

## *Chapter 1*

# Introduction

### 1.1 GENERAL

The study of metal oxides has attracted the attention of materials scientists due to their optical, electrical, magnetic, mechanical, and catalytic properties, which make them technologically useful. Ferromagnetic iron oxides,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , spinels, and hexaferrites are materials of choice for data storage and transmission. Ferroelectric and dielectric oxides like  $\text{BaTiO}_3$ ,  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  with perovskite structure are extensively used in electronic devices. Physical properties of perovskite oxides such as electrical, electronic, magnetic, and optical vary with composition. For example,  $\text{LaNiO}_3$  is a metallic oxide while  $\text{LaMnO}_3$  is an antiferromagnetic insulating oxide. Partial substitution of La ion by Sr, Ca, Ba, or Pb, makes it metallic as well as ferromagnetic. The discovery of superconductivity in  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , popularly known as 1-2-3 compound, with superconducting property at 90 K spurred interest in the chemistry of oxide materials. The relation between the structure and properties (both physical and chemical) of oxide materials and their applications are of great importance.<sup>1</sup>

Some important oxide materials and their applications have been summarized in Table 1.1.

Currently considerable interest in nanocrystalline oxide materials exists owing to their unusual properties. Decreasing particle size results in some remarkable phenomenon. It has been found that smaller the particles, the

- Higher the catalytic activity ( $\text{Pt}/\text{Al}_2\text{O}_3$ ).
- Higher the mechanical reinforcement (carbon black in rubber).
- Higher the electrical conductivity of ceramics ( $\text{CeO}_2$ ).

- Lower the electrical conductivity of metals (Cu, Ni, Fe, Co, and Cu alloys).
- Higher the photocatalytic activity ( $\text{TiO}_2$ ).
- Higher the luminescence of semiconductors.
- Higher the blue-shift of optical spectra of quantum dots.
- Higher the hardness and strength of metals and alloys.
- Superparamagnetic behavior of magnetic oxides.

Table 1.1. Properties and applications of oxide materials.

Oxides	Property	Applications
$\text{Al}_2\text{O}_3$ , $\text{CeO}_2$	Hardness	Abrasive
$\text{TiO}_2$ , $\text{CeO}_2$ , $\text{Fe}_2\text{O}_3$	Catalysts	Air and water purification
$\text{M}^0/\text{Al}_2\text{O}_3$ ( $\text{M}^0 = \text{Cu, Ag, Au, Pt, and Pd}$ ) $\text{Ce}_{1-x}\text{M}_x\text{O}_{2-\delta}$ ( $\text{M} = \text{Cu, Ag, Au, Pt, Pd, Rh, and Ru}$ )	Redox catalyst	Three-way catalyst for automobile exhausts
$\text{Ti}_{1-x}\text{M}_x\text{O}_{2-\delta}$ ( $\text{M} = \text{Cu, Ag, Pt, Pd, Mn, Fe, Co, Ni and W}$ )	Photocatalyst	Oxidation of organic matter
$\text{TiO}_2$ , $\text{ZnO}$	UV-Vis sunlight absorbing	Photocatalyst, sunscreen, and paint
$\text{MTi/ZrO}_3$ ( $\text{M} = \text{Ca, Sr, Ba, and Pb}$ ); PZT	Dielectric	Sensors, MEMS
$\gamma\text{-Fe}_2\text{O}_3$ , $\text{BaFe}_{12}\text{O}_{19}$ , $\text{MFe}_2\text{O}_4$	Super paramagnetic	Cancer detection and remediation, sensors and memory devices
$\text{TiO}_2$ , $\text{Fe}_2\text{O}_3$ , $\text{Cr}_2\text{O}_3$ , $\text{MAl}_2\text{O}_4$ , $\text{MCr}_2\text{O}_4$ ( $\text{M} = \text{transition metal ions}$ )	Colors	Ceramic pigments
$\text{M/Al}_2\text{O}_3$ ( $\text{M} = \text{Cr}^{3+}, \text{Co}^{2+}, \text{Ni}^{2+}$ )		
$\text{M/ZrO}_2$ , $\text{RE/M:ZrSiO}_4$ ( $\text{M} = \text{Fe}^{3+}, \text{Mn}^{2+}, \text{V}^{4+}$ ; $\text{RE} = \text{rare earth ion}$ )		
$\text{Eu}^{3+}/\text{Y}_2\text{O}_3$ (red), $\text{Eu}^{2+}$ , $\text{Tb}^{3+}/\text{Ba-hexaaluminate}$	Luminescence	Phosphors-CFL, color TV picture tube
$\text{Al}_2\text{O}_3$ , $\text{ZrO}_2$ , ZTA, mullite, cordierite, tialite	Refractory	Toughened ceramics
$\text{MgO}$ , $\text{CaO}$ , and $\text{ZnO}$	Adsorbent	Defluoridation and COD from paper mill effluents
YSZ( $\text{Y}_2\text{O}_3\text{-ZrO}_2$ )	Electrolyte	Solid oxide fuel cell materials
Ni/YSZ	Anode	
$\text{La}(\text{Sr})\text{MO}_3$ , $\text{M} = \text{Mn, Cr}$	Cathode/interconnect	

Unusual optical and electrical properties in these materials take place due to a phenomenon known as quantum confinement. The large surface area to volume ratio of nanomaterials leads to their use as catalysts. Excellent sintering characteristics of these fine powders are useful in ceramics and composites. Dispersion of minute particles in various fluids allows the fabrication of corrosion resistant coatings and thin films.

## 1.2 PREPARATIVE METHODS

One of the challenges faced by materials scientists today is the synthesis of materials with desired composition, structure, and properties for specific applications. While one can evolve a well-reasoned approach to the synthesis of oxide materials, serendipity has played an important role in making new materials. Rational synthesis of materials require knowledge of crystal chemistry, besides thermodynamics, phase equilibrium, and reaction kinetics. The physicochemical properties of many materials are determined by the choice of synthetic methods. Selection of the synthetic route is crucial to control the composition, structure, and morphology of a chosen material. For instance, barium hexaferrite ( $\text{BaFe}_{12}\text{O}_{19}$ ) can be used either as a permanent magnet or as a recording media depending on the morphology of the compound, which in turn is dependent on the preparation route.

Oxide materials are usually prepared by solid-state reactions, i.e., either by the ceramic method or by precipitation from solution and subsequent decomposition. A variety of metal oxides, both simple and complex, are prepared by the conventional ceramic method. This involves the mixing of constituent metal oxides, carbonates, etc., and their repeated heating and grinding. These methods are used on both laboratory and industrial scale. However, there is an increasing demand for alternate routes to the synthesis of oxide materials that give superior properties when compared with those available from conventional methods. It should not be construed that conventional methods are substandard in any way; they are still used in the industrial production of several oxide materials. Nonetheless, the need for alternate synthesis routes for oxide materials has arisen because of intrinsic problems relating to:

1. Inhomogeneity of the products obtained by ceramic methods.
2. Incorporation of chemical impurities during repeated grinding and heating operations. Impurities have a deleterious effect on the high-temperature

mechanical behavior of engineering ceramics and on the electrical properties of electroceramics.

3. Coarseness of particles obtained from conventional routes, which make them unsuitable for coatings.

Nonuniform powder compositions make reproducible component fabrication difficult because of chemical inhomogeneity and voids in microstructure. Greater purity and homogeneity from novel methods can lead to improved physical properties.

The present trend is to avoid brute force methods in order to have a better control of stoichiometry, structure, and phase purity of metal oxides. Soft chemical routes are now increasingly becoming important to prepare a variety of oxides including nanocrystalline oxide materials. These approaches make use of simple chemical reactions like coprecipitation, sol-gel, ion exchange, hydrolysis, acid leaching, and so on, at considerably low temperatures compared to the ceramic method. Use of precursors, intercalation reactions, electrochemical methods, hydrothermal process, and self-propagating high-temperature synthesis (SHS) are some of the other contemporary methods. Several books and review articles on the synthesis of oxide materials have been published over the years.<sup>2-12</sup> Among these methods, combustion or fire synthesis (SHS) is quite simple, fast, and economical.

Although SHS has been successfully used to make non-oxide materials, its application for synthesis of oxide materials was delayed due to economic reasons. Furthermore, it being a solid-state method, phase purity and particle size control is not possible. Also, due to its high-temperature course it is not suitable for the preparation of nanocrystalline materials. In this context, a low-temperature initiated combustion method<sup>13,14</sup> developed by Patil *et al.* at Indian Institute of Science, Bangalore has carved a niche. This low-temperature initiated self-propagating combustion process is different from the well-known Pechini (citrate process) which uses external heating at high temperatures to burn away the extra carbon.<sup>10</sup>

Combustion process is different from pyrolysis since once ignited it does not require external heating. In the synthesis of nanomaterials by soft routes there are two approaches: (i) breaking-down and (ii) building-up processes. Solution combustion synthesis of nanocrystalline oxide materials while appearing to be a breaking-down process is in fact an integrated approach, as the desired oxide products nucleate and grow from the combustion residue.

### 1.3 SCOPE OF THE BOOK

Future technologies based on nanoscale inorganic solids will hinge on the production of a controlled size, shape, and structure of nanocrystalline oxide material to make a working device. Today, solution combustion synthesis of oxide materials is becoming popular and is being used by materials scientists all over the world.<sup>13–17</sup> This process is particularly useful for preparing such nanocrystalline oxides. Yet, research and development of the process and its application to nano-oxide materials has not caught the full attention of Nanoscientists and Engineers. The objective of this book is to comprehensively present the solution combustion process and give ready recipes to prepare a wide range of oxide materials. It is gratifying to note that the preparation of nanophosphors<sup>18</sup> and aluminas<sup>19</sup> by the solution combustion method has been described as simple laboratory experiment for undergraduate students.

This book contains 10 chapters. The introductory section has already highlighted the importance of the chemistry of oxide materials, their properties and applications, and the need for a novel method for the preparation of nanocrystalline oxide materials.

Chapter 2 describes the preparation of nanocrystalline oxide materials by the combustion of solid precursors. The precursors discussed are: metal hydrazine carboxylates like formate, acetate, oxalate, and hydrazine carboxylate and their solid solutions. Unlike the precursors described in literature which decompose at high temperatures, these complexes ignite at low temperatures and undergo autocatalytic combustion with the evolution of large amount of gases to yield voluminous nanocrystalline oxides. Several nanocrystalline metal oxides prepared by the combustible solid precursor method are useful as catalysts, magnetic, and dielectric materials.

Chapter 3 introduces the reader to the unique solution combustion synthesis route of making oxide materials with desired composition, structure, and properties for specific applications. Combustion being an exothermic redox chemical reaction requires an oxidizer and a fuel. The oxidizers used are water soluble metal nitrates; the fuels employed are readily available compounds like urea, glycine, metal acetates, and hydrazides, all of which are also water soluble. Synthesis of metal oxides is achieved by rapidly heating an aqueous solution containing stoichiometric quantities of the redox mixture. Calculation of stoichiometry is very critical and important to solution combustion

synthesis. This calculation is based on the principles used in propellant chemistry and consists of balancing elemental oxidizing and reducing valences of the compounds utilized in combustion. The chapter deals with the theory of combustion reaction and its thermodynamic calculation. Typical procedures for preparation of desired oxides are given. The role of fuels and the conditions for synthesis of the nanocrystalline oxide materials are discussed. Advantages of the solution combustion method over other methods are highlighted.

Chapter 4 deals with the synthesis of technologically important alumina and related oxide materials. Urea appears to be an ideal fuel for the combustion synthesis of  $\alpha$ - $\text{Al}_2\text{O}_3$ , metal aluminates, and metal-ion-doped aluminas. Nanocrystalline aluminas are also prepared by using glycine and metal acetate precursors. Luminescent materials like  $\text{Cr}^{3+}$ -doped alumina, aluminates, and garnets, as well as  $\text{Ce}^{3+}$ -,  $\text{Tb}^{3+}$ -, and  $\text{Eu}^{2+}$ -doped hexaaluminates have been prepared and investigated. The synthesis of cobalt ( $\text{Co}^{2+}$ )- and chromium ( $\text{Cr}^{3+}$ )-doped blue and pink aluminas as ceramic pigments are examined. Synthesis and properties of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ - $\text{TiO}_2$  composites are also presented.

Chapter 5 gives an account of the preparation and catalytic properties of nanocrystalline  $\text{CeO}_2$ ,  $\text{Ce}_{1-x}(\text{Zr/Ti})_x\text{O}_2$ , and metal-ion-substituted ceria ( $\text{Ce}_{1-x}\text{M}_x\text{O}_{2-\delta}$  where  $\text{M} = \text{Cu}, \text{Ag}, \text{Au}, \text{Pt}, \text{Pd}, \text{Rh}, \text{and Ru}$ ). Platinum-ion-substituted ceria and palladium-ion-substituted ceria are discovered as catalysts for  $\text{H}_2$ - $\text{O}_2$  recombination and three-way catalytic converter for automobile exhaust, respectively. Oxalic acid dihydrazide (ODH) is the preferred fuel to obtain nanocrystalline ceria.

Chapter 6 contains the preparation and properties of nanocrystalline magnetic oxides based on  $\text{Fe}_2\text{O}_3$ . The materials prepared are simple ferrites ( $\text{MFe}_2\text{O}_4$ ), mixed (Li-Zn, Mg-Zn, and Ni-Zn) ferrites, orthoferrites ( $\text{LnFeO}_3$ ), garnets, and hexaferrites. ODH appears to be an ideal fuel for the preparation of iron-containing nanocrystalline magnetic oxides, since combustion is flameless or smoldering type.

Chapter 7 discusses the synthesis and photocatalytic properties of nanocrystalline anatase titania ( $\text{TiO}_2$ ). Preparation and photocatalytic properties of metal-ion-substituted  $\text{TiO}_2$  are investigated for the degradation of organic dyes and compared with anatase titania and metal-impregnated titania. Titanate-based minerals have been prepared and studied as Synroc materials

for nuclear waste immobilization. Both, tetraformyl trisazine and glycine are suitable for combustion synthesis of titania and titania-based oxide materials.

Synthesis of t-, m-, c-ZrO<sub>2</sub>, and related oxide materials is the topic of Chap. 8. The oxides studied are stabilized forms of ZrO<sub>2</sub>, rare earth ion doped zirconia and zircon pigments, zirconia–ceria (ZrO<sub>2</sub>–CeO<sub>2</sub>), zirconia–titania (ZrO<sub>2</sub>–TiO<sub>2</sub>), and pyrochlores (ZrO<sub>2</sub>–Ln<sub>2</sub>O<sub>3</sub>) systems. Synthesis of NASICONs has also been reviewed. Carbohydrazide is the chosen fuel for the preparation of zirconia and related oxides.

Chapter 9 describes the synthesis, properties, and applications of perovskite oxides (ABO<sub>3</sub>) — metal titanates (MTiO<sub>3</sub>), zirconates (MZrO<sub>3</sub>), LnMO<sub>3</sub>, and strontium-substituted perovskites (Ln(Sr)MO<sub>3</sub>, where M = Cr, Mn, Fe, Co). Dielectric oxide materials like MTiO<sub>3</sub>, MZrO<sub>3</sub> (where M = Ca, Ba, Sr, and Pb), PZT, and lead niobates have also been prepared and their properties are studied.

The synthesis and properties of technologically important oxides not covered in the earlier chapters constitutes the subject matter of Chap. 10. The oxides prepared include simple metal oxides, metal borates, silicates, and vanadates. The properties of combustion synthesized metal chromites, rare earth oxide based pigments, and high-T<sub>c</sub> materials are also examined.

An ‘Appendix’ giving details regarding the preparation of hydrazine-based fuels used for solution combustion synthesis of oxide materials as well as the oxidizer titanium nitrate is provided. Also some important tips for the preparation of oxides using heterogeneous solutions are given.

It is hoped that this book will serve as a handbook on solution combustion synthesis of oxide materials and will prove to be useful to Chemists, Physicists, Materials Scientists, and Students in this field. The information on the synthesis of nanocrystalline oxide materials is a significant contribution to the field of nanoscience and nanotechnology and in the final analysis is expected to inspire entrepreneurship.

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