

Synthesis, Structure and Electric Transport Properties of $\text{La}_3\text{NaMn}_3\text{O}_{10}$

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Abstract

RP-type of phases with the general composition $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ form a well known class of materials exhibiting interesting structural and electric transport properties. In the present study a new phase in this class of materials with the composition $\text{La}_3\text{NaMn}_3\text{O}_{10}$ has been synthesised in the solid state. Study of its crystal structure shows that it crystallizes in a tetragonal unit cell in the space group I4/mmm . Its structural parameters have been calculated and unit cell structure drawn. Its electrical resistivity in the temperature range 10-300 K shows that it is insulator in nature and ionic conduction plays major part due to the presence of Na ion in the structure.

Keywords: RP-type phase, $\text{La}_3\text{NaMn}_3\text{O}_{10}$, X-ray diffraction, Electrical resistance, Insulator

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1. Introduction

The RP-type phases with the composition $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ (where usually A = rare-earth/alkaline metal ion and B = transition metal ion) are an important class of compounds which exhibit interesting structural and electric transport properties [1-4]. Many of such compounds show giant magnetoresistance accompanied by I-M transition when resistance is measured as a function of temperature [5-7]. This phenomenon is attributed to existence of transition metal ion in the mixed valence state and the motion of electron is through double exchange mechanism. In the event of the presence of an alkali metal ion, the conductivity has major component of ionic conduction.

In the work presented in this paper, a new phase with the composition $\text{La}_3\text{NaMn}_3\text{O}_{10}$ has been synthesised. Its crystal structure has been determined by powder X-ray diffraction, while

electrical resistance has been measured as a function of temperature in the temperature range 10-300 K.

2. Experimental

2.1 Synthesis

The title compound $\text{La}_3\text{NaMn}_3\text{O}_{10}$ was prepared by the standard ceramic method by using the reactants La_2O_3 , Na_2O and MnO_2 (Aldrich make, 99.9 % purity). The initial reactants were pulverized, mixed in the stoichiometric ratio corresponding to the composition of the phase $\text{La}_3\text{NaMn}_3\text{O}_{10}$, homogenised by grinding and mixing in cyclohexane, dried, pressed into pellets in a hydraulic press. The pellets were heat-treated in a tube furnace at 1325 K (± 10 K) in static air atmosphere for 72 hours with a number of intermediate grindings and pelletization. The resultant product was pulverized and preserved for investigation.

2.2 X-ray diffraction Study

The room temperature X-ray diffraction data of the phase were recorded on a Philips diffractometer 1820/1710 using $\text{CuK}\alpha$ radiations. The experimental data are given in the Table 1, while the diffraction pattern is plotted in the Fig. 1.

Table 1: Powder X-ray diffraction data of $\text{La}_3\text{NaMn}_3\text{O}_{10}$ Space group: I4/mmm $a = 3.851 \text{ \AA}$; $c = 27.458 \text{ \AA}$.

h	K	l	$d_{\text{obs}}(\text{\AA})$	$d_{\text{cal}}(\text{\AA})$	I_{obs}	I_{cal}
0	0	6	4.780	4.576	5	9
1	0	1	3.840	3.814	20	11
1	0	7	2.748	2.748	100	100
1	1	0	2.723	2.824	88	86
1	0	9	2.243	2.391	30	11
1	1	8	2.185	2.134	10	29
2	0	0	1.938	1.926	65	55
1	1	12	1.740	1.751	7	10
2	1	1	1.727	1.718	5	4
2	0	6	1.591	1.591	20	5
2	1	5	1.585	1.576	42	38
2	2	0	1.378	1.361	15	15
1	0	13	1.365	1.373	12	12



Figure1:X-ray diffraction pattern of $\text{La}_3\text{NaMn}_3\text{O}_{10}$

2.3 Electrical Resistance Study

The electrical resistivity of the sintered pellets of the phase was measured in the temperature range 10-300 K in a Laybold closed cycle helium Cryostat using Keithley

electrometer/voltmeter. The temperature versus log data are plotted in the Fig. 2.

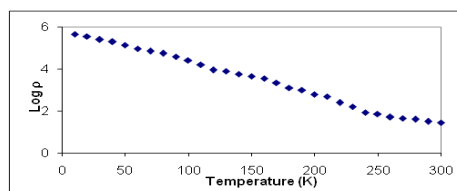


Figure 2: log versus temperature (K) for $\text{La}_3\text{NaMn}_3\text{O}_{10}$

3. Results and Discussion

The X-ray diffraction data (Table 1) could be indexed on the basis of the tetragonal unit cell. The cell parameters, as refined by the programme 'Cell', are given in the Table 1. The standard deviations in the cell parameters were calculated with the least squares method. The factor (R) is better than 0.00001.

The theoretical X-ray diffraction data were generated with the Lazy-Pulverix[8] programme using the cell parameters refined from the programme 'Cell' and the initial structural parameters (positional co-ordinates and the space group I4/mmm) used for the well known phase $\text{Sr}_4\text{V}_3\text{O}_{19}$ [9]. The best fit structural parameters are given in the Table 2. The calculated d-values along with their intensities are given in the Table 1 along with the experimental values.

Table 2: Positional coordinates for $\text{La}_3\text{NaMn}_3\text{O}_{10}$

Atom	x	y	z	Occupancy
La1	0.0	0.0	0.4485	0.75
La2	0.0	0.0	0.2978	0.75
Na1	0.0	0.0	0.4485	0.25
Na2	0.0	0.0	0.2978	0.25
Mn1	0.0	0.0	0.0	1
Mn2	0.0	0.0	0.1398	1
O1	0.0	0.5	0.0	1
O2	0.0	0.0	0.0697	1
O3	0.0	0.5	0.1373	1
O4	0.0	0.0	0.2083	1

Comparison of the experimental data with the theoretically calculated values shows good agreement considering that any preferential orientation effects have not been taken into consideration. The X-ray diffraction results confirm the formation of the RP-type ($n=3$) phase $\text{La}_3\text{NaMn}_3\text{O}_{10}$. The unit cell structure of the title phase $\text{La}_3\text{NaMn}_3\text{O}_{10}$ has been drawn with the programme 'PowderCell' and the same is given in the Fig. 3.

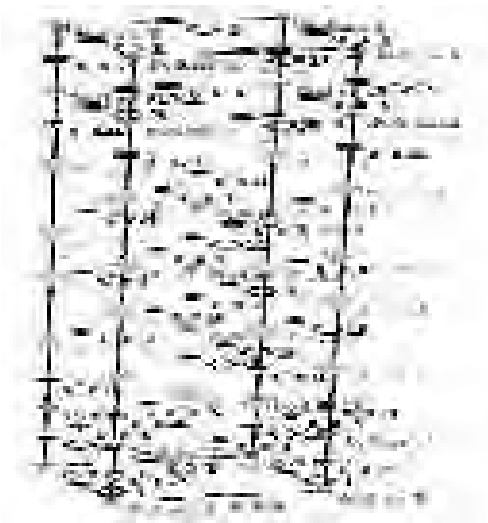


Figure 3: Unit cell structure of $\text{La}_3\text{NaMn}_3\text{O}_{10}$

In the log versus temperature (K) plot the temperature co-efficient of resistivity is negative showing that the phase is insulator in nature. Although Mn ion is in the mixed valence state (3/4) the phase does not show any I-M transition as reported in such phases [5-7] because of the presence of the sodium ion in the cell structure, which hinders the electron exchange through the double exchange mechanism. Presence of the sodium ion suggests that the conduction in the phase would be mainly ionic in nature.

4. Conclusions

RP-type phase of composition $\text{La}_3\text{NaMn}_3\text{O}_{10}$ has been synthesised by traditional ceramic method. X-ray diffraction studies show that it is intergrowth phase and crystallises in tetragonal unit cell with $a = 3.851$ and $c = 27.458 \text{ \AA}$ in the space group $I4/mmm$. The phase is insulator in nature and ionic conduction plays dominant role in the electrical conduction because of the presence of Na ion in the matrix.

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