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Elemental Analysis and Microstructure of 3d-4f Oxides

Elemental analysis is very important step that enable us to test our compound if it is formed in the proper way or we have strange elements in our compound. Elemental analysis and microstructure micrographs were performed for both ytterbium [56-57] and europium [54] managnites. The details of these studies will be presented in the following sections.

3.1 Ytterbium Manganites

The elemental analysis using EDXS was carried out for europium and ytterbium manganites in order to test the elements which constitute the proposed compounds. The used accelerating voltage was 25KeV within resolution of 128 eV of EDXS spectra for both $Yb_{0.6}Sr_{0.4}MnO_3$ and $Yb_{0.6}Sr_{0.4}Mn_xFe_{1-x}O_3$. The following standards; K quartz, K Mn, L SrF_2 and YbF_3 were used for identifying the elements that constitute $Yb_{0.6}Sr_{0.4}MnO_3$ (Oxygen, manganese, Strontium and Ytterbium). The obtained peaks correspond to Oxygen, Manganese, Strontium and Ytterbium which form the $Yb_{0.6}Sr_{0.4}MnO_3$ are noted [16]. From analysis of the measured spectra it is found that ytterbium, strontium, manganese and oxygen are the elements which form $Yb_{0.6}Sr_{0.4}Mn_xFe_{1-x}O_3$ where X=1 while ytterbium, strontium, manganese, iron and oxygen are observed for X=0.98 with the proper concentration. The concentration of each element in the compound is in agreement with the theoretically calculated concentrations (see table 3.1). For identification of the elements constituting the $Yb_{0.6}Sr_{0.4}Mn_{0.98}Fe_{0.02}O_3$ composite the same standards for identifying the $Yb_{0.6}Sr_{0.4}MnO_3$ were used in addition to *K*Fe for identifying iron. It is quite clear that the experimentally observed percentages of elements (which constitute the proposed composites) are in agreement with those calculated.

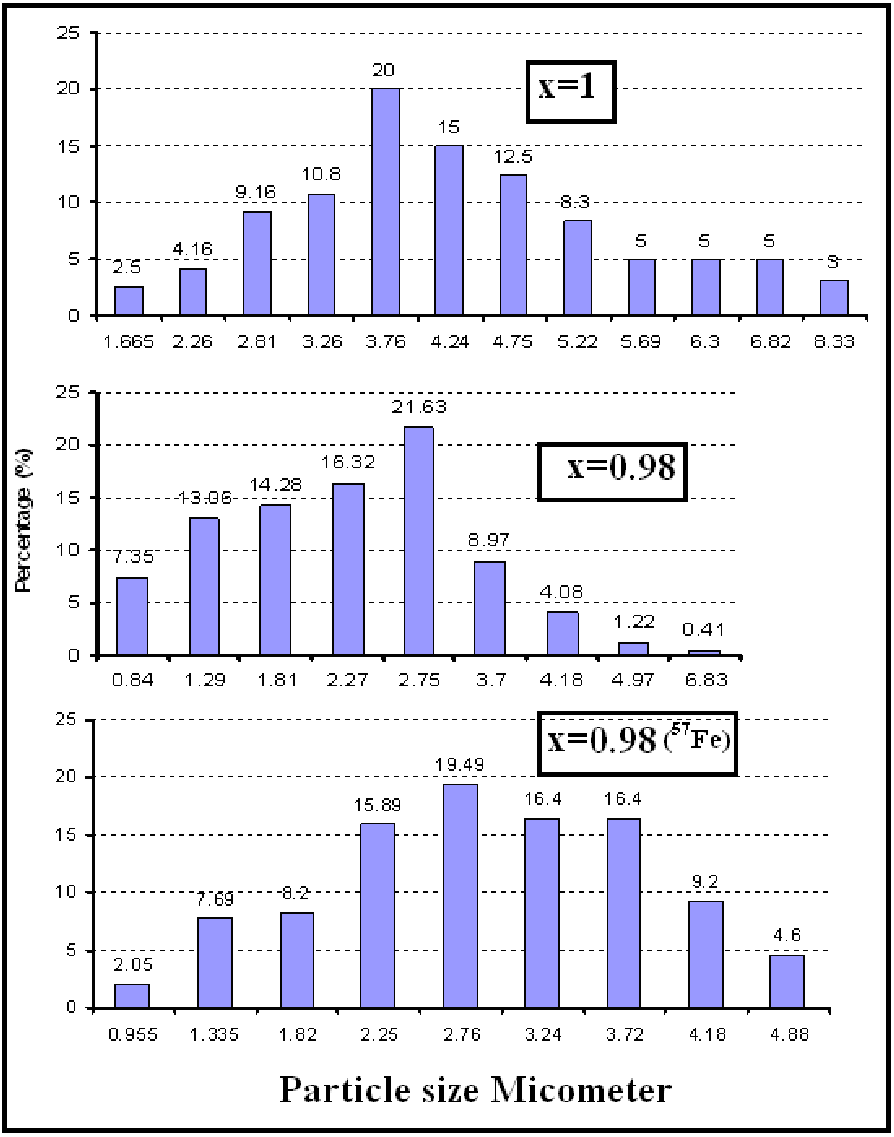


Fig. 3.1 *The particle size distribution of* $Yb_{0.6}Sr_{0.4}Mn_xFe_{1-x}O_3$.

The elemental analysis reveals that the synthesized composites of the proposed structure are in proper stoichometry. Particle size distribution of $Yb_{0.6}Sr_{0..4}MnO_3$, $Yb_{0.6}Sr_{0.4}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ and $Yb_{0.6}Sr_{0.4}Mn_{0.98}Fe_{0.02}O_3$ was done.

The obtained micrographs were analyzed according to digital imaging processing method. The particle size distribution of the $Yb_{0.6}Sr_{0.4}Mn_xFe_{1-x}O_3$ is illustrated in Fig. 3.1. It is quite clear that the minimum observed size of the composite where x=1 is of 1.665 μm. Those particles represent 2.5%. The maximum particle size was 8.33 μm which is 3%. The maximum percentage is 20% for 3.76 μm. In the case of x=0.98 (for ^{57}Fe) it is noted that 2.05% of minimum size of 0.955 μm while 4.6% of maximum size of 4.88 μm. 2.76 μm particle size is the peak of this distribution within 19.49%. The minimum size of 0.84 μm represents 7.35% while 4.6% the maximum size of 6.83 μm represents 0.41% and 2.756 μm is the peak of this distribution within 21.63%. One can note that the particle size of both $Yb_{0.6}Sr_{0.4}Mn_{0.98}{}^{57}Fe_{0.02}O_3$ and $Yb_{0.6}Sr_{0.4}Mn_{0.98}Fe_{0.02}O_3$ is identical and the difference in particle size is obtained in the sample x=1.

The elemental analysis using EDXS was carried out for $Yb_{0.9}Sr_{0.1}MnO_3$ and $YbMnO_3$ as shown in Fig. 3.2 and Fig. 3.3. The used accelerating voltage was 15KeV. The following standards; quartz, Mn, SrF_2 and YbF_3 were used for identifying the elements that constitute $Yb_{0.9}Sr_{0.1}MnO_3$ (Oxygen, manganese, Strontium and Ytterbium). The obtained peaks correspond to Oxygen, manganese, Strontium and Ytterbium which form the $Yb_{0.9}Sr_{0.1}MnO_3$ are illustrated in Fig. 3.2 On the other hand the obtained peaks correspond to Oxygen, manganese and Ytterbium which form the $YbMnO_3$ are illustrated in Fig. 3.3. The concentrations of each element in both compounds theoretically calculated and experimental are listed in table 3.1.

Table 3.1 *Elements identifications of $Yb_{0.6}Sr_{0.4}Mn_xFe_{1-x}O_3$.*

X	Element	Exp. Percentage, %	Cal. Percentage, %
	Yb	41.84 (18)	42.93
	Sr	14.04 (11)	14.49
1.00	Mn	25.05 (11)	22.72
	Fe	00.00	00.00
	O	19.07 (16)	19.85
	Yb	46.00 (19)	42.92
	Sr	11.97 (11)	14.49
0.98	Mn	24.21 (12)	22.72
	Fe	00.19 (60)	00.46
	O	19.85 (19)	19.85

It is quite clear that the experimentally observed percentages of elements are in a good agreement with those calculated. So one can say that, the elemental analysis reveals that the synthesized composites of the proposed structure are in the proper stoichiometry. The microstructure graphs $Yb_{0.9}Sr_{0.1}MnO_3$ and $YbMnO_3$ are taken using Field Emission Scanning Electron Microscope FE-SEM – JEOL (JSM-5600) at 15KeV and magnification X - 43000, see Fig. 3.4 and Fig. 3.5. From Fig. 3.6, it is clear that the particle size of $Yb_{0.9}Sr_{0.1}MnO_3$ composite fired at 850 ℃ at 12h are on the range of 80 nm. One can say there is homogeneity in the size of particles all over the graph.

Looking at the microstructure of $YbMnO_3$ one can note that the composite which fired at 750 ℃ has nano tube structure of size 60 nm. In the same composite but fired at 1000 ℃ the particles aggregated and the particle size increased (110 nm).

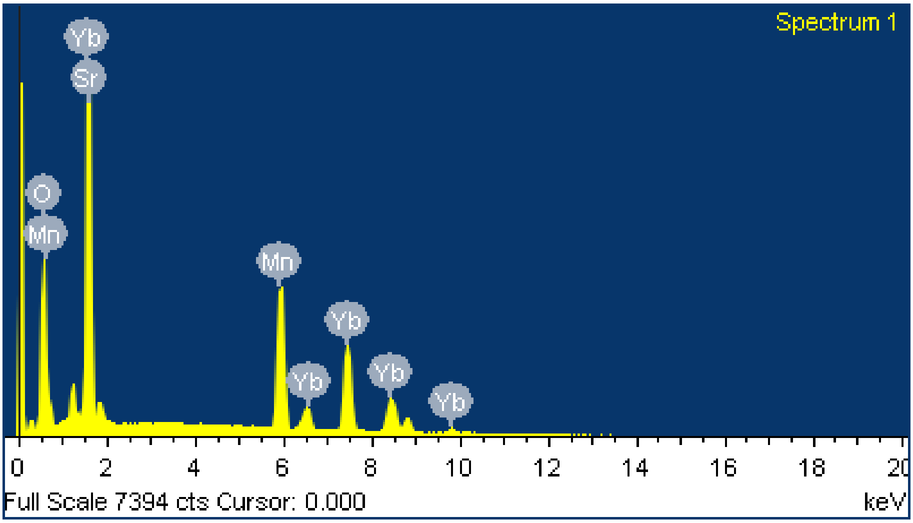


Fig. 3.2 *EDX spectra of* $Yb_{0.9}Sr_{0.1}MnO_3$.

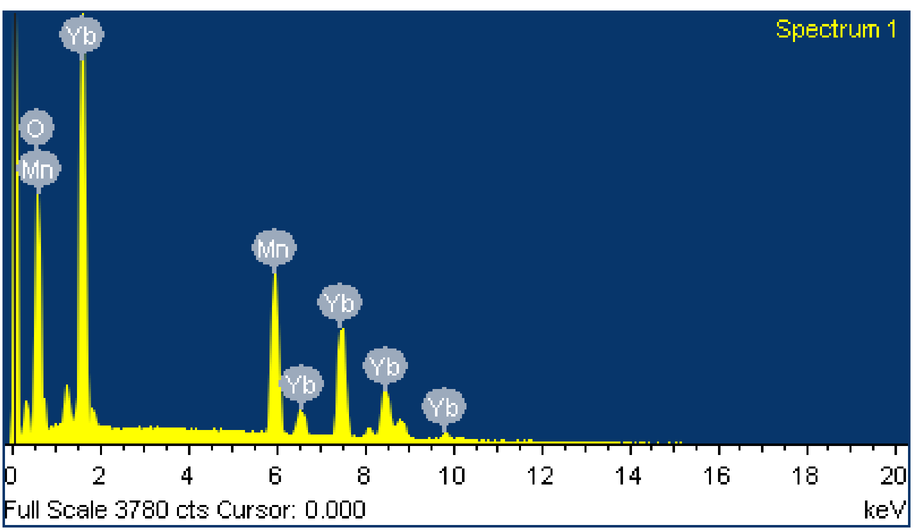


Fig. 3.3 *EDX spectra of* $YbMnO_3$.

Table 3.2 *Element identification of Yb* $_xSr_{1-x}MnO_3$.

X	Element	Exp. Percentage, %	Cal. Percentage, %
0.9	Yb	55.27	58.23
	Sr	2.19	3.28
	Mn	19.10	20.54
	O	23.44	17.95
1	Yb	56.70	62.70
	Mn	16.98	19.91
	O	26.31	17.39

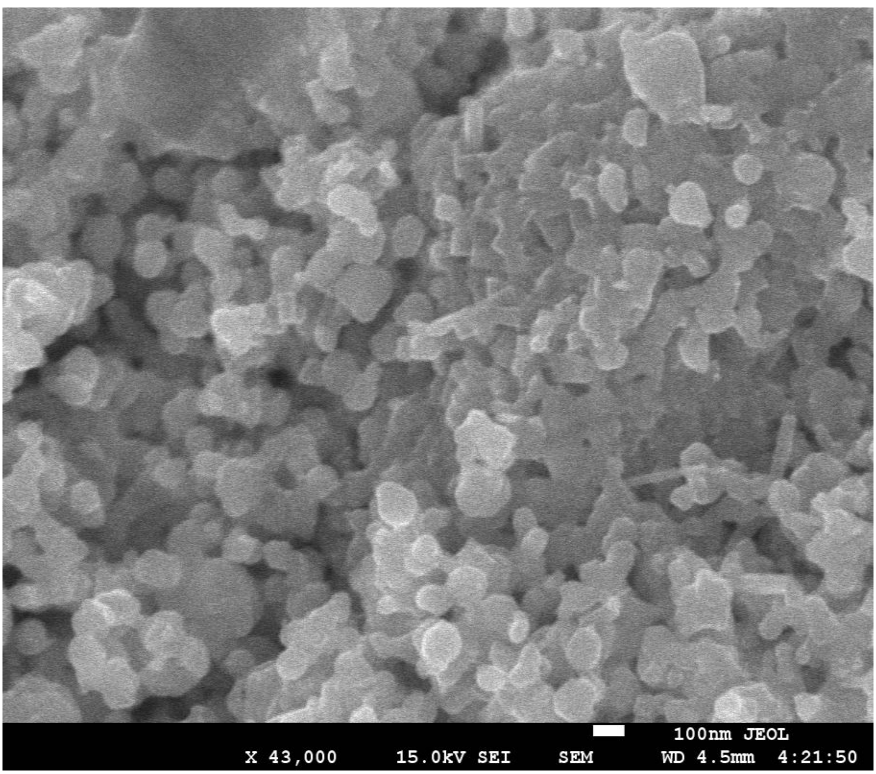
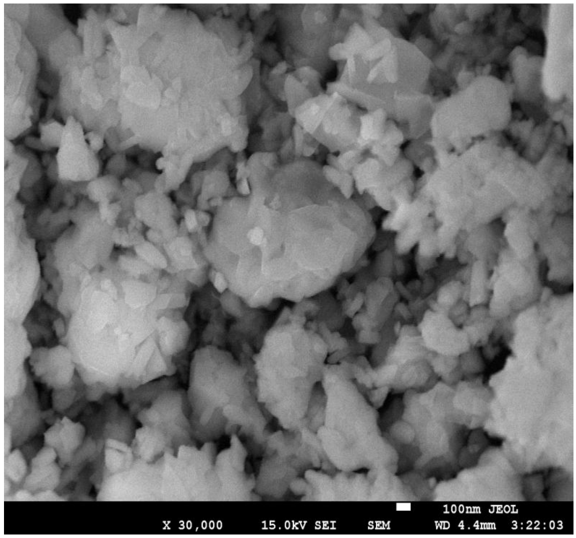
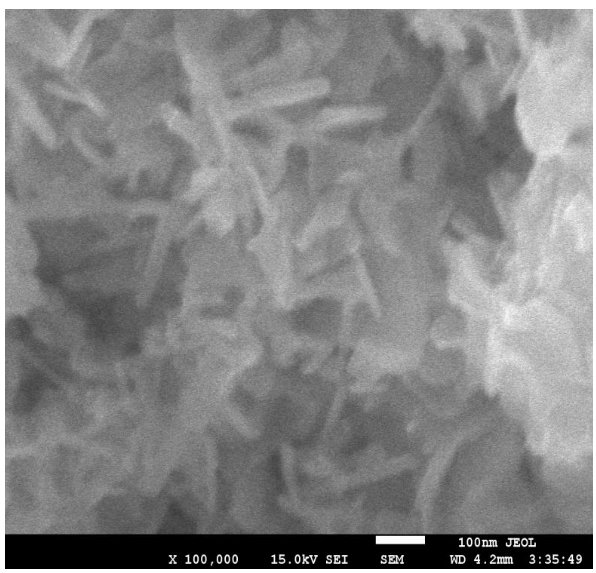


Fig. 3.4 *Microstructure of the* $Yb_{0.9}Sr_{0.1}MnO_3$ *composite.*



(a)



(b)

Fig. 3.5 *Microstructure of the $YbMnO_3$ composite; (a) fired at 1000 ℃ and (b) fired at 750 ℃.*

The particle size of the composite as prepared is closed to 50 nm. Recently reported by Rößler et. al [58] that the morphology of thin films has a strong influence on the local conductivities in manganite thin films. The magnetic properties of manganites also depend on the morphology of these manganites. It was reported by Marttinez et. al. [59], that the magnetoresistance and the magnetization of ceramic $La_{2/3}A_{1/3}MnO_3$ (A = Sr, Ca) oxides have been studied as a function of the grain size. It was found that [2] these ceramics become magnetically harder when reducing the particle size exhibiting a large magnetic anisotropy that increases when reducing the grain size.

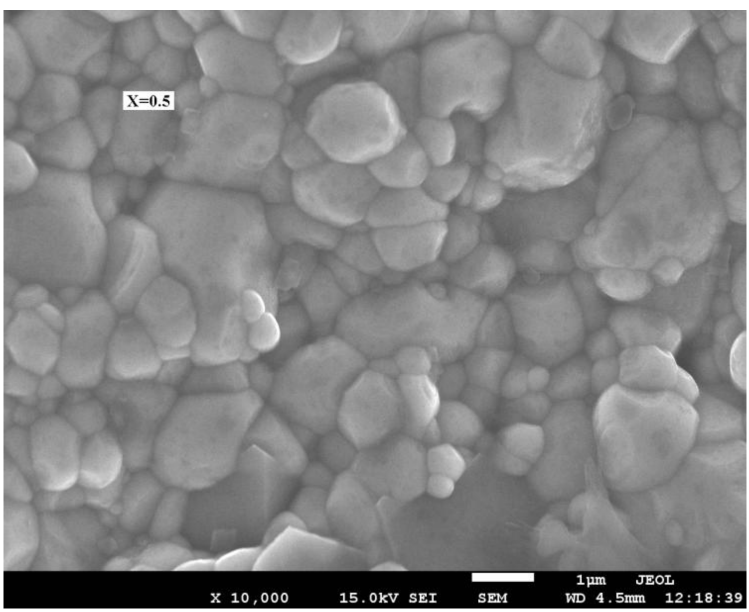
3.2 Europium Manganites

The elemental analysis using EDXS was carried out for $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ (x=0.1 and 0.5) samples [54]. The following standards; SiO_2, Mn, Fe, SrF and EuF were used for identifying Oxygen O, manganese Mn, Iron Fe, Strontium Sr and Europium Eu elements respectively that constitute $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$. The obtained peaks correspond to Oxygen, Manganese, Iron, Strontium and Europium which forms the $Eu_{0.65}$ $Sr_{0.35}$ $Mn_{1-x}Fe_xO_3$ that is good indication for the absence of impurities in synthesized compounds (see table 3.3). This means the quality of synthesis.

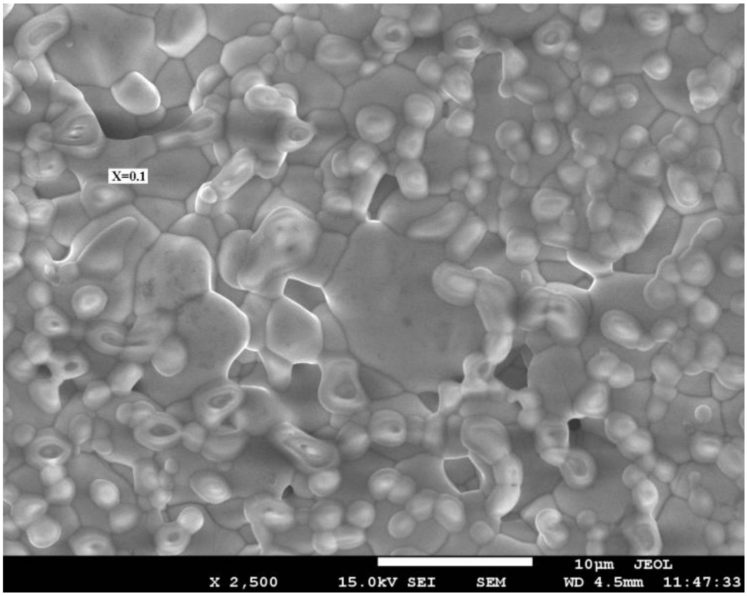
Table 3.3 *Elements identifications of $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$.*

X	**0.1**		**0.5**	
Element	**Exp. Weight %**	**Cal. Weight %**	**Exp. Weight %**	**Cal. Weight %**
O	18.67	20.65	28.49	20.62
Mn	21.05	21.27	10.41	11.80
Fe	3.56	2.40	11.26	11.99
Sr	7.05	13.19	11.38	13.17
Eu	49.67	42.49	38.46	42.43
Totals	100.0	100.0	100.0	100.0

The concentration of each element in the compound are in good agreement with the theoretically calculated, see table 3.3. As it is quite clear that the experimentally observed percentages of elements (which constitute the proposed composites) are in good agreement with those calculated. The elemental analysis reveals that the synthesized composites of the proposed structure are in proper stoichiometry and this is in a good agreement with the crystal structure analysis using X-ray diffraction which reported in ref., [53]. The microstructure graphs $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ are taken at 15KeV and magnification X-43000, see Fig. 3.2. From Fig. 3.2, it is clear that the grain size of in the composite where x=0.1 is on the range of 2.5 – 3.5 μm. One can say that the homogeneity size of grains is not completely represented. Looking at the microstructure of composite where x=0.5 one can note that the lower grain size is quite clear compared with the grain size in x=0.1. The grain size in the case of x=0.5 in the range 0.5 – 1 μm.



X=0.5



X=0.1

Fig. 3.6 *Micrographs of $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ (X= 0.1 and 0.5) measured at 15 kV.*

3.3 Neodymium Manganites

The elemental analysis using EDXS was carried out for one sample $Nd_{0.6}Sr_{0.4}Mn_{0.7}Co_{0.3}O_3$ as shown in fig. 3.7. The used accelerating voltage was 15KeV. Looking at table 3.4, it is quite clear that the experimentally observed percentages of elements are in a good agreement with those theoretically calculated. So, one can say that the elemental analysis reveals that the synthesized composites of the proposed structure ($Nd_{0.6}Sr_{0.4}Mn_{0.7}Co_{0.3}O_3$) are in the proper stoichiometry.

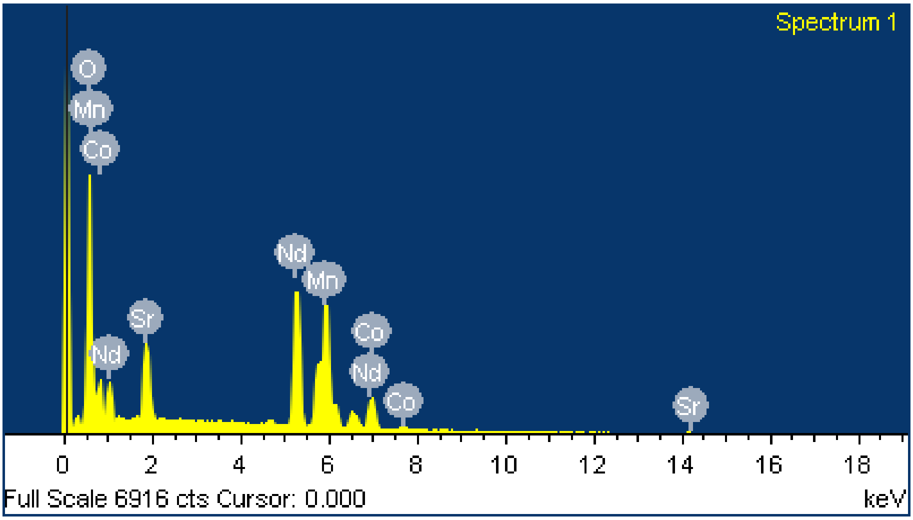


Fig. 3.7 *EDX spectra of $Nd_{0.6}Sr_{0.4}Mn_{0.7}Co_{0.3}O_3$.*

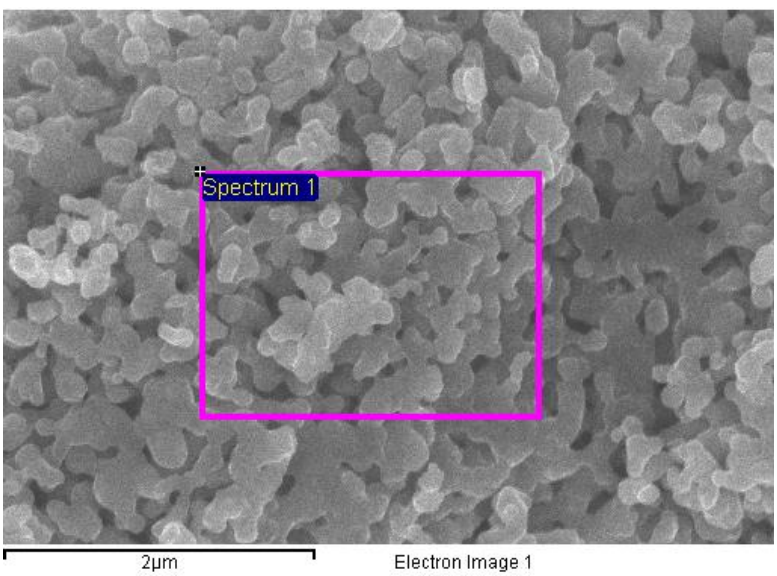


Fig. 3.8 *Micrograph of $Nd_{0.6}Sr_{0.4}Mn_{0.7}Co_{0.3}O_3$ annealed at 850 ℃ for 12h.*

Table 3.4 *Element identification of* $Nd_{0.6}Sr_{0.4}Mn_{0.7}Co_{0.3}O_3$.

Element	**Exp. Percentage, %**	**Cal. Percentage, %**
Nd	38.81	38.34
Sr	10.25	15.53
Mn	16.42	17.04
Co	6.00	7.83
O	28.50	21.26

The microstructure graphs $Nd_{0.6}Sr_{0.4}Mn_{0.7}Co_{0.3}O_3$ are illustrated in Fig. 3.8. It is quite clear that say there is homogeneity in the size of particles all over the graph. The minimum particle size is 119.05 nm while the maximum particle size is 190.48 nm. The mean value of the particle size is 150.80 nm which in good agreement with the crystalline size deduced from XRD measurements (147.4 nm).