

Chapter 1

Introduction

1.1 Motivation

Sensor applications in advanced aerospace and hypersonic propulsion systems involve high temperature and heat flux environments where stability and reliability under extremely harsh environments are principal concerns. Also, compatibility of the sensors with the ceramic and/or nonmetallic materials used for the fabrication of the propulsion systems and their endurance to hostile temperature, flow and thermal cycling environments is very important. The demanding requirements have initially led to the use of Platinum/Platinum-Rhodium based thin film thermocouples. However, earlier studies by several researchers indicated many problems associated with their use at temperatures exceeding 900 K. These include Rhodium oxidation at around 900 K, poor adhesion to the substrate, reaction with the substrate at high temperatures and coalescing of the films due to electromigration resulting in electrical discontinuity at higher temperatures.

The fundamental research to be performed is geared towards identifying novel materials that can withstand the above-mentioned severe environments, studying their feasibility as well as their limits of operation.

1.2 Objectives

The aim of this research is to identify novel high temperature conducting materials, which possess stability in terms of phase, chemical composition, and microstructure in the thin film form. In this regard, the following objectives were proposed.

- Identify several candidate materials from the literature, which have shown excellent high temperature stability in the bulk form.
- Fabricate an experimental set up to measure the properties of these candidate materials in the thin film form as a function of temperature. The primary properties of interest were high temperature stability, stable and fairly high seebeck coefficient and electrical conductivity throughout the temperature range of operation.
- Study the thermal and electrical stability of these materials and predict the limits of operation of the thin film thermocouples based on these materials.

1.3 Dissertation Organization

This dissertation begins with a review on the different areas that will be exposed in this research. Chapter 2 reviews in brief, thin film thermocouples, their advantages over bulk thermocouples, the selection criteria of candidate materials, the candidate materials selected from literature and their properties in the bulk form. Chapters 3-5 consist of papers presented, and to be submitted, to various journals, focussing on high temperature thin film properties of materials. Because of this layout, the reader will find repetitions in some of these chapters. Therefore, each of these chapters comprises introduction, experimental procedure, results and discussion of results as well as conclusions or summary separately. Chapter 6 summarizes all the results and proposes some recommendations for further research.

Chapter 2

Literature Review

2.1 Temperature Measurements - Thin Film Thermocouples

Thermocouples are devices primarily used for temperature measurement. The principle of operation of thermocouples is based on the findings of Seebeck that a closed circuit composed of two dissimilar conductors, when their two junctions are maintained at different temperatures (known as cold and hot junctions) yields a current through the circuit. In other words, a thermocouple converts thermal energy into electrical energy. Therefore, by monitoring the current through the circuit (or voltage), a very accurate measurement of the temperature of the hot junction can be made, knowing the temperature of the cold junction. The cold junction is also called the reference junction.

Several types of thermocouples are in use today, some of which include wire thermocouples, rod thermocouples, thin film thermocouples and so on. For surface temperature measurements, especially under high temperature, high heat flux and high speed flow environments, thin film thermocouples offer numerous advantages over the other types of thermocouples primarily due to their small size. For instance, a typical thin film thermocouple has the dimensions of < 1 micron thickness and < 1 mm width, as compared to wire thermocouples (> 500 microns thickness and atleast a few mm length). Consequently, thin film thermocouples provide extremely fast response ($1 \mu\text{sec}$), excellent spatial resolution ($< 1\text{mm}^2$), minimal disturbance to the surface being monitored and simplicity. In recent years, developments in CMOS fabrication methods have offered high volume production of thermocouple materials compatible with integrated circuit technology and thereby lowered cost of production. All these advantages have led to renewed interest for various applications such as, thin film thermocouple pressure gauges¹, turbine engines², diesel engines³, thermopiles⁴, AC-DC converters⁵, thermoelectric devices⁶ and miniature temperature controllers⁷.

For high temperature applications, thin films provide several problems along with the above-mentioned advantages. The smaller size of these thermocouples also reduces the diffusion distances significantly as compared to wire or rod thermocouples. In most cases, these distances are shorter than a few microns, rendering the thin film

thermocouples extremely sensitive to the environments. For example, silicide thermocouples are used in conventional furnaces up to temperatures around 1600 °C in rod form, whereas thin film silicide thermocouples have been shown to oxidize even in extreme vacuum conditions at temperatures no greater than 1100 °C⁸. Although silicides are excellent candidates for high temperature applications in the rod form, in the thin film form, they are practically useless under operating temperatures exceeding 1100 °C. Therefore, the objective of identifying a candidate thin film thermocouple material suitable for operation in both vacuum as well as oxidizing atmospheres is extremely challenging.

2.2 Criteria of Selection of Candidate Materials

High temperature thin film thermocouples to be used in advanced aerospace propulsion systems, diesel engines or turbine systems are expected to perform in rapidly fluctuating environments of temperature, heat flux and high speed flows. In order for the candidate materials to withstand such harsh and severe environments, there are several requirements these materials need to satisfy. Based on these requirements, the following criteria are formulated for the selection of candidate materials for high temperature thin film thermocouple applications.

- *High Melting Point*: This is an indication of the material high temperature stability. Therefore materials with high melting points exhibit great potential as candidate materials for high temperature sensor applications.
- *Stable and fairly high Seebeck Coefficient and Electrical Conductivity*: The performance of the thermocouple fabricated depends on the seebeck coefficient as well as the electrical conductivity of the material. It is required that the candidate material possess stable and fairly high seebeck coefficient and electrical conductivity in the temperature range of operation, as the greater these properties, the higher the thermocouple output and hence, the better the sensitivity of the thermocouple fabricated.
- *Stability of Phase, Structure, Chemical Composition and Microstructure*: In most materials, the thermoelectric properties are a function of the chemical composition, phase and microstructure. Changes in these properties in the temperature range of operation translate as changes in the thermocouple output, thereby losing the

reproducibility of the thermocouples after repeated tests of temperature cycling.

- *Single and Stable Charge Carrier Transport Mechanism in the Temperature Range of Interest:* In many materials, the electrical conduction and charge transport mechanisms are functions of temperature. Changes in the crystal structure, variation in the lattice parameter etc., are some of the numerous reasons for such behavior. These could render discontinuities in the thermocouple output when measured as a function of temperature. Therefore, it is important that the candidate material possess a single and stable electrical conduction as well as charge carrier transport mechanism throughout the temperature range of interest.
- *Compatibility with Ceramic/Nonmetallic Substrates:* The candidate materials should be compatible with the substrates unlike Platinum/Platinum-Rhodium based thermocouples, even at high temperatures.
- *Easy and Straightforward Process of Fabrication in the Thin Film form:* For cost effective thermocouple production, it is judicious to select candidate materials with easy and straightforward processibility in thin film form.

2.3 Non-Metallic Thin Film Thermocouple Materials

From literature, several candidate nonmetallic materials were selected for high temperature thin film thermocouple applications. As the properties of most of these materials are available only in bulk form, the following table is formulated from the bulk Table1. Nonmetallic materials selected from literature

Material	Melting Point (°C)	Electrical Resistivity (μOhm-cm)	Thermoelectric Power (μV/C)	Temperature of Oxidation (°C)
TiC	3257	55-60	-4.5 to -11.2	1100-1200
TaC	3925	20-30	-11.7	900-1000
HfC	3900	30-39	-5 to -11.5	1100 – 1200
TiN	2950	30-40	-2.6 to -7.7	1100 – 1200
HfN	3000	33	-2.9	700 – 900
MoSi ₂	2030	21.6	-3	1600-1700
TaB ₂	3100	32-37	-2.8 to -3.1	800 - 900

data⁹⁻¹². In the case of nonmetallic thermocouple materials, oxidation resistance plays a significant role and therefore, was used as an additional criterion for selection. Based on the above data from literature, the following thermocouple pairs have been selected.

(a) TiC/TaC, (b) ZrC/HfC (c) TiN/HfN (d) MoSi₂/WSi₂

In literature, several researchers have identified sputtering as an easy, reproducible and straightforward method of deposition of these thin films. Chapter 3 focuses on the deposition, thermoelectric properties and thermal stability of one such pair of materials viz., TiC/TaC, and reports the feasibility of use in high temperature thin film thermocouple applications involving vacuum or inert environments.

2.3 Conducting Oxides for Thin Film Thermocouple applications

Although nonmetallic refractory ceramic materials possess excellent thermoelectric properties and very high melting points, one major drawback with their use lies in their poor oxidation resistance at high temperatures particularly in the thin film form limiting their range of applications to those involving vacuum or inert environments. Therefore, it was proposed that multicomponent conducting perovskite oxides be investigated for applications involving oxidizing or air environments. Conducting perovskite oxides possess stable and fairly large electrical conductivity and Seebeck coefficients, stability of phase, structure, composition as well as microstructure in both oxidizing and reducing atmospheres. In addition, these materials are easy to fabricate in thin film form, i.e., they do not require very high deposition temperatures or high oxygen partial pressures for phase formation. Therefore, these materials offer excellent potential in high temperature thin film thermocouple applications.

In general, conducting oxides are essentially narrow band semiconductors, with the major crystal structures being rutile, pyrochlore, NaCl type, perovskite, spinel, Mo/W bronze and K₂NiF₄ structure¹³. The materials of interest in this research belong to perovskite type. Conduction in these materials occurs through a thermally activated process called small polaron hopping. A polaron refers to a charge carrier, localized over an area of the order of a lattice constant. Electrical conduction occurs when a polaron hops between equivalent or nonequivalent hopping sites by the motion of electrons or holes through the narrow energy bands. In these materials, polarons are created by several mechanisms. For instance, in the case of CaMnO₃, the valence states of Ca and

Mn are +2 and +4 respectively. When the A site (Ca site) is doped with a +3 valence state donor, charge compensation occurs through either formation of one oxygen vacancy for every two lattices doped, or by Mn changing its valence state from +4 to +3. The latter results in the formation of a charge carrier. This is however, localized over the area of the lattice. Conduction occurs through hopping of such charge carriers between two hopping sites.

In literature, several perovskite conducting oxide systems have been investigated for numerous applications ranging from superconductivity to electrodes. Most of the information, however, is limited to bulk form and hence will be used as reference to select the candidate materials. Although one could expect the properties of materials to be different in bulk form and thin film form, in most cases, they follow the same trend and differ only by a small factor. The following materials have been selected for investigation in this research.

Table. 2: Candidate Materials selected from literature (data on bulk)^{14, 15}

Material	Temperature range (K)	Resistivity (Ohm.cm)	Seebeck coefficient ($\mu\text{V/C}$)
$\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$	300 – 1200	0.003	15 - 20
$\text{La}_{(1-x)}\text{Ca}_x\text{MnO}_3$	300 - 1500	0.0003 – 0.0474	-0.01 to -0.03
$\text{Y}_{(1-x)}\text{Ca}_x\text{MnO}_3$	500 - 1600	0.0005 – 0.05	-0.02 to –0.05
$\text{La}_{(1-x)}\text{Ca}_x\text{CrO}_3$	400 - 1500	0.1 - 1	0.29 – 0.35
$\text{Y}_{(1-x)}\text{Ca}_x\text{CrO}_3$	400 - 1500	0.1 - 1	0.3 – 0.6

Each of the following chapters presents the work done on some of the above mentioned materials, both nonmetallic as well as conducting oxides

Chapter 3

Thin Film TiC/TaC Thermocouples

3.1 INTRODUCTION

In this study, titanium and tantalum carbide thin films were investigated, for the first time, for high temperature thin film thermocouple applications in inert or vacuum environments. Earlier, transition metal carbides were studied extensively as interesting engineering materials, (e.g., as cermets in hard metals industry) owing to their extremely high melting points, strength and good corrosion resistance¹⁶. Among many transition metal carbides, titanium carbide based composites particularly are used as cutting tools, plasma and flame spraying processes in air etc¹⁷. Tantalum carbide on the other hand also has extremely high melting point (3983 °C, one of the highest known) as well as high mechanical hardness¹⁸. Its electronic and optical similarities with group IV nitrides (such as TiN) are also of interest¹⁹. However, the range of applications of the transition metal carbides is limited due to their poor oxidation resistance. There are several reports of physical vapor deposition (PVD) of these carbides in literature and the deposition of TiC and TaC is easy and straightforward. All these properties of TiC and TaC have prompted the present investigation for high temperature thin film thermocouple applications in vacuum or inert environments.

3.2 EXPERIMENTAL PROCEDURE

1. Thin film deposition and characterization

Thin films of TiC and TaC were deposited using r.f sputtering technique in a Denton Vacuum sputtering system. Sheet resistance of the deposited thin films was measured using a four point probe. The deposition conditions were varied to obtain the optimum sheet resistance of the thin films as well as substantial deposition rates. The r.f. power during deposition was varied from 50 to 100 watts. A TiC (99.5% pure) target, 2 inches in diameter, 0.125 inches thick and a TaC target with identical specifications were used for deposition. The base pressure in the chamber was maintained between $3-10 \times 10^{-7}$ torr. Argon was used as the sputter gas, and the deposition pressure was varied from 2 to 30 mtorr. Electronic grade alumina was used as substrate and the substrate temperature

during deposition was varied from room temperature to 850 °C.

Thickness of the deposited films was measured using Dektak profilometer and weight measurements. X-ray diffraction technique was used to study the phase development in the films. A Scintag diffractometer was used to record the XRD patterns using Cu K α radiation. Chemical composition of the films was studied using electron scattering for chemical analysis (ESCA) technique. Auger electron spectroscopy was used to study the interface characteristics and oxidation mechanism of the carbide thin films after exposure to high temperatures.

II. Thin film thermoelectric properties measurement

Thin films of TiC and TaC were deposited on alumina substrates using the optimized deposition conditions in the same sputtering system. From the deposited samples, resistors of width 4-4.5 mm were cut. These resistors were pasted on electronic grade alumina samples. The height of the samples was about 12 mm. The principle of measurement of Seebeck coefficient is shown in Fig. 1. Platinum and Platinum-10%Rhodium thermocouples were used to measure the thermoemf of the film. Each thermocouple was inserted in an alumina tube having two isolated holes for the two thermocouple legs. The two thermocouples were placed one on top of the other at a distance of 8 mm from each other. They were sealed using high temperature alumina cement. This was fixed to a stainless steel holder which could be slid length wise. The whole system was spring loaded to ensure contact with the resistor. Fig. 2 shows the experimental setup for high temperature thin film thermoelectric properties measurement system. The top thermocouple was insulated during seebeck coefficient measurement using molybdenum radiation shield to incorporate a temperature difference of about 15 °C. The detailed description of the apparatus with the dimensions and performance analysis is given elsewhere²⁰. The voltages generated between the Pt and Pt-Rh legs of the thermocouple and the temperatures of the hot and cold junctions were measured using a Tempbook 7-channel thermocouple readout system. The whole system was inserted in a high vacuum furnace, which has a built in temperature controller system and also maintains pressures less than 5×10^{-7} torr. From the data collected, seebeck coefficients were plotted as a function of temperature. The equations employed to evaluate the Seebeck coefficient are listed below. S_{Pt} and S_{PtRh} correspond to the voltage drops in the

Pt and PtRh legs of the two thermocouples respectively, ϵ_{film} , ϵ_{Pt} and ϵ_{PtRh} are the Seebeck coefficients of the film, Pt and PtRh respectively and T_h and T_c are the temperatures of the hot and cold junctions respectively.

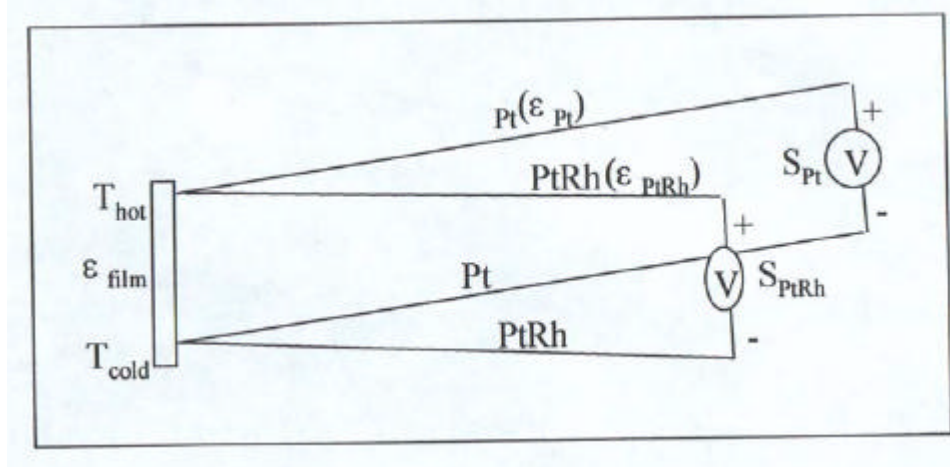


Fig.1 Principle of measurement of seebeck coefficient of thin films as a function of temperature

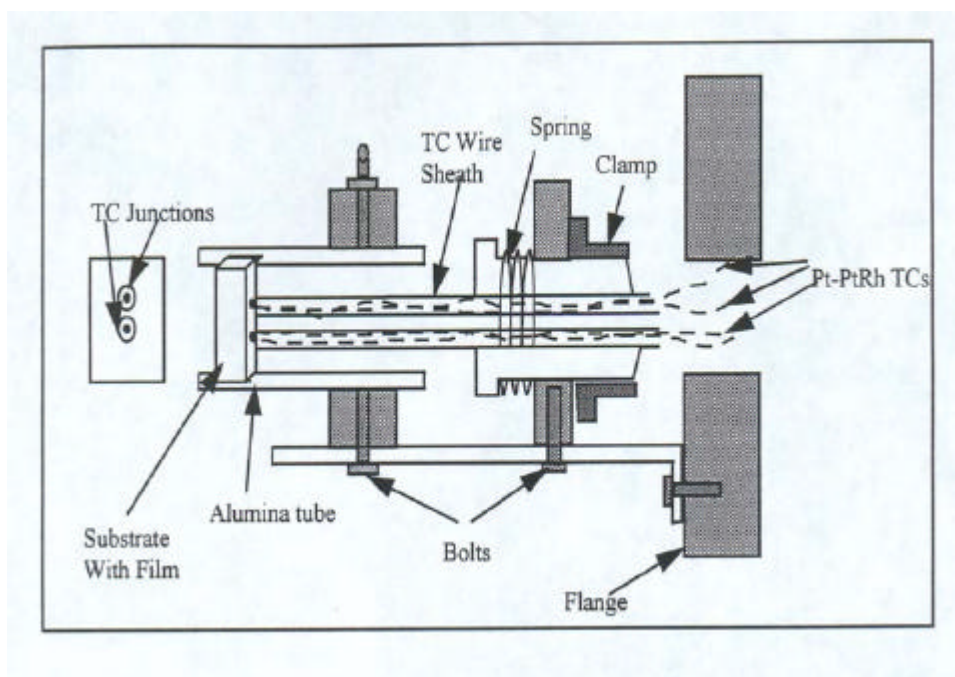
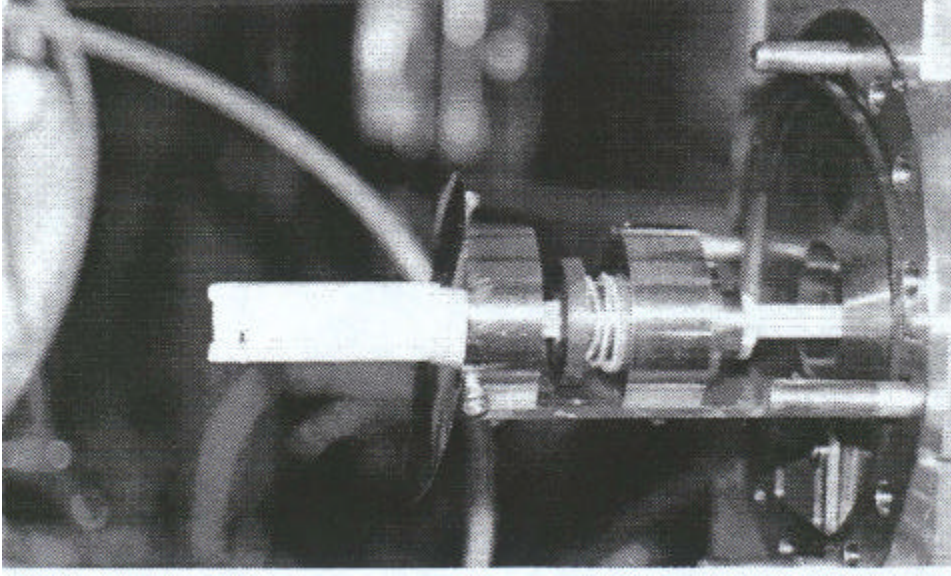


Fig.2 Experimental setup for the thin film thermoelectric properties measurement

(a): Schematic



(b) Photograph

$$\begin{aligned}
 S_{Pt} &= -e_{Pt}(T_h - T_c) + e_{film}(T_h - T_c) \\
 S_{PtRh} &= -e_{PtRh}(T_h - T_c) + e_{film}(T_h - T_c) \\
 e_{film} &= \frac{S_{Pt}}{(T_h - T_c)} + e_{Pt} = \frac{S_{PtRh}}{(T_h - T_c)} + e_{PtRh} \\
 \Delta T_{theoretical} &= (T_h - T_c) = \frac{S_{Pt} - S_{PtRh}}{e_{PtRh} - e_{Pt}}
 \end{aligned}$$

III. Thin film thermocouple calibration and testing

Test thermocouples were deposited on alumina substrates using the optimized deposition conditions in the same sputtering system. Each leg of the thermocouples was deposited separately, and it was found that upon annealing, there is very good electrical continuity in the thermocouples. These thermocouples were calibrated using standard Pt/Pt-Rh thermocouples. Fig. 3(a) shows a photograph of the high vacuum furnace fabricated for thin film thermocouple calibration and Fig. 3(b) shows a schematic of the

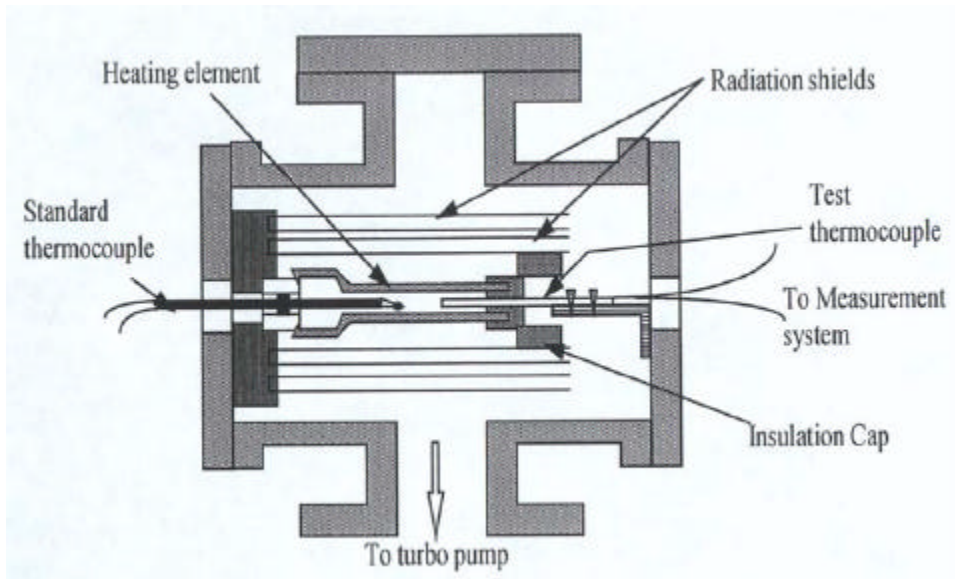
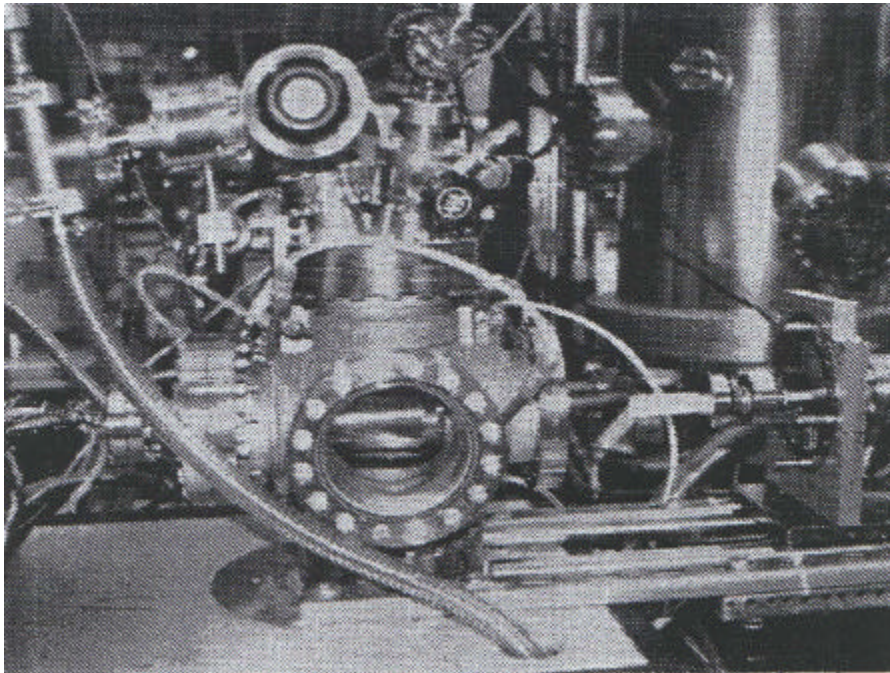


Fig.3 High vacuum furnace fabricated for thin film thermocouple calibration

(a) Schematic



(b) Photograph

test chamber. The furnace was heated using boron nitride heating element by radiation. The test specimen was surrounded by several layers of molybdenum foil to prevent

heating of the exterior of the chamber. Similar foil as well as a thick alumina disc were

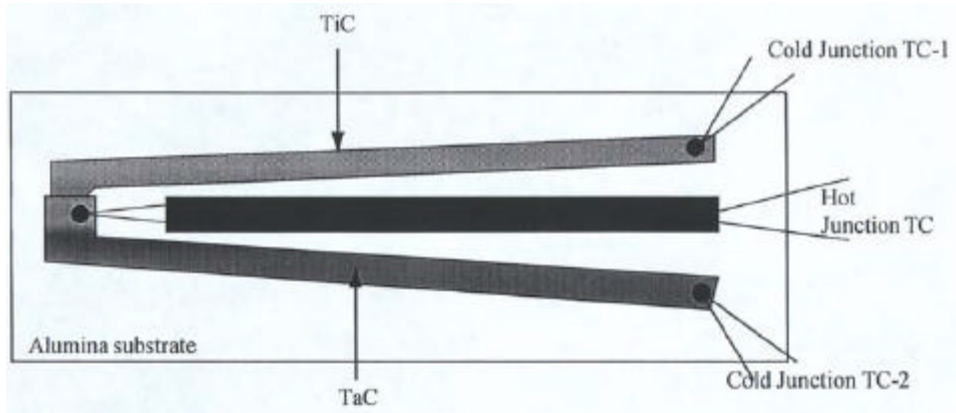


Fig.4 A typical TiC/TaC thermocouple fabricated on alumina substrate

used as insulation caps to prevent the cold junctions of the test thermocouples from getting heated to high temperatures. Added to that, the cold junctions of the test thermocouples were fastened on to a stainless steel block, which was maintained at close to room temperature using circulated cooling water. The chamber was maintained at extremely low base pressures using a cryo pump. Fig. 4 shows the schematic view of a typical TiC/TaC test thermocouple. S-type platinum/platinum-10%rhodium wire thermocouples were used to determine the temperatures of the two cold junctions and the hot junction of the test thermocouples. The thermocouple output was measured using a Tempbook 7-channel thermocouple readout system. The thin film thermocouple output was measured between the two cold junctions as shown in Fig.4.

3.3 RESULTS AND DISCUSSION

I. Sheet resistance of the deposited films

(A) Dependence on r.f. power

Fig. 5 shows the variation of sheet resistance of the TiC and TaC thin films with r.f. power. With increasing r.f power of deposition, the sheet resistance decreases till 100 W beyond which there is little dependence. This effect could be attributed to the difference in the sputter yields of titanium, tantalum and carbon. From literature, it can be found that the sputter yields decrease in the order tantalum, titanium and carbon²¹. The effect of r.f. power of deposition on the sputter yields is more dominant at lower r.f.

powers, whereas at higher r.f. powers, there is smaller difference in the sputter yields. Accordingly, at lower r.f. powers, the deposition rate of tantalum is higher than that of titanium which in turn is higher than that of carbon. At higher r.f. powers, there is little difference in the relative deposition rates. Therefore, at lower r.f. powers, it is reasonable to expect that TaC is more deficient in carbon when compared to TiC. Earlier reports on the dependence of electrical resistivity of TiC and TaC indicate that as the carbon deficiency in TaC and TiC increases, the electrical resistivity increases²². In our experiments, we observe that at higher r.f. powers, the sheet resistance is much lower compared to that at lower r.f. powers, which follows the above discussion. Also, this effect is more evident in the case of TaC when compared to TiC. There was no significant difference in the porosity of the films and hence such effects are neglected. From these experiments, it was found that 100 W was the optimum r.f. power taking into account, the limitations of the equipment.

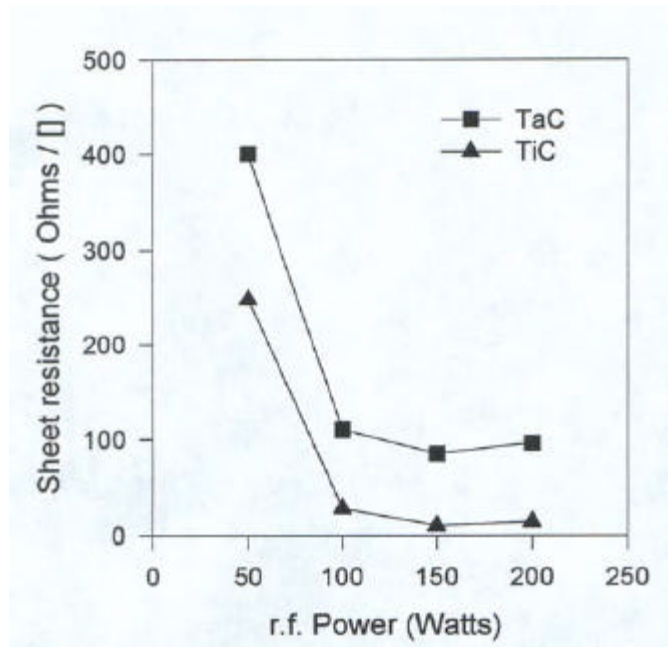


Fig.5 Effect of r.f. power on the sheet resistance of TiC/TaC thin films

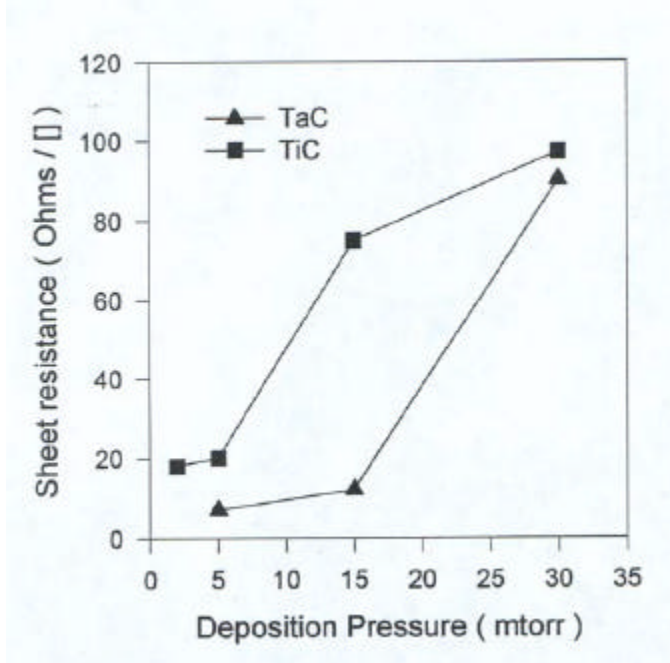


Fig. 6 Effect of deposition pressure on the sheet resistance of TiC/TaC thin films

(B) Effect of sputter gas pressure

Fig. 6 shows the variation of sheet resistance of TiC as well as TaC thin films with sputter gas pressure during deposition. Both TiC as well as TaC show a marked increase in the sheet resistance with increase in the sputter gas. This effect could also be explained on the basis of differences in sputter yields of tantalum, titanium and carbon. At higher sputter gas pressures during deposition, there is a larger difference in the deposition rates of tantalum, titanium and carbon resulting in greater deviation in the stoichiometry which in turn increases the sheet resistance considerably. Also, there was oxygen incorporation into the films at higher pressures of deposition as indicated from composition analyses as well as depth profile analyses arising possibly due to the limitations of the equipment. The presence of oxygen in the films could also result in the increase in the sheet resistance of the films. From these results, it can be seen that lower pressures of sputter gas (argon) result in lower electrical resistivities.

(C) Effect of substrate temperature

Fig. 7 shows the influence of the substrate temperature during deposition on the sheet resistance of TiC and TaC thin films. In the case of TaC, the sheet resistance

decreases sharply when the substrate temperature is increased from room temperature to 400 °C. Further increase in the substrate temperature results in a slight increase in the sheet resistance. This trend can be explained on the basis of two effects viz., densification or grain growth and oxidation of the surface layers of the films. The former results in a decrease in the thin film resistivity while the latter results in an increase in the resistivity. Although a base pressure less than 5×10^{-6} torr is maintained before the argon gas is input into the chamber, there is a possibility of formation of a monolayer of oxide on the top of the carbide films which could result in an increase in the resistivity. However, it can be seen that, the increase in resistivity of the films is extremely small and could also be because of the difference in the deposition rates of the films. These results indicate that a temperature of about 400 °C is optimum for the deposition of carbide thin films.

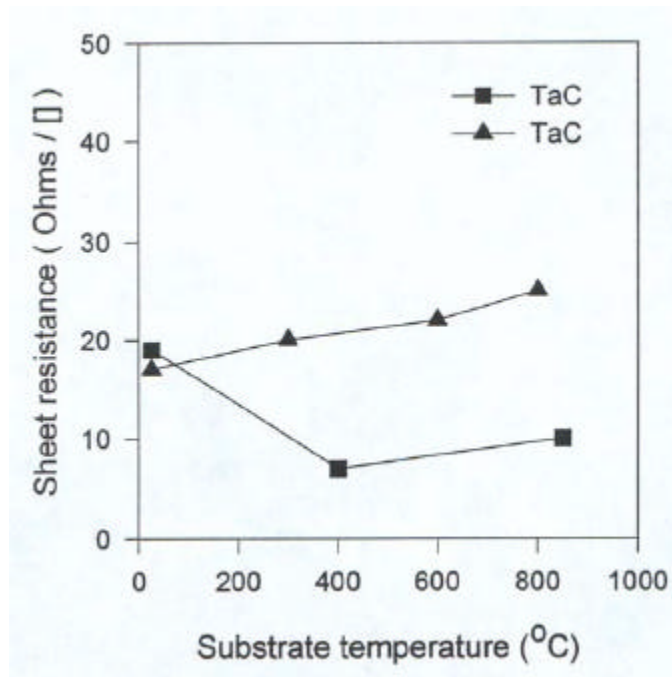


Fig. 7 Effect of substrate temperature on the sheet resistance of TiC/TaC thin films

II Influence of sputter parameters on the deposition rates of TiC and TaC thin films

The influence of r.f. power on the rate of thin film deposition is plotted in Fig.8(a) while Fig. 8(b) shows the corresponding effect of sputter gas pressure. Both figures illustrate that at a constant sputter gas (argon) pressure of 15 mtorr, the higher the r.f.

power or sputter gas pressure during deposition, the higher is the deposition rate. This is expected because as the r.f. power is increased, the number of particles striking the surface of the target is increased, resulting in a greater number of species released from the target. Consequently, the deposition rate is increased. This effect is observed both in

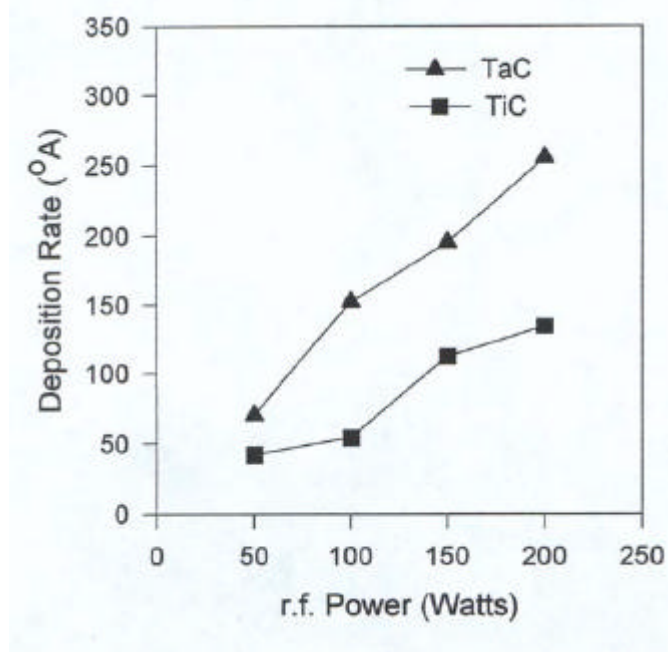


Fig. 8(a) Effect of r.f. power on the deposition rate of TiC/TaC thin films

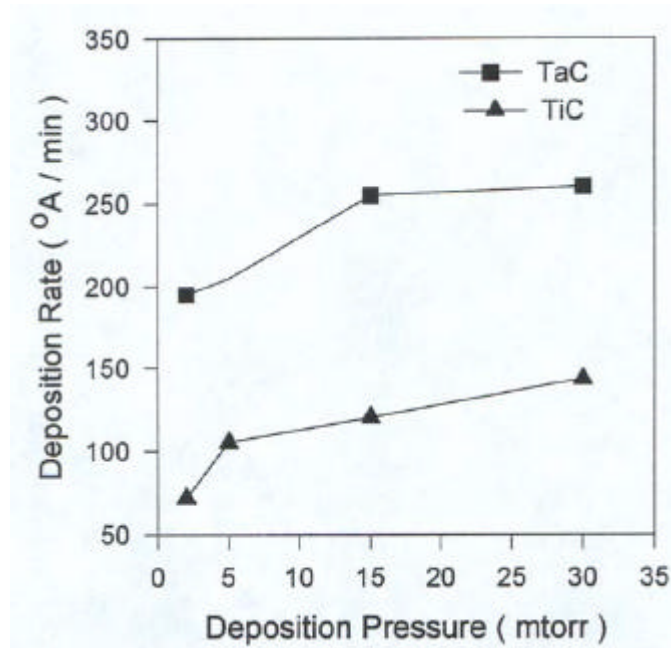


Fig. 8(b) Effect of deposition pressure on the deposition rate of TiC/TaC thin films

TaC as well as TiC thin films. At a constant r.f. power of 150 W, it was observed that increasing the sputter gas pressure increases the deposition rate of the thin films. This can be attributed to the fact that, as the sputter gas pressure in the chamber increases the ion density in the plasma increases, resulting in greater deposition rates. Similar effects have been observed by several researchers and reported in literature²¹.

From all these results it was found that the optimum deposition conditions to obtain substantial deposition rates and at the same time low sheet resistance were, r.f. power of 150 W, substrate temperature of 400 °C and argon pressure of 2 mtorr during deposition. The thickness of the films was measured using a Dektak profilometer and was found to be about 3000 °A. All the results reported hereafter will be on thin films of TaC and TiC on alumina substrates deposited under the optimized sputter conditions. The fabrication of thin film thermocouples was also done using these parameters.

III Thermoemf data of TaC and TiC thin films

Thermoemf of TaC as well as TiC thin films was measured using the thin film thermoelectric properties measurement system shown in Fig.2. Fig. 9 shows the thermoemf as a function of the absolute temperature for TiC and TaC thin films. During the measurement of the thermoemf of the films, it was not possible to control the temperature difference between the hot and cold junctions of the films accurately, and this accounts for the large amount of scatter in the data presented. The trend however, appears to be similar to that reported earlier in literature²³. From the thermoemf data in the thin film form, the thermocouple output of TiC/TaC thermocouples was estimated using a simple linear model. Test thermocouples were fabricated on alumina substrates and calibrated.

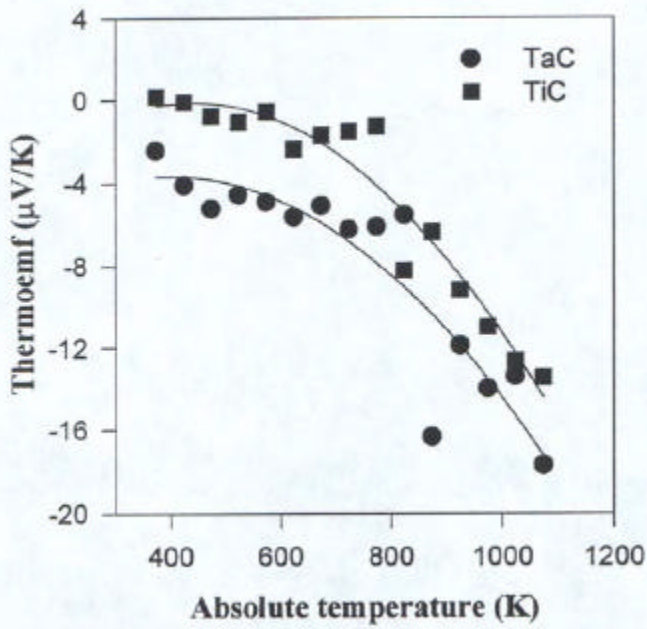


Fig. 9 Thermoemf of TiC/TaC thin films as a function of temperature

IV Thin film TiC/TaC test thermocouple calibration and performance

Fig. 10 shows the performance of two thin film TiC/TaC thermocouples as a function of temperature in vacuum (pressure less than 5×10^{-7} torr). Also shown in the figure is the estimated output of the thermocouple calculated from the thermoemf of TiC and TaC thin films measured separately. From the figure, it is clear that there is very little difference in the thermocouple output of the two thermocouples testifying the consistency of the fabrication and the reproducibility of the data. The difference between the estimated and the experimentally determined values of the thermocouples could be attributed to the inaccuracies in the calculations arising possibly due to lack of control over the temperature difference between the hot and cold junctions of the thin films during thermoemf measurements. The second thermocouple was subjected to a temperature higher than the first (>1350 K) and this resulted in the breakdown of the thermocouple. From this observation, the temperature limit of operation of TiC/TaC

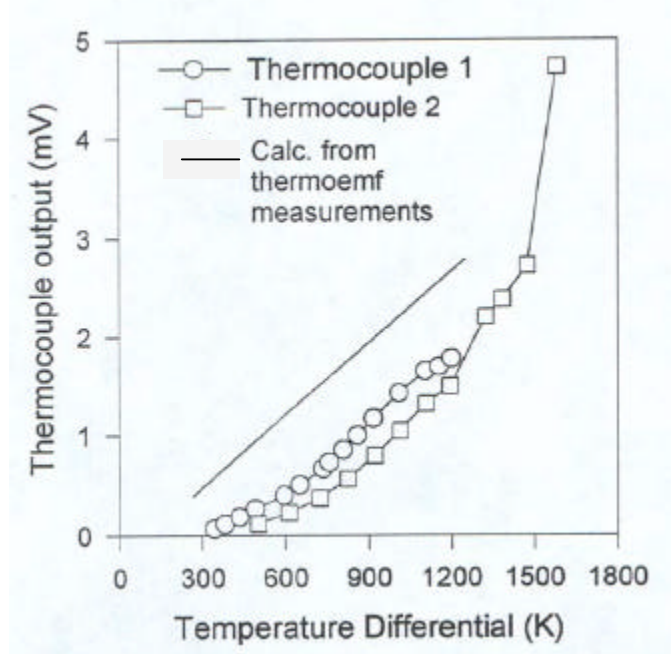


Fig.10 Thermocouple output of two TiC/TaC test thermocouples

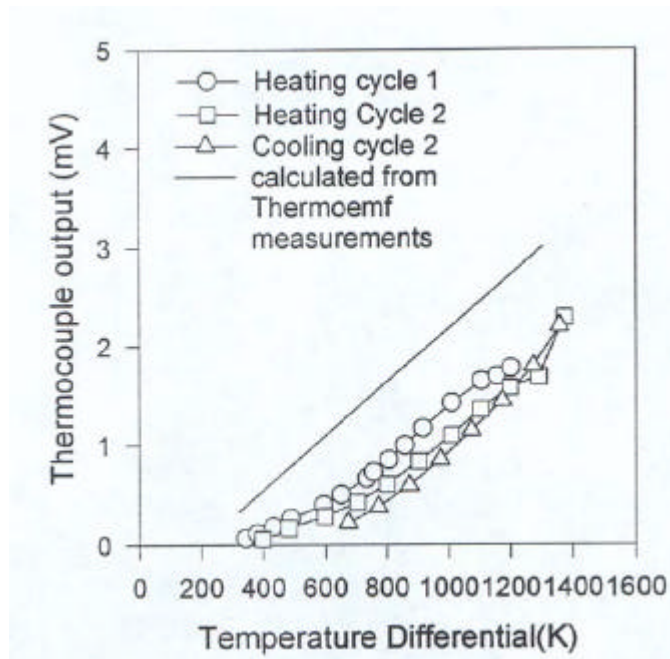


Fig.11 Thermocouple output of a TiC/TaC test thermocouple after repeated thermal cycling

thermocouples was determined to be about 1350 K.

Fig. 11 illustrates the thermocouple output of thin film TaC/TaC thermocouples tested under several repeated cycles of heating and subsequent cooling. It can be observed that there is no significant change in the output of the test thermocouples during heating and cooling indicating stability of chemical composition, phase and thermoelectric properties of the films. The minor changes in the thermocouple outputs between heating and cooling cycles of operation could be attributed to any grain growth or densification of the films. The thermocouple, which was subjected to temperatures beyond the maximum temperature of operation, developed electrical discontinuities, which could be seen clearly with naked eye.

Chapter 4

$\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ for Thin Film Thermocouple Applications

4.1 INTRODUCTION

Thin film thermocouples have been demonstrated to possess several advantages arising mainly due to their small size (1 micron thick and less than 1 mm wide). They offer excellent spatial resolution, low cost in large volume production and extremely fast response²⁴⁻²⁷. In the past, Platinum/Platinum-Rhodium based thin film thermocouples have been used for surface temperature measurements. However, for high temperature applications, these thermocouples have indicated several problems some of which include poor adhesion to the substrate, rhodium oxidation, reaction with the substrate at high temperatures and coalescing of the films due to electromigration resulting in electrical discontinuity at higher temperatures.

Subsequently, alternate materials were investigated for this purpose, some of which are carbides, borides, silicides and nitrides. These refractory ceramics have high melting points and also possess excellent electrical conductivities and Seebeck coefficients at high temperatures. Most of these materials however, exhibit poor oxidation resistance at high temperatures even in vacuum. For instance, recent studies indicated that carbide (TiC and TaC) thin films oxidize completely at 1200K, even under a pressure less than 10^{-4} torr resulting in the thermocouple breakdown. Silicide thin films (ReSi_2 and WSi_2) have also been found to oxidize completely at temperatures above 1100 K.

The important criteria to be satisfied by candidate thin film thermocouple materials are chemical stability and phase stability, stable and fairly large electrical conductivity and Seebeck coefficient, presence of a single charge transport mechanism for electrical conduction, resistance to oxidation in the entire temperature range of operation and easy processibility in the thin film form. Previously investigated material families have demonstrated the absence of at least one of the above mentioned properties. Earlier studies for different applications show that some of the mixed oxide families (perovskite type) have good chemical and phase stability in both oxidizing and reducing

atmospheres, good thin film processibilities, and large electrical conductivities. Some cobaltites, manganates and chromites have demonstrated large seebeck coefficients and one dominant charge carrier mechanism for electrical conductivity in bulk form throughout the temperature range of interest. This prompted the study of conducting oxides for thin film thermocouple applications. In this paper, one such family (LSCO) is investigated and high temperature electrical and thermoelectric properties have been studied.

Lanthanum strontium cobalt oxides with the perovskite structure have been studied for several applications which include catalysts for toluene oxidation²⁸ oxygen electrodes in various solid and liquid electrolyte electrochemical devices²⁹, oxygen membranes³⁰, electrodes in ferroelectric memory devices³¹ and solid oxide fuel cells (SOFCs)³². Consequently, there have been several independent reports of electrical resistivity³³ and Seebeck coefficients³² of these compounds mostly in the bulk form. However, there has not been a report of a comprehensive study of these oxides in the thin film form correlating the phase, composition, electrical resistivity, and Seebeck coefficient dependence on temperature and annealing conditions. In order to be applicable as thin film thermocouple materials, the candidate materials should possess excellent chemical and phase stability, fairly high and stable electrical conductivity and Seebeck coefficient and one stable charge carrier transport mechanism. This makes it desirable to carry out a detailed investigation of the thermal stability and thermoelectric properties of LSCO and their dependence on the parameters mentioned above.

LSCO belongs to the family of perovskite-type mixed oxides. Most of these mixed oxides are narrow band semiconductors. The outer electrons of the atoms in these materials are more localized, therefore, only a narrow band of energy forms. In solids, electrons or holes in narrow bands move either by tunneling through a potential well or by hopping. Though the hopping mobilities at room temperature are low, usually, the density of charge carriers is very large resulting in metallic conductivity. These mixed oxides essentially have the general formula ABO_3 where the A site is substituted by another cation. A and B in this case correspond to La and Co, respectively, while the substitution cation is Sr. Conduction in these compounds occurs in two ways. La and Co in unsubstituted $LaCoO_3$ each has a valence of +3. When the La atom is substituted with

Sr (valence +2), to maintain charge neutrality, the valence of Co changes from +3 to +4. This causes the “creation” of an electronic charge carrier, in this case, a hole. This hole, however, is localized over an area of the order of a lattice constant unlike metallic charge carriers and is often referred to as a polaron. On the other hand, any oxygen vacancy present in the compound acts as ionic charge carrier. However due to low mobility of ionic charge carriers as compared to polarons, the former do not play significant role in charge transport. The mobility of polarons occurs through a thermally activated process known as hopping. Thus, conduction in LSCO occurs through small polaron hopping.

Several researchers have formulated the electrical conductivity(σ) and Seebeck coefficient(α)³⁴ of materials with predominantly small polaron hopping conduction mechanism as follows.

$$\sigma = \frac{(1-c)}{kT} n e^2 a_0 \gamma \exp\left(\frac{-E_a}{kT}\right)$$

$$\alpha = \left(\frac{k}{e}\right) \ln\left[\frac{2(1-c)}{c}\right] + \left(\frac{k}{e}\right) \frac{zJ^2 k T}{E_B^3}$$

where, c-fraction of sites occupied by polarons, E_a -activation energy of hopping, n-small polaron concentration, e-electron charge, a_0 -distance between sites, γ -optical phonon frequency, z-number of nearest neighbors, J-intersite transfer energy during hopping process, E_B -binding energy of polaron and k-Boltzmann constant. In other words, the electrical conductivity of these compounds varies exponentially with temperature while the Seebeck coefficient follows the empirical relation $\alpha=A+BT$.

All the above mentioned properties are sensitive to both the thin film deposition technique used and the substrate on which the film is deposited. It is important that the stoichiometry and phase of the thin films is consistent and this depends critically on the deposition technique. Pulsed laser deposition has demonstrated excellent stoichiometry and phase control of the films and hence was chosen as the deposition technique. The substrate, on the other hand plays an important role at high temperatures. There should not be any changes in the chemical and electrical characteristics of the substrate and also, there should be minimal reaction between the film and the substrate in the entire temperature range of experiments. Moreover, the substrate should not play any role in the

microstructural and morphological development of the thin film. Taking all these into consideration, sapphire (1102) has been used as the substrate for all the films deposited in this study.

4.2 EXPERIMENTAL PROCEDURE

Thin films of $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ ($x=0.3, 0.5, 0.7$) were fabricated on sapphire ($\bar{1}102$) substrates by pulsed laser deposition (PLD) from bulk targets prepared by the standard powder method. The films were characterized for phase, composition, microstructure and thickness. The electrical resistivity and Seebeck coefficient of the films both in as deposited condition and annealed at 800 °C for 30 mins were measured as a function of temperature in air by a home made device. Also, the room temperature resistivity of the films after annealing at different temperatures was measured. The experimental details are given below.

Thin film deposition

Powders of La_2O_3 , SrCO_3 and CoO_3 (99.99%) in the required stoichiometric ratios were mixed thoroughly in ethanol solution and the resulting mixture dried overnight at 90 °C. After drying, the powder was then calcined at 900 °C for 3 hours. Then a bulk target for pulsed laser deposition was made by compacting the powder at 5 Mpa, and then sintering at 1300 °C for 3 hours in air. This bulk sample was used as the target in PLD.

A KrF_2 (248 nm) excimer laser was used to ablate the target. The target and the substrate are mounted in different holders and are separated by a prefixed distance. Both could be independently rotated. There is provision for independent heating of the substrate during deposition. The substrate (sapphire) was heated to 650 °C during deposition. The two holders are inserted into a high vacuum chamber (10^{-6} torr). The laser beam was collimated and focused onto the target. Both the target and the substrate were rotated to ensure uniform film deposition on the substrate. The energy of the laser used was 700 mJ, at a replate frequency of 30 Hz. the deposition time was 25 mins. During deposition, there was an input of oxygen gas and the pressure inside the deposition chamber was maintained at 400 mtorr. After deposition, the films were characterized for thickness, phase, composition and microstructure.

Characterization

After deposition, the thickness of the films was measured by a Dektak profilometer. Then, X-ray diffraction studies were conducted on all the films using a Scintag diffractometer. After the phase was studied, composition was analyzed using Electron spectroscopy for chemical analysis (ESCA). Then, the grain size, microstructure and surface roughness were characterized by Atomic force microscopy (AFM). The room temperature resistivity of the films were measured by a four point probe. Then electrical resistivity and seebeck coefficient were measured in air as a function of temperature.

Electrical resistivity and Seebeck coefficient measurement

From the samples deposited as described earlier, resistors of width 4-4.5 mm were cut. These resistors were pasted on electronic grade alumina samples. The height of the samples was about 12 mm. Platinum and Platinum-10%Rhodium thermocouples were used to measure the thermoemf of the film. Each thermocouple was inserted in an alumina tube having two isolated holes for the two thermocouple legs. The two thermocouples were placed one on top of the other 8 mm distant from each other. They were sealed using high temperature alumina cement. This was fixed to a stainless steel holder which could be slid length wise. The whole system was spring loaded to ensure contact with the resistor. The resistance of the sample was measured by a Keithley 2000 digital multimeter and resistivity calculated from the resistance using the dimensions of the resistor. The top thermocouple was insulated during Seebeck coefficient measurement using fiber glass to incorporate a temperature difference of about 10-15 °C. The detailed description of the apparatus with the dimensions and performance analysis is given elsewhere³⁵. The voltages generated between the Pt and Pt-Rh legs of the thermocouple and the temperatures of the hot and cold junctions were measured using a Tempbook 7-channel thermocouple readout system. The whole system was inserted in a furnace which has a built in temperature controller system. From the data collected electrical resistivity and Seebeck coefficients were plotted as a function of temperature.

The equations employed to evaluate the Seebeck coefficient are listed below.

$$S_{Pt} = -e_{Pt}(T_h - T_c) + e_{film}(T_h - T_c)$$

$$S_{PtRh} = -e_{PtRh}(T_h - T_c) + e_{film}(T_h - T_c)$$

$$e_{film} = \frac{S_{Pt}}{(T_h - T_c)} + e_{Pt} = \frac{S_{PtRh}}{(T_h - T_c)} + e_{PtRh}$$

$$\Delta T_{theoretical} = (T_h - T_c) = \frac{S_{Pt} - S_{PtRh}}{e_{PtRh} - e_{Pt}}$$

where, S_{Pt} and S_{PtRh} correspond to the voltage drops in the Pt and PtRh legs of the two thermocouples respectively, e_{film} , e_{Pt} and e_{PtRh} are the Seebeck coefficients of the film, Pt and PtRh respectively and T_h and T_c are the temperatures of the hot and cold junctions respectively. Two sets of data were taken on as deposited films and on films annealed at 800 C in air for 30 mins prior to measurement.

4.3 RESULTS AND DISCUSSION

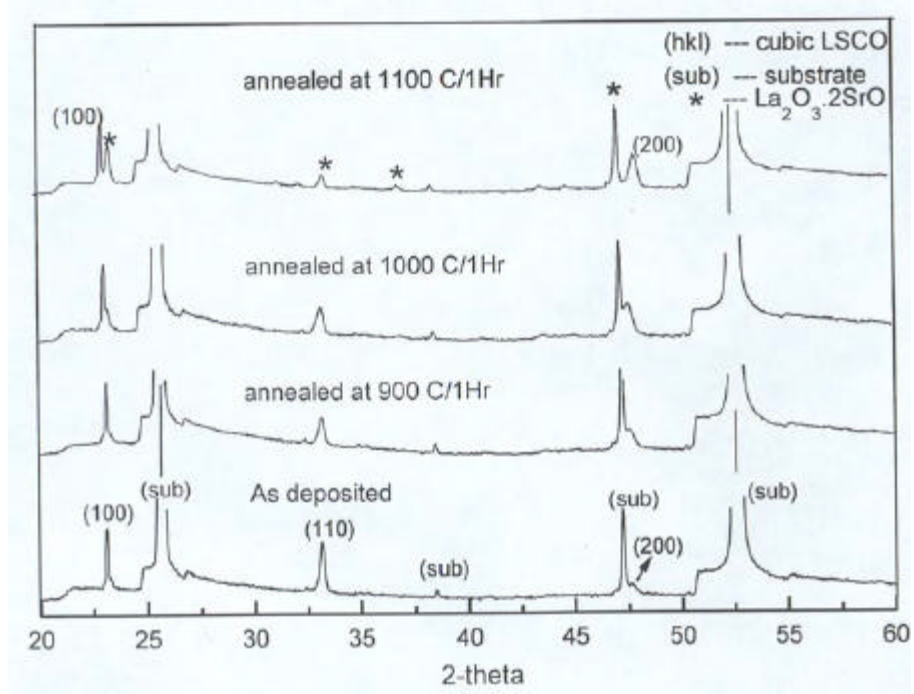


Fig.12 XRD pattern of $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ thin films on sapphire substrate

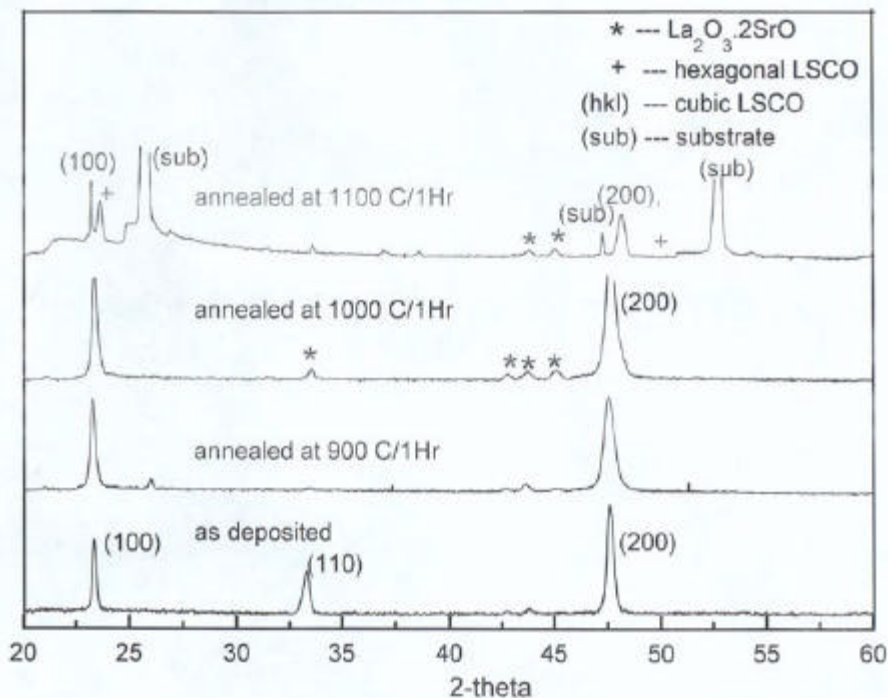


Fig.13 XRD pattern of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ thin films on sapphire substrate

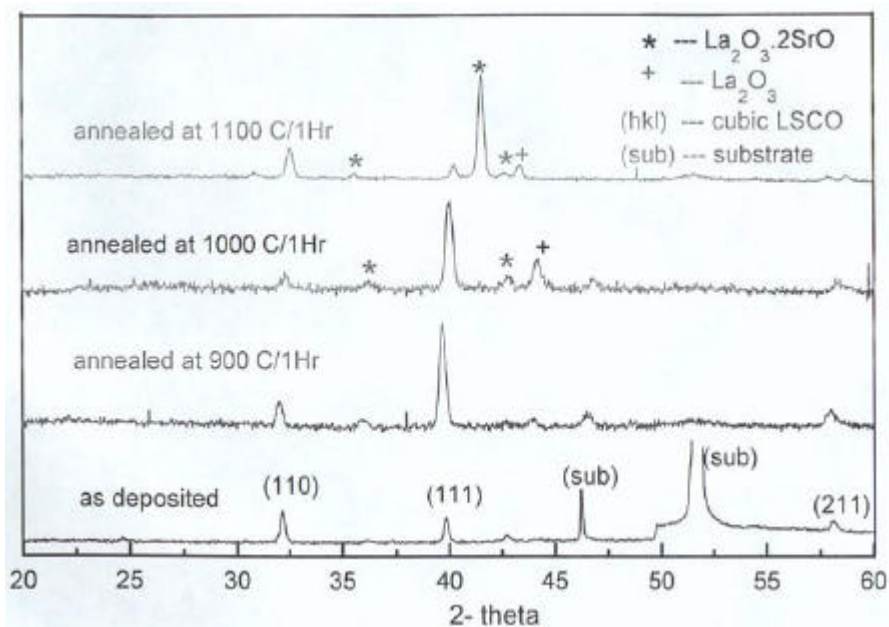


Fig.14 XRD pattern of $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_3$ thin films on sapphire substrate

The lattice parameter from each peak in XRD was plotted against $\cos^2\theta/\sin\theta$ where θ is the Bragg angle for that reflection to correct any measurement errors in the calculation. By extrapolation of the obtained straight line (fit) to $\cos^2\theta/\sin\theta = 0$, a more precise

determination of the lattice parameter is obtained. Morphological studies using atomic force microscopy (AFM) indicate a steady increase in the grain size as a function of temperature in all the three compositions. The results from AFM are shown in the figs. 15,16,17. The electrical conductivity of as deposited samples and prior annealed (800 °C/30 mins) samples is given in figs. 18 and 19 respectively. The results indicate no significant change in the resistivity of the films after annealing. The Seebeck coefficients are plotted in figs. 20 and 21. Also, the room temperature resistivities of the samples as measured by the four point probe are tabulated in table. 1. These indicate a steady decrease of resistivity with annealing temperature till about 1100 °C when the resistivity increases sharply due to loss of the film. All the above mentioned results are discussed below in separate sections.

Phase, Composition and Microstructure Analysis

X-ray diffraction results on the as deposited samples of all three compositions indicated a predominantly cubic perovskite structure. The lattice parameter of LSCO was found to be in the same range as was reported in literature earlier (3.805 Å). As the samples were annealed at temperatures beyond 1000 °C, LSCO cubic perovskite breaks down and phase separation occurs. After annealing the films at 1000 and 1100 °C, La₂O₃.2SrO phase was observed in all the three compositions. This can be explained on the basis of results from electron spectroscopy for chemical analysis ESCA, which indicate loss of cobalt at high temperatures and relative strontium enrichment. An earlier report on the electrical conductivity and thermal stability of lanthanum cobaltite perovskite indicates that undoped lanthanum cobaltite decomposes at high temperatures and low pressures to give cobalt oxide. In this study, we observe lanthanum cobaltite with lower strontium levels of doping (La_(0.7)Sr_(0.3)CoO₃) decomposes at high temperatures to lose cobalt and lanthanum oxide remains. This La₂O₃ along with traces of rhombohedral (hexagonal) phase could be seen in the XRD data of La_(0.7)Sr_(0.3)CoO₃ films annealed at 1100 °C. In the case of La_(0.5)Sr_(0.5)CoO₃ films annealed at similar temperatures, both La₂O₃ and La₂O₃.2SrO phases were detected. That means as the Sr doping in lanthanum cobaltite increases, the breakdown of LSCO into La₂O₃.2SrO becomes increasingly easier. This can be seen from the XRD of La_(0.3)Sr_(0.7)CoO₃ films annealed at 1100 °C which is predominantly La₂O₃.2SrO. From all these results it can be concluded that

LSCO decomposes at high temperatures to lose Co and the phase stability of LSCO decreases with increase in the Sr content. From the X ray diffraction and composition

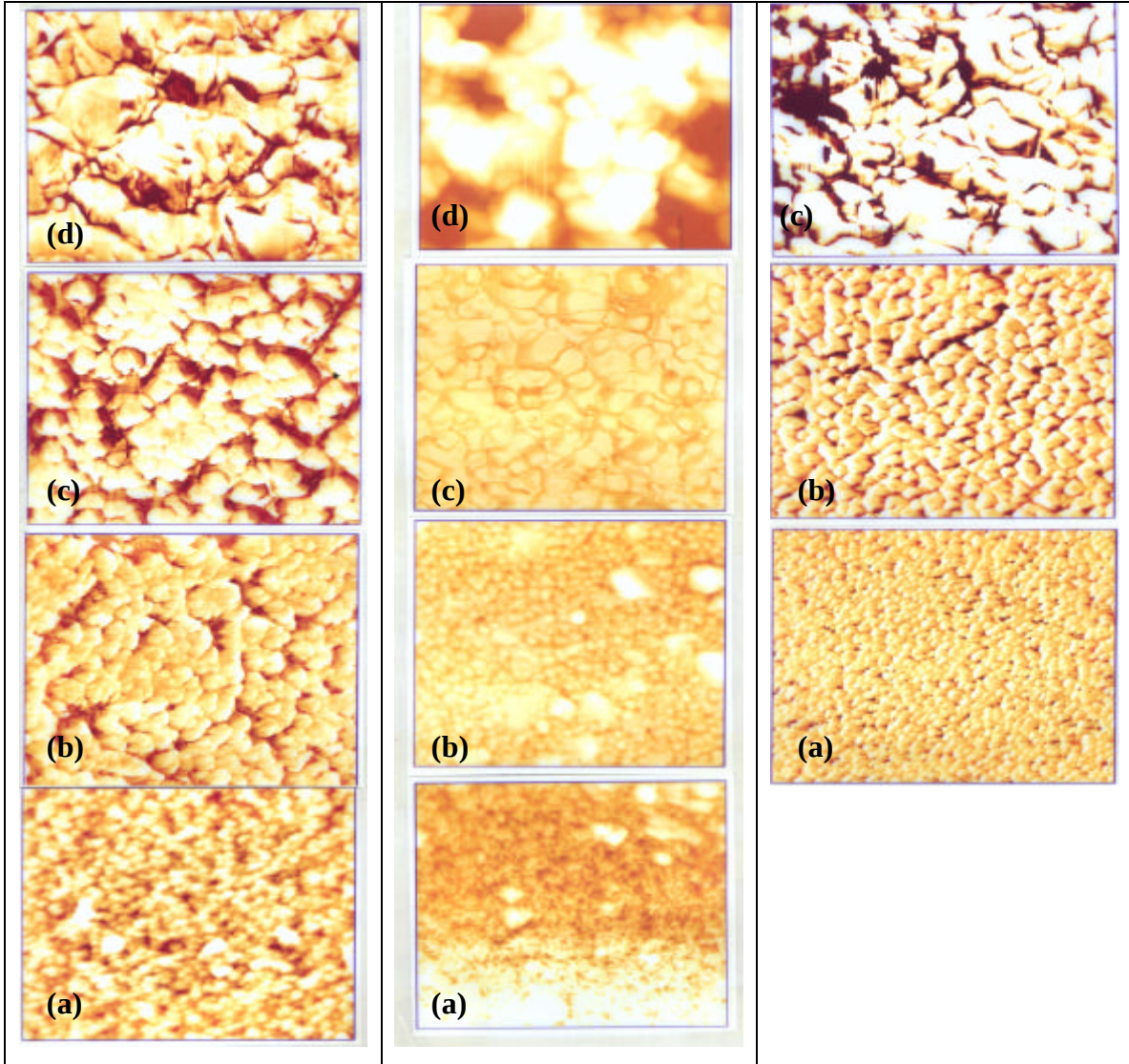


Fig.15, 16, 17 AFM micrographs of $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ thin films ($x=0.3, 0.5, 0.7$) on sapphire substrates as a function of annealing temperatures

- (a) – as deposited
- (b) - annealed at $900^\circ\text{C}/1\text{hr}/\text{air}$
- (c) – annealed at $1000^\circ\text{C}/1\text{hr}/\text{air}$
- (d) – annealed at $1100^\circ\text{C}/1\text{hr}/\text{air}$

analysis results, the following mechanisms of breakdown of LSCO can be proposed.

Cubic $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ with $x < 0.5$ decomposes at high temperatures to give La_2O_3 , rhombohedral $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ along with only traces of $\text{La}_2\text{O}_3 \cdot 2\text{SrO}$, with loss of cobalt oxide.

Cubic $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ with $x > 0.5$, on the other hand decomposes at high temperatures losing cobalt oxide and forms predominantly $\text{La}_2\text{O}_3 \cdot 2\text{SrO}$.

This transformation in the phase of $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ thin films at high temperatures is considered to be due to changes in the film composition. Among the three compositions studied, $\text{La}_{(0.7)}\text{Sr}_{(0.3)}\text{CoO}_3$ was observed to possess the best phase stability.

The phase separation at high temperatures can be seen in the atomic force microscope (AFM) micrographs. The as deposited films show a fine grained uniform microstructure. The grain size progressively increases with annealing till 1000 °C. At 1100 °C, however, the grain structure is not well defined and the image is hazy, indicating phase separation and loss of material.

Electrical Resistivity

The electrical resistance measured between the Pt legs of the thermocouples is converted into electrical conductivity based on the dimensions of the resistors (6000 Å thick, 8 mm long and 4-5 mm wide). The conductivity was multiplied by the absolute temperature, and plotted against the reciprocal temperature in figs. 18 and 19. Fig. 18 shows the conductivity plot of as deposited films and Fig. 19 shows the plot of films annealed at 800 °C for 30 mins prior to measurement. The plots are linear indicating small polaron hopping conduction mechanism as mentioned earlier in this paper.

In the case of conduction through small polaron hopping the electrical conductivity follows

$$\sigma = \frac{(1-c)}{kT} ne^2 a_0 g \exp\left(\frac{-E_a}{kT}\right)$$

When $\ln(\sigma T)$ is plotted against $1/T$, the plot should be linear, the slope being equal to $-E_a/k$ where E_a -activation energy of hopping and k -Boltzmann constant. From the graphs, the Activation energy of hopping in $\text{La}_{(1-x)}\text{Sr}_{(0.x)}\text{CoO}_3$ can be found to be 0.1492 eV, 0.1356 eV, and 0.1144 eV, for $x=0.7, 0.5, 0.3$ respectively. The increase in the activation energy of hopping with Sr content increase can be explained on the basis of oxygen vacancies. It was reported earlier that as the Sr content in LSCO increases, the oxygen

deficiency in the films increases. This causes an increase in the oxygen vacancies which could result in a decrease in the available sites for small polaron hopping. Consequently, the activation energy increases with increase in Sr content. The linear nature of the plot of films annealed at 800 °C for 30 mins prior to measurement indicates that on annealing the films at 800 °C, there is no difference in the mechanism of conduction. It also shows that LSCO the electrical characteristics of these thin films are stable to annealing temperatures.

Seebeck coefficients

The thermoemf created between the two Pt and Pt-Rh legs of the thermocouples due to a temperature difference of about 10 °C was converted into Seebeck coefficient and plotted as a function of temperature. For thin film thermocouple applications, it is important that the material electrical and thermoelectric properties be stable to annealing temperatures. Therefore, the Seebeck coefficients of LSCO films annealed at 800 °C for 30 mins have been measured along with the as deposited films. All the films show a

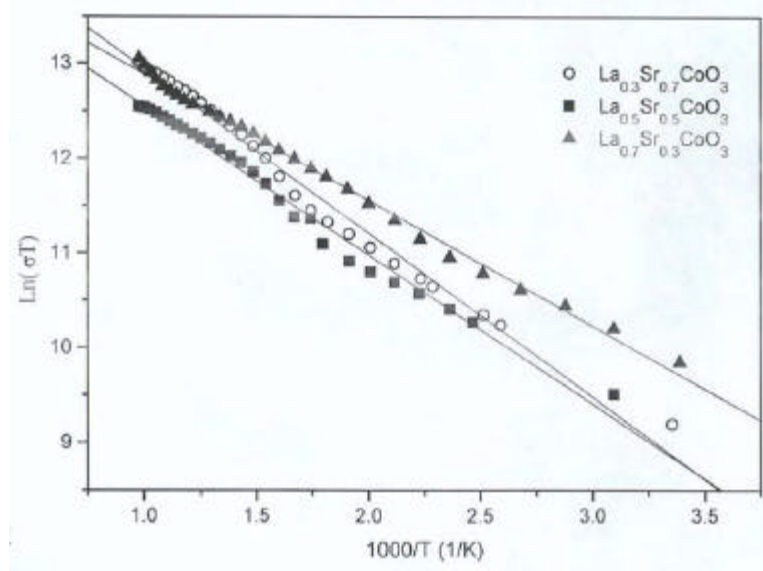


Fig. 18 Electrical conductivity of as deposited $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ thin films on sapphire substrates measured in-situ as a function of temperature

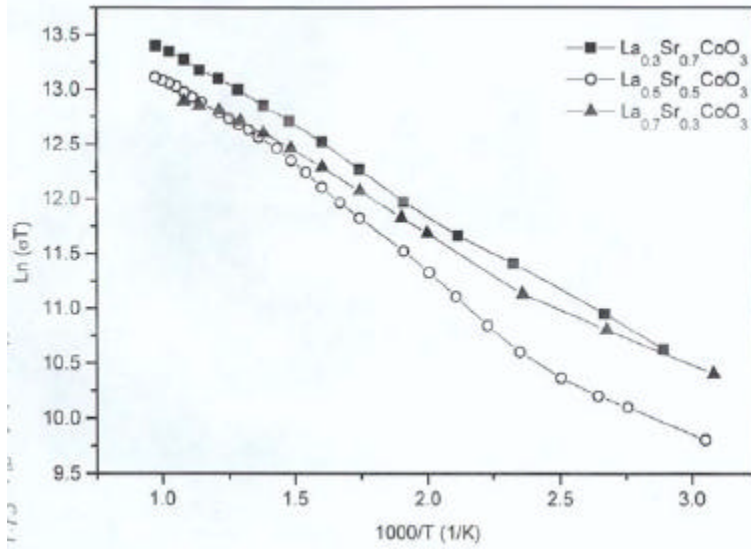


Fig. 19 Electrical conductivity of $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ thin films on sapphire substrates annealed at $800^\circ\text{C}/1\text{hr}/\text{air}$ prior to measurement as a function of temperature

positive seebeck coefficient. This indicates a positively charged charge carrier based on the equation for seebeck coefficient in materials with small polaron hopping conduction mechanism. In LSCO, this can be explained as follows. In this case, lanthanum cobaltite is the parent perovskite and Sr is the dopant. Lanthanum in LaCoO_3 has a valence of +3. Doping of Sr on the A site (La site) forces the valence of Co to change from +3 to +4 thereby creating a hole as the charge carrier.

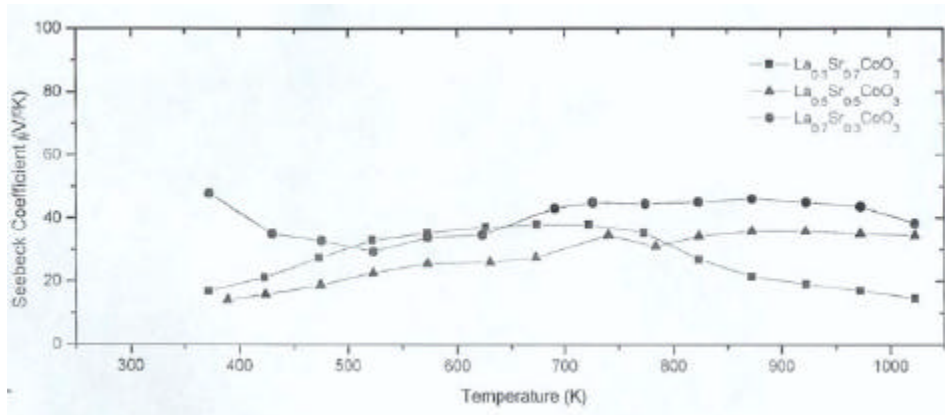


Fig.20 Seebeck coefficients of as deposited $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ thin films on sapphire as a function of temperature

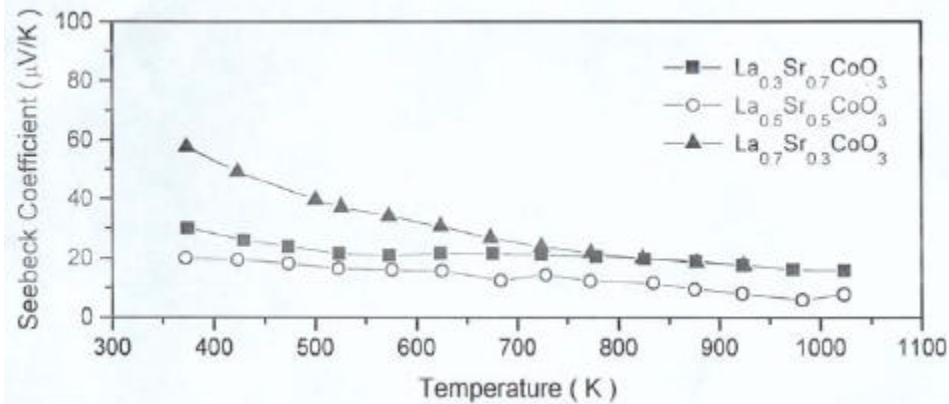


Fig.21 Seebeck coefficients of $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ thin films on sapphire annealed at 800°C for 1hr prior to measurement, as a function of temperature

The Seebeck coefficients were found to be stable upto 1023K and linear with respect to temperature following a relationship close to $S = A + B.T$. Attempts to accurately determine the constants A and B from the graphs were frustrated by the inaccuracies in the measurement of thermoemf $<100 \mu\text{V}$. However, the trend appears to follow what is expected from a material with small polaron hopping as the predominant conduction mechanism. On annealing the films at 800°C for 30 mins, there is no significant change in the temperature dependence of seebeck coefficient indicating stable thermoelectric property of LSCO films even after annealing. There is no observable dependence of Seebeck coefficients on the composition at least up to 1023 K. Therefore it can be said that all three compositions possess stable seebeck coefficients up to 1023 K. From the electrical conductivity plots and the seebeck coefficient plots, it can be inferred that, for the three compositions studied, small polaron hopping is the dominant conduction mechanism.

4.4 CONCLUSIONS

Three different compositions of lanthanum strontium cobalt oxides with varying amounts of Sr doping were studied for thin film thermocouple applications. Thin films of $\text{La}_{(1-x)}\text{Sr}_x\text{CoO}_3$ ($x=0.3, 0.5, 0.7$) were prepared on sapphire substrates by pulsed laser deposition. They were examined for phase, composition, microstructure, electrical conductivity and seebeck coefficients. It was evident that, the thermal stability (phase and

chemical compositional stability) of LSCO depends critically on the amount of Sr doping. Among the three compositions examined, $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ possessed the best thermal stability. At temperatures beyond 1273 K, LSCO decomposes to lose cobalt and results in lanthanum oxide (La_2O_3) or lanthanum strontium oxide ($\text{La}_2\text{O}_{3.2}\text{SrO}$). The electrical conductivity and seebeck coefficients were found to be stable upto 1023 K. The electrical and transport property results can be explained on the basis of small polaron hopping mechanism. All these results indicate that LSCO family holds excellent promise for high temperature thin film thermocouple applications.

Chapter 5

High Temperature Structural and Electrical Transport

Properties of $M_{(1-x)}Ca_xMnO_3$ Thin Films ($M=La, Y$)

5.1 INTRODUCTION

$La_{(1-x)}M_xMnO_3$ ($M=Ca, Sr, Ba$) type compounds have been studied with renewed interest ever since the discovery of giant magnetoresistance effects in these perovskite type oxides. These compounds have shown unusually large negative magnetoresistance at low temperatures, commonly referred to as giant magnetoresistance. In all these perovskite oxide systems a mixed valence ion state (+3/+4) in the Mn ion is created for charge compensation resulting in the creation of a “polaron”. The transport of polarons has been extensively studied in the investigation of giant or colossal magnetoresistance in these compounds^{36,37}. Apart from the giant magnetoresistive effects in these perovskite oxides, $La_{(1-x)}Ca_xMnO_3$ and $Y_{(1-x)}Ca_xMnO_3$ have also been studied as candidate cathode materials for solid oxide fuel cells (SOFCs)^{38,39}. Their oxidation-reduction behaviour, electrical resistivity and thermoelectric properties have been studied in the bulk form both at low temperatures as well as at high temperatures by several researchers for the above mentioned applications. Although substantial amount of information on these perovskite oxides is available in the bulk form, there have been few reports in thin film form.

The purpose of this study is to investigate the high temperature thermal stability, electrical resistivity and seebeck coefficient as a function of temperature for the rare earth metal doped $CaMnO_3$ systems. An attempt is made to identify the optimum composition from each of the Y and La doped $CaMnO_3$ systems from the point of view of high temperature thin film thermocouple applications. A systematic study of stability of phase, structure, composition and morphology of these perovskite oxides is presented. The temperature dependence of electrical resistivity as well as seebeck coefficients is also reported.

5.2 EXPERIMENTAL PROCEDURE

Thin films of $La_{(1-x)}Ca_xMnO_3$ as well as $Y_{(1-x)}Ca_xMnO_3$ ($x=0.3, 0.5$) were fabricated on sapphire (1102) substrates by pulsed laser deposition (PLD) from bulk

targets prepared by the standard powder method. The films were characterized for phase, composition, microstructure and thickness. The electrical resistivity and Seebeck coefficient of the films annealed at 1000 °C for 30 mins were measured in-situ, as a function of temperature in air up to 750 °C, by a home made device. The experimental details are given below.

Thin film deposition

Powders of La_2O_3 , CaCO_3 and MnCO_3 (99.99% purity) in the required stoichiometric ratios were mixed thoroughly in ethanol solution and the resulting mixture dried overnight at 90 °C. After drying, the powder was then calcined at 900 °C for 3 hours. A bulk sample was made by compacting the powder at 5 Mpa, and then sintering at 1350 °C for 3 hours in air. This bulk sample was used as the target in PLD.

A KrF_2 (248 nm) excimer laser was used to ablate the target. The target and the substrate are mounted in different holders and are separated by a prefixed distance. Both could be independently rotated. There is provision for independent heating of the substrate during deposition. The substrate (sapphire) was heated to 650 °C during deposition. The two holders are inserted into a high vacuum chamber (10^{-6} torr). The laser beam was collimated and focused onto the target. Both the target and the substrate were rotated to ensure uniform film deposition on the substrate. The energy of the laser used was 700 mJ, at a replate frequency of 30 Hz. the deposition time was 25 mins. During deposition, there was an input of oxygen gas and the pressure inside the deposition chamber was maintained at 400 mtorr. After deposition, the films were characterized for thickness, phase, composition and microstructure.

Characterization

After deposition, the thickness of the films was measured by a Dektak profilometer. Then, X-ray diffraction (XRD) studies were conducted on all the films using a Scintag diffractometer. After the phase was studied, composition was analyzed using Electron spectroscopy for chemical analysis (ESCA). Then, the grain size, microstructure and surface roughness was characterized by atomic force microscopy (AFM). The room temperature resistivity of the films were measured by a four point probe. Then electrical resistivity and seebeck coefficient were measured in air as a function of temperature.

Electrical resistivity and Seebeck coefficient measurement

From the samples deposited as described earlier, resistors of width 4 to 4.5 mm were cut. These resistors were pasted on electronic grade alumina samples. The height of the samples was about 12 mm. Platinum and Platinum-10 weight %Rhodium thermocouples were used to measure the thermoemf of the film. Each thermocouple was inserted in an alumina tube having two isolated holes for the two thermocouple legs. The two thermocouples were placed one on top of the other 8 mm distant from each other. They were sealed using high temperature alumina cement. This was fixed to a stainless steel holder which could be slid length wise. The whole system was spring loaded to ensure contact with the resistor. The resistance of the sample was measured by a Keithley 2000 digital multimeter and resistivity calculated from the resistance using the dimensions of the resistor. The top thermocouple was insulated during Seebeck coefficient measurement using fiberglass to incorporate a temperature difference of about 10-15 °C. The detailed description of the apparatus with the dimensions and performance analysis is given elsewhere³⁵. The voltages generated between the Pt and Pt-Rh legs of the thermocouple and the temperatures of the hot and cold junctions were measured using a Tempbook 7-channel thermocouple readout system. The whole system was inserted in a furnace which has a built in temperature controller system. From the data collected electrical resistivity and Seebeck coefficients were plotted as a function of temperature.

The equations employed to evaluate the Seebeck coefficient are listed below.

$$\begin{aligned} S_{Pt} &= -e_{Pt} (T_h - T_c) + e_{film} (T_h - T_c) \\ S_{PtRh} &= -e_{PtRh} (T_h - T_c) + e_{film} (T_h - T_c) \\ e_{film} &= \frac{S_{Pt}}{(T_h - T_c)} + e_{Pt} = \frac{S_{PtRh}}{(T_h - T_c)} + e_{PtRh} \\ \Delta T_{theoretical} &= (T_h - T_c) = \frac{S_{Pt} - S_{PtRh}}{e_{PtRh} - e_{Pt}} \end{aligned}$$

where, S_{Pt} and S_{PtRh} correspond to the voltage drops in the Pt and PtRh legs of the two thermocouples respectively, e_{film} , e_{Pt} and e_{PtRh} are the Seebeck coefficients of the film, Pt and PtRh respectively and T_h and T_c are the temperatures of the hot and cold junctions

respectively.

5.3 RESULTS AND DISCUSSION

I. Phase, composition and microstructure

The thickness of the deposited films as measured using a Dektak profilometer was 6000 Å. The phase of the films was studied by X-ray diffraction (XRD) using Cu-K α radiation as a function of annealing temperature to observe the phase stability of the thin films. All the films were annealed in air in conventional annealing furnaces. Fig. 22 and 23 show the XRD patterns of La_{0.7}Ca_{0.3}MnO₃ and La_{0.5}Ca_{0.5}MnO₃ as a function of annealing temperature, whereas Fig. 24 shows those of Y_{0.5}Ca_{0.5}MnO₃ thin films. XRD patterns of most of the films show well crystallized single phase orthorhombic perovskite structures of both La_(1-x)Ca_xMnO₃ as well as Y_(1-x)Ca_xMnO₃ (x=0.3,0.5) thin films even as deposited. This could be attributed to the fact that the films were deposited using pulsed laser deposition (PLD) at a temperature of 650 °C. There were no observable deviations in the phase of the all the films shown in the figures upto 1100 °C indicating excellent perovskite phase stability of the thin films.

Earlier studies on Y_(1-x)Ca_xMnO₃ in the bulk form by several researchers have

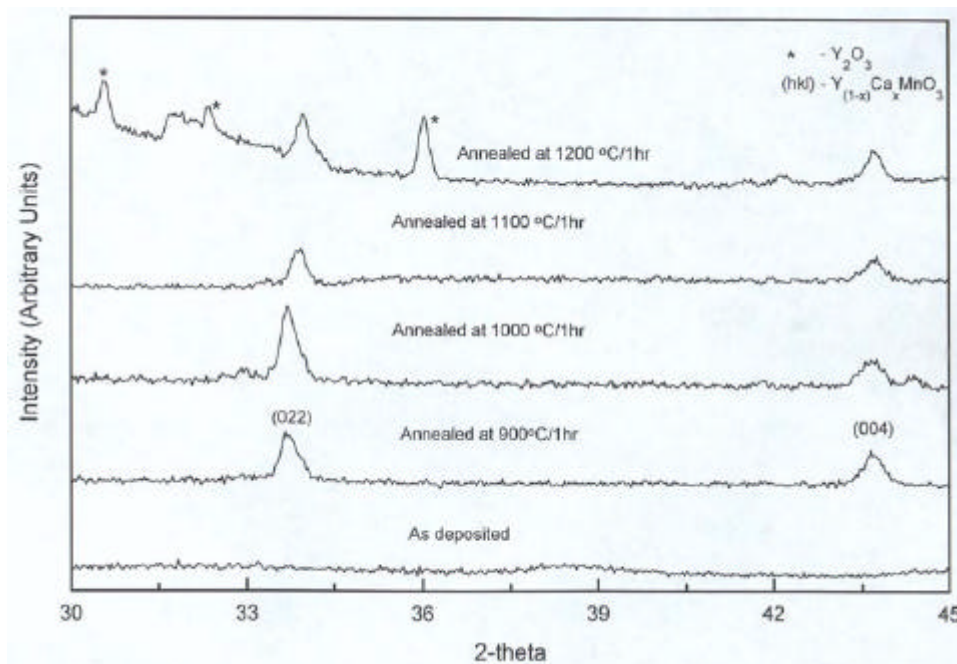


Fig.22 XRD pattern of Y_(0.5)Ca_(0.5)MnO₃ thin films on sapphire as a function of annealing temperature

indicated that, YMnO_3 has two polymorphs viz., orthorhombic perovskite and hexagonal nonperovskite structures. The former is found to be stable at high pressures and high temperatures whereas at lower temperatures and normal pressures, the nonperovskite phase is dominant^{40,41}. Stevenson et al explained the instability of YMnO_3 on the basis of the ionic radius and the coordination number of the Y 3+ ion in the two structures⁴². In

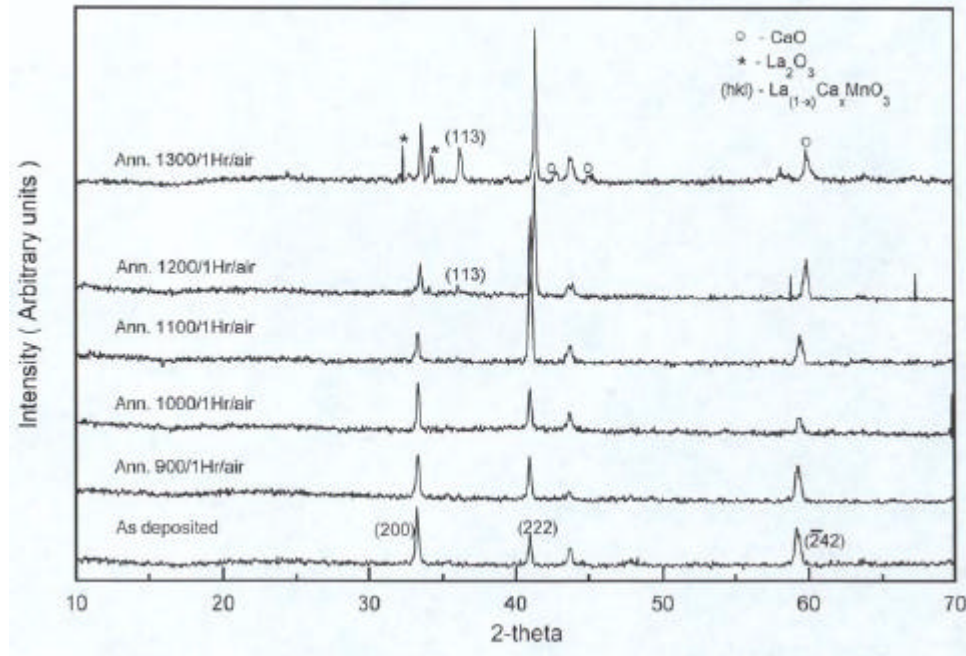


Fig.23 XRD pattern of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ thin films on sapphire

the hexagonal structure, the coordination number of Y is smaller than in the case of orthorhombic structure, thereby increasing its stability. They also observed the presence of a miscibility gap in the YMnO_3 and CaMnO_3 systems for the compositions of $\text{Y}_{(1-x)}\text{Ca}_x\text{MnO}_3$ $0 < x < 0.3$. In our case, as the composition of the films was beyond the miscibility gap, it was observed that the films both as-deposited as well as annealed at temperatures below 1100 °C has a stable orthorhombic perovskite structure. XRD data from the films annealed 1200 °C and 1300 °C however, showed extraneous peaks which were identified as individual oxides such as La_2O_3 , CaO and Y_2O_3 . This indicates that the perovskite phase is not stable beyond 1100 °C and hence these materials cannot be used for thin film thermocouple applications involving temperatures greater than 1100 °C.

Studies on the thin film composition using electron spectroscopy for chemical

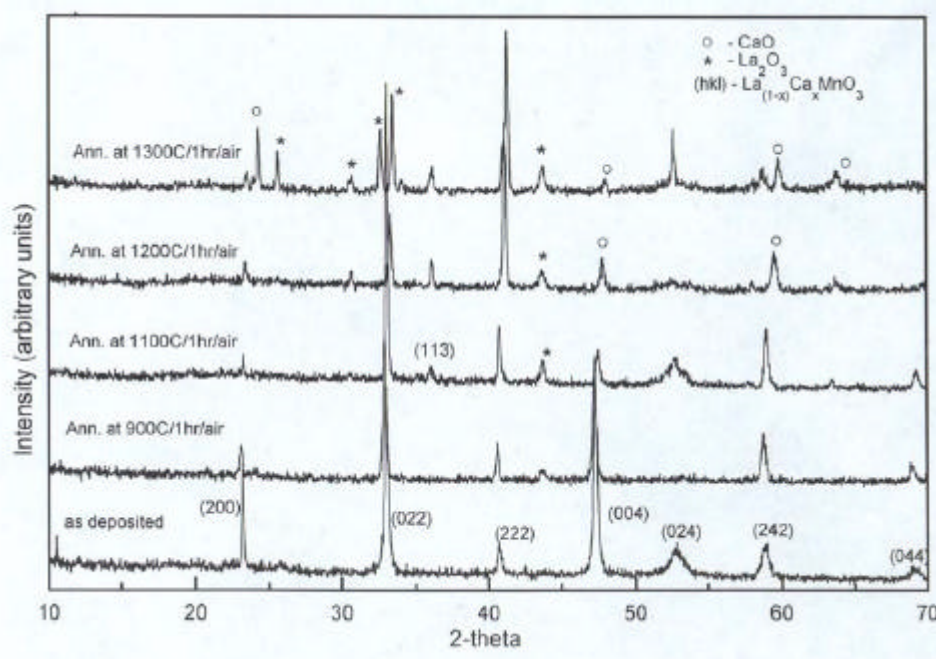


Fig.24 XRD pattern of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ thin films on sapphire as a function of annealing temperature

analysis (ESCA) also confirmed that at these materials are stable up to 1100 °C temperatures above which, there was an observable loss of manganese from the system. Microstructural studies on the films using atomic force microscopy (AFM) showed a progressive increase in the grain size up to 1100 °C and bimodal grain size distribution in the films annealed at 1200 °C or 1300 °C indicating the instability of these materials to annealing temperatures greater than 1100 °C.

One of the primary objectives of this study was to identify the optimum composition in each of the $\text{Y}_{(1-x)}\text{Ca}_x\text{MnO}_3$ and $\text{La}_{(1-x)}\text{Ca}_x\text{MnO}_3$ systems. From the point of view of thermal stability, it was observed that in the $\text{La}_{(1-x)}\text{Ca}_x\text{MnO}_3$ as well as $\text{Y}_{(1-x)}\text{Ca}_x\text{MnO}_3$ systems, compositions with $x=0.5$ possesses better phase stability than those with $x=0.7$ as observed from the XRD patterns and results from composition analyses. There was little difference in the microstructure of the films. It can be concluded that the above mentioned compositions of $\text{Y}_{(1-x)}\text{Ca}_x\text{MnO}_3$ and $\text{La}_{(1-x)}\text{Ca}_x\text{MnO}_3$ systems show remarkable stability in phase, structure, compoaiton and microstructure up to 1100 C and hence show great promise for thin film thermoelectric device applications.

II. Electrical conductivity

The as deposited thin films were annealed at 1000 °C for 1 hour in air prior to the measurement of electrical resistivities to avoid any grain growth effects. Electrical resistivity of the films was measured using both Pt as well as the PtRh legs of the thermocouples in the experimental setup explained earlier. From the resistivities, electrical conductivities were calculated using the specimen geometry and plotted as a function of temperature as shown in Fig. 25. All the films show fairly large electrical

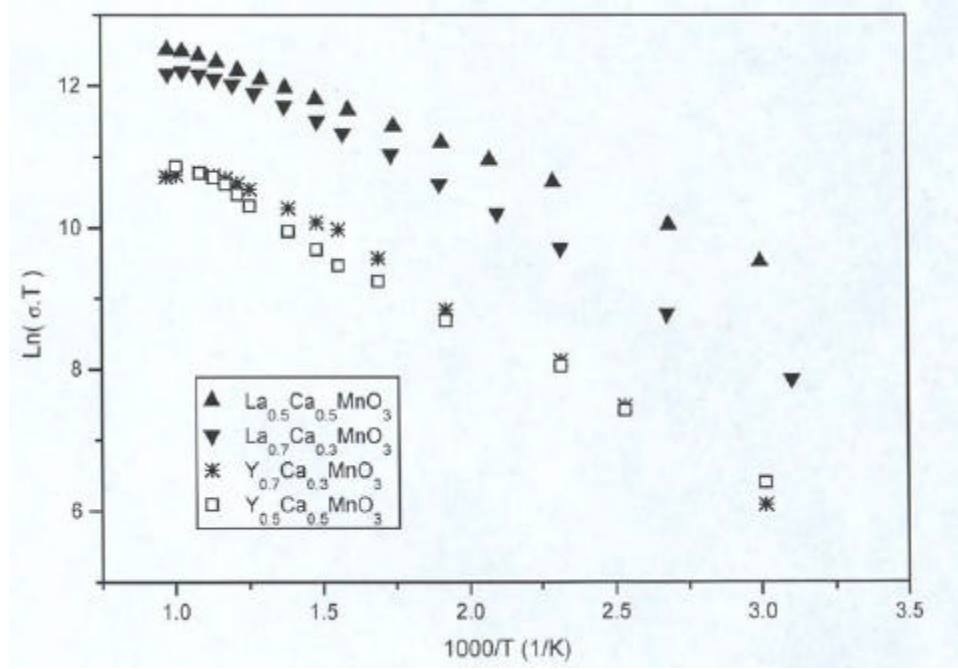


Fig.25 Electrical conductivities of $\text{La}_{(1-x)}\text{Ca}_{(x)}\text{MnO}_3$ and $\text{Y}_{(1-x)}\text{Ca}_{(x)}\text{MnO}_3$ thin films on sapphire as a function of temperature ($x=0.3, 0.5$)

conductivities and the linearity of the plots of $\text{Ln}(\sigma T)$ vs $1/T$ indicates that electrical conduction in these materials occurs through a thermally activated small polaron conduction mechanism consistent with the results from literature. Although increase in the dopant concentration should result in an increase in the electrical conductivity, experimental results indicate little or no difference in the electrical conductivities of the samples. At this point the reason for such behavior is unclear, however, it could be speculated that the films differ in the oxygen stoichiometry resulting in a difference in the oxygen vacancy concentrations, although such a difference in the oxygen concentration

in the films could not be detected from ESCA studies. A difference in the concentrations of the oxygen vacancies results in a change in the charge carrier concentration thereby accounting for a change in the electrical conductivity of the films. Several researchers have postulated that for materials in which conduction occurs through small polaron hopping mechanism, its electrical conductivity (σ) follows the relation⁴²:

$$\sigma = \frac{(1 - c)}{kT} n e^2 a_0 \gamma \exp\left(\frac{-E_a}{kT}\right)$$

where, c -fraction of sites occupied by polarons, E_a -activation energy of hopping, n -small polaron concentration, e -electron charge, a_0 -distance between sites, γ -optical phonon frequency, z -number of nearest neighbors and k -Boltzmann constant.

Therefore, a linear plot of $\ln(\sigma T)$ vs $1/T$ indicates that conduction occurs predominantly through small polaron hopping as is the case with our films. An important aspect to note, from the data is that there is no observable deviation in the linearity of the curves, indicating no change in the mechanism of conduction throughout the temperature range of measurement. This is a significant factor in choosing candidate materials for thin film thermocouple applications indicating that these materials are excellent candidates for the thin film thermoelectric device applications.

III Seebeck coefficient

The seebeck coefficient of the films was measured in-situ as a function of temperature simultaneously with the electrical conductivity measurement. The temperature differential between the hot and cold junctions during the measurement was maintained at around 10-15 °C. Thermoemf was measured between both the platinum as well as the platinum/rhodium legs of the thermocouples as mentioned earlier in this paper. The seebeck coefficient was calculated from the thermoemf based on the temperature differential measured. Fig. 26 shows the seebeck coefficients of $Y_{(1-x)}Ca_xMnO_3$ and $La_{(1-x)}Ca_xMnO_3$ systems as a function of temperature. It can be seen that

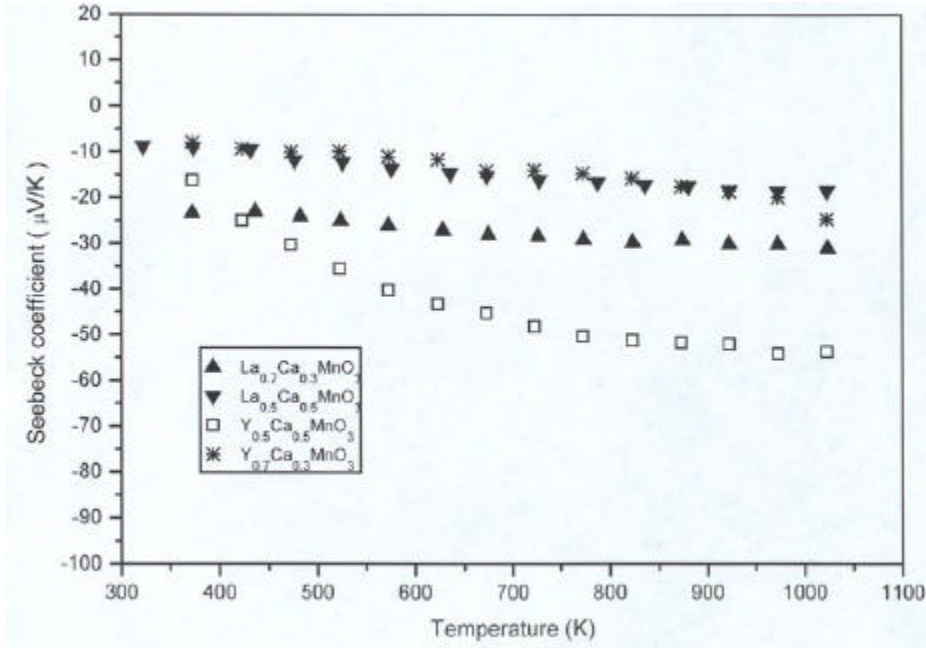


Fig.26 Seebeck coefficients of $\text{La}_{(1-x)}\text{Ca}_x\text{MnO}_3$ and $\text{Y}_{(1-x)}\text{Ca}_x\text{MnO}_3$ thin films on sapphire as a function of temperature ($x=0.3, 0.5$)

all the films showed a negative seebeck coefficient and there is little dependence of the seebeck coefficients of the films with temperature. It is well established in literature that the sign of the seebeck coefficient indicates the nature of the charge carriers (electrons or holes). In our case, electrons appear to be the predominant charge carriers. This can be explained as follows: CaMnO_3 is the host perovskite and when the A site in the perovskite (Ca +2 valence) is doped with La or Y (+3 valence state donors), the valence of the Mn ion (+4 in CaMnO_3) changes to +3 for charge compensation. This results in the formation of a localised charge carrier, an electron, commonly referred to in such cases as a polaron.

Several researchers have identified the temperature dependence of seebeck coefficient(α) of materials with predominantly small polaron hopping conduction mechanism as follows⁴².

$$\alpha = \left(\frac{k}{e} \right) \ln \left[2 \left(\frac{1-c}{c} \right) \right] + \left(\frac{k}{e} \right) \frac{zJ}{E} \frac{k}{T}$$

where, c -fraction of sites occupied by polarons, E_a -activation energy of hopping, e -electron charge, z -number of nearest neighbors, J -intersite transfer energy during hopping process, E_B -binding energy of polaron and k -Boltzmann constant.

Fig. 26 shows that these materials have stable and fairly large seebeck coefficients in thin film form throughout the temperature range of measurement and hence show excellent promise for thin film thermoelectric device applications. Also noteworthy from Fig. 6 is the fact that among the two compositions in the systems $M_{(1-x)}Ca_xMnO_3$ ($M=La, Y$) studied, $x=0.5$ shows a higher seebeck coefficient value compared to $x = 0.3$. This is important because, the absolute value of the seebeck coefficient determines the output of the thin film thermocouple fabricated from these materials and the higher the seebeck coefficient, the greater the thermocouple output and the higher the sensitivity of the thermocouple.

IV Charge Transport

From Fig. 25 it is clear that the charge transport occurs through a thermally activated small polaron hopping mechanism consistent with other reports in literature. The slope of the plot gives the activation energy of hopping (E_a). Table 3 shows the activation energy of hopping as a function of amount of Y or La doping. These values are consistent with earlier reports of Stevenson et. al⁴¹ of 0.19 eV and 0.1 eV for $Y_{0.7}Ca_{0.3}MnO_3$ and $Y_{0.5}Ca_{0.5}MnO_3$ respectively and several other researchers^{43,44}. This also confirms that electrical conduction occurs predominantly through thermally activated small polaron hopping conduction mechanism.

In addition to activation energy, table. 3 also shows the calculated values of fraction of available hopping sites that are occupied (C). The details of calculation of C are available in literature and hence, not reported here⁴¹. From the table, it is clear that as the Y doping increases from 0.5 to 0.7, the fraction of available sites for hopping that are occupied decreases. Assuming electronic charge compensation, the amount of Y doping directly determines the concentration of $[Mn^{3+}]$ and $[Mn^{4+}]$ ions in the lattice i.e., as the concentration of $[Y^{3+}]$ or $[La^{3+}]$ increases, the concentration of $[Mn^{3+}]$ should increase. Assuming Mn is present in only +3 or +4 valence states, and exact oxygen stoichiometry, the amount of $[Mn^{3+}]$ directly determines the number of charge carriers. As the amount of Y or La doping increases, the number of charge carriers, in this case electrons assuming

CaMnO_3 as the host lattice, should increase. This results in a decrease in the number of available sites for hopping. If the fraction of available sites that are occupied (C) is defined as the probability of occupancy of an available hopping site by a charge carrier multiplied by the number of available sites for hopping, C is expected to decrease. This is exactly what we observe from Table. 3

Table. 3: The Activation energy of hopping and the fraction of available sites for hopping that are occupied for the systems $\text{M}_{(1-x)}\text{Ca}_x\text{MnO}_3$ (M = La, Y), $x = 0.5, 0.3$.

Material	E_a (eV)	C
$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$	0.18	0.55
$\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$	0.128	0.589
$\text{Y}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$	0.196	0.554
$\text{Y}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$	0.164	0.651

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

In this dissertation, several novel materials have been investigated for high temperature thin film thermocouple applications. Thin films have been deposited primarily using r.f. sputtering and pulsed laser ablation deposition techniques. The high temperature thermal stability of the thin films in terms of phase, composition, microstructure has been tested. In addition, electrical conductivity and Seebeck coefficient were measured in-situ as a function of temperature. The following are the principal conclusions of this research.

I TiC/TaC Thermocouples

- It was observed that the electrical properties of the thin films both TiC as well as TaC are extremely sensitive not only to stoichiometry but also to the deposition conditions
- The thermoemf of TiC and TaC thin films decreases as the temperature is increased.
- Thermocouple output was recorded as a function of temperature and the maximum temperature of stability of thermocouples was determined to be 1350 K. No significant change was observed in the output of the test thermocouples when they were subjected to several repeated cycles of heating and cooling indicating thermal and electrical stability of the thermocouples.
- The reproducibility of the thermocouple data was also tested and found to be satisfactory.

II LSCO Thin Films

- It was evident that, the thermal stability (phase and chemical compositional stability) of LSCO depends critically on the amount of Sr doping. Among the three compositions examined, $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$ possessed the best thermal stability.
- At temperatures beyond 1273 K, LSCO decomposes to lose cobalt and results in lanthanum oxide (La_2O_3) or lanthanum strontium oxide ($\text{La}_2\text{O}_3 \cdot 2\text{SrO}$). The electrical conductivity and seebeck coefficients were found to be stable upto 1023 K.
- The electrical and transport property results can be explained on the basis of small polaron hopping mechanism.

III Manganate Thin Films

- Both $Y_{(1-x)}Ca_xMnO_3$ and $La_{(1-x)}Ca_xMnO_3$ thin films crystallize in a single phase orthorhombic perovskite structure. This phase is stable up to annealing temperatures of 1100 °C, above which, the perovskite structure is no longer stable. Loss of manganese from the systems results in the formation of individual oxides of La, Y and Ca. This limits the temperature range of operation of thermoelectric devices based on these materials up to 1100 °C.
- Electrical conductivity and seebeck coefficient studies indicate that these materials have fairly large and stable conductivities and seebeck coefficients throughout the temperature range of measurement. The linearity of the $\ln(\sigma T)$ vs $1/T$ plot indicates that small polaron hopping conduction mechanism is the predominant conduction mechanism in these perovskite oxides.
- From the phase, composition analyses, as well as from the seebeck coefficient and electrical conductivity measurements, it is clear that for both $Y_{(1-x)}Ca_xMnO_3$ and $La_{(1-x)}Ca_xMnO_3$ systems, $x = 0.5$ is the optimum composition.

All these materials exhibit significant improvements over Pt/PtRh thermocouples in terms of thermal stability and substrate compatibility and hence, show excellent potential for use in high temperature thin film thermocouple applications.

5.1 Recommendations

In this dissertation, several results were presented some of which show excellent potential for applications involving high temperature thin film thermocouples. A major drawback with all these materials lies in their limitations of thermal stability. One approach towards solving this problem could be deposition of a diffusion barrier layer such as high purity alumina on top of these materials and fabricate thermocouples. Also, in this research, hafnates have been identified from bulk data in literature to possess high thermal stability. However, they have poor thermoelectric properties at high temperature. Therefore, it could be recommended that by judicious combination of hafnates and chromites or any such high thermoelectric materials, the problem of finding materials which could withstand the rigorous demands of high temperature thin film thermocouples could possibly be solved.

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