PROPERTIES AND APPLICATIONS OF PEROVSKITE-TYPE OXIDES

Stainless Steel Net

Heater Coil

Semiconductor Oxide

Lead Wire

Terminal

edited by
L. G. Tejuca
J. L. G. Fierro

PROPERTIES AND APPLICATIONS OF PEROVSKITE-TYPE OXIDES

CHEMICAL INDUSTRIES

A Series of Reference Books and Textbooks

Consulting Editor

HEINZ HEINEMANN
Berkeley, California

ADDITIONAL VOLUMES IN PREPARATION

PROPERTIES AND APPLICATIONS OF PEROVSKITE-TYPE OXIDES

edited by

L. G. Tejuca
J. L. G. Fierro

Instituto de Catálisis y Petroleoquímica
CSIC
Madrid, Spain

This book is printed on acid-free paper.

In Memoriam

With my deepest regret, I must report the unexpected death of Dr. L.G. Tejuca, who first accepted the task of editing this book almost three years ago. Born on September 25, 1939 in Asturias, Dr. Tejuca received the master's degree in chemistry from Oviedo University in 1965 and the doctoral degree, also in chemistry, from the Complutense University in 1970. After serving as Associate Scientist from 1971 to 1975, he assumed a position as Staff Senior Scientist in 1976 at the Institute of Catalysis and Petrochemistry of the National Council for Scientific Research. He was also a postdoctoral research fellow at the University of Nottingham (Great Britain), Princeton University, and the University of Dundee (Great Britain).

Dr. Tejuca was best known for his pioneering research on the perovskite-type oxides, including synthesis, structural characterization, and application in several catalytic test reactions. His most important contribution was the establishment of the relationship between the local symmetry of the 3d transition cations in perovskite surfaces and the surfaces' adsorption and catalytic properties. The close parallelism he found between the extent of oxygen adsorption and the rate of carbon monoxide and low-molecular-weight olefin oxidations permitted him to discuss catalytic trends in terms of crystal field effects. Another major area of Dr. Tejuca's work involved the use of adsorption models to evaluate the number of surface sites on unsupported and supported metal oxides. These efforts of Dr. Tejuca resulted in over 130 original publications which have stimulated research in this paticular area of heterogeneous catalysis over the past decade.

As his friend and coworker, I decided to continue with the task of editing this pivotal book. All friends at the Institute, authors of the different chapters, the publisher, and readers of the book mourn the passing of Dr. Tejuca.

J.L.G. Fierro

Preface

Many progress reports and a large body of publications in specialized surface science and catalysis journals have provided a convincing description of the processes taking place at the surface of perovskite-type structures. Accordingly, it has been our endeavor to offer the reader of this book an overview of the bulk and surface properties of these marvelous materials and how they can be related to the catalytic performance in many model and practical reactions.

Chapter 1 surveys the methods of preparation of bulk perovskites and offers the possibility of synthesizing these compounds on moderate- or high-surface-area carriers. Special emphasis is placed in Chapter 2 on the methods employed in the processing of high temperature superconductive cuprates. Chapter 3 provides a comprehensive review of the oxidative nonstoichiometric behavior of perovskites, including not only the excess oxygen but also the cation vacancies. This analysis is extended in Chapter 4 to several high-temperature superconductive cuprates for which a careful crystallographic analysis is made. Chapter 5 deals with the thermoelectric properties of various cuprates and the comparative analysis of the critical behavior of thermopower and electrical conductivity in the mean field region. Chapter 6 is concerned with the optical properties of perovskites and doped perovskites in which the ions may adopt a large variety of configurations.

Chapters 7 and 8 focus on methods used to evaluate the surface sites, including poisoning with sulfur dioxide, the study of the vibrational modes of adsorbed molecules, and the analysis of the desorption products of chemisorbed probe molecules. The role of surface impurities and phase segregation and the relevance of the surface structure on chemisorptive and catalytic properties are discussed in Chapter 9. Chapters 10 to 17 survey several practical and model catalytic reactions such as total oxidation of hydrocarbons, hydrogenation and hydrogenolysis of hydrocarbons, hydrogenation of carbon oxides, CO oxidation and NO reduction, partial oxidation of hydrocarbons and oxygenates, hydrogen evolution from water, reduction of sulfur dioxide, and decomposition of nitrous oxide. Finally, the use of these compounds as solid state chemical sensors is reviewed in Chapter 18.

The overall view depicted in this book indicates clearly how these model compounds provide basic information for the study of structure-activity relationships and also for catalytic design based on the flexible perovskite structure which can tolerate multiple ion substitution.

I acknowledge with gratitude the contributions made by the different authors, the technical staffs of the Institutes supporting this work, and the collaboration of the publisher, all of whose cumulative efforts and patience have made this book possible. Last but not least, my thanks go to Mrs. B. Pawelec whose indefatigable secretarial assistance has been invaluable.

J.L.G. Fierro

Contents

Contributors

Professor T. Arakawa   Department of Industrial Chemistry, Faculty of Engineering, Kinki University in Kyushu, Iizuka, Fukuoka 820, Japan

Dr. M. Avudaithai   Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Professor G. Blasse   Debye Research Institute, University of Utrecht, 3508 TA Utrecht, The Netherlands

Dr. O. Cabeza   Laboratorio de Física de Materiales (LAFIMAS), Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain

Dr. M. T. Casais   Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas (CSIC), Serrano 113, 28006 Madrid, Spain

Dr. C. Cascales   Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas (CSIC), Serrano 113, 28006 Madrid, Spain

Dr. J. Christopher   Research and Development Centre, Indian Oil Corporation, Ltd., Faridabad 121 007, India

Professor P. Duran   Instituto de Cerámica y Vidrio, Consejo Superior de Investigaciones Científicas (CSIC), Electroceramics Department, 28500 Arganda del Rey, Madrid, Spain

Dr. J. L. G. Fierro   Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas (CSIC), Serrano 119, 28006 Madrid, Spain

Professor P. K. Gallagher   Departments of Chemistry and Material Science and Engineering, The Ohio State University, Columbus, OH   43210

Professor M. Hervieu   Laboratoire CRISMAT, Institut des Sciences de la Matière et du Rayonnement (ISMRA), Boulevard du Maréchal Juin, 14050 Caen Cédex, France

Professor D. Brynn Hibbert   Department of Analytical Chemistry, University of New South Wales, Kensington, New South Wales 2033, Sidney, Australia

Professor K. Ichimura   Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami, Kumamoto 860, Japan

Professor Y. Inoue   Department of Chemistry, Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan

Professor T. R. N. Kutty   Department of Inorganic and Physical Chemistry, and Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India

Professor Li Wan   Department of Chemistry and Environmental Engineering, Beijing Polytechnic University, Beijing 100871, People's Republic of China

Dr. J. Maza   Laboratorio de Física de Materiales (LAFIMAS), Universidad de Santiago de Compostela, 15706 Santiago de Compsotela, Spain

Professor C. Michel   Laboratoire CRISMAT, Institut des Sciences de la Matière et du Rayonnement (ISMRA), Boulevard du Maréchal Juin, 14050 Caen Cédex, France

Professor C. Moure   Instituto de Cerámica y Vidrio, Consejo Superior de Investigaciones Científicas (CSIC), Electroceramics Department, 28500 Arganda de Rey, Madrid, Spain

Professor I. Rasines   Instituto de Ciencia de Materiales, Consejo Superior de Investigaciones Científicas (CSIC), Serrano 113, 28006 Madrid, Spain

Professor B. Raveau   Laboratoire CRISMAT, Institut des Sciences de la Matière et du Rayonnement (ISMRA), Boulevard du Maréchal Juin, 14050 Caen Cédex, France

Professor T. Seiyama   Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816, Japan

Professor T. Shimizu   Hakodate National College of Technology, Hakodate, Tokura-cho 14-1, 042 Japan

Professor D. M. Smyth   Department of Materials Science and Engineering, Lehigh University, Bethlehem, PA 18015

Professor C. S. Swamy   Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Dr. J. M. D. Tascón   Instituto Nacional del Carbón y sus Derivados, Conjejo Superior de Investigaciones Científicas (CSIC), Apartado 73, 33080 Oviedo, Spain

Dr. L. G. Tejuca (deceased)   Instituto de Catálisis y Petroleoquimica, Conjejo Superior de Investigaciones Científicas (CSIC), Serrano 119, 28006 Madrid, Spain

Dr. J. Twu Pharmaceutical R&D Laboratories, Development Center for Biotechnology, Taipei, Republic of China

Dr. J. A. Veira Laboratorio de Física de Materiales (LAFIMAS), Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain

Professor F. Vidal   Laboratorio de Física de Materiales (LAFIMAS), Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain

Professor B. Viswanathan   Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

Dr. Y. Yadava Laboratorio de Física de Materiales (LAFIMAS), Universidad de Santiago de Compostela, 15706 Santiago de Compostela, Spain

Professor I. Yasumori Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Yokohama 221, Japan

PROPERTIES AND APPLICATIONS OF PEROVSKITE-TYPE OXIDES

Chapter 1

Preparation of Bulk and Supported Perovskites

J. Twu[1] and P.K. Gallagher[2]

[1]Pharmaceutical R&D Laboratories, Development Center for
Biotechnology, Taipei, Republic of China

[2]Departments of Chemistry and Materials Science & Engineering,
The Ohio State University, Columbus, OH 43210

I. Introduction

Perovskite-related materials are represented by the general formula ABO_3 in which A ions can be rare earth, alkaline earth, alkali and other large ions such as Pb^{2+} and Bi^{3+} that fit into the dodecahedral site of the framework. The B ions can be 3d, 4d and 5d transitional metal ions which occupy the octahedral sites. A complete list of A and B ions is given in Table 1 (1). In general, the perovskite structure is formed if the tolerence factor, t, is in the range 0.8 - 1.0 (R is the ionic radius of the A, B, or oxide ion) (2):

$$t = (R_A + R_0)/\sqrt{2}(R_B + R_0)$$

Large classes of perovskite-like materials are comprised of basic perovskite cells separated by intervening layers such as alkaline earth oxides. There are many stacking sequences possible that give rise to such compounds as Sr_2FeO_4 or $Sr_3Fe_2O_7$ (2). In addition to the diversity of compositions mentioned above, perovskite materials can tolerate significant partial substitution and non-stoichiometry while still maintaining the perovskite structure. For example, metal ions having different valences can

1

replace both A and B ions. This may generate a non-integral number of oxygen atoms. These flexible compositions can be represented by the related family of layered grossly oxygen deficient perovskites such as Sr_2FeO_{4-x} and $Sr_3Fe_2O_{7-x}$ (2), and the superconducting variety, $Y_1Ba_2Cu_3O_{6+x}$ (3).

Because of their varied structure and composition, perovskite materials have attracted intense interest in many applied and fundamental areas of solid state chemistry, physics, advanced materials, and catalysis. A partial list of their potential applications is presented in Table 2 (4). Because of their diverse applications, the optimum preparation of these materials has proved challenging, requiring many synthetic approaches determined by the ultimate end use. For example, materials-oriented applications require densification by high temperature

Table 1. Radii of Cations A and B for ABO_3-Type Perovskite[a]

Dodecahedral A-site				Octahedral B-site			
Na^+	1.06	1.32?	(IX)	Li^+		0.68	0.74
K^+	1.45	1.60?		Cu^{+2}		0.72	0.73
Rb^+	1.61	1.73		Mg^{+2}		0.66	0.72
Ag^+	1.40	1.30	(VIII)	Ti^{+3}		0.76	0.67
Ca^{+2}	1.08	1.35		V^{+3}		0.74	0.64
Sr^{+2}	1.23	1.44		Cr^{+3}		0.70	0.62
Ba^{+2}	1.46	1.60		Mn^{+3}		0.66	0.65
Pb^{+2}	1.29	1.49		Fe^{+3}		0.64	0.64
La^{+3}	1.22	1.32?		Co^{+3}	(LS)	–	0.52
Pr^{+3}	1.10	1.14	(VIII)	Co^{+3}	(HS)	0.63	0.61
Nd^{+3}	1.09	1.12	(VIII)	Ni^{+3}	(LS)	–	0.56
Bi^{+3}	1.07	1.11	(VIII)	Ni^{+3}	(HS)	0.62	0.60
Ce^{+4}	1.02	0.97	(VIII)	Rh^{+3}		0.68	0.66
Th^{+4}	1.09	1.06	(VIII)	Ti^{+4}		0.68	0.60
				Mn^{+4}		0.56	0.54
				Ru^{+4}		0.67	0.62
				Pt^{+4}		0.65	0.63
				Nb^{+5}		0.69	0.64
				Ta^{+5}		0.69	0.64
				Mo^{+6}		0.62	0.60
				W^{+6}		0.62	0.58

[a] The coordination number is in parentheses if the radii given are not for 12-coordination. HS and LS refer to the spin states.

sintering to minimize both surface area and surface free energy in order to maximize mechanical strength. In contrast, catalytic materials have to maintain sufficiently high surface area in order to maximize their participation and activity in chemical reactions.

In this chapter, studies of the synthetic approach to produce high performance perovskite powders for both catalysis and advanced materials will be reviewed. Since other chapters are devoted to their applications and structures, the discussion here will be limited only to the synthetic aspects and related work. The literature on this topic is very extensive, and no attempt at an exhaustive coverage is attempted. Instead, a series of typical examples is selected to illustrate various approaches to the synthesis of perovskites and related materials.

II. Solution Preparation

Traditional ways of making perovskite materials usually adopt mixing the constituent oxides, hydroxides and/or carbonates. However, since these materials generally have a large particle size, this approach frequently requires repeated mixing and extended heating at high temperature to generate a homogeneous and single phase material. In order to overcome the disadvantages of low surface area and limited control of the micro-structure

Table 2. Applications of Perovskites in Materials

Multilayer Capacitor	$BaTiO_3$
Piezoelectric Transducer	$Pb(Zr,Ti)O_3$
P. T. C. Thermistor	$BaTiO_3$, doped
Electrooptical Modulator	$(Pb,La)(Zr,Ti)O_3$
Switch	$LiNbO_3$
Dielectric Resonator	$BaZrO_3$
Thick Film Resistor	$BaRuO_3$
Electrostrictive Actuator	$Pb(Mg,Nb)O_3$
Superconductor	$Ba(Pb,Bi)O_3$ layered cuprates
Magnetic Bubble Memory	$GdFeO_3$
Laser Host	$YAlO_3$
Ferromagnet	$(Ca,La)MnO_3$
Refractory Electrode	$LaCoO_3$
Second Harmonic Generator	$KNbO_3$

inherent in the high temperature process, precursors generated by sol-gel preparations or coprecipitation of metal ions by precipitating agents such as hydroxide, cyanide, oxalate, carbonate, citrate ions, etc., have been used.

These gel or coprecipitated precursors can offer molecular or near molecular mixing and provide a reactive environment during the course of subsequent heating and decomposition. Because of the improved solid state diffusion resulting from the improved mixing, they need a relatively lower temperature to produce similar materials compared to the traditional methods. These methods frequently offer additional advantages, such as better control of stoichiometry and purity, greater flexibility in forming thin films and new compositions, and an enhanced ability to control particle size. Consequently, they have opened new directions for molecular architecture in the synthesis of perovskites.

A convenient way of classifying the methods which start from solution is to consider the means used for solvent removal. Two basic classes exist. The first is based upon precipitation with subsequent filtration, centrifugation, etc., used to separate the solid and liquid phases. The second basic method depends upon thermal processes, e.g., evaporation, sublimation, combustion, etc., to remove the solvent. An additional consideration in the latter method is the possible simultaneous conversion of the residue into the desired product.

The principal advantages of starting from solution are better homogeneity and improved reactivity. No amount of mixing of solid particles will approach that obtained in solution and most of the other advantages are a direct result of this mixing on essentially an atomic scale. The necessary solid state reactions proceed more rapidly and at lower temperatures. As a consequence, the desired product can be obtained with a smaller particle size and greater reactivity.

Solubility is one of the most important considerations in designing solution techniques. Not only is it desirable that solubility be high in order to minimize the amount of solvent which must subsequently be removed, but also the particular components must be compatible, e.g., iron sulfates could not be combined with barium chloride in order to produce barium ferrite because barium sulfate would precipitate. Cost, purity and toxicity are other obvious factors.

A more subtle concern is the choice of the presumably inert anions, which will be determined by the pH values, ionic strength,

degree of supersaturation and impurities. This is important firstly because of the tendency of these ions to become incorporated in the final product and secondly because their subsequent effects can vary dramatically. Conditions which favor large particle size, slow growth and equilibrium will generally produce the purest precipitate.

A. Precipitation

1. **Oxalate**-based preparations of ceramic and superconducting materials have been used extensively. However, due to the incorporation of extraneous ions by occlusion, adsorption and substitution, a special method has been applied to alleviate the deleterious effects. This method is based on digestion of the appropriate carbonates, hydroxides, or oxides with oxalic acid, and the only products of this process are the metal oxalates, water and carbon dioxide (5). Since the pH value of the resulting solution is close to 7, it minimizes the solubility problem. However, if solubility remains a problem, the solution could be reused to ensure a saturated solution as the starting point. Such recycling also reduces the potential enviromental impact by decreasing the disposal problem.

During calcination, an atmosphere that is sufficiently oxidizing has to be adopted in order to prevent carbon residues and carbide formation (6). In general, an oxygen atmosphere is maintained to prevent free carbon or metal formation by oxidation of CO and or any other metal formed from the more easily reduced oxides such as copper.

Clabaugh et al. precipitated from an aqueous chloride solution the unique and novel complex compound $BaTiO(C_2O_4)_2 \cdot 4H_2O$ as a precursor for the preparation of finely divided, stoichiometric $BaTiO_3$ (7). Modifications were made to this process to partially substitute Sr, Pb, or La for Ba in order to change the transition temperature and modify electrical conductivity (7-10). Gallagher et al. (11) reported the synthesis of $BaSnO_3$ by thermal decomposition of $BaSn(C_2O_4) \cdot 0.5H_2O$ or $Ba_2Sn(C_2O_4) \cdot 6H_2O$ to form $BaCO_3$ and SnO_2, which then subsequently react to form $BaSnO_3$. The intimate mixing resulting from the precursor method avoids the formation of Ba_2SnO_4 as an intermediate which is a problem during the conventional preparation. This avoidance of undesirable intermediates occurs because of the shorter solid state diffusion paths achieved during thermal decomposition of the precursor. The major use of an oxalate

precursor for the synthesis of perovskites has been associated
with the formation of alkaline earth titanates but $BaFeO_{3-x}$ and
$SrFeO_{3-x}$ can also be generated from $Ba_3[Fe(C_2O_4)_2 \cdot 8H_2O$ and
$Sr_3[Fe(C_2O_4)_3]_2 \cdot 2H_2O$ (12).

   2. **Hydroxide** formation is often used because of its low
solubility and the variety of precipitation schemes possible.
Because of its advantages over traditional methods, e.g.,
chemical homogeneity, low temperature calcination, controlled
hydrolysis for thin film formation, and room temperature
deposition, the sol-gel process has been utilized for producing
a wide range of new materials as well as improving existing
materials. A general procedure can be divided into following
steps: (i) preparations of metal alkoxides, (ii) conducting
controlled hydrolysis and polymerization, (iii) drying, and (iv)
firing. Blum et al. (13) reported the synthesis of $PbTiO_3$ using
$Pb(CH_3COO)_2$ and $Ti(OC_3H_7)_4$ dissolved in methoxymethanol. The gel
was formed by introducing water and nitric acid and then drying
at room temperature for about three weeks. The dried gel was
annealed at 873 K for several cycles. X-ray diffraction
indicated that a tetragonal structure was formed at 673 K after
sufficient time. However, absence of the ferroelectric anomaly
was observed when heating below 823 K and the lack of extended
crystallinity or long range order was proposed as an explanation.
An alternative procedure is to start directly with a colloidal
solution of one of the components. Commercial sols of many oxides
are available, e.g., silica, alumina and titania. High T_c
superconducting powders and thin films of $Y_1Ba_2Cu_3O_7$ have also
been synthesized by sol-gel preparations (14).
   Homogeneous and stoichiometric $LiNbO_3$ fibers were prepared
by the sol-gel process (15). By controlling the concentration of
the alkoxide solution and the amount of water used for partial
hydrolysis, gel fibers having a uniform diameter were achieved.
The gel fibers, prepared by drawing, crystallized directly to
single-phase $LiNbO_3$ fibers by heating from 723 to 873 K. The
density of the crystalline $LiNbO_3$ fibers was higher than 4.22
g/cm^3, and the dielectric constant at room temperature was about
10 at 10 Mhz.
   Another approach via hydroxide formation involves
hydrothermal synthesis. The hydrothermal synthesis of $BaTiO_3$-
perovskite has been reported by Christensen (16). More recently,
$Ba(Ti,Zr)O_3$, $SrTiO_3$ and $BaSnO_3$ have been reported by Kutty et al.
(17). Reactive gels of hydrated TiO_2 and ZrO_2 were formed by the

addition of NH_4OH to a mixed aqueous solution of $TiOCl_2$ and $ZrOCl_2$. The gel was washed free of chloride ions and suspended in a 0.2 M $Ba(OH)_2$ solution. Then the resulting slurry was placed in a sealed teflon container and heated to 358-403 K for 2-6 h under hydrothermal conditions. The product was filtered and washed with dilute acetic acid to remove excess $Ba(OH)_2$. The sample was air dried before being calcined. The perovskite structures of $BaTiO_3$ and $BaZrO_3$ can be detected by X-ray diffraction (XRD) for samples heated at 403 K for 6h. Adding polyvinyl alcohol during the hydrothermal treatment and LiF during the sintering process has been used to promote reactivity. Transmission electron microscopy (TEM) studies indicate that the hydrothermally prepared $BaTiO_3$ powder contains individual crystallite as well as aggregates of acicular crystallites. Mazdiyasni (18) also compared hydrothermally generated samples of fine (5 nm) of $BaTiO_3$ by heating at 323 K under vacuum. These are significantly smaller than the 30.5 nm formed at 973 K for 60 min.

3.   **Acetate** ions have been used alone or together with nitrate ions to generate different perovskites and have shown some advantage over the traditional and oxalate methods. For instance, Nakamura et al. (19) reported the synthesis of $La_{1-x}Sr_xCoO_3$ compounds with x = to 0, 0.2, 0.4 and 0.6 by using acetate precursors followed by calcination at 1123 K in air for 5 h. From XRD, it was confirmed that the perovskite structure had been generated. Zhang et al. (20) reported the synthesis of $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ using lanthanum, strontium, and cobalt acetates and iron nitrate, then calcining at 1123 K in air between 5-10 h. XRD data showed that all of the oxides except $SrCoO_{2.5}$ showed a perovskite structure.

4. **Citrate** precursors have been investigated by Zhang et al. (21). The decomposition mechanism of these precursors was studied during the course of producing $LaCo_{0.4}Fe_{0.6}O_3$. By using thermogravimetry (TG), XRD and infrared (IR), it was found that citrate precursors undergo several decomposition steps before the perovskite structure is obtained. These steps correspond to the breakup of the citrate complexes, and the elimination of residual CO_3^{2-} and NO_3^- ions. The perovskite framework was detected by IR but was not observable by XRD, indicating that the perovskite was still lacking extended crystallinity. When the temperature was raised to 823 or 873 K, the diffractions due to perovskite were observed. Since the calcination temperature of citrate precursors

about 473 to 573 K lower than the acetate preparation for the same compositions, the resulting surface areas of both preparations were measured in order to compare them. Because of the lower calcination temperature, citrate preparations have a surface area increased by a factor between 3 and 7. It was proposed that the citrate complexes at the precursor stage have localized the metal ions more effectively resulting in a more homogeneous dispersion requiring a lower calcination temperature.

5. **Complex cyanides** have been used to prepare rare earth orthoferrites ($REFeO_3$) and the analogous cobalt compounds ($RECoO_3$) by the thermal decomposition of the appropriate rare earth ferricyanide and cobalticyanide compounds (22). These compounds such as $LaFe(CN)_6 \cdot 6H_2O$, $LaCo(CN)_6 \cdot 5H_2O$ and even ferrocyanides such as $NH_4LaFe(CN)_6 \cdot 5H_2O$ are readily precipitated from aqueous solution. A major advantage of such a process is that, since the excess of either component remains in solution, the precise control of stoichiometry is guaranteed. Because the mixing and stoichiometry are achieved on a atomic scale, the desired compounds are generated by relatively low temperature calcination and without any subsequent milling or contamination. Similar studies have been conducted for europium and other rare earth hexacyanoferrate compounds (23).

Monitoring the nature of the decompositions and identification of the intermediate and final products requires a wide range of techniques such as XRD, Mossbauer spectroscopy, IR, Raman, scanning electron microscopy (SEM), surface area, and TEM. The most convenient and powerful general method is thermal analysis, however. The use of TG, differential thermal analysis (DTA), and evolved gas analysis (EGA) techniques will determine weight loss, phase transitions, solid state reactions, oxidation/reduction, and the gas evolved or consumed. For example, the perovskite $BaPtO_3$ has been prepared by the thermal decomposition of a $BaPt(OH)_6$ precursor (24). TG and DTA were utilized to monitor the decomposition of $BaPt(OH)_6$ in both O_2 and vacuum. The decomposition pathway can be described by the reactions:

$$BaPt(OH)_6 \cdot 0.5H_2O \longrightarrow BaPt(OH)_6 + 0.5H_2O \qquad (2)$$
$$BaPt(OH)_6 \longrightarrow BaPtO_3 + 3H_2O \qquad (3)$$
$$BaPtO_3 \longrightarrow BaPtO_{3-x} + x/2\ O_2 \qquad (4)$$
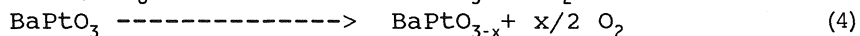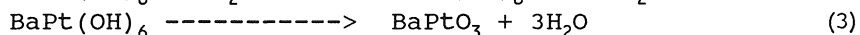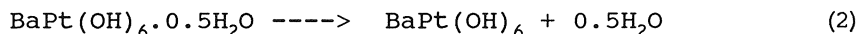
The degree of nonstoichiometry (value of x in eq. 4) could be readily determined by weight loss to form $Ba(OH)_2$ + Pt as

determined by TG in H_2. Similar studies have characterized the decomposition or conversion for most of the precursors described herein.

B. Thermal Treatment

1. Combustion

Hydrolysis of aluminum, titanium and silicon in a flame around 1073-1673 K has long been used to prepare these oxides in a fine particulate form. Wenkus and Leavitt (25) first prepared a number of ferrites in a similar fashions by dissolving metal nitrates in alcohol, atomizing the resulting solution with oxygen through a nozzle, burning the alcohol, and finally collecting the resulting powder. The process, which is also referred to as self-propagating high temperature synthesis (SHS), provides energy- and cost-saving advantages over the more conventional processing routes for these materials (26). At the same time, the rapid heating and cooling rates provide a potential for the production of metastable materials with new and, perhaps, unique properties.

A novel combustion process for the synthesis of $YBa_2Cu_3O_7$ superconductor involves ignition of a metal nitrates-organic salts mixture and results in an intimate mixture of partially reacted oxides (27-29). Another modification uses a nitrate-urea mixture. The mixture is given a second combustion with NH_4NO_3 and urea followed by subsequent heat treatment and oxygenation. This produces a single phase superconducting $YBa_2Cu_3O_7$ powder (30).

Pankajavalli et al. discuss a procedure for the preparation of improved quality $YBa_2Cu_3O_{7-x}$ by the citrate pyrolysis method and optimization of parameters for annealing were presented (31). The characterization of the product of citrate pyrolysis and the quality control tests employed for the 1-2-3 compounds produced were discussed. Combustion of the citrate from the aqueous phase yielded uniform mixtures of Y_2O_3, $BaCO_3$, and CuO in the desired 1:4:6 molar ratio. The higher reactivity of this powder was observed in TG traces.

2. Freeze-Drying

The freeze-drying technique is conceptually simple. It involves: (i) dissolving salts in a suitable solvent, usually water; (ii) freezing this solution rapidly to preserve chemical homogeneity; (iii) freeze-drying the frozen solution to give

dehydrated salts without involving a liquid phase; and (iv)
decomposing the salts to give the desired oxide powder. The
freezing and drying process can be comprehended easily with the
aid of the schematic diagram in Fig. 1 (32). The most important
criterion for the freezing step is the rate of heat transfer out
of the solution. This should be as great as possible in order to
minimize the ice-salt segregation and more importantly for
multicomponent solutions, to prevent large scale segregation of
the cation components. This can be accomplished by spraying the
liquid through a small orifice into an immiscible liquid such as
hexane chilled by dry ice-acetone, or directly into liquid
nitrogen.

Early applications of this technique to forming mixed
compounds involved ferrites (33,34) and lithium niobate (6). More
recently freeze-drying was applied to prepare complex Bi-Pb-Sr-
Ca-Cu-O powders which subsequently required sintering at 1113 K
for 30 h to form the 110 K (2223) phase (35). Freeze-drying
provided highly reactive, intimately mixed, and carbon-free
precursors. The latter is important because the presence of
carbonate in the uncalcined powders was the major cause of phase
segregation and sluggishness of the 110 K phase formation.

The effect of the choice of precursor salts on the surface
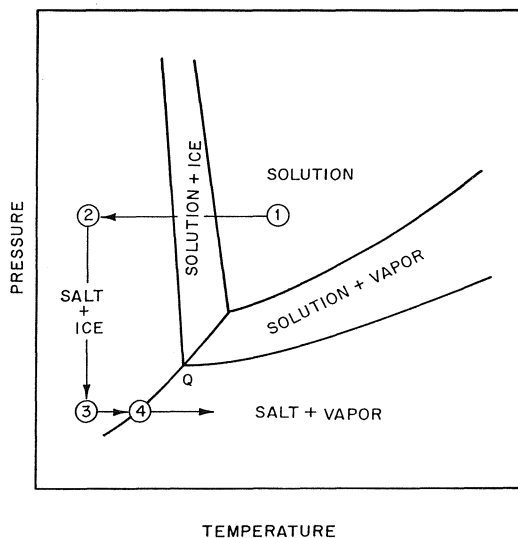area of mixed metal oxides prepared by freeze-drying was studied

Fig. 1. Phase diagram of an aqueous solution illustrating the
freeze-drying method (32).

using the nitrate of Ni or acetates and nitrates of La, Sr, and Co. The $NiCo_2O_4$ produced via the thermal decomposition of freeze-dried Ni Co nitrate had a greater surface area and lower decomposition temperature than $La0_.5Sr_{0.5}CoO_3$ prepared from the freeze-dried nitrates (36). The latter needed heating above 773 K to decompose the $Sr(NO_3)_2$, which fractionates from the mixed nitrates. The mist of a mixed solution of $Co(NO_3)_2$, $La(NO_3)_3$ and an additive was produced by supersonic atomization and treated in three temperatures to produce fine particles (37). These temperatures were adjusted to achieve evaporation of the water, decomposition of the mixed metal salts, and the crystallization of the mixed oxides, respectively. The surface area of these samples was increased from 11 m^2/g to 55 m^2/g when NH_4Cl and polyvinyl alcohol were added.

3. Plasma Spray-Drying

Plasma techniques can be divided into two main stages: the injection of reactants and the generation and interaction of the molten droplets (either with the substrate or with the previous generated droplets). They have been applied to various precursors which include gaseous, liquid and solid materials. Since this process offers improved performance in various aspects such as economy, purity, particle size distribution and reactivity, it has been applied to various ceramic, electronic and catalytic materials. This technique has recently been applied to produce thick $YBa_2Cu_3O_x$ films covering large areas (38). The deposition conditions, such as plasma parameters and substrate temperatures, as well as post-deposition treatment of films, were varied in order to obtain the optimum superconducting oxide phase.

III. Solid State Reactions

Conventional processing of perovskite-related materials uses solid state reactions between metal-carbonates, hydroxides, and oxides. A typical case is represented by $BaTiO_3$ (39). Impurities are introduced from raw materials, milling media, and the calcination container. Because of the high temperature required for complete reaction and coarse particles, problems such as multiphases have to be minimized in order to generate homogeneous high performance $BaTiO_3$. Low temperature approaches described in the previous sections have been tested by various

groups. The formation of the $Ba_2YCu_4O_8$ superconducting compound initally required a high pressure oxygen process (40). It was later found that the reactivity could be promoted and the desired product obtained at atmospheric pressure by adding an extra (0.2-0.5) molar ratio of an alkaline metal carbonate (41,42). The 124 perovskite formed in this way was more nearly single phase compared to the sample without the addition of alkaline metal carbonates. The formation of a low melting eutectic phase by the addition facilitates reactivity. The additive volatilizes during subsequent processing at higher temperatures.

Rather than starting with the individual components, it may be advisable to begin with prereacted powders (43). This approach has been applied to the synthesis of $Pb(FeW)O_3$ and $Pb(FeNb)O_3$ in order to obtain materials having high dielectric constants with a low temperature dependence. Presumably, the prereacted phases facilitate initial homogeneity leading to reduced diffusion paths during the formation of product.

Oxidation reactions during solid state reactions can be facilitated by using highly oxidized starting materials, e.g., BaO_2 and Fe_2O_3 were used to synthesize $BaFeO_3$ by utilizing the oxidizing ability of the peroxide ion (44). Fe_2O_3 was prepared by thermal decomposition of $FeC_2O_4 \cdot H_2O$ and then mixed with the BaO_2. The cubic structure of $BaFeO_3$ was observed at 633 K and the tetragonal structure of $BaFeO_{2.75}$ at 848 K by XRD. High pressure oxygen systems have also been used to prepare these difficult materials.

A float zone technique was used to prepare single crystal and textured ceramics of incongruently melting perovskites (45). A CO_2 laser produced a stable float zone of $Bi_2CaSr_2Cu_2O_x$ in air or in O_2 pressure up to 2.6 atm. In the best case, nearly 100% single crystal can be obtained. This technique shows great promise for preparing ceramic materials even when the detailed phase diagrams are not available.

Perovskite-related compounds have demonstrated a wide range of oxygen non-stoichiometry. This property determines the vacancy content of the materials which can affect the temperature of melting, electrical properties and catalytic performance (46). The degree of non-stoichiometry depends upon several parameters such as oxygen partial pressure, calcination temperature and substitution of metal ions with different valences. As an example Lindemer et al. reported the influence on oxygen stoichiometry exhibited by variations in P_{O2} and calcination temperature for YBa_2Cu_3O superconducting materials, see Fig. 2 (47). The transi-
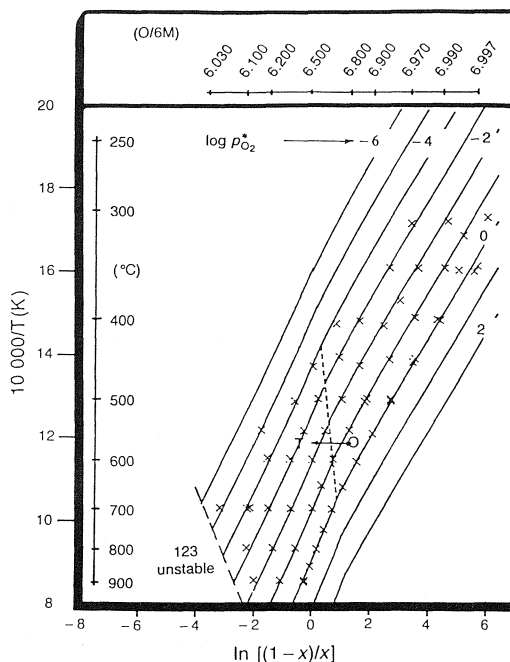
Fig. 2. Oxygen stoichiometry in $YBa_2Cu_3O_{7-x}$ perovskite-related structure (47). The orthorhombic-to-tetragonal transition (O <—> T, dashed line) is from Specht et al. (48).

tion from orthorhombic to the tetragonal phase is indicated by the dashed line based on the data of Specht (48). Since high temperature superconductivity has been shown to depend upon a high oxygen content, the need for a low anneal temperature is clearly evident. This low temperature anneal can be accomplished using oxidizing agents other than the conventional molecular oxygen, e.g., ozone, oxygen plasmas, etc.

IV. Gas Phase Preparations and Reactions

The deposition of perovskite films with a specific thickness and composition generally requires gas phase reaction or transport. Many physical techniques have been developed for gas phase deposition such as laser ablation (49), molecular beam epitaxy (50), dc sputtering (51), magenetron sputtering (52), electron beam evaporation (53) and thermal evaporation (54). In

general they can be divided into two categories based on the target they use. The first type uses separate targets where a different speed of deposition for each element has to be determined. The second method uses the preformed perovskite material itself as target and the stoichiometric phase is transported to the substrate by sputtering or ablation techniques. Gas phase depositions can be divided further into three categories: (i) deposition at a low substrate temperature followed by a post-annealing at elevated temperatures, (ii) deposition at an intermediate temperature of 873 to 1073 K followed by a post-annealing treatment, and (iii) deposition at the crystallization temperature under an appropriate atmosphere.

Films of $YBa_2Cu_3O_7$ have been made by co-evaporation of Y, Cu, and BaF_2 and subsequent annealing in wet O_2 (54). Addition of water vapor to the annealing gas at high temperatures greatly reduces the annealing time and thus the substrate interaction. Transition temperatures (zero resistance) of 89 to 92 K are obtained on $SrTiO_3$ and cubic ZrO_2 substrates. Critical current densities on $SrTiO_3$ as high as 10^6 A/cm^2 at 81 K were obtained.

PZT thin films were deposited by radio frequency magnetron sputtering of a multi-element metal target (55). Control of the composition of PZT film was accomplished by adjusting the relative surface areas of the individual metallic targets. The perovskite structure was obtained by a post-annealing treatment. $Pb(BaPb_{1-x}Bi_x)O_3$ and $(Ba_{0.95}Sr_{0.05}PbO_{.75}Bi_{0.25})O_3)$ were prepared. The original films were deficient in Pb and Bi but this tendency was reduced by a higher partial pressure of O_2.

V. Support

Because of the ease in adjusting the composition of perovskites over a wide range, these materials can be investigated in a systematic way and correlation made between their performance and structure. This unique feature has made perovskites an ideal system for both fundamental studies in solid state chemistry and physics as well as useful electronic and catalytic materials. On the other hand, catalytic materials require a combination of advantages to achieve maximum activity and stability, such as high surface area, redox reactivity, product selectivity, and a stable framework. Some perovskites, such as cobaltate and manganite, exhibited competitive activity for the oxidation of CO and reduction of NO compared with noble

metal catalysts (56). However, due to their poisoning by SO_2, low surface areas, and weak mechanical strength, most perovskites have not been able to compete successfully in many catalytic applications (57).

In order to overcome these problems, developing a well dispersed pervoskite on support has been a attractive strategy to optimize the performance except for poisoning. In the preparations of a supported perovskite from solution, the method of drying can be extremely important. Gallagher et al. reported the preparation of supported $LaO_{.5}Pb_{0.5}MnO_3$ using different supports with various impregnation and drying techniques and then compared the catalytic performance of these materials (58). Various drying techniques were applied to maximize the homogeneity and stoichiometry on different supports and their conversion activity examined for the oxidation of CO (59). The immobility of the solution during the freeze-drying process can be invaluable to uniformly distribute the catalyst throughout a porous support, as shown clearly in Figs. 1 and 2 of reference 58.

At this point the discussion will be divided into sections based upon the choice of supports.

A. Cordierite

Mizuno et al. (60) reported the preparation of $La_{1-x}Sr_xCoO_3$ on a cordierite surface ($2Al_2O_3 \cdot 5SiO_2 \cdot 2MgO$) starting from metal citrates and nitrates. Attempts to use Al_2O_3 have not been successful because of the incorporation of Co atoms into the aluminate framework to form spinel. This precludes their participation in the catalytic reactions. Since the generation of the pervoskite depends upon the loading of lanthanum ions, it was proposed that lanthanum oxide was formed at the interface between the pervoskite and support and consequently reduced the diffusion of cobalt ions. Partial substitution of La^{3+} by Sr^{2+} ions results in a similar pervoskite structure and enhanced propane oxidation.

B. $La_2O_3 \cdot 19Al_2O_3$ (LA)

Zhang et al. (61) reported the preparation of $La_{1-x}Sr_xMnO_3$ or MnO_2 supported on LA by pre-treating LA with citrate precursors. XRD of 20 wt% samples supported on LA was performed from 873 to 1173 K and the pervoskite reflections were observed only for

calcinations above 1073 K. Comparing this result with that for
an unsupported pervoskite generated by citrate precursors
indicated a difference of 473 K for the appearance of pervoskite
reflections. This was attributed to the monolayer dispersion (20
wt%) of the pervoskite on the supports. When LA was treated with
10 % Mn_2O_3, a new phase was observed by XRD when calcined above
1273 K. This was proposed to be a new phase of La. These
supported perovskites show better stability and activity in
methane oxidation when compared with a Pt/Al_2O_3 catalyst.

C. ZrO_2

Fujii et al. (62) studied the structure and catalytic
activity of $LaCoO_3$ and $La_{1-x}Sr_xCoO_3$ when supported on ten metal
oxides. Acetate precursors were used and the supported pervoskite
were calcined in air at 1123 K for 5 h. Formation of the
pervoskite phases was confirmed by XRD. Catalytic activity for
propane oxidation of these supported pervoskites is shown in Fig.
3. Because of the outstanding activity on ZrO_2, additional
pyridine adsorption, TEM and loading analysis were employed to
study the structure developed on ZrO_2 surface. These studies
indicated that both $LaCoO_3$ and $La_{1-x}Sr_xCoO_3$ had developed a well
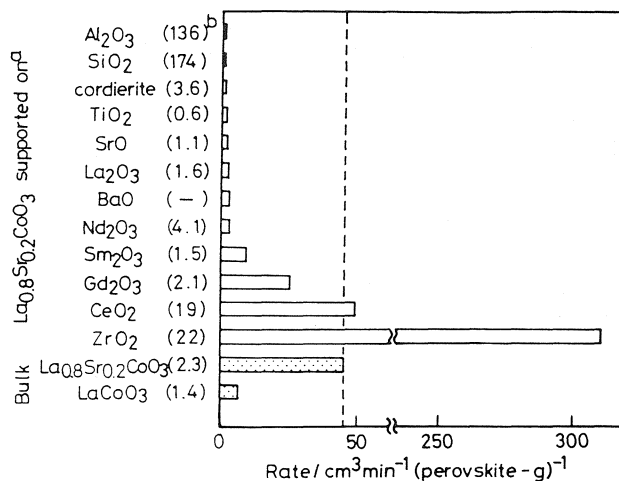dispersed pervoskite on the ZrO_2 surface which were responsible

Fig. 3. Catalytic activities of perovskite supported on oxides
(62). The amount of $La_{0.8}Sr_{0.2}CoO_3$ loaded was 5.8 wt%. Surface
areas of the supports (m^2/g) are given in parentheses.

for the unusual activity. A similar observation was made using a ZrO_2 supported pervoskite electrode.

D. Perovskite as a Support

Perovskites have been tested extensively for CO oxidation and NO_x reduction since these have the most impact for the control of automobile emissions. However, one of the serious obstacles in developing these catalysts to replace the noble metal catalysts is the poisoning produced by the SO_2 reaction to form sulfide and/or sulfate ions which incapacitate the catalytic activity. Addition of Pt to the supported perovskite can help sustain the activity in the presence of sulfur poisoning significantly. From ESCA studies, it can be concluded that the Pt can exist in tetravalent and +4 state when added to the perovskites (63). However, for a similar amount of Pt, the $BaPtO_3$ shows much less activity for CO oxidation. This implies that pervoskite may be critical in developing a unique Pt structure. More studies have to be done to understand and optimize these interactions.

VI. Conclusion and Perspectives

The synthesis of new perovskite materials has been an ongoing interest and challenge of material scientists interested in catalysis and solid state chemistry or physics. Since the discovery of high T_c superconductors, however, there has been even greater interest in perovskites and related materials and brought about many new studies on processing these materials. In the past decade, molecular architecture and micro-structural control have been advanced by using molecular precursor and low temperature treatments. In addition, a combination of perovskites with other materials has proved to be an efficient approach to enhance the desired properties and develop new applications. Based on this new understanding and development, several promising directions emerge for further studies, such as oxygen sensors (64), NO decomposition (65), and emission control catalyst. Novel methods of chemical synthesis and processing will undoubtedly play an ever more important role in the future.

References

1.   Voorhoeve, R.J.H., D.W. Johnson, Jr., J.P. Remeika and P.K.

Gallagher, Perovskite oxides: materials science in catalysis, *Science*, **195**: 827 (1977).

2. Gallagher, P.K., J.B. MacChesney and D.N.E. Buchanan, Mössbauer effect in the system $Sr_3Fe_2O_{6-7}$, *J. Chem. Phys.*, **45**: 2466 (1966).

3. Gallagher, P.K., H.M. O'Bryan, S.A. Sunshine and D.W. Murphy, Oxygen stoichiometry in $Ba_2YCu_3O_x$, *Mat. Res. Bull.*, **22**: 995 (1987).

4. Newnham, R.E., Structure-propertity relationship in perovskite electroceramics, in *Perovskite: a structure of great interest to geophysics and materials science*, A. Navrotsky and D.J. Weidner (Eds.), American Geophysical Union, Washington, D.C. (1989).

5. Gallagher, P.K. and D.A. Fleming, Influence of oxygen partial pressure on the synthesis of $Ba_2YCu_3O_7$ from a novel oxalate precursor, *Chem. Mat.*, **1**: 659 (1989).

6. Gallagher, P.K. and F. Schrey, The thermal decomposition of freeze-dried tantalum and mixed lithium-niobium oxalates, *Thermochim. Acta*, **1**: 465 (1970).

7. Clabaugh, W.S., E.M. Swiggard and R.J. Gilchrist, Preparation of barium titanyl oxalate tetrahydrate for conversion to barium titanate of highly purity, *J. Res. Natl. Bur. Std.*, **56**: 289 (1956).

8. Gallagher, P.K., F. Schrey and F.V. DiMarcello, Preparation of semiconducting titanates by chemical methods, *J. Am. Ceram. Soc.*, **46**: 359 (1963).

9. Northover, W.R., *J. Am. Ceram. Soc.*, **48**: 173 (1965).

10. Shrey, F., Effect of pH on the chemical preparation of barium-strontium titanate, *J. Am. Ceram. Soc.*, **48**: 359 (1965).

11. Gallagher, P.K. and D.W. Johnson, Kinetics of the formation of $BaSnO_3$ from barium carbonate and tin(IV) oxide or oxalate precursors, *Thermochim. Acta*, **4**: 283 (1972).

12. Gallagher, P.K., Thermal decomposition of barium and strontium trisoxalatoferrates(III), *Inor. Chem.*, **4**: 965 (1965).

13. Blum, J. B. and S.R. Gurkovich, Sol-gel-derived lead titanate, *J. Mater. Sci.*, **20**: 4479 (1985).

14. Ravindranathan, P., S. Komarneni, S.C. Choi, A.S. Bhalla and R. Roy, Sol-gel process for the preparation of fine electroceramic powders, *Ferroelectrics*, **87**: 133 (1988).

15. Hirano, S., T. Hayashi, K. Nosaki and K. Kato, Preparation of stoichiometric crystalline lithium niobate fibers by

sol-gel processing with metal alkoxides, *J. Am. Ceram. Soc.*, **72**: 707 (1989).

16. Christensen, A.N., Hydrothermal preparation of barium titanate by transport reactions, *Acta Chem. Scand.*, **24**: 2447 (1979).

17. Kutty, T.R.N., R. Vivenkanandan and P. Murugrraji, Precipitation of rutile and anatase (TiO_2) fine powders and their conversion to metal titanate ($MTiO_3$) (M = barium, strontium, calcium) by the hydrothermal method, *Mater. Chem. Phys.*, **19**: 533 (1978).

18. Mazdiyasni, K.S., Fine particle perovskite processing, *Am. Ceram. Soc. Bull.*, **63**: 591 (1984).

19. Nakamura, T., M. Misono and Y. Yoneda, Reduction-oxidation and catalytic properties of perovskite-type mixed oxide catalysts ($La_{1-x}Sr_xCoO_3$), *Chem. Lett.*, 1589 (1981).

20. Zhang, H.M., Y. Shimizu, Y. Teraoka, N. Miura and N. Yamazoe, Oxygen sorption and catalytic properties of lanthanum strontium cobalt iron oxide ($La_{1-x}Sr_xCo_{1-y}Fe_yO_3$) perovskite-type oxides, *J. Catal.*, **121(2)**: 432 (1990).

21. Zhang, H.M., Y. Teraoka and N. Yamazoe, Preparation of perovskite-type oxides with large surface area by citrate process, *Chem. Lett.*, 665 (1987).

22. Gallagher, P.K., A simple method for the prepararion of $(RE)FeO_3$ and $(RE)CoO_3$, *Mat. Res. Bull.*, **3**: 225 (1967).

23. Gallagher, P.K. and B. Prescott, Further studies of the thermal decomposition of europium hexacyannoferrate (III) and ammonium europium hexacyanoferrate (II), *Inor. Chem.*, **9**: 2510 (1970).

24. Gallagher, P.K., D.W. Johnson, Jr., E.M. Vogel, G.K. Wertheim and F.J. Schnetter, Synthesis and structure of $BaPtO_3$, *J. Catal.*, **21**: 277 (1977).

25. Wenkus, J.F. and W.Z. Leavitt, Papers of the Conf. on Mag. and Mag. Mater., *AIEE Publication T-91*, 526 (1957).

26. Munir, Z.A., Synthesis of high-temperature materials by self-propegating combustion methods, *Am. Ceram. Soc. Bull.*, **67**: 342 (1988).

27. Kourtakis, K., M. Robbins and P.K. Gallagher, Synthesis of $Ba_2YCu_3O_7$ powder by anionic oxidation of (NO_3^{-1}) - reduction ($RCOO^{-1}$, where R is H, CH_3, and CH_3CH_2), *J. Solid State Chem.*, **83**: 230 (1989).

28. Kourtakis, K., M. Robbins and P.K. Gallagher, A novel synthetic method for the preparation of oxide superconduc-

tors: anionic oxidation-reduction, *J. Solid State Chem.*, **82**: 390 (1989).

29.   Kourtakis, K., M. Robbins, P.K. Gallagher and T. Tiefel, Synthesis of $Ba_2YCu_4O_8$ by anionic oxidation-reduction, *J. Mater. Res.*, **4**: 1289 (1989).

30.   Varma, H., K.G. Warrier and A.D. Damodaran, Metal nitrate-urea decomposition route for Y-Ba-Cu-O powder, *J. Am. Ceram. Soc.*, **73**: 3103 (1990).

31.   Pankajavalli, R., J. Janaki, O.M. Sreedharan, J.B. Gnanamoorthy, G.V.N. Rao, V. Sankarasastry, M. Janawadkar, Y. Hariharan, T.S. Radhakrishnan, Synthesis of high quality 1-2-3 compound through citrate combustion, *Physica C*, **156(5)**: 737 (1988).

32.   Schnettler, F.J., F.R. Monforte and W.W. Rhodes, A cryochemical method of prparing ceramic materials, *Science in Ceramics*, Vol. 4, G.H. Stewart (Ed.), H. Blacklock Co., Manchester, 1968.

33.   Johnson, D.W., P.K. Gallagher, D.J. Nitti and F. Schrey, Effect of preparation technique and calcination temperature on the densification of lithium ferrites, *Am. Ceram. Soc. Bull.*, **53**: 163 (1974).

34.   Gallagher, P.K., D.W. Johnson, E.M. Vogel and F. Schrey, Microstructure of some freeze dried ferrites, in *Ceramic Microstructures'76*, R.M. Fulrath and J.A. Pask (Eds.), Westview Press, Bouler, CO, 1976, p. 423.

35.   Song, K.H., H.K. Liu, S.X. Dou and C.C. Sorrell, Rapid formation of the 110 K phase in bismuth lead strontium calcium copper oxide through freeze-drying powder processing, *J. Am. Ceram. Soc.*, **73(6)**: 1771 (1990).

36.   Hibbert, B.D., J. Lovegrove and A.C.C. Tseung, A critical examination of a cryochemical method for the preparation of high-surface-area semiconducting powders. Part 3. Factors which determine surface area, *J. Mater. Sci.*, **22(10)**: 3755 (1977).

37.   Imai, H., K. Takami and M. Naito, Preparation of $CoLaO_3$ catalyst fine particles by mist decomposition method II effect of additives for the increase of surface area, *Mat. Res. Bull.*, **19**: 1293 (1984).

38.   Cuomo, J.J., C. Guarnieri, M. Richard, S.A. Shivashankar, R.A. Roy, D.S. Yee and R. Rosenberg, Large area plasma spray deposited superconducting $YBa_2Cu_3O_7$ thick films, *Adv. Ceram. Mater.*, **2(3B)**: 422 (1989).

39. Phule, P.P. and S.H. Risbud, Low-temperature synthesis and processing of electronic materials in the $BaO-TiO_2$ system, (1990).

40. Karpinski, J., E. Kaldis, E. Jilek, S. Rusiecki and B. Bucher, Bulk synthesis of the 81-K superconductor yttrium barium copper oxide ($YBa_2Cu_4O_8$) at high oxygen pressure, *Nature*, **336:** 660 (1988).

41. Cava, R.J., J.J. Krajewski, W.F. Peck, B. Batlogg, L.W. Rupp, R.M. Fleming, A.C.W.P. James and P. Marsh, Synthesis of bulk superconducting $Ba_2YCu_4O_8$ at one atmosphere oxygen pressure, *Nature*, **338:** 328 (1989).

42. Pooke, D.M., R.G. Buckley, R. Presland and J.L. Tallon, Bulk superconducting $Y_2Ba_4Cu_7O_{15-}$ and $YBa_2Cu_4O_8$ prepared in oxygen 1 atm, *Phys. Rev. B*, **41:** 6616 (1990).

43. Takahara, H., Preparation and dielectric properties of mixed-sintering ceramics, *Jpn. J. Appl. Phys. Part 1*, **24:** 427 (1985).

44. Martinez, E., E. Sanchez Viches, A. Beltran-Porter and D. Beltran-Porter, Low temperature synthesis of Ba-Fe mixed oxides having perovskite structures, *Mat. Res. Bull.*, **21:** 511 (1985).

45. Brody, H.D., J.S. Haggerty, M.J. Cima, M.C. Flemings, R.L. Barns, E.M. Gyorgy, D.W. Johnson, W.W. Rhodes, W.A. Sunder and R.A. Laudise, Highly textured and single crystal bismuth calcium strontium copper oxide ($Bi_2CaSr_2Cu_2O_x$) prepared by laser-heated float zone crystallization, *J. Crystal. Growth.*, **96:** 225 (1989).

46. Vogel, E.M., D.W. Johnson, Jr. and P.K. Gallagher, Oxygen stoichiometry in $LaMn_{1-x}Cu_xO_{3+y}$ by thermogravimetry, *J. Am. Cer. Soc.*, **60:** 31 (1977).

47. Lindemer, T.B., J.F. Hunley, J.E. Gates, A.L. Sutton, Jr., J. Byrnestad, C.R. Hubbard and P.K. Gallagher, Experimental and thermodynamic study of nonstoichiometry in $YBa_2Cu_3O_{7-x}$, *J. Am. Ceram. Soc.*, **72:** 1775 (1989).

48. Specht, E.D., C.J. Sparks, A.G. Dhere, J. Brynestad, O.B. Cavin, D.M. Kroeger and H.A. Oye, Effect of oxygen pressure on the orthorhombic-tetragonal transition in the high-Temperature superconductor $YBa_2Cu_3O_x$, *Phys. Rev. B, Condens. Matter.*, **37:** 7426 (1988).

49. Dijkkamp, D., T. Venkatesan, X.D. Wu, S.A. Shaheen, N. Jisrawi, Y.H. Min-Lee, W.L. McLean and M. Croft, Preparation of Y-Ba-Cu-O oxide superconductor thin films