

## Rietveld Refinements of $K_2NiF_4$ -Type Phases $Ln_{0.5}Sr_{1.5}Mn_{0.5}Fe_{0.5}O_4$ ( $Ln = La, Nd, Gd, \text{ and } Dy$ )

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### INTRODUCTION

Transition metal oxides of composition  $A_2BO_4$  ( $A$  is usually a rare-earth, alkaline-earth, or alkali ion and  $B$  can be a 3d or 4d transition-metal ion) with the layered  $K_2NiF_4$  structure type have long been studied because they display a variety of unusual structural and magnetic properties. They have received considerable interest in recent years, particularly since the discovery of superconductivity in  $La_{2-x}Ba_xCuO_4$  and  $Sr_2RuO_4$ .<sup>1-3</sup> The two dimensional  $A_2BO_4$  consists of perovskite-like corner linked  $BO_6$  sheets interleaved by the rock-salt AO layers, in which the large  $A$  cations are arranged in the plane formed by O atoms at the top (or bottom) of the octahedral with nine nearest O neighbors.

One important factor that determines the structure of the  $A_2BO_4$  compounds is the matching between the perovskite-like  $BO_6$  layers and the A-type cations. A measure of the bond length matching can be calculated from a version of the Goldschmidt tolerance factor  $t = (r_A + r_O) / \sqrt{2}(r_B + r_O)$  for perovskite and perovskite-derived structure; ideal matching between the A cation and one layer of linked  $BO_6$  octahedra occurs for  $t \approx 1$  and the structure formed is tetragonal described in the space group  $I4/mmm$  (no. 139).

In our earlier work,<sup>4</sup> we have reported the synthesis, electric transport and magnetic properties of  $K_2NiF_4$ -type phases  $Ln_{0.5}Sr_{1.5}Mn_{0.5}Fe_{0.5}O_4$  ( $Ln = La, Nd, Gd, \text{ and } Dy$ ). In this reported work, much has been left about the structural characterization of the phases. In the present work, we report structural characterization of the  $Ln_{0.5}Sr_{1.5}Mn_{0.5}Fe_{0.5}O_4$  phases ( $Ln = La, Nd, Gd, \text{ and } Dy$ ) by Rietveld analysis using *GSAS* program. The bond angles and bond distances have been determined on the basis of structural parameters derived from structural refinements.

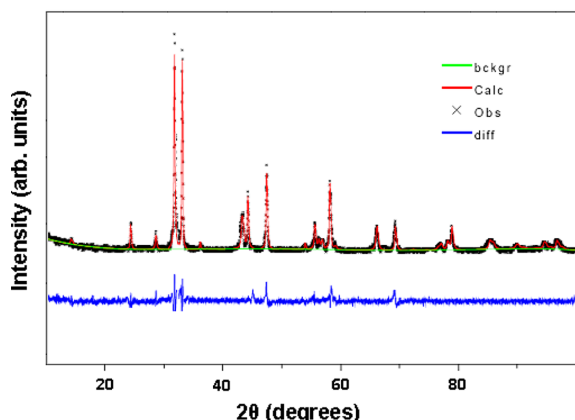
### EXPERIMENTAL

$Ln_{0.5}Sr_{1.5}Mn_{0.5}Fe_{0.5}O_4$  phases ( $Ln = La, Nd, Gd, \text{ and } Dy$ ) have been synthesized by standard ceramic method from  $La_2O_3$ ,  $Nd_2O_3$ ,  $Gd_2O_3$ ,  $Dy_2O_3$ ,  $SrCO_3$ ,  $MnO_2$  and  $Fe_2O_3$  (All were Aldrich made, purity 99.9%), the details have been described elsewhere.<sup>4</sup>

The samples were characterized by room temperature X-ray powder diffraction (XRD) measurements (Bruker AXS diffractometer type D 76181 Karlsruhe, Germany using  $CuK_{\alpha}$  radiations) for phase purity and crystal structure determination. The XRD patterns were obtained between  $10^\circ$  and  $100^\circ$  in steps of  $0.02^\circ$  with a counting time of 2s per step and analyzed by Rietveld refinements using the *GSAS* program.<sup>5</sup> The bond angles and bond distances have been determined on the basis of structural parameters derived from structural refinements.

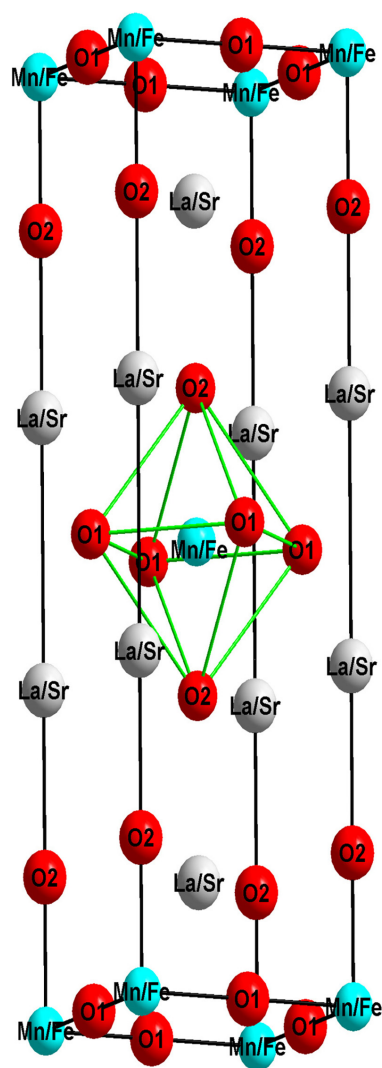
### RESULTS AND DISCUSSION

The present structure refinements for the phases were carried out using the tetragonal unit cell in the space group  $I4/mmm$ . The background Rietveld refinement was fitted with a shifted Chebyshev polynomial function, and pseudo-Voigt function was employed to model the peak shapes in all cases. The initial positional parameters were obtained from the data previously reported for  $Sr_2TiO_4$ .<sup>6</sup> Isotropic thermal displacement parameters, initially set at  $0.025 \text{ \AA}^2$ , were refined first for the metal atoms and then for the oxygen atoms with full occupancy. The occupation factors for the metals were fixed by taking sample stoichiometry into account, assuming that the  $Ln/Sr$  cations were randomly distributed over the 4e site while those of oxygen atoms were refined. No evidence of oxygen non-stoichiometry could be obtained from the XRD structural refinements



**Figure 1.** Rietveld refinement profile for the fit to the XRD pattern of  $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_4$ .

and the oxide ion sites were therefore fixed at full occupancy. The Rietveld plot of the phase  $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_4$  is shown in Fig. 1, while the final refinement values of the structural parameters and R-factors in the Rietveld analysis are given in the Table 1. The values of  $R_p$ ,  $R_{wp}$  and  $\chi^2$  confirmed the formation of the phases. The unit cell structure of  $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_4$ , as drawn with software “DIAMOND” on the basis of refinement parameters, is shown in Fig. 2. The unit cell parameters obtained from the Rietveld refinements (Table 1) are slightly different from those reported in our earlier work.<sup>4</sup> The data in Table 1 suggest that both the unit cell parameters  $a$  and  $c$  and cell volume decreases from La to Dy compound which is consistent with the decrease in the ionic radii of lanthanide ion. This can be attributed to the cumulative effect of reduced lanthanide radii along the  $c$  direction where the layers are



**Figure 2.** Unit cell structure of  $\text{La}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_4$ .

**Table 1.** Structural parameters obtained from the Rietveld refinement of X-ray diffraction pattern for samples  $\text{Ln}_{0.5}\text{Sr}_{1.5}\text{Mn}_{0.5}\text{Fe}_{0.5}\text{O}_4$  ( $\text{Ln} = \text{La, Nd, Gd, and Dy}$ ). The atomic sites are:  $\text{Ln/Sr } 4c[0, 0, z]$ ;  $\text{Mn/Fe } 2a[0, 0, 0]$ ;  $\text{O}(1) 4c[0, 0.5, 0]$ ;  $\text{O}(2) 4e[0, 0, z]$  in the space group  $I4/mmm$

Ln		La	Nd	Gd	Dy
$a$ (Å)		3.8365(1)	3.8297(2)	3.8102(1)	3.8092(1)
$c$ (Å)		12.5100(12)	12.4764(16)	12.3989(8)	12.3956(6)
$V$ (Å <sup>3</sup> )		184.13(2)	182.99(3)	180.00(1)	179.86(1)
$z$	Ln/Sr	0.3572(3)	0.3581(3)	0.3569(3)	0.3563(2)
	O(2)	0.1713(17)	0.1625(19)	0.1624(18)	0.1648(14)
$U_{iso}$ (Å <sup>2</sup> )	Ln/Sr	0.0155(12)	0.0151(12)	0.0151(11)	0.0157(9)
	Mn/Fe	0.0244(6)	0.0290(9)	0.0246(6)	0.0211(10)
	O(1)	0.0610(7)	0.0380(7)	0.0498(4)	0.0336(6)
	O(2)	0.0403(9)	0.0349(9)	0.0501(6)	0.0366(7)
X-ray density (gcm <sup>-3</sup> )		5.776	5.861	6.078	6.131
$R_{wp}$		0.1303	0.1073	0.0788	0.0720
$R_p$		0.0886	0.0803	0.0565	0.0536
$\chi^2$		3.387	2.438	2.054	1.714

**Table 2.** Selected bond lengths of  $Ln_{0.5}Sr_{1.5}Mn_{0.5}Fe_{0.5}O_4$  ( $Ln = La, Nd, Gd, \text{ and } Dy$ )

Ln	La	Nd	Gd	Dy
Mn/Fe – O(1)×4	1.91826(7)	1.91487(9)	1.90514(6)	1.90464(4)
Mn/Fe – O(2)×2	2.02809(21)	2.02750(26)	2.01382(13)	2.04278(10)
La/Sr – O(1)×4	2.62087(13)	2.60768(17)	2.60306(9)	2.60704(7)
La/Sr – O(2)	2.44111(22)	2.44062(31)	2.41183(15)	2.37487(12)
La/Sr – O(2)×4	2.72426(10)	2.72024(13)	2.70494(8)	2.70634(6)
Mean Mn/Fe – O	1.95487	1.95241	1.94136	1.95068
Mean La/Sr – O	2.64684	2.63914	2.62709	2.62537

stacked.

The structure of  $Ln_{0.5}Sr_{1.5}Mn_{0.5}Fe_{0.5}O_4$  phases can be represented by the sequence of layers, ....[(Mn/FeO<sub>2</sub>)<sub>o</sub> (Ln/SrO)<sub>c</sub>(Ln/SrO)<sub>o</sub>(Mn/FeO<sub>2</sub>)<sub>c</sub>(Ln/SrO)<sub>o</sub>(Ln/SrO)<sub>c</sub>](Mn/FeO<sub>2</sub>)<sub>o</sub>.... where the symbols in each parenthesis give the chemical composition of the layer, the subscripts o and c indicate if the cation is at the origin or in the center of the layer's mesh, and the square brackets include the content of one unit cell.<sup>7</sup> This atomic arrangement is practically identical to that of  $La_2CuO_4$ .<sup>8</sup> The selected bond lengths, calculated from the structural parameters, are tabulated in the Table 2. Mn/Fe is six-fold coordinated and the (Mn/Fe)O<sub>6</sub> octahedra are not perfectly regular consisting, typically, of four short in-plane (Mn/Fe)–O1 distances (equatorial) and two (Mn/Fe)–O2 slightly longer apical distances (Table 2). The coordination polyhedron may therefore be described as an elongated octahedron with distances (Mn/Fe)–O1 ranging from 1.90464(4) to 1.91826(7) Å and those of (Mn/Fe)–O2 from 2.01382(13) to 2.02809(21) Å. This arrangement is significantly more regular than that found, for example, in  $La_2CuO_4$ <sup>8</sup> and  $La_{1.85}Sr_{0.15}CuO_4$ ,<sup>9</sup> where these distances range from 1.896 to 2.398 Å and from 1.890 to 2.412 Å, respectively. The (Mn/Fe)–O bond distances change due to tilting of the (Mn/Fe)O<sub>6</sub> octahedra, and their mean values (Table 2) are in good agreement with that obtained from the sum of Shannon's ionic radii (1.9875 Å).<sup>10</sup> Ln/Sr is nine-coordinated and the coordination polyhedron is a capped square antiprism with the Ln/Sr atom displaced considerably from antiprism center towards the capped face with one relatively short (Ln/Sr)–O bond (Table 2) linked with the apical O atom of the above or below (Mn/Fe)O<sub>6</sub> octahedral, a feature also present in  $La_2CuO_4$  and its Sr- and Ba-doped derivatives. A careful examination of the bond lengths (Table 2) indicates that from La to Dy compound, the mean values of (Ln/Sr)–O bond distances decrease as expected and these values are in good agreement with those obtained from the sum of Shannon's ionic radii (2.686, 2.67325, 2.65925, and 2.65325 Å for La, Nd, Gd, and Dy

samples respectively).<sup>10</sup> The decrease in (Ln/Sr)–O bond distance is consistent with the decrease in the ionic radii of lanthanide ion.

## CONCLUSIONS

Rietveld refinements of the phases  $Ln_{0.5}Sr_{1.5}Mn_{0.5}Fe_{0.5}O_4$  ( $Ln = La, Nd, Gd, \text{ and } Dy$ ) have been reported for the first time using *GSAS* program. The (Mn/Fe)–O1 and (Mn/Fe)–O2 distances suggest that (Mn/Fe)O<sub>6</sub> octahedra are not perfectly regular. The (Ln/Sr)–O bond distance decreases from La to Dy compound, which is consistent with the decrease in the ionic radii of lanthanide ion.

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