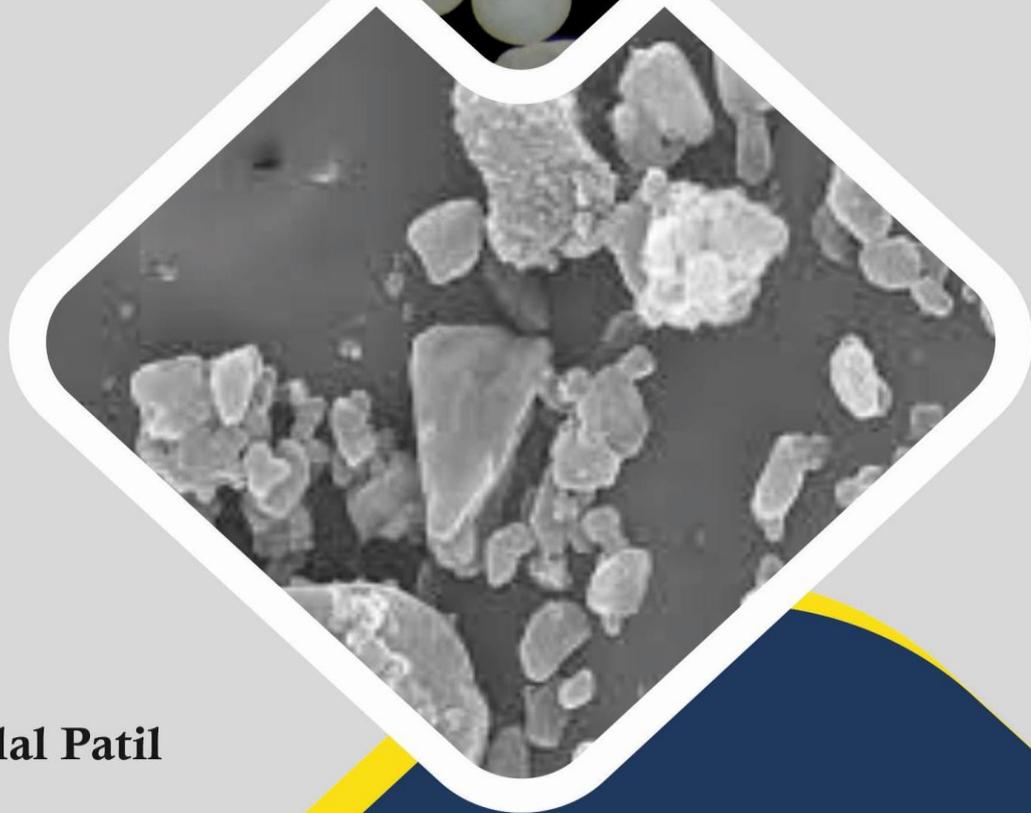


Characterization of Gel Grown Tartrate Crystals of Lanthanide Series Elements



Dr. Hiralal Motilal Patil

Kripa Drishti Publications, Pune.

CHARACTERIZATION OF GEL GROWN TARTRATE CRYSTALS OF LANTHANIDE SERIES ELEMENTS

Dr. Hiralal Motilal Patil

Associate Professor,
Department of Physics,
J.E.S'S Arts, Science and Commerce College,
Nandurbar, M.S, India.

Kripa-Drishti Publications, Pune.

Book Title: **Characterization of Gel Grown Tartrate Crystals
of Lanthanide Series Elements**

Author By: **Dr. Hiralal Motilal Patil**

Price: ₹499

1st Edition

ISBN: 978-81-976840-1-2



Published: **August 2024**

Publisher:



Kripa-Drishti Publications

A/ 503, Poorva Height, SNO 148/1A/1/1A,
Sus Road, Pashan- 411021, Pune, Maharashtra, India.

Mob: +91-8007068686

Email: editor@kdpublications.in

Web: <https://www.kdpublications.in>

© Copyright Dr. Hiralal Motilal Patil

All Rights Reserved. No part of this publication can be stored in any retrieval system or reproduced in any form or by any means without the prior written permission of the publisher. Any person who does any unauthorized act in relation to this publication may be liable to criminal prosecution and civil claims for damages. [The responsibility for the facts stated, conclusions reached, etc., is entirely that of the author. The publisher is not responsible for them, whatsoever.]

PREFACE

Crystals have ever fascinated mankind. The growth of crystals occurs either in nature or artificially in a laboratory. The Mother Nature has grown a variety of crystals in the crust of earth, which are mainly diamond and other precious stones. Systematic study of the growth and properties of crystals is covered under the subject "Crystal Growth." Today, the growth of crystals does not remain the phenomena only occurring in nature, but it has become a well advanced as well as widely used laboratory technique. There always has been a requirement of good quality crystals for various applications. In this regard the crystals having specific properties can be treated as the backbone of today's technological development. This led the investigators and scientists to concentrate on the developments of new variety of defect-free crystals of high degree of purity. Earlier crystal growth techniques were considered an art rather than science. Theories are now available on the growth of crystals so that crystal growth is no more an art. A variety of experimental techniques are developed and modified to such a level as to grow tailor made crystals for specific applications.

This book reports the detailed study on various physical properties of gel grown tartrate crystals of lanthanide series elements. Materials in the form of tartrate compounds deserves special attention because of their many interesting physical properties such as dielectric, piezoelectric, ferroelectric and optical second harmonic generation. The rare earth compounds have attracted considerable attention on account of their luminescent and magnetic properties. Among the rare earth compounds lanthanum, cerium and neodymium tartrate crystals were selected because of their promising technical applications in optics and magnetism. Beside this the lack of work on the growth of these materials prompted the initiation of this work.

This book is a comprehensive account of the characterization of lanthanum tartrate, cerium tartrate and neodymium tartrate crystals. It contains the observations and results of the characterization of lanthanum tartrate, cerium tartrate and neodymium tartrate crystals.

The scope of the book is straight forward and designed in five chapters.

Chapter 1 contains a brief note on the experimental techniques employed in the study. They include XRD, FTIR, SEM, EDAX, UV-spectroscopy, thermal analysis, surface characterization.

Chapter 2 deals with characterization of lanthanum tartrate crystals. All observations and findings are correlated to the theories. This chapter also presents the details of the systematic study of the characterization of the crystals. Characterization of the grown crystals has been done using different techniques. The minute surface details are examined using a recently developed technique, the scanning electron microscopy (SEM). X-ray analysis gives the nature of the crystallinity of the crystals and the cell parameters have been evaluated. The FT-IR spectroscopy and thermal studies (TGA, DTA, DTG, DSC) studies throw light to the functional group and molecular (chemical) formula of the crystals. The thermal analysis results obtained are discussed and it confirms the molecular formula. The percentage of incorporation of different rare earth ions were determined by energy dispersive X-ray analysis (EDAX). UV-vis spectroscopy results are discussed in detail. Pore size, Surface area, pore volume are obtained from surface characterization technique.

Chapter 3 gives a detailed account of the characterization of gel grown cerium tartrate crystals.

Chapter 4 covers the characterization of neodymium tartrate crystals in detail.

Chapter 5 devoted to the summary and comparative study of characterization of this gel grown crystals.

H.M. Patil

Dedicated To

My parents

For

Their Inspiration,

Their Warmth,

But Mostly

For

Their Ethics

Acknowledgement

I wish to express my deep sense of gratitudes to **Dr. Dilip. S. Bhavasar**, Department of electronics, Pratap College, Amalner, whose deep interest and inspiring guidance throughout the course of this investigation made this work possible.

I am greatly indebted to the **Hon. President Smt. Shobhatai D. More, Vice President Dr. Vikrant D. More and Secretary Dr. Abhjit D. More** of Jijamata Education Society for their constant motivation.

My special gratitudes are to **Dr. K.D. Girase**, S.V.S. Arts, Science and Commerce College Dondaicha and **Dr. D.K. Sawant** for constant encouragement throughout the course of the work. My sincere thanks are to **Dr. V. R. Borane, Mr. D.V. Sonawane, Dr. B. R. Shinde, Mr. A. K. Zodge, Mr. P. B. Wagh and Mr. C. V. Nandre.**

I am thankful to the Principal and Head of the physics Department, Pratap College, Amalner for providing facilities for present work. I am also thankful to former Principal **Dr. D. L. Kulkarni** and Principal **Dr. S. V. Deore**, Jijamata Education Society's Arts, Science and Commerce College, Nandurbar for giving permission to do this work.

I extend my special thanks to **Dr. A. H. Jobanputra**, Head Department of Microbiology for her helpful suggestions.

I owe special appreciations to my ever-co-operating wife **Jayashree**, my daughter **Rashmi** and son **Venu** for their encouragement in my research work. Good wishes of my family members are appreciated.

Finally, I thank the staff members of teaching and nonteaching of Pratap College, Amalner and J.E.S.'s Arts, Science and Commerce College, Nandurbar for their co-operation throughout this work.

Finally, I would like to thank all the people who assisted directly or indirectly for the success of this work.

H. M. PATIL

Abstract

Pure crystals of lanthanum tartrate, cerium tartrate and neodymium tartrate were grown by the diffusion of aqueous solutions of lanthanum chloride, cerium chloride and neodymium chloride as an upper reactant into the set gel embedded with tartaric acid. The single diffusion gel growth technique was employed for the growth of these crystals. The growth conditions were optimized by varying various parameters such as gel density, pH, gel setting time, aging of the gel, concentration of the reactants and temperature. Crystals of various dimensions and morphologies were obtained. Most of them were platelet, acicular and spherulites in shape.

The as grown crystals were characterized by various characterization techniques. The surface morphology of the spherulites grown is illustrated by scanning electron microscopy. The X-ray powder diffraction studies were carried to find out lattice parameters, grain size and texture coefficient. The X-ray powder diffraction studies reveal that all these crystals are polycrystalline. FTIR spectra for these crystals show all the bands expected from metal tartrate with water of hydration. It is seen from the band assignment that each metal atom is coordinated with one $-OH$ and one carboxylic group from a tartrate molecule.

The thermal behaviour of the grown material was studied using TGA, DTA, DTG and DSC. The thermal stability and decomposition pattern of the grown crystals was established. Thermogravimetric analysis supports the correctness of the suggested chemical formula of the grown crystals. The percentage weight loss calculations from the thermogram were supplemented by EDAX and FTIR. The decomposition pattern of these crystals is reported to be typical of a hydrated metal tartrate with the rare earth oxides as the stable residue.

The energy dispersive X-ray analyses (EDAX) establish the presence of heavy rare earth elements qualitatively and to a good extent quantitatively. In addition, the optical characteristics were studied by UV-visible spectral studies. Surface area, pore size and pore volume analysis of powder sample was carried out using automated gas sorption system. The findings of these techniques of characterization are in good agreement with those reported in the literature. The implications are discussed.

Abbreviations

LaT	Lanthanum tartrate
CeT	Cerium Tartrate
NdT	Neodymium Tartrate
TG	Thermogravimetric
TGA	Thermogravimetric analysis
DTA	Differential thermal analysis
DTG	Derivative Thermogravimetric / Differential scanning calorimetry
DSC	Differential scanning calorimetry
UV-vis	Ultraviolet-visible spectroscopy
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscope
NLO	Nonlinear Optics
KDP	Potassium di-hydrogen phosphate
DKDP	potassium di-deuterium phosphate
TGS	tri-glycine sulphate
KAP	potassium acid phthalate
LAP	Lithium Arginine Phosphate
SMS	Sodium Metasilicate
RHT	Rubidium hydrogen tartrate
CHPD	Calcium Hydrogen Phosphate Dihydrate
SHP	Strontium Hydrogen Phosphate
(BHP)	Barium Hydrogen Phosphate (BHP)
FT-I R	Fourier Transform Infrared
CCD	Charge-Coupled Device
DH	Dollimore-Heal
BJH	Barrett, Joyner and Halenda
DFT	Density Functional Theory
t-plot	Statistical thickness method
DR	Dubinin-Radushkevich
BET	Brunauer, Emmett and Teller

INDEX

Chapter 1: Experimental Techniques and Methodologies.....	1
1.1 Introduction:.....	1
1.2 X-ray Diffraction Technique:.....	2
1.3 Infrared Spectroscopy:.....	6
1.4 Thermo-analytical Techniques:.....	9
1.4.1 Thermogravimetric Analysis (TGA):.....	9
1.4.2 Differential Thermogravimetric Analysis (DTG):.....	10
1.4.3 Differential Thermal Analysis (DTA):.....	10
1.4.4 Differential Scanning Calorimetry (DSC):.....	12
1.5 Ultraviolet-Visible Spectroscopy (UV-Vis):	12
1.6 Scanning Electron Microscopy (SEM):.....	17
1.7 Energy Dispersive Analysis of X-rays (EDAX):	20
1.8 Surface Area and Pore Size Analysis:	22
1.9 References:.....	25
Chapter 2: Characterization of Gel Grown Lanthanum Tartrate Crystals ...	27
2.1 Introduction:.....	27
2.2 Scanning Electron Microscopy:	27
2.3 XRD Analysis of Lanthanum Tartrate:	29
2.4 FT-IR Absorption Studies of Lanthanum Tartrate Crystals:	33
2.5 UV-Vis Absorption Spectroscopy:.....	36
2.6 Energy Dispersive X-Ray Analysis (EDAX) Of Lanthanum Tartrate	38
2.7 Thermal Analysis of Gel Grown Lanthanum Tartrate Crystals:	39
2.8 Surface Characterization of Lanthanum Tartrate Crystals:	47
2.9 Conclusions:.....	52
2.10 References:.....	53
Chapter 3: Characterization of Gel Grown Cerium Tartrate Crystals	55
3.1 Introduction:.....	55
3.2 Scanning Electron Microscopy:	56
3.3 XRD Analysis of Cerium Tartrate:	60
3.3.1 Determination of Grain Size from XRD Spectra:.....	60
3.3.2 Texture Coefficient:	61

3.4 FT-IR Absorption Studies of Cerium Tartrate Crystals:	63
3.5 UV-Vis absorption Spectroscopy:	65
3.6 Energy Dispersive X-Ray Analysis of Cerium Tartrate Crystals:	66
3.7 Thermal Analysis of Gel Grown Cerium Tartrate Crystals:	68
3.8 Surface Characterization of Cerium Tartrate Crystals:	75
3.9 Conclusions:	79
3.10 References:	80

Chapter 4: Characterization of Gel Grown Neodymium Tartrate Crystals.. 82

4.1 Introduction:	82
4.2 Scanning Electron Microscopy:	83
4.3 XRD Analysis of Neodymium Tartrate:	85
4.4 FT-IR Analysis of Neodymium Tartrate Crystals:	88
4.5 UV-Vis Absorption Spectroscopy:	90
4.6 Energy dispersive X-ray analysis of neodymium tartrate Crystals:	91
4.7 Thermal Analysis of Gel Grown Neodymium Tartrate Crystals:	93
4.8 Surface Characterization of Neodymium Tartrate Crystals:	99
4.9 Conclusions:	104
4.10 References:	105

Chapter 5: Summary and Comparative Study on Characterization 107

5.1 Summary on Characterization:	107
5.2 Comparative Study on Characterization:	109
5.2.1 Comparison of X-ray Analysis:	109
5.2.2 Comparison of EDAX:	111
5.2.3 Comparison of FTIR:	112
5.2.4 Comparison of Thermal Analysis:	113
5.2.5 Comparison of UV Analysis:	114
5.2.6 Comparison of Surface Analysis:	114
5.3 References:	115

List of Figures

	Figures Name	Page No.
Figure 1.1:	Simplified Sketch of X-Ray Diffractometer	5
Figure 1.2:	Rigaku Miniflex Diffractometer in The Laboratory	6
Figure 1.3:	Internal Mechanism of Rigaku Diffractometer	6
Figure 1.4:	FT-IR Spectrophotometer in The Laboratory	8
Figure 1.5:	Block Diagram of a Modern Thermo-Gravimetric Analysis Instrument	10
Figure 1.6:	Differential Thermal Analysis Apparatus	11
Figure 1.7:	Differential Scanning Calorimetry Apparatus	12
Figure 1.8:	Diagram of a Single-Beam UV-Vis Spectrophotometer	15
Figure 1.9:	A Simple Double Beam Spectrophotometer.	15
Figure 1.10:	Schematic Diagram of an SEM	19
Figure 1.11:	A Typical SEM Instrument, Showing the Electron Column, Sample Chamber, EDS Detector, Electronics Console, And Visual Display Monitors.	20
Figure 1.12:	Element Identification Based on Electron Transfer from Higher Energy Shell to Lower Energy Shell	21
Figure 1.13:	A Section of One Greatly Enlarged Particle of a Solid	24
Figure 1.14:	The Monolayer of Adsorbed Molecules; Typically, 15-20% Saturation	24
Figure 1.15:	The multilayer capillary condensation stage approximately 70% saturation	24
Figure 1.16:	Total Pore Volume Filling; Approximately 100% Saturation	25
Figure 2.1:	Scanning Electron Micrograph of Lanthanum Tartrate Crystals at Magnification 1000x	28
Figure 2.2:	Scanning Electron Micrograph of Lanthanum Tartrate Crystals at Magnification 5000x	29
Figure 2.3:	Scanning Electron Micrograph of Lanthanum Tartrate Crystals at Magnification 10000x	29
Figure 2.4:	X-ray diffractogram of lanthanum tartrate	32
Figure 2.5:	FT-IR Spectrum of Lanthanum Tartrate Crystals Grown in Silica Gel	36
Figure 2.6:	UV-Vis Spectra of Lanthanum Tartrate Crystal	37
Figure 2.7:	The EDAX Pattern of Lanthanum Tartarte Crystals	38
Figure 2.8:	TG and DTA Curve of Lanthanum Tartrate	43
Figure 2.9:	TG and DTG Curve of Lanthanum Tartrate Crystals	44

	Figures Name	Page No.
Figure 2.10:	DSC Curve of Lanthanum Tartrate Crystals	46
Figure 2.11:	Structure of lanthanum tartrate	47
Figure 2.12:	Adsorption / Desorption Isotherm for Lanthanum Tartrate	49
Figure 2.13:	BJH Desorption Dv(log d)	49
Figure 2.14:	DFT differential pore volume distribution	50
Figure 2.15:	DFT Histogram	50
Figure 3.1:	Scanning Electron Micrograph Depicting a Spherulites of Cerium Tartarte Crystals at Magnification 1000xsize of The Spherulites = 9.02um	57
Figure 3.2:	Scanning Electron Micrograph Depicting a Spherulites of Cerium Tartarte Crystals at Magnification 2500xSize of the Spherulites = 9.33um	57
Figure 3.3:	Scanning Electron Micrograph Depicting a Spherulite of Cerium Tartarte Crystals at Magnification 5000x.	58
Figure 3.4:	Scanning Electron Micrograph Depicting a Spherulite of Cerium Tartarte Crystals at Magnification 12000xsize of The Spherulites = 10.13um Average size of the spherulites = 9.49um	58
Figure 3.5:	Enlarged view of regions A, B, C, D, E, F, of the inset of Figure 3.3.	59
Figure 3.6:	X-ray Diffractogram of Cerium Tartrate	62
Figure 3.7:	FT-IR Spectrum of Cerium Tartrate Crystals Grown in Silica Gel.	65
Figure 3.8:	UV-Vis Spectra of Cerium Tartrate Crystal	66
Figure 3.9:	EDAX spectrum of neodymium tartrate	67
Figure 3.10:	TG and DTA Curve of Cerium Tartrate	70
Figure 3.11:	TG and DTG curve of cerium tartrate	71
Figure 3.12:	DSC Curve of cerium tartrate crystals	72
Figure 3.13:	Structure of Cerium Tartrate	74
Figure 3.14:	Adsorption / Desorption Isotherm for cerium tartrate	76
Figure 3.15:	Pore Size Distribution by BJH Method	76
Figure 3.16:	Pore Size Distribution by DFT method	77
Figure 3.17:	Volume Histogram by DFT Method	77
Figure 4.1:	Scanning Electron Micrograph of Neodymium Tartrate Crystals at Magnification 2500x	84
Figure 4.2:	Scanning Electron Micrograph of Neodymium Tartrate Crystals at Magnification 5000x	84

	Figures Name	Page No.
Figure 4.3:	Scanning Electron Micrograph of Neodymium Tartrate Crystals at Magnification 10000x	85
Figure 4.4:	X-ray Diffractogram of Neodymium Tartrate	87
Figure 4.5:	FT-IR Spectrum of Neodymium Tartrate Crystals Grown in Silica Gel	90
Figure 4.6:	UV-Vis Spectra of Neodymium Tartrate Crystal	91
Figure 4.7:	EDAX Spectrum of Neodymium Tartrate	92
Figure 4.8:	TG and DTA Curve of Neodymium Tartrate	94
Figure 4.9:	TG and DTG Curve of Neodymium Tartrate Crystals	94
Figure 4.10:	DSC Curve of Neodymium Tartrate Crystals	98
Figure 4.11:	Structure of Neodymium Tartrate	99
Figure 4.12:	Adsorption / Desorption Isotherm for Neodymium Tartrate	101
Figure 4.13:	Pore Size Distribution by BJH Method	101
Figure 4.14:	Pore Size Distribution by DFT Method	102
Figure 4.15:	DFT Histogram	102

List of Tables

Table Name	Page No.
Table 1.1: Applications of powder diffraction	4
Table 2.1: Powder X-ray diffraction data for lanthanum tartrate	32
Table 2.2: FT-IR Band Assignment	35
Table 2.3: Quantitative EDAX Results of La Tartrate	39
Table 2.4: Result of decomposition process of $\text{Ce}_2(\text{C}_4\text{H}_4\text{O}_6) \cdot 6\text{H}_2\text{O}$	43
Table 2.5: DTA data of lanthanum tartrate crystals	44
Table 2.6: DTG data of lanthanum tartrate crystals	45
Table 2.7: DSC data of lanthanum tartrate crystals	45
Table 3.1: Powder X-ray diffraction data for cerium tartrate	62
Table 3.2: FT-IR Band assignment	64
Table 3.3: Quantitative EDAX Results of Ce Tartrate.	67
Table 3.4: TGA Data	70
Table 3.5: DTA Data	71
Table 3.6: DTG data of cerium tartrate crystals	72
Table 3.7: DSC data of Cerium tartrate crystals	73
Table 4.1: Powder X-ray diffraction data for neodymium tartrate	88
Table 4.2: Assignment of some selected FT-IR bands of neodymium tartrate hydrate	89
Table 4.3: Quantitative EDAX Results of Nd Tartrate	93
Table 4.4: Result of decomposition process of $\text{Nd}_2(\text{C}_4\text{H}_4\text{O}_6) \cdot 7\text{H}_2\text{O}$	95
Table 4.5: DTA Data of Neodymium Tartrate	95
Table 4.6: DSC Data of Neodymium Tartrate	98
Table 5.1: Comparison of crystallographic parameters	109
Table 5.2: Crystallographic data of other tartrates	110
Table 5.3: Comparative EDAX data	112
Table 5.4: The UV transparency cutoff limits	114
Table 5.5: Surface area/Pore volume/Pore size comparison data	114

ABOUT THE BOOK

This book is intended for use as reference book for undergraduate, postgraduate and research scholars as well as the beginners who desire to work in the field of characterization of crystals grown by gel method. The book provides a complete and comprehensive material on various characterization techniques. The subject matter is divided into five parts in simple and lucid language. Easy to understand most of the difficult and intricate topics. Book provides detailed study on the characterization of gel grown Lanthanum Tartrate, Cerium Tartrate and Neodymium Tartrate crystals.

ABOUT THE AUTHOR



Dr. Hiralal Motilal Patil graduated from prestigious Pratap College, Amalner affiliated to Poona University, Pune in 1987 with First Class. He passed his M.Sc. degree examination in Physics from M.J. College, Jalgaon affiliated to Poona University in 1989 with First Class. He obtained M.Phil. Degree from Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon (Formerly known as North Maharashtra University,

Jalgaon) in 1997 and now he holds a Ph.D. degree in Physics from a prestigious Kavayitri Bahinabai Chaudhari North Maharashtra University, Jalgaon and has conducted research at renowned institutions. He has 34 years of teaching experience at undergraduate level. Presently he is working as an Associate Professor at renowned Jijamata Education Society's Arts, Science and Commerce College, Nandurbar. He has authored one Text Book for undergraduate students. Dr. Hiralal Motilal Patil is a renowned researcher and scholar in the field of materials science and crystallography. He has made significant contributions to the development of novel crystal growth techniques, including the gel method. Their research focuses on understanding the properties and applications of gel-grown crystals, with a particular emphasis on thermal properties. Dr. Hiralal Motilal Patil has published numerous papers in esteemed scientific journals and has presented their work at various national and international conferences. He is actively involved in the scientific community; continue to advance the field of crystal growth by gel method through his innovative research.



Kripa-Drishti Publications

A-503 Poorva Heights, Pashan-Sus Road, Near Sai Chowk,

Pune – 411021, Maharashtra, India.

Mob: +91 8007068686

Email: editor@kdpublishations.in

Web: <https://www.kdpublishations.in>

Price: ₹ 499

ISBN: 978-81-976840-1-2



9 788197 684012