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INTRODUCTION

Intergrowth crystal structures in inorganic systems have provided a fertile field of solid state chemical research for many years and the discovery of high-T_c superconducting cuprates has focused attention on intergrowth structures based on perovskite blocks. Ruddlesden and Popper (R-P hereafter) (1) have described intergrowth structures with the general formula $Sr_{n+1}Ti_nO_{3n+1}$ where n is the number of perovskite layers separated by SrO layers. Indeed, La_2CuO_4 corresponds to the n = 1 phase in which the decreased ionic charge of the octahedral ion is compensated by the increased ionic charge of the dodecahedral ion.

Numerous structures have been derived from these parent compounds by the replacement of Ti^{4+} with lower valent transition metals and charge compensation with higher valent ions on the alkaline earth site. In this manner the series of compounds $Ln_2AM_2O_7$, Ln^{3+} = La, Nd, Sm, Eu, Gd, Tb, A^{2+} = Sr, Ba, M^{3+} = Mn, Fe, has been synthesized and they are isomorphous with the n = 2 R-P phase (2,3). The replacement of Ti^{4+} by Cu^{2+} to form $La_2SrCu_2O_6$ requires the removal of an oxygen ion for overall charge neutrality. The apical oxygen bridging the two octahedra is missing resulting in layers of copper pyramids whose bases face each other (4). The lowering of the valence of the octahedral ion from 4+ to 3+ is charge compensated by trivalent rare earth ions and maintains the octahedral double layer. However, the replacement of the 4+ ion with Cu^{2+} introduces a modification in the structure by the removal of the apical O^{2-} to create separate copper pyramids. The replacement of $2Ti^{4+}$ in the parent compound by $Fe^{3+}Cu^{2+}$, to create an intermediate valence state +2.5, again causes the removal of an oxygen ion, but now the unshared apex of the octahedron is lost. The structure of $YBaFeCuO_5$ contains double layers of apex-sharing Fe/Cu pyramids separated by a single layer of Y in 8-fold coordination - a fluorite unit (5). Its structural relationship to the R-P parent compound with n=2 is not apparent from the stoichiometry. To emphasize it requires the formula to be written as

$(YBa\square)(FeCu)O_{7-\delta}$, but no cation vacancies exist in this structure. We synthesized a compound that contains the apex-sharing double pyramidal layer as a structural motif and has all the alkaline earth sites filled.

Relatively few compounds with n=3 have been investigated. We have synthesized and investigated the properties of $LaSr_3Fe_3O_{9\pm\delta}$ and report here some of the results.

$Y_2SrFeCuO_{6.5}$

The substitution of 2Y and FeCu for 2Sr and 2Ti in $Sr_3Ti_2O_7$ led to a new phase $Y_2SrFeCuO_{6.5}$. Its crystal structure and magnetic properties were investigated using single crystal X-ray diffraction, powder neutron diffraction, Mössbauer spectroscopy, and magnetic susceptibility measurements. $Y_2SrFeCuO_{6.5}$ is orthorhombic, Ibam, a = 5.4036(8) [5.4149(1)] Å, b = 10.702(1) [10.7244(1)] Å, c = 20.250(2) [20.2799(2)] Å; values in square brackets are neutron data. The structure is derived from the R-P phase $Sr_{n+1}Ti_nO_{3n+1}$ with n = 2. The Fe/Cu atoms occupy randomly the approximate center of oxygen pyramids. The pyramids share the apical bridging oxygen and articulate laterally by corner sharing of oxygen to form a double pyramidal layer perpendicular to *c*. The pyramidal slabs are separated by double layers of Y that are in 7-fold coordination to oxygen, forming a defect fluorite unit, Fig. 1.

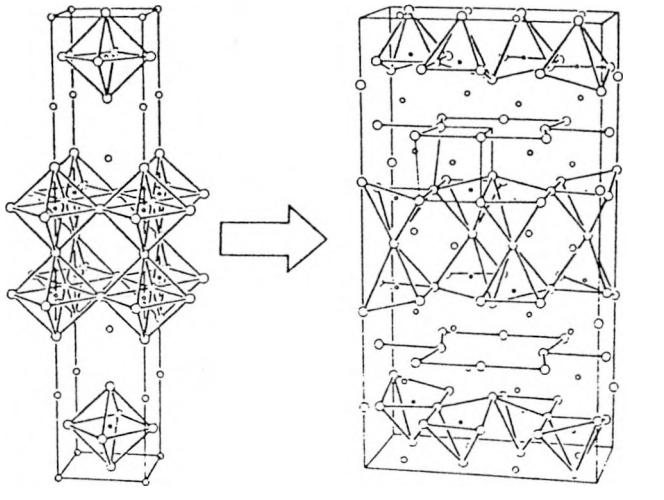

Fig. 1. The evolution of the $Y_2SrCuFeO_{6.5}$ from the parent compound. Large circles are O, smaller circles are Y, and the smallest are Fe/Cu. The defect fluorite unit is outlined around one Y.

The oxygen layer between the Y layers contains a vacant site. The surrounding oxygen ions within the layer and oxygen ions from the pyramidal bases situated above and below the vacant site are displaced toward it and distort the pyramids. The average bond length Sr-10 O is 2.793(10)Å and for Y-7 O is 2.331(6)Å. The Fe/Cu-O distances vary from 1.940(6) to 2.002(2)Å.

Mössbauer spectra indicate a unique iron environment and magnetic ordering at about 265 K. The paramagnetic phase coexists with the magnetic phase over an approximate temperature range 300 - 263 K, characteristic of low dimensionality (1 or 2D) magnetic interactions. The temperature dependence of the molar magnetic susceptibility is consistent with the Mössbauer data and also suggests low-dimensionality with a broad maximum in χ_M vs. T at 260 K. The isomer shift and quadrupole splitting are consistent with Fe^{3+} in 5-fold coordination and H_{int} values also indicate classic high spin Fe^{3+}, Table 1, Fig. 2.

Table 1. Isomer shifts δ*, quadrupole splittings ΔE, and internal fields H_{int} for $Y_2SrFeCuO_{6.5}$.

Temperature (K)	ΔE (mm/sec)	δ	H_{int} (kG)
306	0.56	0.26	0
295.7	0.57	0.25	0
295	0.54	0.25	0
285	0.61	0.28	>0
253.4			252
241.2			270
216.8			333
199.3			362
181.7			385
181.1			382
145.7			418
120.7			440
77			467
4.8			499

*Relative to natural iron metal foil.

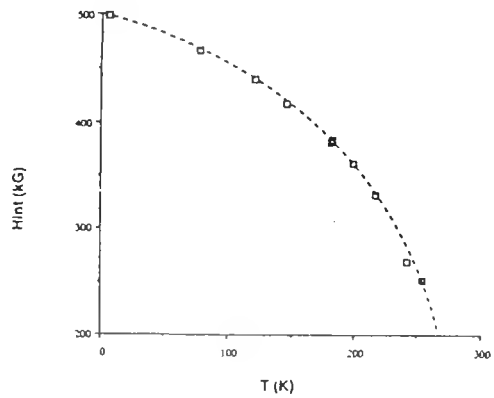

Fig. 2. Internal magnetic field vs. temperature for $Y_2SrFeCuO_{6.5}$

Powder neutron diffraction data at 10K show several new peaks that were absent in the room temperature data. They could be indexed on the basis of a *primitive* unit cell of the same dimensions as the original body-centered cell. Numerous models for the magnetic structure were tried but none accounted satisfactorily for the observed magnetic line intensities. It is interesting to note that no magnetic structural studies of R-P related phases have been reported. These structures ($AO{\cdot}2ABO_3$) may be regarded as intermediate between the 3D perovskite (ABO_3) and 2D Sr_2FeO_4 ($AO{\cdot}ABO_3$) structure types and would be of interest in studying pseudo-2D magnetic properties.

This phase does not display detectable deviation from the 1:1 Fe-Cu ratio. Substitution of 0.20 Ca for Y is possible. This phase can also be synthesized with Gd and Er. It is a semiconductor.

$LaSr_3Fe_3O_{9\pm\delta}$

Compounds based on the parent structure with n = 3, $Sr_4Ti_3O_{10}$, have not been investigated extensively. Brisi and Rolando (6) studied the system Sr-Fe-O and report an oxygen deficient $Sr_4Fe_3O_{10-x}$ phase. We prepared $LaSr_3Fe_3O_x$ by standard ceramic techniques as single phase material by reacting the oxides and carbonates at about 1450°C. A single crystal from the reaction product was selected for the determination of the crystal structure by X-ray diffraction. The compound is isostructural with $Sr_4Ti_3O_{10}$, Fig. 3, but is oxygen deficient, with composition $LaSr_3Fe_3O_{9\pm\delta}$.

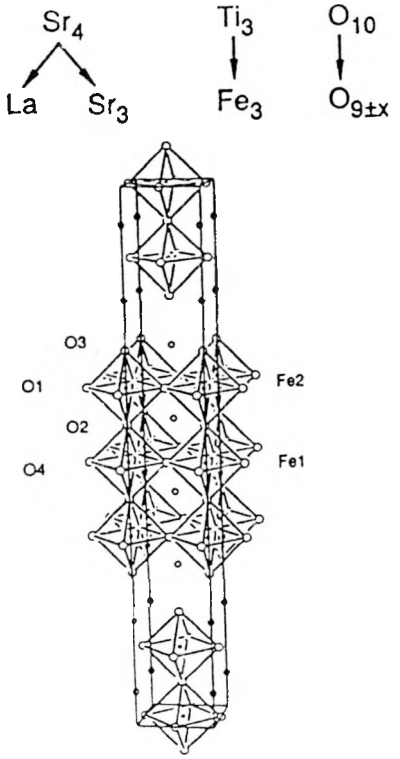

Fig. 3. The structure of $LaSr_3Fe_3O_{9\pm\delta}$. The oxygen vacancies are primarily in the equatorial plane of Fe1. The crystallographically distinct atoms are labled. Sr are shown as small non-bonded circles.

The value of δ is approximately ± 0.25. The oxygen vacancies are concentrated around the central Fe1 octahedron and oxygen can be reversibly intercalated. The equatorial Fe-O lengths for the octahedra are equal, 1.939(5)Å, but the apical Fe1 - O2 lengths for the central octahedron are significantly shorter, 1.8785(2)Å, than for the flanking octahedra. The Fe2 - O2 length of 2.0982(15)Å to the shared O2 is also significantly longer than Fe2 - O3, 2.058(8)Å, to the unshared apex. One La/Sr is in a dodecahedral site and the other crystallographically independent La/Sr is in 9-fold coordination, a monocapped square antiprism. Bond-valence calculations (7) using the expression $V = \sum_i \exp\left(\frac{r_o - r_i}{0.37}\right)$, $r_o\ (Fe^{3+}) = 1.759$, $r_o\ (\frac{1}{4} La^{3+} + \frac{3}{4} Sr^{2+}) = 2.132$, yield +3.92 for Fe1, +3.33 for Fe2, +2.28 for La/Sr1, and +2.20 for La/Sr2. If the oxygen stoichiometry for this phase can be increased to 9.5, the Fe1 most likely becomes the tetravalent ion. The valence sums for La/Sr are equal to the weighted value for the site occupant in the structure.

Mössbauer spectra and magnetic susceptibility data indicate 3D antiferromagnetic ordering temperatures of ~75K for the low oxygen content material and 150 K for the high oxygen content phase. The compound decomposes when oxygen content is less than about 8.6. We have determined that the Sr/La ratio is 3:1 within the limits of second-phase detection by powder X-ray diffraction. This phase forms with La, Nd, Pr, and Gd but not with Er; Ca and Ba do not substitute for Sr.

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