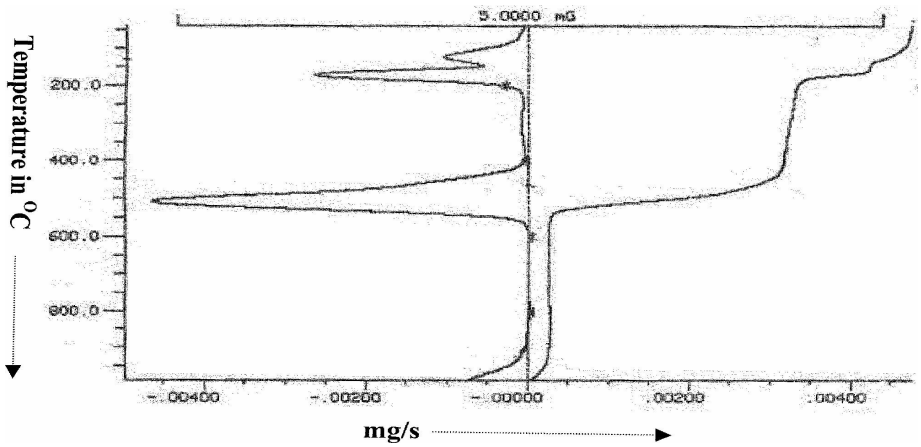


Figure 8. Thermal analysis (DTA/TGA) of barium oxalate.

Conclusion :

Based on the aforementioned studies, the following observations were made:

(I) The gel growth technique is found to be suitable for the growth of barium oxalate crystals.

(II) The growth mechanisms exhibited variations in the case of single diffusion with respect to molarity of solution.

(III) XRD results, particularly the 'd' values, exhibited a match with the standard JCPDS data.

(IV) Analysis of characteristic peaks obtained through IR spectroscopy indicated the presence of metal-oxygen bonds.

(V) Dehydration of the crystal resulted in the loss of 0.5 water molecules at temperatures ranging from 142.7°C to 217.3°C (endothermic). Additionally, the evolution of CO occurred between 408.7°C and 558°C (exothermic), followed by the release of CO2 at 992°C (exothermic). Beyond 992°C, stable residual barium oxide was obtained.

References :

1. *Agrawal B P, Chauhan K M and Bhadbhade M M 1999 Indian J. Pure & Appl. Phys.* ***37*** *395*
2. *Armington A F and O'Cornnar J J 1968 J. Cryst. Growth* ***3/4*** *367*
3. *Arora S K 1981 Prog. Crystal Growth Charact.* ***4*** *345*
4. *Arora S K and Tony Abraham 1981 Indian J. Pure & Appl.Phys.* ***19*** *199*
5. *Bangera Kasthuri V and Mohan Rao P 1992 Bull. Mater. Sci.* ***15*** *339*
6. *Barkley J R, Brixner L H and Hogan E M 1971 IEEE symposium on the application of ferroelectrics (New York: York Town Heights)*
7. *Barkley J R, Brixner L H, Hogan E M and Waring R K 1972 J. Ferroelectrics* ***3*** *191*
8. *Brezina B and Harvankova M 1991 Mater. Res. Bull.* ***87*** *537 Caillaud F, Baumard J F and Smith A 1988 Mater. Res. Bull.* ***23*** *1273*
9. *Dennis J and Henisch H K 1967 J. Electrochem. Soc.(USA)* ***114*** *263*
10. *Ittyachen M A and Kurien K V 1979 J. Cryst. Growth* ***47*** *743 Jayakumari Isac, Raju K S and Ittyachen M A 1995 Bull. Ma-ter. Sci.* ***19*** *495*
11. *Joshi M S and Trivedi S G 1970 Kryst. Und Technol.* ***15*** *1131 Joshi M S, Mohan Rao P and Antoni A V 1981 Bull. Mater. Sci.* ***2*** *127*
12. *Pactor A 1977 Krist. & Technol.* ***12*** *729*
13. *Prasad N V, Prasad G, Bhimasankaram T, Suryanarayana S V and Kumar G S 1996 Bull. Mater. Sci.* ***19*** *639*
14. *Raju K S, Varughese John and Ittyachen M A 1998 Bull. Mater.Sci.* ***21*** *375*
15. *Ranadive D, Blank Z, Brenner W and Okamoto Y 1969 Nature* ***223*** *829*
16. *Sapriel J and Vacher R 1977 J. Appl. Phys.* ***48*** *1191*
17. *Sheftal N N 1968 Growth of crystals (New York: ConsultantsBureau)*
18. *Sushma Bhat, Kotru P N and Raju K S 1995 Curr. Sci.* ***69*** *607*
19. *P V DALAL* and K B SARAF Bull. Mater. Sci., Vol. 29, No. 5, October 2006, pp. 421–425.Indian Academy of Sciences*