

from the stoichiometry and determined using powder data. The optimal structure model was predicted by minimization of the global instability index of the difference between the calculated bond valency sum and the formal valency (oxidation state) of each ion (optimize the bonding in the structure) using SPuDS program [1]. Three expected space groups (R-3c, I4/mcm and Pnma) and the corresponding lattice parameters and fractional atomic coordinations were given. On the other hand, the experimental diffraction pattern was indexed by CRYSFIRE and the possible best space groups (R-3c, P2/c and C2/m) and the corresponding lattice parameters were specified by CHEKCELL program. These three space groups were used one-by-one in turn to determine the approximate structure solution by "direct-space" approach using Monte Carlo method [2, 3] and a combined cost function of global optimization of the difference between the calculated and the measured diffraction pattern and of the potential energy of the system, which is implemented in ENDEAVOUR program [4]. The predicted structures as well as the approximate ones were refined by Rietveld method using FULLPROF program. Almost, acceptable fitting with good reliability factors (R_{wp} and χ^2) was reached in all cases. However, in order to pick out the most reliable space group, careful inspection of the tick marks that represent the positions of the possible Bragg reflections in Reitveld plot was considered; their presence where no peaks or their absence where weak peaks are observed. The rhombohedral (R-3c) space group was found to be the reasonable accepted choice for $\text{La}_{0.77}\text{Sr}_{0.23}\text{MnO}_3$, which is the common space group between the two approaches. Considering the number of diffraction peaks as well as their positions and relative intensities, the three samples showed almost the same XRD patterns. So, the accepted model was applied successfully for the two Cu-doped samples. The light Cu B-site doping does not change the crystal structure; only a small increase in lattice volume occurs due to the larger average ionic size of Cu (Cu^{2+} and Cu^{3+}) relative to Mn (Mn^{3+} and Mn^{4+}). In conclusion, the prediction methods, as a useful guide, coupled with direct-space methods and proper cost function is an approach of great help in *ab-initio* structure determination from powder data.

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A_2FeSbO_6 (A=Sr,Ca) double perovskites oxides: Crystal structures, phase's transitions and ^{57}Fe Mössbauer spectroscopy study. A. Faik^a, J. M. Igartua^a, J. Pizarro^b and J. J. S. Garitaonandia^a. ^a*Fisika Aplikatua II Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, Apdo. 644, Bilbao 48080, Spain.* ^b*Dpto. de Mineralogía y Petrología, Facultad de Ciencia y Tecnología, Apdo. 644, E-48080 Bilbao, Spain.*
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A_2FeSbO_6 (A=Sr,Ca) double perovskite have been elaborated by the standard solid state reaction method.

Rietveld analysis of X-ray powder data at room temperature, shows that $\text{Sr}_2\text{FeSbO}_6$ crystallize in the monoclinic system (space group $\text{P}2_1/n$) with unit cell parameters $a = 5.6148(1) \text{ \AA}$; $b = 5.5954(4) \text{ \AA}$; $c = 7.9002(1) \text{ \AA}$; $\beta = 90.02(4)^\circ$ the ordering scheme is 92%, in good agreement with the crystal structural data from the first synthesis of this compound[1]. The $\text{Ca}_2\text{FeSbO}_6$ phase has been synthesized for the first time, and from conventional x-ray powder diffraction data, it has been found that it crystallizes in the $\text{P}2_1/n$ monoclinic space group; the Rietveld analysis results show the following cell parameters: $a = 5.4425(1) \text{ \AA}$; $b = 5.5413(6) \text{ \AA}$; $c = 7.7451(8) \text{ \AA}$; $\beta = 90.06(3)^\circ$. The Fe and Sb cations are almost completely ordered in the B sites (95%). ^{57}Fe Mössbauer spectroscopy measurements, at room temperature, showed a single Fe^{3+} cation in two six-coordinated sites, with the same ordering degree deduced from the powder diffraction data: 92% for $\text{Sr}_2\text{FeSbO}_6$, and 95% for $\text{Ca}_2\text{FeSbO}_6$.

The temperature evolution of the crystal structure of A_2FeSbO_6 (A=Sr,Ca) has been studied using both x-ray powder diffraction and ^{57}Fe Mössbauer spectroscopy. A_2FeSbO_6 (A=Sr,Ca) were found to present the $\text{P}2_1/n$ (monoclinic) – I4/m (tetragonal) – Fm-3m (cubic) phase transitions sequence observed for similar materials Sr_2MWO_6 (M=Ca,Zn,Co) [2, 3]. The first phase transition, from the monoclinic structure with the $\text{P}2_1/n$ space group to tetragonal structure with I4/m space group, is starts to take place at $\approx 400 \text{ K}$, for $\text{Sr}_2\text{FeSbO}_6$, with a temperature interval, 400 to 420 K, in which both phases, monoclinic and tetragonal, co-exist; for $\text{Ca}_2\text{FeSbO}_6$, the phase transition takes place at 920 K, with no co-existence interval. The mechanism of these phase transition is related to the mismatch between the size of the A cation and the cuboctahedral space between the FeO_6 and SbO_6 octahedra: the smaller size of the Ca^{2+} cation, with respect to that of Sr^{2+} cation, leads to a structure with a higher monoclinic distortion, at room temperature for the calcium containing compounds. This fact can explain the higher phase-transition temperature, 920 K for $\text{Ca}_2\text{FeSbO}_6$, compared to that 420 K for $\text{Ca}_2\text{FeSbO}_6$. The second phase transition, from the tetragonal structure with I4/m space group to the cubic structure with the Fm-3m space group, observed above 500 K for the strontium compound and above 1150 K for the calcium compound.

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