

# 2

## Synthesis of 3d-4f Oxides



The rare earth manganites are synthesized using different methods. The well known methods for fabrication manganites are solid state reaction, co-precipitation method, hydrothermal reaction method, sol gel method.

## 2.1 Solid State Method

Solid state reaction method is called conventional method of preparation manganites. In this method pure oxides or carbonates of transition metal and rare earth are mixed together with the proper ratio [13-20].

*Let us take an example how to synthesis SmMnO<sub>3</sub>?*

The steps of solid state reaction method could be represented in the schematic diagram shown in Fig. 2.1. First of all, the reaction which is used to get SmMnO<sub>3</sub> could be written as follow;



We need to calculate the atomic weight of each oxide to know how much oxides needed to get SmMnO<sub>3</sub> (From periodic table see Fig. 2.2 Atomic Wt (Mn) = 54.93805, Atomic Wt (O) = 15.9994, Atomic Wt (Sm) = 150.36). This is so called calculations step and results are shown in table 2.1.

**Table 2.1** Calculations of initial Oxides.

	<b>Initial oxides 0.5 (Sm<sub>2</sub>O<sub>3</sub>)</b>	<b>Initial oxides 0.5 (Mn<sub>2</sub>O<sub>3</sub>)</b>	<b>Final oxides SmMnO<sub>3</sub></b>
Atomic Wt	174.3591	78.9372	253.2963
(Initial oxides/ Final oxides)	0.6884	0.31164	
Mass	0.6884 g	0.3116 g	1.0000 g

Let us return back to our example to get 1g of SmMnO<sub>3</sub> we need to weighting 0.68836g of pure Sm<sub>2</sub>O<sub>3</sub> (99.9%) and 0.31164g of pure Mn<sub>2</sub>O<sub>3</sub> (99.9%) to mix, then grinding carefully using agate mortar to get homogenous and well mixed

powder. Next step is to press the well mixed powder from initial oxides into disc form or into any other forms (pressure range 2-3 ton). The pressed pelt (disc) is place inside furnace and setting the temperature of the firing at the calcinating temperature of rare earth manganites which in our case starts from 1000°C. The calcinating firing process talks 12h - 24h and could be done in environmental or in the presence of oxygen gas. The obtained disc is grinded again and repeating firing but with increasing firing temperature up to 1100°C in environmental condition or in the presence of oxygen gas. Each time we must test the fired powder using X-Ray diffraction in order to know how much from our phase is formed. The calcination process may be made for the well mixed and grinded powder form without pressing. The last step is to fire the disc formed from our powder at sintering temperature ( $T_{\text{sintering}} \approx 1200^{\circ}\text{C} - 1400^{\circ}\text{C}$ ). The instrumental equipments which are used in solid state reaction method are shown in Fig. 2.3. The sintered disc is examined again with X-Ray diffraction to define the structural parameters and carrying out different characterizations (optical, electrical and magnetic transport).

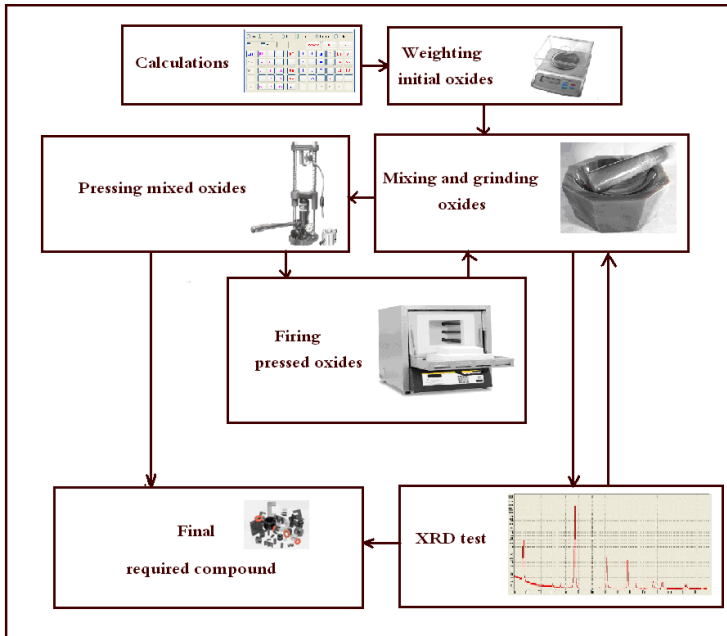


Fig. 2.1 Schematic representation of the solid state reaction process.

### Periodic Table of Elements

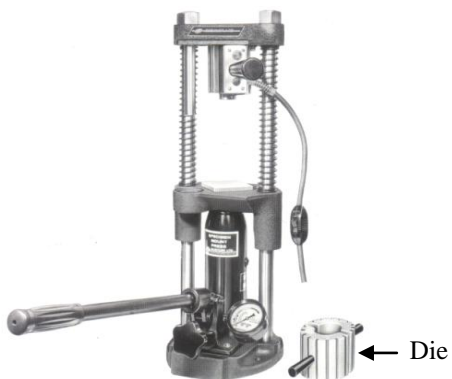
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Electronic Balance



Agate Mortar



High pressure Press (20 Ton)



Furnace

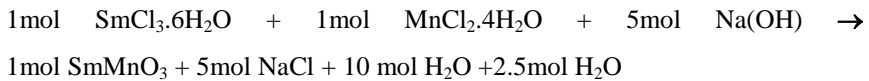
*Fig. 2.3 Experimental equipments for solid state synthesis.*

## 2.2. Co-precipitation Method

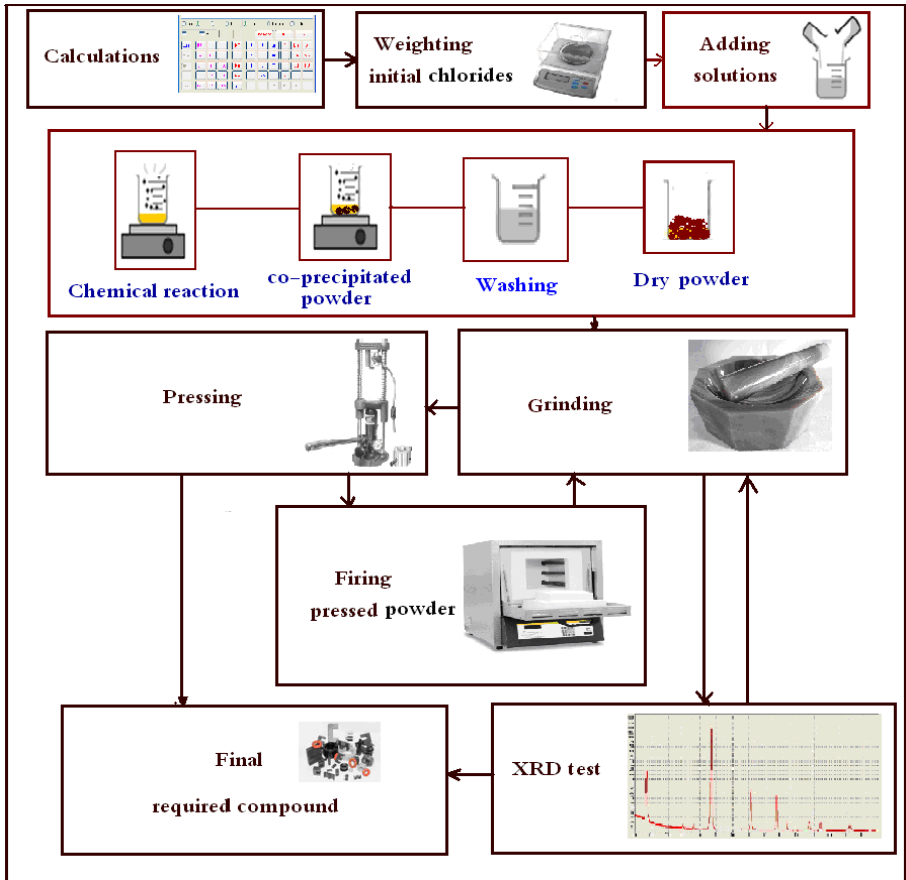
The synthesis of manganites using chemical reaction methods are widely used in fabrication nano-sized manganites. Co-precipitation [21-30], hydrothermal reaction, sol gel are the well known example chemical reaction method, where we are using chlorides, nitrates or phosphates as initial chemical to start our reaction.

Let us take the same example (synthesis  $\text{SmMnO}_3$  which we discussed before using solid state reaction) but in this case we apply co-precipitation reaction. Looking at the schematic diagram of chemical reaction process shown in Fig. 2.4, one can realize that we need first to make calculations for how much starting precursors required for beginning our reaction.

Calculations step: 1mol of  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  and 1mol  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  react with 5mol  $\text{Na}(\text{OH})$ . The chemical reaction could be represented as:



The details of calculations are required for chemical reactions are represented below in this table 2.2.



*Fig. 2.4 Schematic representation of the chemical reaction process.*





Electronic balance



pH meter



Magnetic stirrer with hot plate



High pressure Press (20 Ton)



Agate mortar



Furnace

**Fig. 2.5** Experimental equipments for chemical synthesis.

**Table 2.2** Calculations details of chemical reaction.

SmCl <sub>3</sub> =256.7181	SmCl <sub>3</sub> .6H <sub>2</sub> O =364.8099		NaCl =58.4425	H <sub>2</sub> O =18.0153
MnCl <sub>2</sub> =125.8435	MnCl <sub>2</sub> .4H <sub>2</sub> O =197.9047	SmMnO <sub>3</sub> =253.29625	5NaCl =292.2125	H <sub>2</sub> O =180.153 +45.0383 =225.1913
Na(OH) =39.9971	5Na(OH) =199.9855			
Total	Input =762.7	Output 770.7		

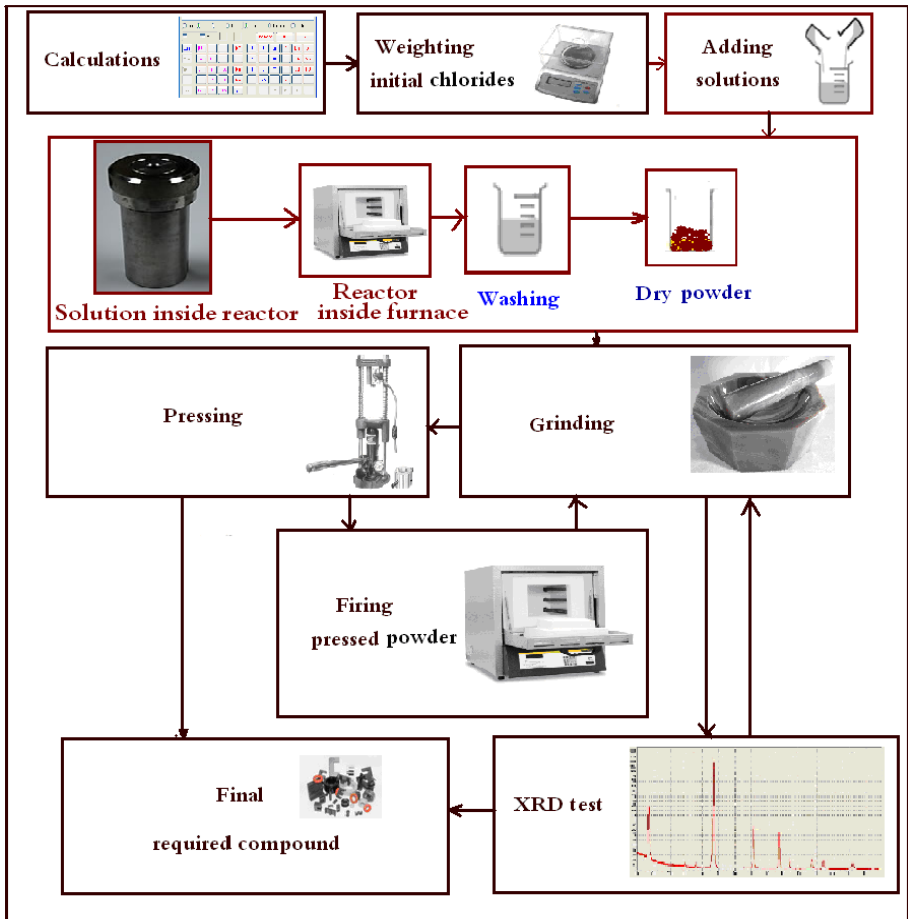
According to our calculation, to get 1g of SmMnO<sub>3</sub> we need to take the following weights of starting precursors; 1.4403g of SmCl<sub>3</sub>.6H<sub>2</sub>O, 0.7813g of MnCl<sub>2</sub>.4H<sub>2</sub>O and 0.7895g Na(OH). One can ask reasonable question; why there is difference in atomic weights of input and output of reaction? The difference in weights is of 0.5 of oxygen weight which equal 8 and it is taken from air.

Following the schematic representation of synthesis process, the next step is to weight starting precursors with the calculated values. Taking into consideration all starting precursors must be of high-purity compounds. After weighting our initial powders the 1.4403g of SmCl<sub>3</sub>.6H<sub>2</sub>O and the 0.7813g of MnCl<sub>2</sub>.4H<sub>2</sub>O are dissolved in distilled water (200 mLiter). The 0.7895g Na(OH) is dissolved in distilled water separately to give us alkaline solution. Then this alkaline solution is slowly poured into the solution of metal ion until the pH of the suspension reach ~ 13 to avoid differences in precipitate composition. Digital pH meter is used and you can use any other pH indicators, all experimental equipments required to sensitize our manganites are shown in Fig. 2.5. Looking at the solution when adding alkaline solution we can see the color of solution is changing we see small particles in this solution. The aqueous mixture stirred magnetically for 180-300 minutes at 85 °C using magnetic stirrer. The precipitated Powder composed of our SmMnO<sub>3</sub> compound and NaCl compound so we need to dissolve NaCl in water and get red of this NaCl which is dissolved in water. This

step is so called washing process and we are washing for several times using distilled water until the pH value of the solution became neutral, or until get rid of sodium chloride. Finally, the precipitated powder is dried at 90 °C for 3h in air using hot plate. The obtained powder grinded using agate mortar to get well disperse  $\text{SmMnO}_3$  powder and testing it with X-Ray diffraction. After this step you may need to thermal treatment for this powder to form required  $\text{SmMnO}_3$  structure. The powder is pressed into a disk- shaped form of 13 mm diameter to be sintered in air for 12 hours at different temperatures 650 °C, 750 °C, 850 °C and 1000 °C. The sintered pellets constituted the final sample and has certain shape (disc, rectangular, or torrid) to examine (electrical, magnetic, optical, ... etc.) properties of our synthesized material according to certain conditions (either heat treatment or chemical reaction).

## 2.3 Hydrothermal Method

The hydrothermal reaction [31-35] is also one of the well known examples of chemical reaction method, where we can use chlorides, nitrates or phosphates as the initial chemicals to start our reaction. Looking at the schematic diagram of hydrothermal reaction process shown in Fig. 2.6, one can realize that next step after calculations is weighting starting precursors; 1.4403g of  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.7813g of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 0.7895g of  $\text{Na}(\text{OH})$ . After weighting our initial powders the 1.4403g of  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$  and the 0.7813g of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  are dissolved in distilled water (200 mLiter). The 0.7895g  $\text{Na}(\text{OH})$  is dissolved in distilled water separately to give us alkaline solution. Then this alkaline solution is slowly poured into the solution of metal ion until the pH of the suspension reach ~ 13. The solution is placed inside the hydrothermal reactor and closed tightly and put them together inside furnace with temperature 200°C for 3h.



*Fig. 2.6 Schematic representation of the hydrothermal reaction process.*

Return to our example (synthesis  $\text{SmMnO}_3$ ) and let us see the difference in the hydrothermal reaction method. For the calculation of how much of initial materials are needed in hydrothermal reaction we can say the same procedure of the co-precipitation method and the same materials could be used. So we can take the same calculations shown in table 2.2 for hydrothermal reaction. According to that calculation, we will repeat “we need to take the following weights of starting precursors; 1.4403g of  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ , 0.7813g of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 0.7895g of  $\text{Na}(\text{OH})$  to obtain 1g of  $\text{SmMnO}_3$ ”.

The precipitated Powder composed of our  $\text{SmMnO}_3$  compound and  $\text{NaCl}$  compound so we need to dissolve  $\text{NaCl}$  in water and get rid of this  $\text{NaCl}$  which is dissolved in water. This step is so called washing process and we are washing for several times using distilled water until the pH value of the solution became neutral, or until get rid of sodium chloride. Finally, the precipitated powder is dried at  $90\text{ }^\circ\text{C}$  for 3h in air using hot plate. The obtained powder grinded using agate mortar to get well disperse  $\text{SmMnO}_3$  powder and testing it with X-Ray diffraction. After this step you may need to thermal treatment for this powder to form required  $\text{SmMnO}_3$  structure. The powder is pressed into a disk-shaped form of 13 mm diameter to be sintered in air for 12 hours at different temperatures  $650\text{ }^\circ\text{C}$ ,  $750\text{ }^\circ\text{C}$ ,  $850\text{ }^\circ\text{C}$  and  $1000\text{ }^\circ\text{C}$ . The sintered pellets constituted the final sample and has certain shape (disc, rectangular, or torrid) to examine (electrical, magnetic, optical, ... etc.) properties of our synthesized material according to certain conditions (either heat treatment or chemical reaction).

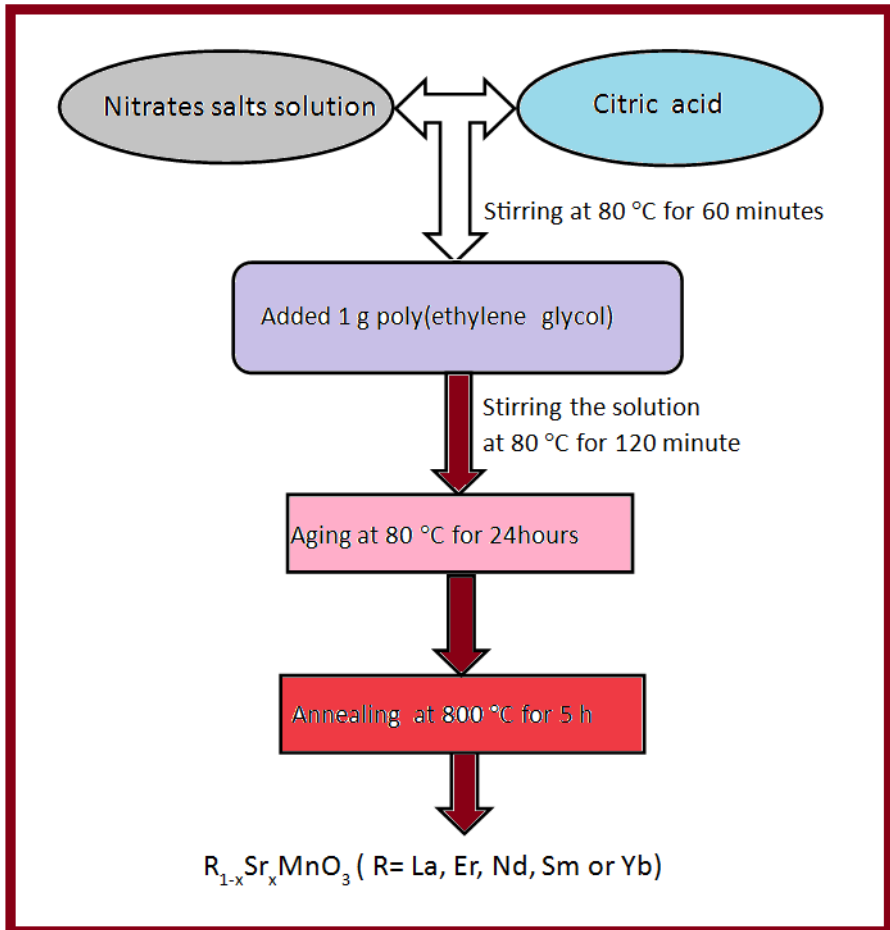
## 2.4 Sol-gel Method

The Sol-gel method is very efficient for producing various functional materials in which particle size, porosity, thin layer thickness, separation of particles of different compositions and structure may be controlled [36-50].

For synthesize rare earth manganites; rare earth acetate hydrate, and manganese (II) acetate tetrahydrate were used as precursors in this method. [37]. For preparing perovskites  $\text{R}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $\text{R} = \text{La}, \text{Er}, \text{Nd}, \text{Sm}$  or  $\text{Yb}$ ), [38] an appropriate amount of  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Yb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in 100 ml  $\text{H}_2\text{O}$ , and then citric acid (the molar ratio of citric acid to nitrate salts is 2:1) was added with continuous stirring at  $80\text{ }^\circ\text{C}$  for 60 minutes. Afterward, 1g of poly (ethylene glycol) was added to mixture with stirring at  $80\text{ }^\circ\text{C}$  for

two hours to get clear solution at pH = 8. The produced sol was aged at 80 °C for 24 hours to evaporate water until the gels formed. The produced gel was calcined at 500 °C for 2 hours and then annealed at 800 °C for 5 hours to obtain  $R_{1-x}Sr_xMnO_3$  (R= La, Er, Nd, Sm or Yb).

So we can say that the proper stoichiometric quantities of the nitrates or chlorides are dissolved in water. This solution was mixed with citric acid solution in 1:1 volume ratio. On heating this mixture in water bath at 80 °C, a yellowish transparent gel was formed on complete evaporation of water. Continued heating caused the gel to swell and fill the beaker with a foamy precursor. Upon subjecting it to a temperature of 400 °C for 2h, the foamy precursor decomposed to give very light, homogenous, black-colored flakes of extremely fine particle size. Further, the powder obtained by crushing these flakes was subjected to final sintering temperature of 800 °C for duration of 2h. The powder was magnetically filtered to ensure that there are no traces of carbon in the sample.



*Fig. 2.7 Schematic representation of the sol gel reaction process.*

Let us see some examples; how we prepared different compounds using different methods. Solid state reaction was used to prepare Samarium [1, 51-52], Europium [53-55] and a part of ytterbium manganites ( $\text{Yb}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ ,  $\text{Yb}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_3$  and  $\text{Yb}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.98}^{57}\text{Fe}_{0.02}\text{O}_3$  samples) [56] while chemical reaction was used to prepare nano crystalline size of ytterbium manganites [57-58].

## 2.5 Samarium Ferrimanganites

Samarium ferrimanganites  $\text{SmFe}_x\text{Mn}_{1-x}\text{O}_3$  [11, 51] were prepared using solid state method from pure oxides;  $\text{Sm}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $^{57}\text{Fe}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$  with the proper ratio.  $^{57}\text{Fe}_2\text{O}_3$  is used to enable measuring Mossbauer spectra which given in ref. [51]. Strontium is doped to samarium manganite in ref [1] where  $\text{Sm}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  was synthesized from initial pure oxides;  $\text{Sm}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and carbonate  $\text{SrCO}_3$ . These oxides and carbonate were mixed together within the appropriate ratios then milled and pressed in disc form. The obtained disc was fired at 950 °C for 12h in air. The sample was fired again at 1350 °C for 72h, after repetition of milling and pressing process.

## 2.6 Europium Ferrimanganites

$\text{Eu}_{0.65}\text{Sr}_{0.35}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$  were prepared from the initial pure oxides ( $\text{Eu}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{SrO}$ ) using the solid state reaction method [52-53]. These pure oxides were well mixed with appropriate ratios to be milled together using agate mortar then pressed in disk form under a pressure = 15 ton/cm<sup>2</sup>. The pressed disks were fired at 1200 °C for 12h in air. The pre-sintered samples were ground again and pressed under the same pressure in the form of disk with 12 mm diameter. All samples were fired again at 1350 °C for 72h with an intermediate grinding to ensure homogenization; this heat treatment was followed by natural furnace cooling.

## 2.7 Ytterbium Manganites

The  $\text{Yb}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ ,  $\text{Yb}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_3$  and  $\text{Yb}_{0.6}\text{Sr}_{0.4}\text{Mn}_{0.98}\text{Fe}_{0.02}\text{O}_3$  samples were prepared using standard solid solution method from pure oxides ( $\text{SrO}$ ,  $\text{Yb}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $^{57}\text{Fe}_2\text{O}_3$ , and  $\text{Mn}_2\text{O}_3$ ) [56]. The purity of the initial oxides was 99.9%. These oxides were carefully mixed, milled and pressed then calcined at a temperature of 1050 °C for 25h. After that, obtained compound



milled and pressed again to be burned at a temperature of 1250 °C for 12h. Finally the last process was repeated but the firing (sintering) temperature was 1350 °C for 40h. The burning was done at the air environment.

Chemical reaction method (co-precipitation method) was used to synthesize  $\text{YbMnO}_3$  and  $\text{Yb}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$  samples from initial pure Chloride solutions;  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  [57]. These Solutions were mixed with NaOH solution within the appropriate molar ratios. The resulting compounds are milled and pressed in the disc form. The obtained discs were fired at 750 °C, 850 °C and 1000 °C in air to give  $\text{YbMnO}_3$  and  $\text{Yb}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ .

