CHAPTER 5

STRUCTURAL CHARACTERIZATION OF CERIUM DIOXIDE
6.1 INTRODUCTION

By structural characterization, one determines, the three-dimensional arrangement of the atoms in a solid ranging from gross features like external morphology, cracks etc. to the details of atomic arrangement. Most modern characterization techniques for thin film structures and compositional analyses are scattering techniques. In scattering techniques usually a beam of photons, X-rays or charged particles are incident on the specimen surface, interacts and may give rise to a scattered beam. By analysing the scattered beam, structural as well as compositional information about the sample can be obtained. The most common is the X-ray technique where the incident and the scattered beams are both X-rays. When the incident and scattered beam, both are electrons, this has given rise to a number of techniques, namely:

(i) Transmission electron microscopy (TEM),
(ii) Scanning electron microscopy (SEM),
(iii) Scanning and transmission electron microscopy (STEM),
(iv) Low energy electron diffraction (LEED), and
(v) High energy electron diffraction (HEED).

The arrangement of atoms is necessarily investigated by diffraction techniques (X-ray, electron, neutron), while the surface structure can be studied using microscopic techniques utilizing optical, electron, scanning electron microscopic methods. Both the microscopic and diffraction methods and the way of interpretation of the data are now standard techniques described extensively in literature. In the present work, we have used X-ray diffraction powder method for the identification of the material cerium dioxide and the electron microscopic techniques have been used for the structural characterization of the films prepared by vacuum evaporation method.

5.2 X-RAY DIFFRACTION STUDIES

The powder photograph is particularly useful for identification. For details regarding the method, text by Asaroff and Buerger (1958) may be referred. The X-ray diffraction pattern of a crystalline substance is characteristic of the atomic arrangement in it. It is similar to a fingerprint and no two substances give rise to identical powder photographs. The principle involved in the production of a powder photograph of the specimen is illustrated in Fig.5.1. The powder sample is introduced in the path of a well collimated X-ray beam. As the beam travels through the
Fig. 5.1 Principle of X-ray powder diffraction
powder sample, it meets thousands of powder grains. In a fine powder, the grains each a tiny crystal are arranged in an entirely chaotic manner. There should be enough particles turned at just the appropriate angle to the incident primary beam of monochromatic radiations to allow strong reflection from one set of parallel planes, other particles turned at another angle will produce reflection from another set of planes. The reflection occurs in a direction making an angle 2θ with the direction of X-ray beam. The locus of direction making an angle 2θ with a given direction, is a cone of angle 4θ. For each solution of Bragg equation

\[ n \lambda = 2d_{hkl} \sin \theta \]  \hspace{1cm} (5.1)

there exists such a cone. Considering a particular cone, the separate reflections from all crystals which satisfy Bragg equation for a particular \( n/d_{hkl} \) lie along the direction of a certain cone of angle 4θ. These rays cut the photographic plate in a circle (for a flat plate) or in a curve (nearly a circular arc in case of a cylindrical plate). From a measurement of the distance between similar arcs (S) and the known crystal to film distance (R), Bragg angle (θ) can be computed using the equation (see Fig.5.2)

\[ S = R \cdot 4\theta \]  \hspace{1cm} (5.2)

The cameras are usually equipped with small motors
Fig.5.1 Measurement of Bragg angles
to rotate the specimen, this smooths out the lines.

We have used X-ray 'Radon House' unit for obtaining powder diffraction patterns of bulk CeO₂. First procedural step is the preparation of powder mount. Powder mount was prepared by fashioning the sample itself in the form of a cylindrical rod. This method is preferred since it introduces no material other than the sample in the path of the X-ray beam. A few milligrams of finely powdered material are mixed with a drop of quickfix (binder) until a homogeneous paste results. The paste is then scooped up on a razor blade and rolled into a rod shaped specimen with clean fingers. Then the rod is rolled between two pieces of clean glass slides to give a more uniform shape to the cylinder. The diameter of the prepared rod is less than 0.5 mm and length approximately 10 mm. After allowing time for the rod to harden, it is affixed to the specimen holder by means of ordinary glue. Proper centering is accomplished so that its axis coincides with the rotation axis of the camera. The camera cover, pin hole assembly and direct beam catcher are removed. The strip of film cut to size and prepunched to permit subsequent insertion of the collimator and beam catcher assemblies is placed in level against the inside wall of the camera. During the exposure, the film must be held tightly against the inside wall of the camera. The collimator, direct beam catcher assembly and the cover are then replaced and the camera is placed on its track on the
Fig. 5.3 Powder diffraction pattern of Cerium dioxide
Fig. 5.4
X-ray unit. The time necessary for an exposure varies with the type of x-radiations used, the specimen to film distance and the amount of x-ray absorption. The powder diffraction pattern shown in Fig. 5.3 was obtained using CuKα radiation for 6 hours.

When the film is fully exposed, it is removed from the camera in a manner reversing the procedure described above. The film is developed and fixed. The distances between arcs of symmetrical pairs are measured using a special film measuring device. Bragg angles of diffraction are computed and from these the interplanary distances (d_{hkl}) are evaluated. These values were compared with ASTM card values given for cerium dioxide (see Table 5.1) and a close fit was found. Thus crystallographic characterisation confirms that the powder employed corresponds to cerium dioxide.

5.3 ELECTRON MICROSCOPY

The electron interaction has given us so many novel techniques of structural characterization as has already been pointed out. The utility of transmission electron microscopy is very well known and excellent general reference sources are available (Kay, 1965; Hawkes, 1972; Mulvey and Webster, 1974). Schematic diagram illustrating the principle of electron microscope is shown in Fig. 5.4. The electron microscope uses high energy electrons to form a magnified
image of a specimen. A beam is allowed to fall on a specimen and the scattered radiation while passing through the material of the specimen is focused by another lens system to form an image. The image characteristic of atomic make up of the specimen is formed by the transmitted part of the original radiation. The electron image can be observed visually on a fluorescent screen, recorded on a photographic plate or films, or even transferred directly as an electric signal onto video-tape for subsequent processing and reconstitution by a digital computer. Its range of magnification can be varied readily from that of a low factor optical microscope to about \( x \times 10^6 \). It renders visible to the naked eye finer details of the specimen and is, therefore, complimentary to that of X-ray or electron diffraction, which furnishes structural information averaged over many millions of atoms, thereby ignoring any deviations of irregularities in individual units. The first practical electron microscope was built in Berlin by E. Ruska in 1933. A comprehensive account of currently available instruments can be found in reviews by Cossett (1970) and Mulvey and Webster (1974). Schematic diagram of a typical high voltage electron microscope is shown in Fig.5.5.

An electron source usually a heated tungsten hairpin filament, emits electrons which are then accelerated through a potential difference which may be varied, generally between 50 KV and 100 KV. The source (called as electron gun) and
Schematic diagram of a typical high-voltage electron microscope. The accelerator and generator may be in separate tanks as shown here or within a single tank.

Fig.5.5
condenser lenses form the illuminating system. The lenses below the specimen constitute the imaging system. There are usually three of these, known as objective, intermediate and projector lenses. For greater range of magnification especially for electron diffraction patterns an additional intermediate lens may be provided. The image produced by the objective is magnified by the help of other lenses. Objective is by far the most important since the resolving power depends upon its perfection and state of cleanliness. The whole electron path is under vacuum. The sample itself must be sufficiently thin to scatter incoming electrons without appreciable loss of energy. The scattered electrons carry essential information about the object. Removing these electrons by means of a suitable aperture stop produces image contrast. The intensity distribution in the back focal plane constitutes a diffraction pattern of the entire specimen. The plane is also known as the Fourier Transform Plane, since the diffraction pattern formed may be regarded as the Fourier transform of the wave transmitted by the specimen. The electrons which form the diffraction pattern in the back focal plane continue through the system and by combining in the image plane give a recognizable image (Fig. 5.6).

For observation of the pattern by the electron microscope, the specimen is placed in the mechanical stage
(a) Image formation in the electron microscope. Scattered electrons form a diffraction pattern (Fourier transform) in the back focal plane of the objective lens. An aperture in the image plane enables a small area of the sample to be selected for viewing. The projector lens magnifies this image. (b) Weakened projector lens focuses the diffraction pattern onto the screen.

Fig. 5.6
of the instrument through a vacuum airlock. The magnification control is set at an appropriate low value, and the image which appears on a fluorescent screen is focussed by turning a focussing control which alters the magnetizing current of the objective lens. For photographing the patterns, the fluorescent screen is moved out of the way of the beam and electrons fall directly onto a photographic plate. Standard gold pattern is also taken to compute the camera constant. The camera constant of the electron microscope is given by

\[ 2L \lambda = \frac{2R_{\text{gold}} a}{h^{1/2}} \]  

(5.3)

where \(2R_{\text{gold}}\) are the diameters of various rings obtained in the powder pattern of gold. If \(h,k,l\) are the Miller indices of the diffracting planes corresponding to a given ring then \(N\) is given by the expression:

\[ N = h^2 + k^2 + l^2 \]  

(5.4)

\(a\) is the lattice parameter of gold. \(d_{hkl}\) values responsible for various diffraction rings can be calculated using the relation

\[ d_{hkl} = \frac{\text{Camera constant}}{2R} \]  

(5.5)

where \(2R\) is the diameter of a ring under consideration. To take full advantage of the electron microscope, specimen preparation techniques are of major importance. The cerium dioxide films employed for the electron microscopic
investigations were deposited in-situ on the formvar coated copper grids. Grids are discs of 2 to 3 mm diameter containing large number of holes and are usually made of copper, platinum nickel, stainless steel, etc. when the deposition is to be made directly on the grids through thermal evaporation process, it is imperative that grids be coated with some support film before film deposition. The support film is generally made up of structureless plastics such as Formvar (Polyvinyl formaline) or collodion (Nitro cellulose) and have thicknesses of the order of 50-200 Å. These plastic materials consist of elements of low atomic number. Both the low atomic number and small thickness contribute to a reduced scattering and energy loss of the electron beam. This is important and necessary as in the range of 50 to 100 KV, the electrons have low penetrating power, viz. 100 micron thick aluminium sheet or 20 cm air will stop a 50 KV electron beam. Another technique of preparing specimen is to make the film on a clean glass slide and then to remove a small portion (approximately 2 mm²) to mount it on the grid. For this, glass slide is coated with a plastic film and then the deposition of the specimen film is carried out. The small portions are cut with a razor blade and allowed to float on clean water. One of the floating regions is then picked up on the copper grid.
5.4 STRUCTURE OF RARE EARTH OXIDES

The rare earth metal comprise of 15 elements from atomic number 57 (Lanthanum) to 71 (Lutetium). The elements from cerium (58) to lutetium are also often called 4f elements as they arise in terms of atomic structure as a result of the filling up of the 4f sub-shell.

The most widely occurring oxides of the rare earth metals (R) are the so-called sesquioxides, $R_2O_3$, and these represent a series of stable refractories. Lower oxides have been found for the rare earth metals; Samarium, Europium and Ytterbium. SmO and YbO are not stable phases at moderate to high temperatures but YbO may be stable at low temperatures below 100°C.

The elements cerium, praseodymium and terbium also form higher oxides. For all the three, the most oxygen rich phases are the dioxides, $R_2O_2$, and in addition a series of oxides are formed in the composition range $R_01.5$ to $R_02$. It has been suggested that these oxides are members of a homologous series with the general formula, $R_nO_{2n-2}$.

The dioxide possess the fluorite structure. The sesquioxide, on the other hand, may exist in different forms and the relative stability of the different modifications vary systematically with atomic number. The crystal structure of the polymorphs have been termed as $A,B,C,H$ and $X$ type.
structures. The latter two may exist at high temperatures only. Transformations from the C type to either the A or B form occur for all oxides up to holmium (67).

The fluorite structure (shown in Fig. 5.7) is the basis for the understanding of the nonstoichiometric rare earth oxide systems, \( \text{RO}_2 - x(\text{RO}_3 - \text{RO}_2) \), which exhibits several sharply defined compounds. Fluorite structure has been described in terms of a face centred cubic unit cell containing four unit cell of \( \text{RO}_2 \). Thus each metal atom (R) is surrounded by 8 oxygen atoms at the corners of a cube, each cube shares edges with neighbouring cubes and all oxygen distances are the same. It can also be conveniently described in terms of anion centred coordination polyhedra. The oxygen in \( \text{RO}_2 \) is at the centre of a tetrahedron of metallic atoms and the whole structure may be seen as three dimensional framework of OR_4 tetrahedra linked together by their edges.

The C type \( \text{R}_2 \text{O}_3 \) is derived from the fluorite structure type by removing a quarter of the anions. The cation lattice remains nearly unchanged. Thus, now the metal atoms are surrounded by only six oxygen atoms. The missing oxygen atoms are located either on the face diagonals or body diagonals of the fluorite cubes, and they are ordered in such a manner that the missing oxygen atoms lie in straight lines.
(A) CATION LATTICE WITH POSITION OF ANIONS

(B) ANION LATTICE WITH POSITIONS OF CATIONS

○ OXYGEN
● CERIUM

FIG. 5.7 STRUCTURE OF CERIUM DIOXIDE
('FLUORITE STRUCTURE')
through the body diagonals of the cubic crystals. Thus, it is easy to show that C-R\textsubscript{2}O\textsubscript{3} is a three-dimensional building of the same OR\textsubscript{4} tetrahedra but linked together with 5 out of 6 edges.

'\textit{A}' type structure has hexagonal unit cell and has a seven-fold coordination about the metal ions, while '\textit{B}' type has a monoclinic structure and has both six and seven fold coordination numbers. RO\textsubscript{4} tetrahedron packing appears conspicuously in \textit{A} and B-Ln\textsubscript{2}O\textsubscript{3}. In these cases, there are two types of oxygen atoms in the structure, one is inside a tetrahedron of metallic atoms and the other one is six coordinated. It is further removed from the rare earth atoms than the former one (d\textsubscript{0-R}=2.70 Å versus 2.4 Å in A-R\textsubscript{2}O\textsubscript{3}). Based on this picture \textit{A} type R\textsubscript{2}O\textsubscript{3} can be thought of as (RO)\textsubscript{2}O layers. This is so, since the structure is made along the hexagonal c axis of a succession of slabs of a complex group (RO) built of OR\textsubscript{4} tetrahedron edge linked in a manner derived from the fluorite structure, separated by planes of oxygen anions. The layered character of A-R\textsubscript{2}O\textsubscript{3} is very clearly exhibited by easy cleavage of the simple crystal perpendicular to the c axis.

The \textit{B} type is very similar to the \textit{A} type but is monoclinic because the hexagonal symmetry is lost following a small displacement of the (RO) slabs with respect to each other, together with a tetrahedron distortion induced by
lanthanide contraction.

Now the two types of (RO) structural slabs or layers are simply slices of the fluorite (RO₂) structure. One of them (A-R₂O₃) is a slice perpendicular to the C₃ axis in the fluorite structure and involves a R-O-O-R succession of fluorite planes parallel to (111) and the other is a slice perpendicular to C₄ axis and involves a R-O-R succession of planes. Both slices have the same overall formula (RO).

An excellent survey of the phase stability of rare earth metal oxides has been given by Foex and Traverse (1966).

Cerium dioxide is light yellow, praseodymium dioxide is black and terbium dioxide is dark brown. A light coloured TbO₂ has not been observed, even when heated with molecular oxygen at 60 atmosphere pressure. The dark colours of PrO₂ and TbO₂ crystals suggest a deviation from stoichiometry. Between the dioxides of Ce, Pr, Tb and the sesquioxides discussed above is a sequence of oxides of intermediate compositions. The existence of these stable intermediate oxides is indicated by their X-ray diffraction patterns, kinetics of oxygen transport and weight change isotherms. The existence of non-stoichiometry and the intermediate phases will be discussed in the next section.

6.5 NON-STOICHIOMETRY IN RARE EARTH METAL OXIDES

As already pointed out, the element cerium,
Praseodymium and terbium form a series of oxides in the composition range $\text{RO}_{1.5}$-$\text{RO}_2$ and for all the three the most oxygen rich phases are the dioxides. Out of these, praseodymium oxide exhibits the widest variations of compositions and can be taken as a protogenic of all the rare earth metal oxides in as much as the non-stoichiometry is concerned. We shall discuss the crystallographic and compositional characteristics of praseodymium oxide in detail, to be followed by a discussion of other non-stoichiometric oxides of terbium and cerium. An excellent text on non-stoichiometry in binary metal oxides is available due to Kofstad (1972).

5.5.1 The Praseodymium-oxygen System

Praseodymium oxide is known to possess several stable intermediate compositions between $\text{Pr}_2\text{O}_3$ and $\text{PrO}_2$. At constant temperature, the compositions may be expressed as a function of the oxygen pressure. In the temperature range 100-1000°C and the pressure range 2-150 torr, the compositions $\text{PrO}_{1.83}$, $\text{PrO}_{1.818}$, $\text{PrO}_{1.800}$, $\text{PrO}_{1.768}$, $\text{PrO}_{1.714}$, $\text{PrO}_{1.67}$, $\text{PrO}_{1.62}$ and $\text{PrO}_{1.50}$ are stable.

The $\text{PrO}_2$ phase possesses the fluorite structure and has an extensive non-stoichiometry range above 450-500°C. The $\text{Pr}_2\text{O}_3$ crystallizes with the A type rare earth sesquioxide structure. The structures $\text{PrO}_{1.83}$, $\text{PrO}_{1.818}$, $\text{PrO}_{1.80}$, $\text{PrO}_{1.78}$ and $\text{PrO}_{1.714}$ can be derived from the fluorite structure through
withdrawal of oxygen atoms and the vacancies so formed are considered to be ordered in arrays or strings in one or more directions in the fluorite lattice. For example, \( \text{Pr}_2\text{O}_3 \) can be obtained by withdrawing a quarter of anions, while one-seventh of the vacant oxygen site gives \( \text{PrO}_{1.714} \) phase (\( \text{PrO}_{1.67} \)) may be considered as the sesquioxide structure with interstitial oxygen atoms (Hyde, 1966).

Large hysteresis effects have been observed in the transitions between the various oxide phases by several experimenters (in particular by A.W. Czanderna and Honig, 1967). The direction of approach to equilibrium for certain non-stoichiometric compositions is irrelevant, but it is quite critical for others. In the critical region, the pressure ascending isotherms are not superimposable on the pressure descending isotherms and a hysteresis is observed between most of the neighbouring pairs of compositions mentioned above. Hyde (1966) gave a crystallo-chemical interpretation of this phenomenon and discussed the importance of structural relationships of the reactant and product phases in thesolid state reactions. They applied concept of microdomains which in more general involves the proposal that large deviations from stoichiometry constitute structural defects that are much larger than the single point defect.
5.5.2 The Terbium-Oxygen System

The terbium-oxygen system has many similarities to the praseodymium-oxygen system, but fewer phases have been identified in TbO$_{1.8}$-TbO$_2$ composition range. In addition to Tb$_2$O$_3$ and TbO$_2$ phases, the system comprises phases with the compositions TbO$_{1.71}$, TbO$_{1.81}$ and possibly TbO$_{1.83}$. Tb$_2$O$_3$ have a C type structure up to about 1500°C, while TbO$_2$ crystallizes with the fluorite structure. Oxides with an oxygen/metal ratio higher than 1.81 are stable at low temperatures only and their preparation requires the use of atomic oxygen or high pressure molecular oxygen. The TbO phases have higher dissociation pressures than that of praseodymium-oxygen systems. Marked hysteresis effects are observed in transitions between the phases by oxidation and reduction. Oxidation and reduction take place relatively rapidly and it appears that the oxygen is the faster moving species in different phases.

5.5.3 Cerium-Oxygen System

Similar to the case of praseodymium and terbium, cerium also combines with oxygen to produce a series of supposed homologous phases intermediate from end members CeO$_{1.5}$ to CeO$_2$. Numerous studies have been conducted for the purpose of studying the phase relationship in CeO$_3$-CeO$_2$ system. The cerium system has been investigated by X-ray diffraction techniques by Brauer and Gradinger (1954), Bevan (1955),

By reduction of cerium oxide with hydrogen at high temperatures near 1000°C in vacuo, Bevan (1955) has shown that no less than five different phases exist in the composition range from Ce₂O₃ to CeO₂. Brauer and Gingerich (1960) studied the influence of temperature on the phase relations in the cerium-oxygen system by measuring the oxygen dissociation pressure in the region CeO₁.₅ to CeO₂ employing temperature range 600 to 1000°C and by X-ray powder diffraction analysis in the region CeO₁.₇₈ to CeO₂ using the range 20 to 1050°C. Their results indicated a miscibility gap which has the boundaries CeO₁.₈₁ and CeO₂ at room temperature. The gap contracts with the rise in temperature and closes with the composition of approximately CeO₁.₉₂ at 685°C. Above 800°C, a homogeneous cubic solid solution extends from CeO₁.₆₇ to CeO₂ and from CeO₁.₆₇ to CeO₁.₉ a two phase region exists. Another noteworthy point in their investigations is that they observed an increase in lattice parameter with increasing deviations from stoichiometry. Kuznetsov et al (1961) utilized both a Galvanic cell technique and a gas equilibrium method to
obtain the thermodynamic properties of cerium oxide over the composition range CeO$_{1.58}$ to CeO$_{1.98}$. The results of their investigation indicate the existence of single phase region between CeO$_{1.67}$ and CeO$_{1.98}$ above 700°C.

The study of oxygen dissociation pressure and phase relationships in cerium-oxygen system carried out by Bevan and Kordis (1964) covers a wide range of pressure, composition and temperature range 636-1169°C. They observed the intermediate phases of the composition, CeO$_{1.818'}$ CeO$_{1.778}$ and CeO$_{1.714}$ as well as the end members CeO$_2$ and CeO$_{1.5}$. Based on their results they constructed a cerium-oxygen phase diagram at these temperatures between the composition CeO$_2$ and CeO$_{1.5}$. There exists a single nonstoichiometric phase between CeO$_2$ and CeO$_{1.72}$ at all temperatures above 685°C. Below 685°C there is a clear evidence for a biphasic region. This is in agreement with the result of high temperature X-ray investigation and tensiometric studies (Brauer and coworker, 1954, 1960).

Thus we find that the phase field limits of nonstoichiometric cerium oxide determined by high temperature X-ray measurements and thermodynamic measurements appear to be in good agreement. A single phase composition extends from CeO$_2$ to CeO$_{1.72}$ at elevated temperatures above 680°C and a series of sharply defined intermediate phases at lower temperatures are observed. Another interesting point
was noted by Anderson and Wünsch (1973) that cerium oxide crystals in any state of reduction which were achieved would reoxidize in air to single crystal of cerium dioxide in a matter of hours at room temperature. The various phases observed are named as:

\[
\begin{align*}
\text{CeO}_2 & : \lambda \text{ phase} \\
\text{CeO}_{1.818} & : \phi \text{ phase} \\
\text{CeO}_{1.778} & : \phi \text{ phase (Two phase intergrowth of } \phi \text{ and } i \text{ phase)} \\
\text{CeO}_{1.714} & : i \text{ phase} \\
\text{CeO}_{1.683} - \text{CeO}_{1.661} & : \sigma - \text{ phase}
\end{align*}
\]

Cerium dioxide possesses fluorite structure and the intermediate phase are closely related to the parent fluorite structure and is generally felt that they are discrete stoichiometric phases with ordered array of oxygen vacancies. \(\lambda\) phase is a fluorite structure as already stated, \(\phi\) phases are a body centred cubic structure (can be taken as a superstructure on cerium dioxide structure), while \(i\) phase is hexagonal.

5.6 EXPERIMENTAL RESULTS AND DISCUSSION

The main aim of the present investigation is to characterize structurally the cerium oxide films prepared from the 99.99\% pure powder supplied by Indian Rare Earth Limited, Bombay, by employing electron microscope techniques. Before proceeding with this phase of investigation, we
identified the working material by taking its X-ray diffraction powder photograph (shown in Fig.5.3). Its technique and procedure have already been discussed. Measured interplanary distances ($d_{hkl}$) were compared with ASTM card values given for cerium dioxide and a close fit was found, thereby identifying that the powder which we have used in our investigation was cerium dioxide.

The cerium dioxide films for electron microscopic investigation were prepared by vacuum thermal deposition technique using tungsten baskets. The techniques for film preparation has already been described. Since specimen transparency to electrons is a primary consideration films of several thicknesses were initially prepared and tested in the electron microscope. The cerium oxide films were deposited in-situ on the formvar coated copper grids. The preparation technique has already been discussed. The films were prepared under exactly identical conditions as those prevailing while the films for electrical and dielectric measurements were deposited. Evidently, the samples observed in the electron microscope truly corresponded to those used for electrical measurements. Obviously, the influence of the structure and microstructure of the film on the electrical and dielectric measurements can be deduced from those investigated by the electron microscope.
The as-grown films were examined under the low electron beam illumination by suitably energizing both the condenser I and II lenses and inserting in apertures of 100 and 50 μ respectively. This was carried out to avoid the modification in the crystallographic characteristics as a result of the interaction of the film with the electron beam. The films were examined both in the imaging and diffraction modes. Figures 5.8 to 5.10 represent the transmission electron micrographs taken from the as deposited cerium oxide films. As can be noticed, the micrographs represent the film matrix criss-crossed by cracks. These micrographs are for CeO₂ films for which the substrate to source distance were 10, 15 and 20 cm respectively during vacuum evaporation. A noticeable feature of these micrographs is the fact that for the film at the farthest distance (Fig.5.10) represents a comparatively more coherent film with very few cracks. The films for electrical measurements are thought to correspond to this structure, since they were placed at a source to substrate distance of about 20 cm. Occasional electrical short circuiting of the cerium oxides films under cross metal electrodes across the film confirmed the porous nature of the film. It appears that a completely coherent cerium oxide films do not get deposited with the thermal evaporation technique adopted for deposition in the present investigation. The cracks and pores in the as deposited films seem to form due to the
Fig. 5.8. Transmission electron micrograph of CeO₂ film
(Source to substrate distance 10 cm)

Fig. 5.9 Transmission electron micrograph of CeO₂ film
(Source to substrate distance 15 cm.)

Fig. 5.10 Transmission electron micrograph of CeO₂ film
(Source to substrate distance 20 cm)
differential thermal stress, which develops between the film and the substrate. Low substrate temperature would probably lead to the formation of coherent films.

Figures 5.11 to 5.13 represent the diffraction patterns of the as deposited cerium oxide films. These diffraction patterns represent a typically face centred crystal system with fluorite type of structure. An indexing of the diffraction patterns has been suggested in Fig. 5.14. The measurement of the lattice parameter revealed that the measured parameter tallied very closely with that reported for the cerium dioxide (see Table 5.1). Thus the deposited films can be taken to correspond to the cerium dioxide. This observation provides support to the material characterization discussed earlier in Chapters 3 and 4, where the films were presumably taken to correspond to cerium dioxide.

A remarkable feature as shown in the Figs. 5.11 to 5.13 by the diffraction patterns was that the lattice parameter varied from sample to sample and also from region to region in the same sample. Thus for instance the lattice parameter 'a' as deduced from the pattern, Fig. 5.13, varies from 5.41 to 5.55 Å. A careful examination of several diffraction patterns confirmed this variability of the lattice parameter. This feature is vividly brought about by Fig. 5.14 where a comparative sequence of diffraction lines taken from two
Fig. 5.11 F.M. diffraction pattern (Region was chosen from micrograph fig. 5.8)

Fig. 5.12 F.M. diffraction pattern (Region was chosen from fig. 5.9)

Fig. 5.13 F.M. diffraction pattern (Region was chosen from micrograph figure 5.10)
Fig. 5.14 Indexing and comparison of E.M. powder rings. The comparison is done between the films obtained at 10 cm and 20 cm (see text).
<table>
<thead>
<tr>
<th>hkl</th>
<th>I/I₀</th>
<th>d Å</th>
<th>d Å</th>
<th>d Å ± 0.05 Å</th>
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<tr>
<td>111</td>
<td>100</td>
<td>3.124</td>
<td>3.1843</td>
<td>3.13</td>
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<td>200</td>
<td>29</td>
<td>2.706</td>
<td>2.696</td>
<td>2.72</td>
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<td>1.804</td>
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<td>-</td>
</tr>
<tr>
<td>511</td>
<td>9</td>
<td>1.041</td>
<td>1.041</td>
<td>-</td>
</tr>
</tbody>
</table>

*These observed 'd' values tallied closely with the known 'd' values for the standard CeO₂ cubic (fluorite type) with a=5.41 Å. The observed 'a' values for thin films varied from ~5.41 to 5.55 suggesting the existence of a severe non-stoichiometry (see text for details).*
different specimens are shown. As is well known, a variation of lattice parameter for the same chemical material manifests in the existence of non-stoichiometry. The diffraction data for the cerium oxide samples thus clearly suggests the existence of non-stoichiometry in the as deposited films.

It may be mentioned here that Hass, Ramsey and Thun (1958) had prepared evaporated films of cerium dioxide on amorphous substrates such as silicon oxide and quartz glass, and measured their lattice constant. Cerium dioxide is known to crystallize in a face centred cubic lattice with a lattice constant $a=5.41$ Å. They obtained 5.44 Å value for the films deposited at room temperature, 5.41 Å value for the films condensed at temperature between 200 and 270°C. Above 250°C the lattice constant increased slightly. It has already been stated that Brauer and Gingerich (1960) during the course of investigation observed an increase in lattice parameter in the X-ray powder photograph of cerium dioxide, with increasing deviations from stoichiometry.

Another characteristic revealed from the diffraction pattern is in regard to the sharpness of the lines. Whereas for the films represented by Figs. 5.11 and 5.12, the diffraction lines are diffuse, whereas these lines are sharp for Fig. 5.13. The comparative sharpness of the lines represent a larger grain size in the as deposited film. On the other hand, the diffuse lines represent very small grain
size. For very small grains (crystals) the reciprocal lattice points would be broadened thus giving rise to diffuse (broadened) diffraction lines. However, regardless of the state of aggregation, the lattice parameters were found to vary invariably for different films. Thus non-stoichiometry may be taken to be a genuine built in structural feature of the thermally deposited films. It may be opportune to point out that the occurrence of non-stoichiometry has been inferred from the electrical and dielectric measurements also (as per chapters 3 and 4). The present observation on the non-stoichiometry employing electron microscope technique provides credence to the electrical and dielectric measurements, where the details of the observed phenomena becomes explicable only based on non-stoichiometry.

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