DEVELOPMENT OF RARE-EARTH FREE PERMANENT MAGNETS WITH IMPROVED MAGNETIC PROPERTIES

Thesis submitted in partial fulfillment

for the Award of Degree

DOCTOR OF PHILOSOPHY

By

AKANKSHA GUPTA

DEPARTMENT OF CERAMIC ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI – 221005

INDIA

18031007 **2022**

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय

INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

CERTIFICATE

It is certified that the work contained in the thesis titled **"Development of Rare-Earth Free Permanent Magnets with Improved Magnetic Properties"** by "**AKANKSHA GUPTA**" has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. Degree.

Pradip Kumar Roy

Dr. Pradip Kumar Roy
(Supervisor)

Dr. Pradip Kumar Roy
Associate Professor
Department of Ceramic Engineering,
Indian Institute of Tecnology (I.I.T) (BHU),
Banaras Hindu University, Varanasi-221005
Uttar Pradesh (U.P.), INDIA

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय

IIT INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

DECLARATION BY THE CANDIDATE

I, **AKANKSHA GUPTA**, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of **DR. PRADIP KUMAR ROY** from July, 2018 to November, 2022 at the Department of Ceramic Engineering, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

Date : November 10, 2022

Place: IIT (BHU), Varanasi

Akanksha Gupta

AKANKSHA GUPTA

CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

Pradip Kumar Roy

Dr. Pradip Kumar Roy
(Supervisor)

Dr. Pradip Kumar Roy
Associate Professor
Department of Ceramic Engineering,
Indian Institute of Tecnology (I.I.T) (BHU),
Banaras Hindu University, Varanasi-221005
Uttar Pradesh (U.P.), INDIA

Prof. Vinay Kumar Singh
(Head of Department)

HEAD/ विभागाध्यक्ष
Department of Ceramic Engineering
सिरामिक अभियान्त्रिकी विभाग
Indian Institute of Technology (B.H.U.)
भारतीय प्रोद्योगिकी संस्थान (का०हि०वि०वि०)
Varanasi-221005/ वाराणसी-221005

भारतीय प्रौद्योगिकी संस्थान
काशी हिन्दू विश्वविद्यालय

INDIAN INSTITUTE OF TECHNOLOGY
BANARAS HINDU UNIVERSITY

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis : *Development of Rare-Earth Free Permanent Magnets with Improved Magnetic Properties*

Name of the Student : *Akanksha Gupta*

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University), Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the Doctor of Philosophy.

Date : November 10, 2022

Place: IIT (BHU), Varanasi

Akanksha Gupta

AKANKSHA GUPTA

Note: *However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notice are indicated*

Dedicated to My Grandfather

Late Mr. Moti Narayan

&

My Beloved Family

ACKNOWLEDGEMENTS

"We should not give up and we should not allow the problem to defeat us"- *Dr. A.P.J. Abdul Kalam. This line expresses the journey of doctoral life, which is full of challenges and difficulties. Life is nothing without experience, and I am fortunate to possess a wonderful journey at IIT (BHU). I get the direct and indirect support of many people around me to accomplish this journey successfully. It is my immense pleasure to get the mammoth opportunity to thank those people to whom I will be grateful forever.*

At the very beginning, I would like to express my thankfulness to Mahamana Pandit Madan Mohan Malviya, founder of BHU, for his contribution to the education and IIT (BHU), Varanasi, where I have spent a precious time of my life. This place provided me with many learnings of life and its beautiful campus gave me a delightful environment to positively carry out my research work.

I wish to express my sincere gratitude and respect to my research supervisor Dr. Pradip Kumar Roy, Department of Ceramic Engineering, IIT (BHU), for giving me the opportunity to work under his esteemed guidance. I must appreciate him for providing me the prospects to think, work, and express my research work by keeping faith in my capabilities. Moreover, his valuable insights on various technical ideas and his colossal experience in the magnetic material field helped me to sort out research problems that arose in the experimentations.

I am highly grateful to my doctoral committee members, Dr. Mohammad Imteyaz Ahmad and Dr. Shravan Kumar Mishra, for their valuable suggestions and feedback to improve my research work from various perspectives. I express my sincere gratitude to the present Head of Department (HoD), Ceramic Engineering, Prof. Vinay Kumar Singh and former HoDs, Prof. Devendra Kumar, Prof. Ram Pyare, for providing me with various departmental facilities. I am also thankful to all the faculty members and other staff members of the Department of Ceramic Engineering as well.

I wish to convey a special thanks to the Incharge (Prof. Rajiv Prakash) and all the technical staff of Central Instrument Facility (CIF), IIT (BHU) for availing me of various instrumental facilities. I am very much thankful to Dr. Manoranjan Kar, IIT Patna, for his help in magnetic measurements of Cr-Zn and Ni-Al substituted SrM samples.

I would like to extend my sincere gratitude to the Department of Science and Technology (DST), New Delhi (Ref No: IMP/2019/000165) and IIT (BHU) for providing me with financial support for this thesis.

I am fortunate to have labmates Dr. Deepshikha Shekhawat, Dr. Priyanka Verma, Dr. SK Saddam Hossain, Mr. Satyendra Kumar Singh, Mr. Soham Mukherjee, Mr. Sandip Kumar Patel, Mr. Sumit Kumar Singh, and Mr. Akash Sahu who will always be remembered for the wonderful time we shared together. "Life without Friends is like sweet without sugar." I am very grateful to have many of them. I am greatly thankful to my friends, Dr. Mukesh Suthar, Dr. Debarati Pal, Dr. Shanu Mishra, Mrs. Priya Singh, Mr. Pawan Kumar, Mrs. Jyoti Sharma, Mr. Pratyush Shukla, Mrs. Anviti Pandey, Dr. Manisha Singla, Mrs. Mahima Singh, Mrs. Arpita Gupta, and others for adding sparkles in my life.

*Family is the biggest blessing that builds the individual's personality and helps one to become strong and vibrant. I would like to express my special gratitude to the greatest strength of my life, my parents (**Mr. Vinay Narayan** and **Ms. Sunita Gupta**) and my siblings (**Dr. Saksham Gupta** and **Ms. Samridhi Gupta**) for being the backbone of my journey. I am very much grateful to Mr. Atharva, my Dadi (Late Mrs. Chandramukhi Devi), my family members, my Nani, and relatives for their love, care, blessings, and constant support throughout my life.*

At last, my heartiest gratitude to the almighty God for giving me all the strength and courage to face all the difficulties and giving me the opportunity to enjoy this beautiful journey of life with zeal and zest.

Date : November 10, 2022

Place: IIT (BHU), Varanasi

AKANKSHA GUPTA

Table of Contents

List of Figures

List of Tables

List of Abbreviations and Symbols

BaM	Barium hexaferrite ($BaFe_{12}O_{19}$)
B	Magnetic induction/ Magnetic flux density
B_r	Residual magnetic flux density/ Remanent flux density
$(BH)_{max}$	Energy product / Energy density
BD	Bulk density
D	Average crystallite size
Fe_A / Fe_B	$Fe_{(tetrahedral\ site)}$ / $Fe_{(octahedral\ site)}$
G_{avg}	Average grain size
H_a	Intrinsic Coercivity
H_c	Magnetocrystalline anisotropy field
K_{eff}	Effective magnetocrystalline anisotropy
M_r	Remanent magnetization
M_s	Saturation magnetization
NdFeB	Neodymium-Iron-Boron magnet
PM	Permanent magnet
RE / REE	Rare earth / Rare earth elements
R_M	Fe^{3+}/Sr^{2+} molar ratio
SmCo	Samarium-Cobalt magnet
SrM	Strontium hexaferrite ($SrFe_{12}O_{19}$)
T_c	Curie temperature
T_f	Functioning temperature
T_{ann}	Annealing temperature
T_{cal}	Calcination temperature
T_{sin}	Sintering temperature
V	Unit-cell volume
ϵ	Lattice strain
χD	X-ray density
ε	Dielectric constant
$tan\delta$	Dielectric tangent loss
ρ	ac-resistivity
σ	ac-conductivity

PREFACE

Permanent magnets are a significant component in various applications like motor, wind turbine, generator, computer device, medical equipment, and many more. There is a huge demand for permanent magnets which was valued at $17.85 Billion globally in 2018 and are expected to reach $34.7 Billion by 2026. Amond these magnets, NdFeB is the best performing magnet presently available in the market due to their high energy product. However, the market restriction and supply issues of rare-earth elements (REEs) due to the monopoly of China and the negative environmental effects of REEs extraction are demanding less dependency on REEs. It brings the challenge of developing a rare-earth free permanent magnet with high energy density.

Strontium hexaferrite (SrM) magnets represent the largest magnet group being used nowadays by volume. SrM is a ferrimagnetic material whose magnetic properties are inherently linked to the crystal structure and grain morphology. Though, it has a small energy density which is required to improve to reduce the dependency on NdFeB. Energy density is a key figure of merit, which is required to be high for better performance and is linked with the saturation magnetization (M_s) and coercivity (H_c) of the magnetic material. Due to high magnetocrystalline anisotropy, decent magnetism, chemical inertness, and high Curie temperature, these magnets are continuously drawing the attention of research communities to improve the low energy density of SrM with different means. It is found as the most faithful base magnet in terms of abundance and economic balance, which requires more or less reformation and advancement in the aspect of magnetic properties. Improvement in M_s and H_c of SrM magnet, even mildly, could open up the possibilities of large-scale immersion of strontium hexaferrite based magnets in numerous permanent

magnet applications. In the past several years, enormous improvement has been made toward enhancing the magnetic properties of SrM.

The thesis work is focused on the 'development of rare-earth free permanent magnets with improved magnetic properties', where the magnetic properties of strontium hexaferrites have been tried to improve toward the proposed objective. Detailed investigations on the structural, magnetic, and dielectric properties of five different SrM-based compositions (not reported earlier by other authors) have indicated a good improvement in SrM compositions. The results of different SrM-based series are briefly outlined here. It is arranged into nine chapters, and a brief description of each chapter is as follows:

Chapter 1 provides a brief introduction to permanent magnets and the different magnetic properties of a magnetic material. The featured characteristics of strontium hexaferrite magnets are discussed with the requirement of certain criteria that must be fulfilled for developing a permanent magnet. Concerning the significance of these criteria, literature surveys on the effect of synthesis techniques and current progress in magnetic properties of strontium hexaferrite magnets due to the substitution of various non-rare-earth elements are summarized in this chapter. Finally, it is concluded with the scope and objective of the present work.

Chapter 2 provides a detailed overview of the experimental techniques applied in the present thesis work. It includes sample preparation procedures and a detailed introduction to the working principles of different characterizing instruments that are used in the different studies of synthesized samples.

Chapter 3 presents the synthesis of a $SrFe_{12-x-y}Co_xCr_yO_{19}$ ($0 \leq x, y \leq 1$) hexaferrite. The effect of Co-Cr substitution on the structural, magnetic, and dielectric properties of SrM is studied. XRD pattern confirms the formation of magnetoplumbite hexagonal

structure of SrM hexaferrite. Co ion substitution is found favorable to improve the M_s value with a drastic decrease in H_c, resulting in a soft magnetic behavior of samples. In contrast, Cr substitution is observed to significantly enhance the H_c value (almost double) without adversely affecting the M_s, resulting in a better hard magnetic behavior of strontium hexaferrite. Also, both these elements are found liable for improving the ac-resistivity of pristine strontium hexaferrite.

Chapter 4 presents the synthesis of a $Sr_{1-x}Cr_xFe_{12-y}Zn_yO_{19}$ ($0 \leq x \leq 0.8$; $0 \leq y \leq 1$) hexaferrite. The effect of Cr-Zn substitution on the structural, magnetic, and dielectric properties of SrM is studied. XRD pattern confirms the formation of magnetoplumbite hexagonal structure of SrM hexaferrite. Cr substitution at Sr site is also found favorable to improve the H_c value but not as significant as observed at Fe site, with a slight decline in M_s value. Zn substitution at Fe site of SrM is observed to improve M_s value considerably with a drastic reduction in H_c value, resulting in a soft magnetic behavior of the sample. Despite the sharp H_c dilution due to Zn ion, Cr substitution retained the hard magnetic characteristic of samples by maintaining H_c value greater than at least 1 kOe. Also, both these elements are found liable for improving the ac-resistivity of pristine strontium hexaferrite.

Chapter 5 presents the synthesis of a $SrFe_{12-x-y}Ni_xAl_yO_{19}$ ($0.005 \leq x \leq 0.02$; $1 \leq y \leq 4$) hexaferrite. The effect of Ni-Al substitution on the structural, magnetic, and dielectric properties of SrM is studied. XRD pattern confirms the formation of magnetoplumbite hexagonal structure of SrM hexaferrite. Ni substitution is found favorable to improve the M_s value of samples without adversely affecting the H_c. Al substitution is observed to significantly increase the H_c value of SrM, even higher than NdFeB but at the cost of M_s value. Also, both these elements are found liable for improving the ac-resistivity of pristine strontium hexaferrite.

Chapter 6 presents the synthesis of a $SrFe_8Al_4O_{19}$_xBi_2O_3 ($0 \leq x \leq 5$ wt%), where the doping effect of Bi_2O_3 sintering aid and the effect of different sintering temperature is studied on the structural, magnetic, and dielectric properties of Al-substituted SrM. XRD pattern confirms the formation of magnetoplumbite hexagonal structure of SrM hexaferrite. Mainly, the study of this chapter is motivated to compensate for the M_s loss in $SrFe_8Al_4O_{19}$ (a drawback of 4 Al substitution in SrM). The doping concentration of Bi_2O_3 and sintering temperature is optimized to realize better magnetic properties in $SrFe_8Al_4O_{19}$. Both Bi_2O_3 dopings and T_{sin} variation have reduced the ac-resistivity of samples compared to pristine strontium hexaferrite, but it is still higher than NdFeB.

Chapter 7 presents the synthesis of a $SrFe_{8-x}Al_4Zn_xO_{19}$ ($0 \leq x \leq 1$) hexaferrite. The effect of Al-Zn substitution on the structural, magnetic, and dielectric properties of SrM is studied. XRD pattern confirms the formation of magnetoplumbite hexagonal structure of SrM hexaferrite. Al substitution is observed to considerably increase the H_c value, even higher than NdFeB, but at the cost of M_s value. Zn substitution is found more prominent in improving the M_s of compositions but at little expense of H_c. An improvement in both M_s and H_c values is observed for small Zn substitution (x = 0.2). Zn substitution improves the ac-resistivity of Al-substituted SrM, but it is less than pristine strontium hexaferrite (still higher than NdFeB).

Chapter 8 presents the progress in energy density of the three best compositions of different series concerning the improvement in magnetic properties of strontium hexaferrite in comparison to the NdFeB. Three compositions from different series of the thesis work is selected here to demonstrate the enhancement in $(BH)_{max}$, due to their high H_c, either nearly approaching to the H_c of NdFeB (~15.07 kOe) or even higher than that. Also, Curie temperature analysis of these samples is given in this chapter to deliberate the operating temperature efficiency of synthesized permanent magnets.

Chapter 9 briefly summarizes the important findings of the thesis work. A decent improvement in magnetic properties of strontium hexaferrite magnets is deliberated here with the optimal amount of substituted element and optimization in synthesis factors. It also highlights the future scope of research on this material.