Local Structure of Nano powder of Sm_2O_3

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1. Objective

The main objective of the work is to analyze the local structure of nano powder of Sm_2O_3 and to the characterize nano particles using powder X-Ray diffraction and SEM (Scanning Electron Microscopy). The structures are analyzed using powder X-Ray diffraction techniques. For Sm_2O_3, the powder XRD analysis is used for the electronic level characterization using Maximum Entropy Method (MEM). The local structure of the nano particles is analyzed using PDF (Pair Distribution Function) analysis which employs the powder XRD data. Also the size of the nano particle is analyzed using XRD and SEM.

2. Introduction

A chemical element, Sm, atomic number 62, belongs to the rare-earth group. Its atomic weight is 150.35, and there are 7 naturally occurring isotopes; ^{147}Sm, ^{148}Sm, and ^{149}Sm are radioactive and emit α particle. Samarium oxide is pale yellow, is readily soluble in most acids, and gives topaz-yellow salts in solutions (1). Samarium oxide has most common structures: Monoclinic (mS30, Space Group = C2/m, (12). The cubic structure is similar to that of manganese (III) oxide. The monoclinic structure of the cell parameters are a= 14.17Å, b=3.628 Å & c= 8.855 Å , α= 90°, β= 100.03° & γ= 90° [1]. A unit cell of Samarium Oxide structure is as shown in figure 1.

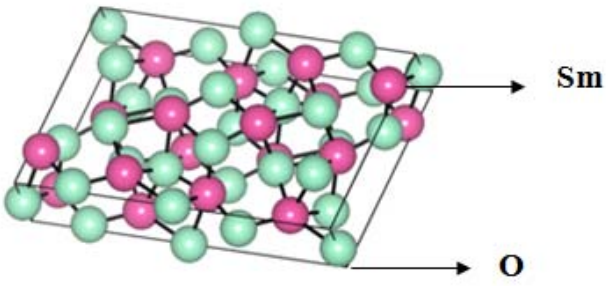

Figure 1: A Unit Cell of Monoclinic Structure of Samarium Oxide

3. XRD Data Collection

The powder X-ray intensity data were collected at NIIST (X-RAY LAB), Thiruvanandhapuram, Kerela, India using X'PERT Software X-ray diffractometer with a monochromatic incident beam of wavelength 1.54056 Å offering pure Cu-K_α stripping procedures. To analyze the bonding and structural behavior of Sm_2O_3 the powder X-ray intensity data was collected using Cu-K_α X-radiation with λ = 1.54056Å from the finely powdered samples. The powder X-ray data set as collected in the 2θ range for XRD data collection is 10° to 120° for Sm_2O_3.

4. Structure Factor

In the work, the powder data of Sm_2O_3 was subjected to sfac.332. in this software program we first created all input file having the basic requirements are name of the element, number of species, cell parameter values and the position of individual elements in a compact [2]. The input files are given in the following table 1. Successful execution of the program gives the output file which contains the values of h k l, F_{cal}, sin (Θ / λ), Θ and the values. A phase file having h k l, F_A and F_B values will also be generated. Finally 'σ' value was calculated by using the values of F_{cal} taken from the output file. Theoretically calculated structure factors of Sm_2O_3 are given in the table 2 respectively. A constant error value of 5% was added so that 'σ' can be calculated by using Fcal * (5/100). Using the values of h k l, F_A, F_B and sigma the input file for MEM analysis was created.

Input file for Sm_2O_3

Name of the element: Sm_2O_3; Name of the species: 2; Occupancy: Sm - 1, O -1
a = 14.17 Å, b = 3.628 Å & c = 8.855 Å, α = 90°, β = 100.03° & γ = 90°.

Table 1: The Position of Atoms in Sm_2O_3

Atoms	*X*	*Y*	*Z*
Sm 1	0.6349	0	0.4905
Sm2	0.6897	0	0.1380
Sm3	0.9663	0	0.1881
O1	0.5	0	0
O2	0.128	0	0.2860
O3	0.824	0	0.0270
O4	0.799	0	0.3740
O5	0.469	0	0.3440

Table 2: The Calculated Structure Factors of Sm_2O_3 Using Structure factor - 332

h	*k*	*l*	F_{cal}	F_{obs}	$\sigma=F_{cal}$ * (5/100)
1	1	1	10.0718	30.0358	1.5840
1	1	3	34.6733	-108.2521	5.6834
1	1	5	92.4980	-29.6242	4.8563
1	1	7	14.5211	25.3796	1.4620
1	1	9	37.3103	-69.7914	3.9569
1	1	1	84.2562	-30.4003	4.4786
1	3	1	58.8095	-21.4946	3.1307
1	3	1	6.3857	19.6691	1.0340
1	3	3	22.1503	-79.2375	4.1137
1	3	5	72.8545	-25.4853	3.8591
1	3	7	12.1700	21.4496	1.2331
0	0	2	10.8111	68.1734	3.4512
0	0	4	5.3411	-59.2290	2.9734
0	0	6	88.3868	-14.9347	4.4820
0	0	8	27.6134	6.2357	1.4154

0	2	0	148.9858	0.0000	7.4493
0	2	2	7.5165	55.6045	2.8055
0	2	4	3.8456	-50.9459	2.5545
0	2	6	76.6672	-13.6547	3.8937
0	2	8	24.8353	5.5348	1.2722
0	4	0	98.8375	0.0000	4.9418
0	4	2	4.7889	41.1240	2.0701
0	4	4	2.4759	-39.0451	1.9561
1	1	3	30.7287	40.9440	2.5596
1	1	5	33.4924	23.5822	2.0481
1	1	7	6.4041	20.9277	1.0943
1	1	9	37.4886	-28.4545	2.3532
1	1	1	84.2562	30.4003	4.4786
1	1	5	33.4925	23.5822	2.0481
1	1	7	6.4041	20.9277	1.0943
1	1	9	37.4886	-28.4545	2.3532
1	3	1	58.8095	21.4946	3.1307
1	3	3	21.6884	31.2620	1.9024
1	3	5	27.0822	18.9350	1.6522
1	3	7	5.1887	17.2768	0.9019
2	0	0	7.0025	64.3801	3.2380
2	0	2	47.5260	44.5166	3.2559
2	0	4	30.5590	-9.8049	1.6046
2	0	6	66.1904	79.4695	5.1712
2	0	8	51.7859	39.5048	3.2567
2	2	0	4.6040	49.5225	2.4868
2	2	2	37.4641	37.3224	2.6441
2	2	4	25.1566	-9.0388	1.3365
2	2	6	57.1482	71.0530	4.5592
2	2	8	47.3051	36.4811	2.9869
2	4	0	2.8001	35.3967	1.7753
2	4	2	26.7864	28.0824	1.9404
2	4	4	18.5506	-7.3146	0.9970
3	1	1	4.6630	-33.7655	1.7043
3	1	1	2.0401	83.3657	4.1695
3	1	3	134.1432	49.2972	7.1457
3	1	5	4.1026	-39.6296	1.9920
3	1	7	19.5451	64.8094	3.3846
3	1	9	49.8139	32.5598	2.9755
3	3	1	4.3971	-25.7875	1.3080
3	3	1	4.6272	63.0307	3.1600
3	3	3	96.8127	36.0449	5.1652
3	3	5	2.8439	-31.8081	1.5967
3	3	7	16.6575	54.7885	2.8632
4	0	0	7.7227	-93.7760	4.7046
4	0	2	9.1954	54.5457	2.7657
4	0	4	90.3524	9.2434	4.5412
4	0	6	29.7481	-12.1091	1.6059
4	0	8	31.2905	4.1558	1.5782
4	2	0	7.0424	-75.4537	3.7891
4	2	2	6.2119	43.8887	2.2163
4	2	4	76.9883	8.0416	3.8703
4	2	6	26.6768	-11.1996	1.4466
4	2	8	28.7880	3.9067	1.4526
4	4	0	5.6335	-54.9217	2.7605
4	4	2	3.7275	31.7974	1.6007
4	4	4	58.5045	6.2208	2.9417
5	1	1	65.9712	-31.5221	3.6557
5	1	1	19.3354	-54.9744	2.9138
5	1	3	37.3704	-28.7793	2.3584
5	1	1	19.3354	-54.9744	2.9138
5	1	5	7.6099	-30.4687	1.5702
5	1	7	39.6816	18.0728	2.1801
5	1	9	67.7341	-39.4296	3.9187
5	3	1	47.6046	-23.7891	2.6609
5	3	1	13.6990	-40.8162	2.1527
5	3	3	27.6884	-24.0799	1.8347
5	3	5	5.6175	-25.3424	1.2979
5	3	7	33.3654	15.6408	1.8424
6	0	0	74.9596	-69.2395	5.1022
6	0	2	8.7148	21.3247	1.1518
6	0	4	34.8366	-79.5408	4.3417
6	0	6	70.6252	-55.2249	4.4826
6	0	8	7.3583	27.8550	1.4405
6	2	0	59.1793	-54.0111	4.0060
6	2	2	6.9922	17.5904	0.9464
6	2	4	31.8235	-70.4992	3.8674
6	2	6	63.4868	-50.0883	4.0433
6	2	8	6.9303	25.8072	1.3360
6	4	0	42.0736	-37.9584	2.8333
6	4	2	5.0313	12.9908	0.6965
6	4	4	25.6545	-55.4855	3.0564
7	1	1	15.5508	-74.4187	3.8013
7	1	1	115.8744	-40.9257	6.1444
7	1	3	13.0895	45.2052	2.3531
7	1	5	17.8773	-55.1162	2.8971
7	1	7	57.7749	-37.2040	3.4358
7	1	9	13.9864	-0.9106	0.7008
7	3	1	11.2813	-55.9928	2.8559
7	3	1	89.6894	-30.9211	4.7435
7	3	3	11.0396	37.2683	1.9434
7	3	5	14.7580	-46.1805	2.4240
8	0	0	8.2197	-29.2901	1.5211
8	0	2	74.9626	0.2263	3.7481
8	0	4	39.3538	27.9604	2.4137
8	0	6	35.3662	-3.0309	1.7748
8	0	8	8.9180	10.4715	0.6877
8	2	0	7.2683	-24.5759	1.2814
8	2	2	65.7001	0.3038	3.2850
8	2	4	34.4990	25.0455	2.1316
8	2	6	32.3227	-2.3183	1.6203
8	2	8	8.3417	9.7426	0.6413
8	4	0	5.6986	-18.4221	0.9641
8	4	2	51.1928	0.3054	2.5597
9	1	1	2.8789	45.4647	2.2778
9	1	1	1.4376	41.5253	2.0775
9	1	3	17.9747	48.4741	2.5849
9	1	5	18.1882	-17.6309	1.2665
9	1	7	55.6584	47.5947	3.6616
9	3	1	2.2830	45.4647	1.8659
9	3	1	3.5094	33.5175	1.6850
9	3	3	14.4060	39.4464	2.0997
9	3	5	15.6523	-14.8932	1.0803

5. Electron Density Distribution in Nano Sm_2O_3

For the determination of the electron density distributions in crystalline materials, recently, the statistical approach, MEM, is gaining popularity, because of less biased information on the electron densities. The MEM is one of the appropriate methods in which the concept of entropy is introduced to handle the uncertainty in the electron density distribution properly **[3]**. The bonding nature and the distribution of electrons in the bonding region can be clearly visualized using this technique. The MEM method

gives actual electron density rather than a normalized one. MEM electron densities are always positive and even with limited number of data one can evaluate reliable electron densities resembling true densities. For the numerical MEM computations, the software package PRIMA **[4, 5]** was used. For the 2D and 3D representation of the electron densities, the program VESTA **[6]** package was used.

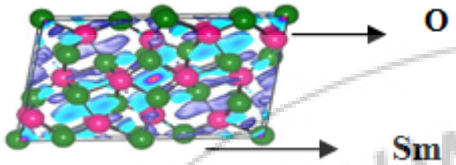

Figure 2: Three Dimensional Electron density of Sm_2o_3

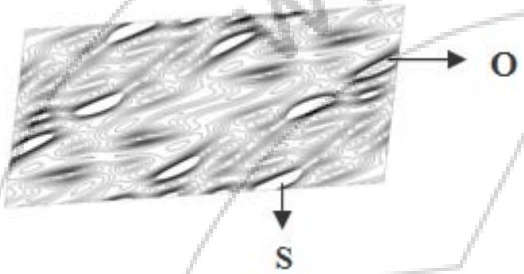

Figure 3 (a): Two dimensional electron configuration of Sm_2o_3 at (011) plane, Contour range is from 0 to 3.5 e/$Å^3$, Contour interval is 0.2 e/$Å^3$.

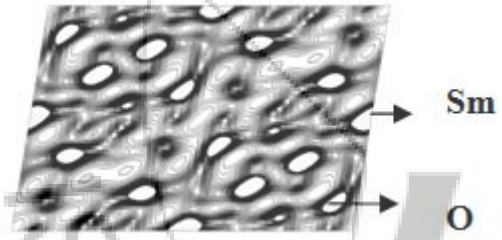

Figure 3 (b): Two dimensional electron configuration of sno_2 at (020) plane, Contour range is from 0.1 to 4.5 e/$Å^3$, Contour interval is 0.15 e/$Å^3$

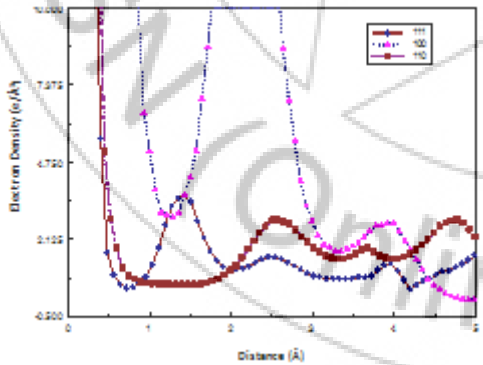

Figure 4: One dimensional electron density profile of Sm_2o_3 at (100), (110) and (111) planes

Table 3: Parameters obtained in MEM refinements

Parameter	*Sm_2o_3*
Number of cycles	4532
Lagrange parameter(λ)	0.231538
R_{MEM} (%)	0.037626
wR_{MEM} (%)	0.076297
Resolution along 'a' axis (Å/pixel)	0.221406
Resolution along 'b' axis (Å/pixel)	0.056687
Resolution along 'c' axis (Å/pixel)	0.138359

Table 4: The one dimensional electron density along three directions

Direction	Sm_2o_3	
	Distance (Å)	Density ($e/Å^3$)
[100]	3.1861	2.4877
[100]	6.0891	0.7011
[110]	1.9723	2.1424
[110]	4.7481	1.9751
[110]	7.2318	6.8219
[110]	9.1310	2.2356
[111]	1.4156	2.0196
[111]	1.9662	2.3131
[111]	2.9886	1.4254
[111]	3.9324	2.5952
[111]	4.1684	1.6190
[111]	4.7976	2.5160
[111]	5.8200	1.5805
[111]	6.4492	1.9068
[111]	7.8649	0.6359
[111]	9.2019	1.9068

6. Pair Distribution Function

Pair distribution function is a method to analyze the powder diffraction data in the real space. The PDF reflects the short-range ordering in a material. This approach has been widely used for studying the structure of materials, glasses and liquids. More recently, it has been applied to disordered crystalline and partially crystallized materials. Quantitative structural information on nanometer length scales can be obtained by fitting a model directly to the PDF. The PDF can be understood as a bond-length distribution between all pairs of atoms within the crystal. A useful characteristic of PDF method is that it gives both *local* and *average* structure information because both Bragg peaks and diffuse scattering are used in the analysis. This method is applicable only for powder diffraction data not for single crystal study. PDF does not require periodicity. The observed PDF's have been obtained from the software package PDFGetX **[7]**. The PDF is then refined using PDFFIT.

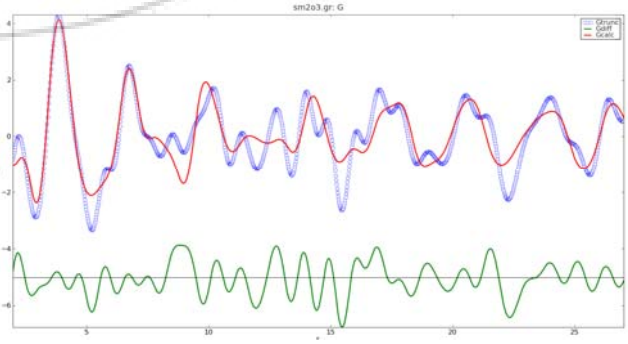

Figure 5: Fitted Pair Distribution of Sm_2o_3

Table 5: Nearest Neighbor Distance from PDF Analysis in Sm_2O_3

Nearest neighbor	Inter atomic distance from PDF analysis r(Å)		Calculated inter atomic distance from Gretep r(Å)		
	Observed	Calculated	Sm-Sm	Sm-O	O-O
I	2.22	2.34	-	2.251	-
II	3.84	3.86	3.856	-	3.628
III	6.47	6.74	6.728	6.789	6.798

7. Particle Size

The particle size of synthesized Sm_2O_3 nano material was evaluated using GRAIN [8] software. The size of the nano Sm_2O_3 particle is analyzed using full width at half maximum of the powder XRD peaks. From this analysis, the average particle size (r_{Xray}) comes out to be 61.0437nm. The SEM picture of nano Sm_2O_3 has been given in Fig. 7. The particle size (r_{SEM}) from SEM measurement is 33.3623nm, and hence there are approximately. Hence, the number of coherently diffracting domains can be obtained using this way, i.e. $N= r_{SEM}/r_{Xray}$.

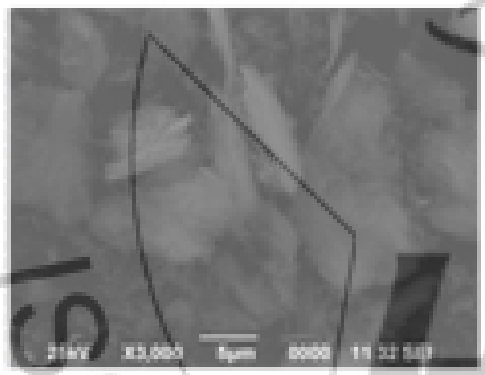

Figure 6: SEM Picture of Nano Sm_2O_3 with a Magnification of 3,000

8. Conclusion

The electronic structure of the Sm_2O_3 nano powder has been analyzed from the electron density evaluated using the MEM technique. The covalent nature of the bonding has been verified from 1D, 2D and 3D density profile map. The local structures of Sm_2O_3 were studied using pair distribution function analysis. The fitting of observed and calculated PDF'S of Sm_2O_3 is excellent. The particle size to be found using SEM analysis and to compare the size from XRD and SEM. Thus, all the evidences point to a strong covalent bond in nano Sm_2O_3.

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