LBL-37569
UC-404
Preprint

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials Sciences Division

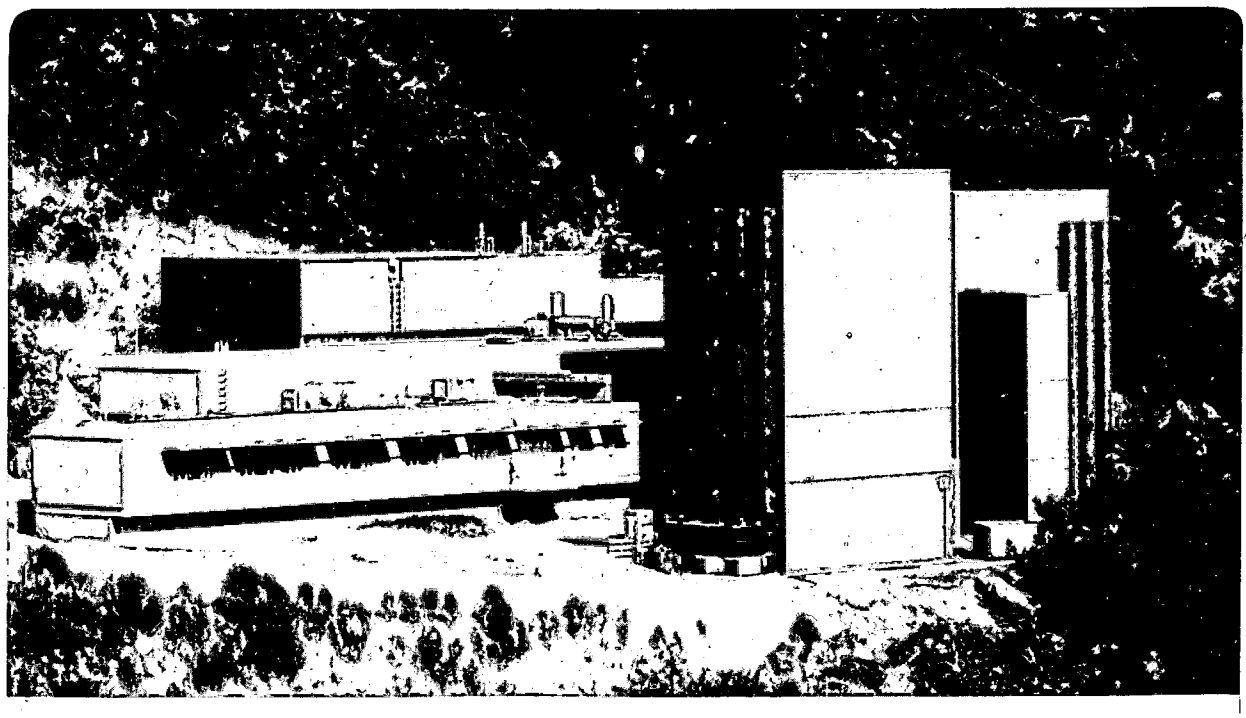
National Center for Electron Microscopy

Submitted to Journal of the American Ceramic Society

Polymeric Sol-gel Synthesis of $La_{1-x}Sr_xMnO_3$ Thin Films Exhibiting Giant Magnetoresistance

A.R. Modak and K.M. Krishnan

August 1995



REFERENCE COPY
Does Not
Circulate
Bldg. 50 Library.
LBL-37569
Copy 1

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-37569

Polymeric Sol-gel Synthesis of $La_{1-x}Sr_xMnO_3$ Thin Films Exhibiting Giant Magnetoresistance

A.R. Modak & K.M. Krishnan

Materials Sciences Division
National Center for Electron Microscopy
Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720

J. Am. Cer. Soc. (submitted)

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Polymeric Sol-gel Synthesis of $La_{1-x}Sr_xMnO_3$ Thin Films Exhibiting Giant Magnetoresistance

Anjaneya R. Modak and Kannan M. Krishnan

Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

We report here, for the first time, a reproducible polymeric sol-gel process for the synthesis of $La_{1-x}Sr_xMnO_3$ thin films exhibiting giant magnetoresistance. We have utilized a combination of metal alkoxide, β-diketonate and carboxylate compounds to form the complex precursor which underwent further processing steps of hydrolysis, spin coating and heat treatment. Key features of the process are its overall simplicity, low processing temperature, ease of composition variation, and ability to produce a wide range of structures. The underlying precursor chemistry, leading to atomic scale mixing of elements that occupy the same crystallographic site, critical to the successful synthesis of these films, has also been established. Single phase LSMO(80/20) thin films with a cubic structure (a = 0.384nm) were obtained and confirmed by x-ray diffraction and transmission electron microscopy observations. Epitaxy with (100) normal orientation was induced by deposition on $LaAlO_3$(100) substrates, while polycrystalline thin films were obtained on Si(100) substrates. Magnetoresistance properties comparable to or better than those of films of similar composition obtained by other techniques were observed, further corroborating the feasibility of the process.

Supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract no. DE-AC03-76SF00098.

I. Introduction

Oxygen octahedral manganites of the form $La_{1-x}M_xMnO_3$ (where M = Sr, Ba or Ca) exhibit a very large magnetoresistance, termed colossal magnetoresistance (CMR) since it is 2-3 orders of magnitude larger than the well known 'giant magnetoresistance(GMR) effect' reported in metallic multilayers. Interest in these compounds stems from their intrinsic antiferromagnetic spin structure which is regarded as an atomic level counterpart of the antiferromagnetically coupled multilayers. Giant magnetoresistance in these compounds was confirmed from studies immediately following the discovery of GMR and MR values of upto 60-70% were reported in $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Ba_xMnO_3$ thin films.[1,2] However, recently, a unusually large magnetoresistance (≈1300% at room temperature and ≈100,000% at 77K) was observed in highly oriented and optimally heat treated $La_{1-x}Ca_xMnO_3$ thin films.[3] This has lead to an upsurge of research activity on understanding their galvanomagnetic properties as well as tailoring the material for potential applications in magnetic field sensors and information storage devices.

To date, laser ablation has been the preferred film deposition technique for fabricating these thin films. Although pulsed laser deposition is an established laboratory scale technique, it poses problems for commercial scale-up due to characteristics such as small deposition area and high substrate temperature. Hence, alternative thin film deposition techniques such as MOCVD, sputtering and e-beam/thermal evaporation are being actively pursued.[4] Since alkoxide based sol-gel routes have been succesfully developed for fabricating thin films of several perovskite compounds such as $PbZr_xTi_{1-x}O_3$, $LiNbO_3$ and $BaTiO_3$,[5,6] they were considered to have potential for synthesizing the manganties which have a similar structure. This prompted us to investigate a sol-gel route for synthesizing these materials, which would be an inexpensive and versatile experimental tool as well as have potential commercial applicability.

We report here, for the first time, a reproducible sol-gel process for synthesizing epitaxial as well as polycrystalline $La_{1-x}Sr_xMnO_3$ thin films, which can be easily extended to Ca and Ba based compositions. Key features of this process are its overall simplicity, compatibility with IC planar technology, low processing temperature, ease of composition variation and ability to

produce a diverse range of structures such as compositionally graded thin films, multilayers, porous structures and complex shapes. Since the process is controlled through polymer solution chemistry it yields atomic level mixing and offers unique possibilites of manipulating the microstructure. In addition, this method has a significant economic advantage over other thin film deposition techniques which involve complex instrumentation and operating procedures.

II. Precursor synthesis and thin film deposition

After evaluating the phase diagram and the critical magnetic transformation temperatures of various compositions in the $LaMnO_3$-$SrMnO_3$ system, we selected a specific composition $La_{0.8}Sr_{0.2}MnO_3$ for establishing the feasibility of the process. Alkoxides of La, Sr and Mn were possible starting materials due to their ability to complex into atomically well-mixed precursors. However, alkoxides of lanthanum and manganese were ruled out since they are known to have limited solubility in organic solvents.[7] Consequently, for lanthanum and manganese the preferred starting compounds were to be either carboxylates or β-diketonates, which have been used before in similar solution based routes.[6] Strontium metal, however, can be readily reacted with different alcohols to form stable alkoxides which are completely soluble in the respective alcohols.[7] After several such considerations and pilot experiments we arrived at lanthanum 2,4-pentanedionate (or Lanthanum acetyl acetonate), manganese(II) acetate and strontium methoxyethoxide as the organometallic precursors. 2-methoxyethanol was used as the base solvent since it has been reported to have advantages over other alcohols in similar sol-gel processes for fabricating perovskite thin films.[8]

The first step was preparation of individual precursors of the constituent elements. Anhydrous lanthanum 2,4-pentanedionate and manganese acetate were individually synthesized from the respective hydrates (which are commercially available) by fractionally distilling off the water of hydration in a Schlenck setup (as shown in Fig. 1) under dry N_2. In another setup, strontium metal was dissolved in 2-methoxyethanol under dry N_2, in a water bath, to form the corresponding methoxyethoxide. The different reactions can be summarized as follows:

$$Sr + 2CH_3OCH_2CH_2OH \text{ -----> } Sr(OCH_2CH_2OCH_3)_2 + H_2 \quad (1)$$

$$La(CH_3COCHCOCH_3)_3.xH_2O \text{ -----> } La(CH_3COCHCOCH_3)_3 + xH_2O \quad (2)$$

$$Mn(CH_3COO)_2.4H_2O \text{ -----> } Mn(CH_3COO)_2 + 4H_2O \quad (3)$$

Individual precursors were then assayed for atomic percentage of metal. Exactly weighed amounts of each precursor were heated at 900°C to form the respective oxides which were weighed to determine metal concentration. Individual elemental precursors were then complexed and refluxed under dry N_2 at 124°C to form the precursor complex.

The next step in a typical sol-gel process is partial hydrolysis of the precursor complex to be able to control the physical properties of the resulting gel. To estimate and optimize hydrolysis, in a pilot experiment, the precursor complex was hydrolysed using varying amounts of water from 1 mole H_2O/mole manganese to 3 moles H_2O/mole manganese. Instead of carrying out gelation tests, each solution was aged for one day and films were deposited. X-ray diffraction was carried out on all the films to determine occurence of extraneous phases resulting from variation in hydrolysis conditions but no difference in the crystal structure was observed for the above range of conditions. This is not unusual because it has been observed before[6] that β-diketonate ligands hydrolyse very slowly, in effect making this process hydrolysis independent. In addition, very large amounts of hydrolysis water led to phase separation and a crosslinked gel. Microstructural characteristics such as porosity and grain size can be tailored by varying hydrolysis and catalysis conditions[6] and the applicability of this modification in our process is currently being investigated. For the purpose of the first demonstration experiments, however, no hydrolysis was used.

Thermogravimetric analysis (TGA) of dried gel (10-15 ml of the complex solution was dried at low temperature (80°C) to give the gel) was carried out for characterizing the effect of thermal processing of the gel and estimate film heat treatment temperature. Fig. 2 shows a plot of the weight of the sample versus temperature from the TGA experiment which was carried out using a heating rate of 10°C/min. The plot reveals an initial gradual weight loss at low temperatures,

related to solvent removal, followed by a rapid weight loss between 350 and 500°C which is associated with the oxidation of the organics with release of CO_2 and H_2O. Also, there is further gradual weight loss after 500°C (about 10% of total weight loss) and the weight remains constant after about 650°C at which temperature the organometallic-to-oxide conversion was presumed to be complete. Hence the heat treatment temperature was fixed at 700°C along with the same heating rate of 10°C/min.

The solution was spin cast at 2000 rpm for 30 seconds on the required substrates (either Si(100) or $LaAlO_3$(100)) to form an amorphous condensed film. Amorphous films were heated at 300°C on a hot plate, immediately after spin coating, for trapped solvent removal. Final heat treatment was carried out at 700°C for 1 hour in air to obtain the oxide thin films. Multiple deposition/drying cycles were used to make thicker films.

III. Thin film characterization

The thin films had a smooth reflecting surface and were completely crack-free. The crystal structure was investigated using x-ray diffraction (XRD). Fig. 3(a) and(b) show normal $\theta/2\theta$ scans taken from LSMO(80/20) thin films grown on Si(100) and $LaAlO_3$(100) substrates respectively. Single phase, polycrystalline and randomly oriented $La_{0.8}Sr_{0.2}MnO_3$ thin films were obtained on Si(100) substrates as revealed by the XRD patterns. The LSMO films had a psuedocubic structure with a = 0.384 nm. However, note that the high angle (111), (102) and (112) peaks show broadening indicating presence of a small rhombohedral distortion. Detailed structural characterization of these films is in progress. The XRD pattern from films grown on the $LaAlO_3$ substrate clearly revealed that the films were highly oriented. Diffraction peaks corresponding to only (100) and (200) crystal planes were observed in the normal $\theta/2\theta$ scans indicating complete (100) normal epitaxy. The films were found to have the same structure as the films on Si(100). The LSMO films grow epitaxially although there is a 1.5 % lattice mismatch with the $LaAlO_3$ substrate (a = 0.377 nm).

The polycrystalline films grown on Si substrates were characterized by transmission electron microscopy using a JEOL 200CX TEM operated at 200 kV. Plan view specimens were prepared using the standard mechanical polishing, dimpling and ion milling technique.[9] Fig. 4 shows the plan view bright field transmission electron micrograph of the LSMO(80/20) thin film. The image shows the polycrystalline structure with a grain size of 1-2 μm (individual grains which are in different diffracting conditions appear as regions of different intensity). There was some evidence of inter- and intra-granular porosity which is typical of sol-gel derived thin films.[10] Additionally the grains seemed to have a sub-grain structure of smaller units as has been observed previously for sol-gel derived PZT thin films.[10] The inset shows a selected area electron diffraction pattern recorded from the same region of the film. The observed ring pattern was indexed to a cubic structure with the same lattice parameters as observed from XRD.

Magnetoresistance measurements were carried out on these thin films and the important results are summarized here. A characteristic resistivity versus temperature behavior along with a resistivity peak and a semiconductor-to-metal transition was observed for these films at their antiferromagnetic-to-ferromagnetic transition temperature. Large magnetoresistance values (≈ 630% for the (100) oriented films and ≈120% for the polycrystalline films) were observed at the respective transition temperatures (200K for the polycrystalline films and 160K for the oriented films). These values are comparable to or better than those obtained on films of similar composition grown by other techniques.[1,2] Details of the magnetic properties along with the effect of crystallinity on the properties and other related issues will be addressed in a separate publication.[11]

IV. Discussion

The above observations confirm that single phase LSMO(80/20) thin films were grown on both Si and $LaAlO_3$ substrates. In this process, condensates with polymeric networks having the rudimentary metal-oxygen-metal bonds were first obtained after the spin coating step. The oxide is nucleated on heat treatment, with the removal of organic groups which combust to form CO_2 and

H_2O. The Si(100) substrates, which usually have a native oxide under our deposition conditions, present an amorphous surface for film nucleation. Hence, with no crystallographic constraints imposed, the nucleating phase attains polycrystallinity and random orientation. However in the case of $LaAlO_3$, the nucleation is strongly influenced by the surface which constrains the films to have an epitaxial relationship. Thus, in principle, it is possible to deposit films with any crystallographic texture by the choice of an appropriate substrate. This characteristic can prove especially useful for future investigation of crystalline anisotropy effects.

In sol-gel derived thin films, since the heating temperature/time (700°C, 1 hr) is insufficient to cause any significant diffusion, the grain size in the film is determined not only by the growth kinetics but also by the nature of the polymeric condensed gel. The relatively large grain size (≈ 1-2 μm) observed indicates that the amorphous films had considerable crosslinking and formed large colloidal units which have ultimately crystallized into large individual grains. The large grain size is thus an indicator of polymeric complexation of the alkoxide, β-diketonate and acetate ligands and is evidence of succesful optimization of precursor chemistry.

Ligand-exchange reactions between metal alkoxides and β-diketonates[12,13] as well as metal alkoxides and carboxylates[12,14] have been observed before and linked to the stoichiometry control of mixed oxides prepared from the respective precursor mixtures. Thus it can be deduced that during refluxing the strontium methoxyethoxide undergoes a partial metal exchange reaction with the La acetyl acetonate to form mixed methoxyethoxide acetyl acetonate species. This represents an atomic scale mixing of two elements which occupy crystallographically identical sites in the final perovskite structure. Furthermore, since transesterification reactions are common between alkoxides and organic esters,[7] some amount of crosslinking is expected to occur between the acetate ligands and the alkoxide acetyl acetonate species. The possible ligand exchange reactions which lead to complexation in this process are summarized as follows:

$$3\ Sr(OCH_2CH_2OCH_3)_2 + 2\ La(CH_3COCHCOCH_3)_3 \longrightarrow 3\ Sr(CH_3COCHCOCH_3)_2 + 2\ La(OCH_2CH_2OCH_3)_3 \quad (4)$$

$$Mn(CH_3COO)_2 + Sr(OCH_2CH_2OCH_3) \longrightarrow Mn(OCH_2CH_2OCH_3)_2 + Sr(CH_3COO)_2 \quad (5)$$

In general, this confirms the feasibility of using mixed alkoxide, β-diketonate and carboxylate precursors for obtaining ternary oxide materials. Since acetyl acetonates and acetates of most transition metals are inexpensive and readily available, they represent attractive alternative precursors for sol-gel processing, especially when alkoxides are not feasible.

V. Summary

A reproducible sol-gel process has been developed for obtaining single phase $La_{1-x}Sr_xMnO_3$ thin films. The crystallinity of the films was controlled by the appropriate choice of substrates: polycrystalline films were obtained on Si(100) and completely (100) oriented epitaxial films on $LaAlO_3$(100). Microstructural examination of the polycrystalline thin films revealed a large grain size (1-2μm) which is indirect evidence of the succesful optimization of precursor chemistry. Acetate-alkoxide and alkoxide-acetyl acetonate ligand exchange reactions lead to complexation and atomic level mixing. The LSMO(80/20) thin films grown by this technique exhibited the characteristic resistance versus temperature behavior and large peak magnetoresistances (≈ 600% for (100) oriented films and ≈ 120% for polycrystalline films) which are comparable to films of the same composition deposited by other current techniques. Overall, this sol-gel process has demonstrated advantages in terms of economics as well as versatility and could prove to be an important research tool in addition to having potential commercial applicability.

References

[1]R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz and K. Samwer, "Giant Negative Magnetoresistance in Perovskitelike $La_{2/3}Ba_{1/3}MnO_x$ Ferromagnetic Films," *Phy. Rev. Lett.*, **71**[14], 2331-33 (1993).

[2]K. Chahara, T. Ohno, M. Kasai and Y. Kozono, "Magnetoresistance in Magnetic Manganese Oxide with Intrinsic Antiferromagnetic Structure," *Appl. Phys. Lett.*, **63**[14], 1990-92 (1993).

[3]S. Jin, M. McCormack, T. H. Tiefel and R. Ramesh, "Colossal Magnetoresistance in La-Ca-Mn-O Ferromagnetic Thin Films," *J. Appl. Phys.*, **76**[10], 6929-33 (1994).

[4]Papers presented at the 'CMR Workshop' at Los Alamos National Laboratory, April 1995.

[5]A. R. Modak and S. K. Dey, "Sol Gel Processing and Characterization of Ferroelectric PZT Thin Films," *Ceramic Transactions*, **15**, 477-88 (1990).

[6]C. J. Brinker and G. W. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-gel Processing, Academic Press, Boston, 1990.

[7]D. C. Bradley, R. C. Mehrotra and D. P. Gaur, Metal Alkoxides, Academic Press, New York, 1978.

[8]K. D. Budd, S. K. Dey and D. A. Payne, "Sol Gel Processing of $PbTiO_3$, $PbZrO_3$, PZT and PLZT Thin Films," *British Ceram. Soc. Proc.*, **36**, 107-21 (1985).

[9]A. R. Modak, S. S. P. Parkin and D. J. Smith, "Transmission Electron Microscopy Observations of Magnetic Multilayers," *Ultramicroscopy*, **47**, 375-82 (1992).

[10]A. R. Modak and S. K. Dey, "Transmission Electron Microscopy Observations of Sol Gel Derived Ferroelectric $PbZrO_3$-$PbTiO_3$ Thin Films with Excess PbO," *Integrated Ferroelectrics*, **5**, 321-31 (1994).

[11]A. R. Modak, Kannan M. Krishnan, Hauyee Chang and X. -D. Xiang, "Colossal Magnetoresistance of $La_{1-x}Sr_xMnO_3$ Thin Films Synthesized by a Novel Sol-gel Process," *in preparation.*

[12]C. D. Chandler, C. Roger and M. J. Hampden-Smith, "Chemical Aspects of Solution Routes to Perovskite-Phase Mixed-Metal Oxides from Metal-Organic Precursors," *Chem. Rev.*, **93**, 1205-41 (1993).

[13]N. N. Sauer, E. Garcia, K. V. Salazar, R. R. Ryan and J. A. Martin, "Isolation and Structural Characterization of the Copper-Barium-Alkoxide Cluster $Ba_2Cu_2(OR)_4(acac)_4.2HOR$ ($R=CH_2CH_2OCH_3$) from Precursor Solutions to $YBa_2Cu_3O_7$ Thin Films," *J. Am. Chem. Soc.*, **112**, 1524-27 (1990).

[14]S. Gurkovich and J. Blum,"Preparation of Monolythic Lead Titanate by a Sol-gel Process," in: Ultrastructure Processing of Ceramics, Glasses and Composites, Edited by L. Hench and D. Ulrich, John Wiley and Sons, New York, 1984.

Figure Captions

Fig. 1. Schematic of Schlenck apparatus for precursor synthesis.

Fig. 2. Thermo-gravimetric analysis of precursor complex gel: weight of gel as a function of temperature measured during heating cycle from 0 - 800°C at 10°C/min.

Fig. 3. Normal $\theta/2\theta$ x-ray scan for LSMO(80/20) thin films: (a) scan for film grown on $LaAlO_3$(100) substrate showing complete (100) normal texture. (b)Scan for film grown on Si(100) substrate. Film is polycrystalline, randomly oriented and has a pseudocubic structure.

Fig. 4. Bright field transmission electron micrograph of a polycrystalline LSMO(80/20) thin film. Inset is a selected area electron diffraction pattern which was indexed to a cubic structure with lattice parameter a = 0.384nm.

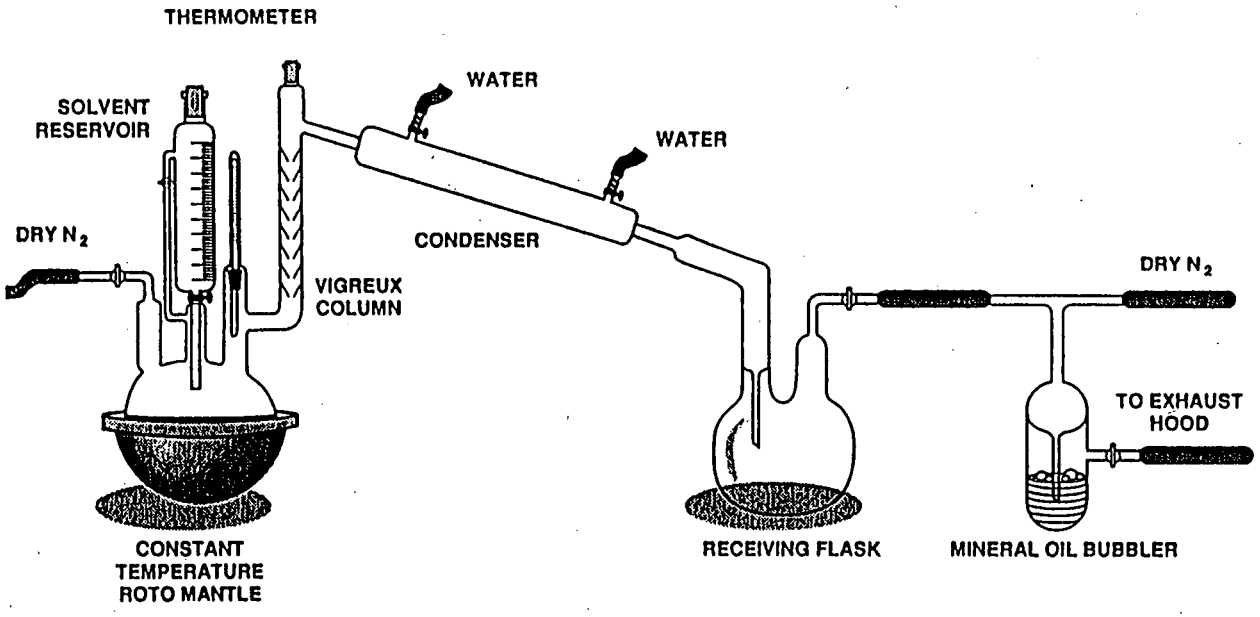


Fig. 1. Schematic of Schlenck apparatus for precursor synthesis.

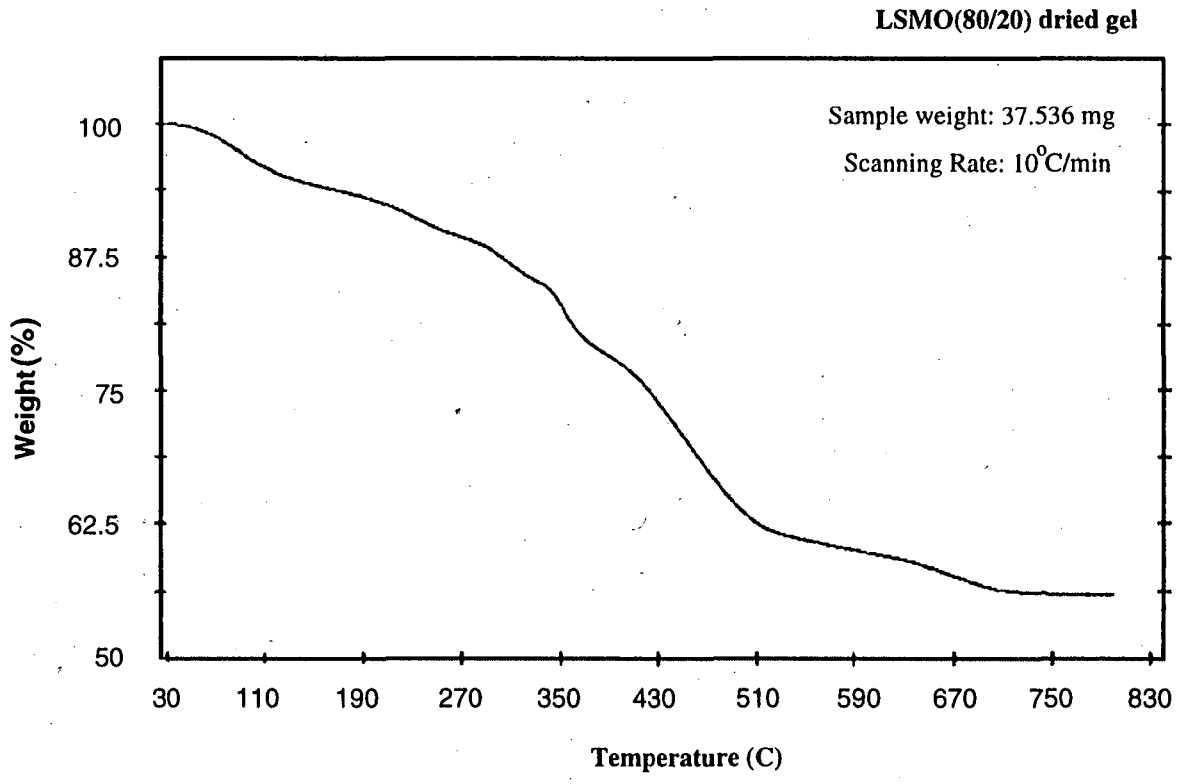


Fig. 2. Thermo-gravimetric analysis of precursor complex gel: weight of gel as a function of temperature measured during heating cycle from 0 - 800°C at 10 °C/min.

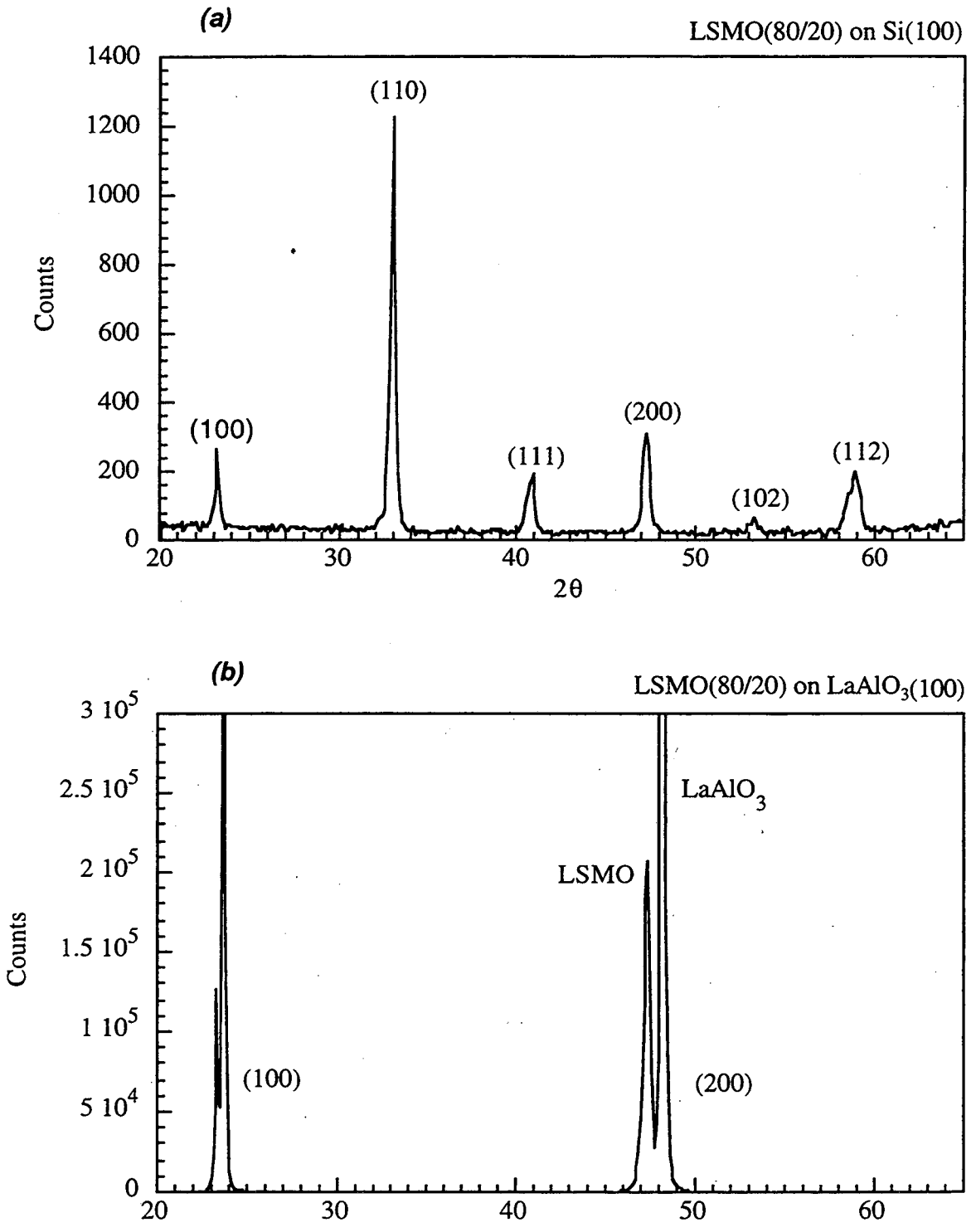


Fig. 3. Normal θ/2θ x-ray scan for LSMO(80/20) thin films: (a) scan for film grown on $LaAlO_3$(100) substrate showing complete (100) normal texture. (b)Scan for film grown on Si(100) substrate. Film is polycrystalline, randomly oriented and has a pseudocubic structure.

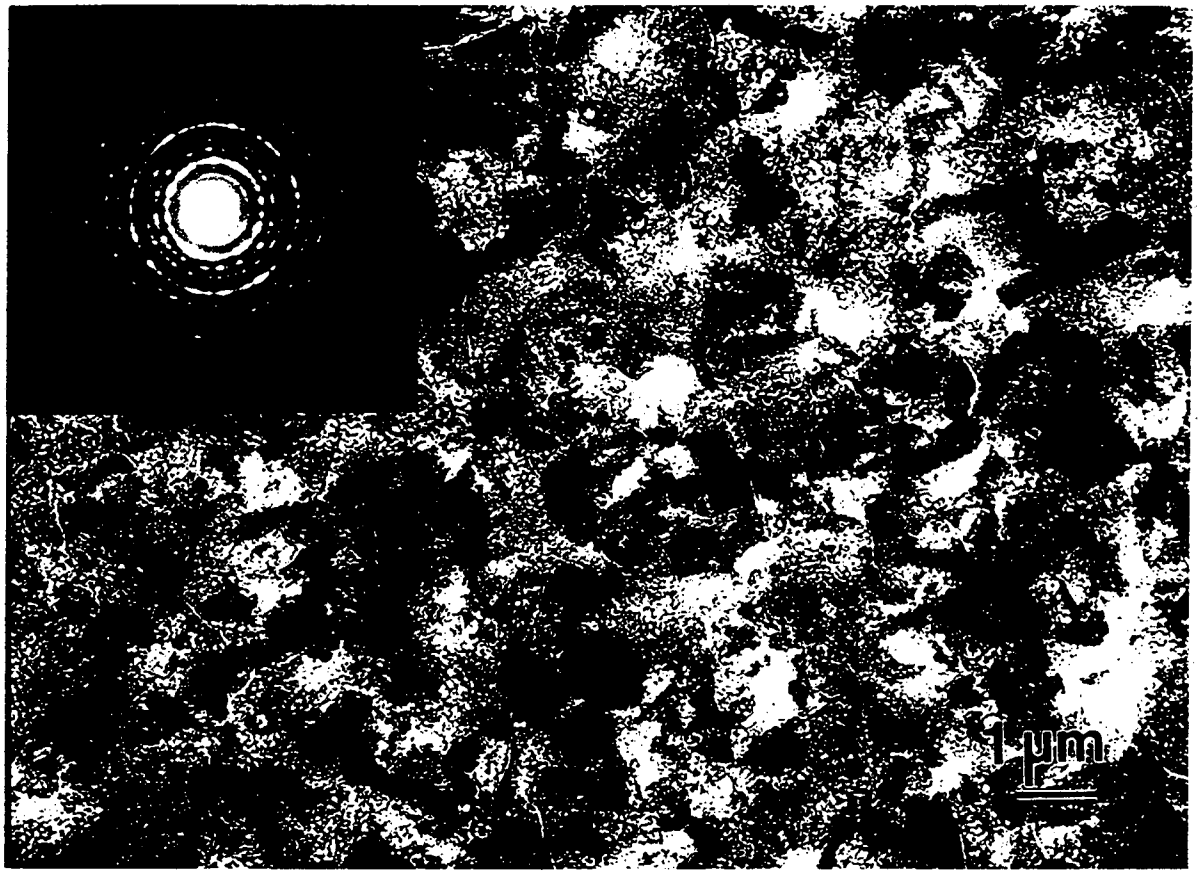


Fig. 4. Bright field transmission electron micrograph of a polycrystalline LSMO(80/20) thin film. Inset is a selected area electron diffraction pattern which was indexed to a cubic structure with lattice parameter a = 0.384nm.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720