

Effect of synthesis temperature on the structural behavior of $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$ compound

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ABSTRACT: $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0, 0.05$ and 0.1) samples are synthesized by both solid solution and mirror furnace methods, and the effect of synthesis temperature on the behaviour structure is investigated. The phase structures are comparatively characterized and studied by means of X-ray powder diffraction. Experimental results reveal that the synthesis temperature has a strong influence on the structure of the synthesized compounds. Samples obtained by solid solution method at 1473 K that they crystallize in the orthorhombic lattice undergoes transition from primitive (*Pnma* space group) to body-centered (*Imma* or *I2mb* space group) up to $x=0.1$, whereas that obtained by mirror furnace method about 1900 K using melting zone technique show the transition at $x=0.05$. Both of synthesis methods were giving same lattice parameters values within the estimated standard deviation. Very high temperature applied during preparation in the "mirror furnace method" has influenced on the arrangement of the FeO_4 tetrahedra, and therefore on the $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$ compound structure.

KEYWORDS: $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$; Chemical synthesis ; Crystal symmetry ; Mirror furnace ; X-ray Powder diffraction.

ملخص: لقد تم تصنيع العينات $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0, 0.05$ و 0.1) بواسطة طريقتي المحلول الصلب و الفرن ذو المرآة، حيث تم دراسة تأثير درجة الحرارة على سلوك بنيتها. لقد قمنا بدراسة البنى البلورية عن طريق انعراج الأشعة السينية على المساحيق. لقد كشفت النتائج التجريبية على أن درجة حرارة التصنيع لها تأثير قوي على الهيكل الداخلي للمركبات المصنعة، حيث وجدنا أن العينات التي تم الحصول عليها بواسطة طريقة المحلول الصلب عند درجة الحرارة 1473 K تتبلور في الشبكة المعينية المستقيمة و تخضع للانتقال من البسيطة (*Pnma*) إلى الممركزة (*Imma* أو *I2mb*) ابتداء من $x=0.1$ ، في حين أن الحصول عليها بواسطة طريقة الفرن ذو المرآة التي تستخدم تقنية منطقة الذوبان عند حوالي 1900 K تظهر التحول فيها عند $x = 0.05$. و لقد أعطت طريقتي التصنيع على حد سواء نفس ثوابت الشبكة في حدود الانحراف المعياري المقدر. فقد أثر تطبيق درجات الحرارة المرتفعة جدا في "طريقة الفرن ذو المرآة خلال عملية التصنيع على ترتيب و توضع رباعيات الأسطح FeO_4 ، وبالتالي على البنية البلورية للمركب $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$.

كلمات دالة: $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ؛ التصنيع الكيميائي ؛ التناظر البلوري ؛ الفرن ذو المرآة ؛ انعراج الأشعة السينية على المساحيق.

RÉSUMÉ: Les échantillons $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0, 0.05$ et 0.1) sont synthétisés par la méthode de solution solide et celle du four à image, et l'effet de la température de synthèse sur le comportement de la structure est étudié. Les structures de phase sont relativement caractérisées et étudiées au moyen de la diffraction des rayons X sur poudre. Les résultats expérimentaux révèlent que la température de synthèse a une forte influence sur la structure interne des composés synthétisés. Les échantillons obtenus par la méthode de solution solide à 1473 K qu'ils se cristallisent dans le réseau orthorhombique subit une transition d'un réseau primitif (groupe d'espace *Pnma*) au réseau centré (groupe d'espace *Imma* ou *I2mb*) jusqu'à $x = 0.1$, alors que celle obtenue par la méthode du four à image utilisant la technique de la fusion de zone autour de 1900 K montrent la transition à $x = 0.05$. Les deux méthodes de synthèse donnaient même valeurs des paramètres de maille au sein de l'écart-type estimé. Très haute température appliquée lors de la préparation dans la méthode du "four à image" a influencé sur l'arrangement des tétraèdres FeO_4 , et donc sur la structure cristalline du composé $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$.

MOTS-CLÉS: $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$; Synthèse chimique ; Symétrie cristalline ; Four à image ; Diffraction des rayons X sur poudre.

1. Introduction:

Among candidate for the ionic conductor materials we can quote the isomorphous compounds $\text{SrFeO}_{2.5}$ and $\text{CaFeO}_{2.5}$ [1-9], which became two interesting areas of research, such as: ceramic membranes for oxygen separation and electrodes of solid oxide fuel cells (SOFCs), electrocatalysis, battery electrodes and sensor materials [10-17]. To date, the information about the structure of $\text{SrFeO}_{2.5}$ is still contradictory at room temperature. It was reported that $\text{SrFeO}_{2.5}$ has either the disordered *Imma* structure (S.G. N° 74) [5, 6, 18, 19] or ordered *I2mb* structure (S.G. N° 46) [20, 21]. On the other hand, there is no dispute that $\text{CaFeO}_{2.5}$ crystallizes in orthorhombic *Pnma* space group (S.G. N° 62) [6, 8, 9, 22, 23]. While FeO_6 octahedra in these structures can not show any preferred orientation, the FeO_4 tetrahedra do. For instance, $\text{SrFeO}_{2.5}$ unlike $\text{CaFeO}_{2.5}$ compound shows the possibility of the electrochemical intercalation of oxygens [2, 24-27]. It seems that the order of the FeO_4 tetrahedra plays an important role in explaining the chemical reactivity in Brownmillerite compounds according to Paulus et al [28]. Deepened study by investigating in the $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ compounds is therefore more requires, considering their important function as a key to better understanding of the ionic conduction mechanism in perovskite-related oxides. In their works, Nemudry & al. [25] were found that the structure of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ compounds obtained by solid solution (*SS*) method change from *Pnma* to body centered space group take place from $x=0.1$ at room temperature. The effect of synthesis conditions on properties of these compounds is essentially unexplored. Recently, we have reported the new synthesis method using the mirror furnace (*MF*) where we are success to synthesize a pure homogenous $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{FeO}_{2.5+\delta}$ compound for the first time [29]. Based on the relationship between structure and physical properties, we will compare in this paper between $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0, 0.05$ and 0.1) brownmillerite compounds obtained by this new method (mirror furnace) with the results of the conventional solid solution method, and assess the effect of applied temperature in different synthesized method on structural behavior of these compounds.

2. Experimental

2.1. Synthesis Method

The $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0, 0.05$ and 0.1) samples have been prepared by the solid solution and mirror furnace using melting zone technique synthesis methods.

2.1.1. Solid solution method

$\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0, 0.05$ and 0.1) compounds oxide was prepared in air by solid-state reaction of stoichiometric amounts of commercial CaCO_3 (ALDRICH, 98%), SrCO_3 (ALDRICH, 99.9+%) and Fe_2O_3 (ALDRICH, 99+%) oxides were well mixed with acetone in an agate mortar for few minutes. The mixture was annealed at 1273 K for 12 hours, and then the powder was compacted in pellets, each of 1 g and 13 mm in diameter. The pellets were heated in air in conventional furnace at 1473 K for 24 hours. Then, the samples were quenched in liquid nitrogen. This operation is repeated several times. The pellets were ground to fine powder for phase characterization. A portion of the obtained powder was used as a starting point of the second method so-called “mirror furnace method” based on melting zone technique.

2.1.2. Mirror furnace method

Each amount of the powder of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ samples was put in a latex tube in order to prepare the feed rod. A hydraulic pressure of 10 bars was applied to obtain a solid bar, and it was calcined in air for 12 h at 1223 K. Afterwards, a high temperature around 1900 K is applied using the mirror

furnace concentrated on a relatively small spot size at the bottom of the rod until melting. The bottom falls down as a molten drop directly in liquid nitrogen (see Fig. 1).

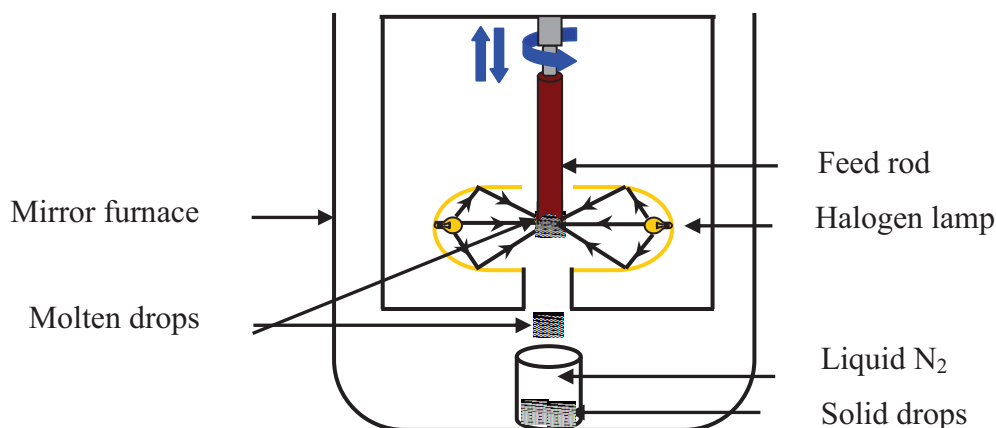


Fig. 1: Schematic representation of the mirror furnace

2.2. Characterisation

2.2.1. X-ray powder diffraction (XRD) measurements:

Phase identification and unit cell parameter determination are checked using powder X-ray diffraction (XRD) at room temperature. Powder X-ray diffraction data were recorded using a Bruker D8 Advance diffractometer (Bragg-Brentano configuration, $\text{CuK}\alpha_1$) equipped by Johanson Ge (111) monochromator.

2.2.2 Crystallite size measurements:

Crystallite sizes were determined from the full-width at half-maximum (FWHM) using the Scherrer formula [30]:

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta}$$

Where D is the crystallite size, k is a shape function for which a value of 0.9 is used, λ is the wavelength of the radiation ($\text{Cu-K}\alpha_1 = 1.54056 \text{ \AA}$) and θ is a diffraction angle and β is full-width at half-maximum (FWHM) of the XRD peak.

3. Results and discussion

The results of X-ray powder diffraction at room temperature of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0, 0.05$ and 0.1) samples prepared by both solid solution (SS) and mirror furnace (MF) methods are presented in Fig. 2a and 2b respectively. As can be seen, evident differences are observed in the pattern for the samples prepared by the two routes. Therefore, we refined the diffractograms of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0.05$ and 0.1) using the lattice constants of $\text{CaFeO}_{2.5}$ as starting parameters [9].

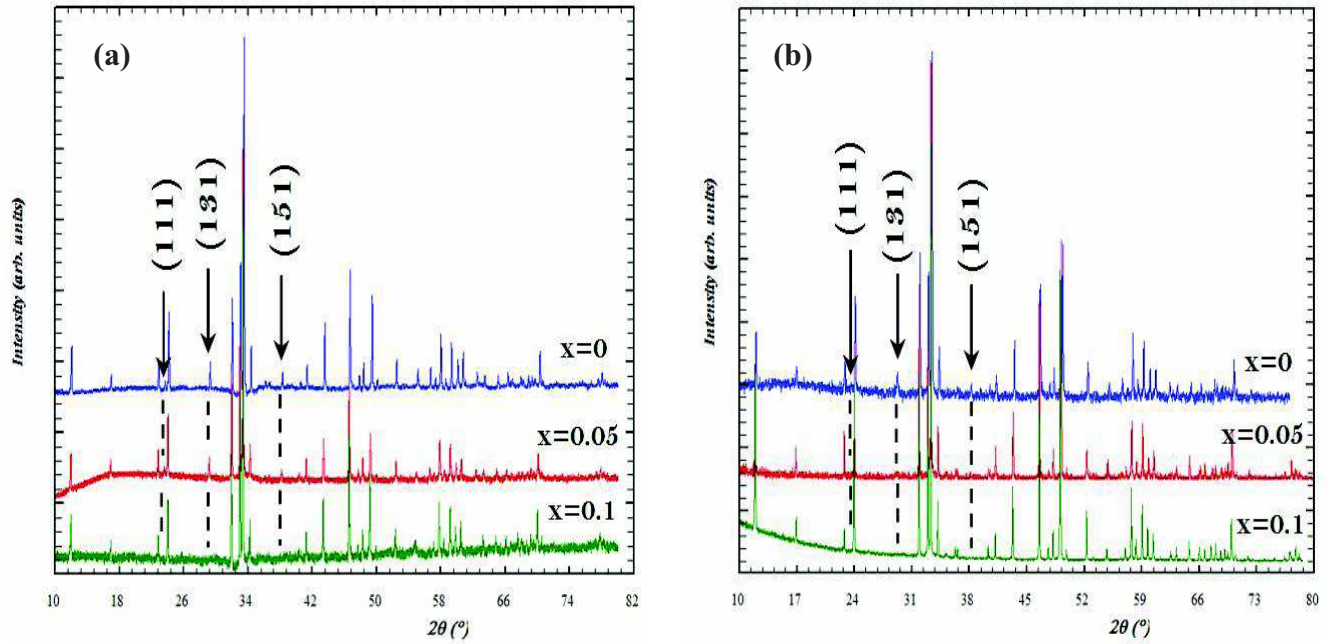


Fig. 2: X-Ray powder diffraction pattern of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0, 0.05$ and 0.1) samples obtained by (a) Solid solution method (b) Mirror furnace method

The lattice parameters of all samples (obtained by *SS* and *MF* method) were refined by means of the FullProf program [31] using le Bail method are summarized in Table 1. Comparison of the values obtained from the indexing of X-ray powder diffraction patterns showed that the results match in case of samples obtained by two methods gave comparable results.

Table 1: Summary of lattice parameters of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ ($x=0, 0.05$ and 0.1) samples synthesized by *SS* and *MF* methods

Sample	Synthesized method	Space group	Lattice parameters (Å)		
			<i>a</i>	<i>b</i>	<i>c</i>
$\text{CaFeO}_{2.5}$	<i>SS</i>	<i>P nma</i>	5.42190 (5)	14.75642 (12)	5.59474 (5)
$\text{CaFeO}_{2.5}$	<i>MF</i>	<i>P nma</i>	5.42455 (11)	14.76309 (24)	5.59668 (10)
$\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$	<i>SS</i>	<i>P nma</i>	5.42877 (8)	14.80476 (21)	5.60034 (8)
$\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$	<i>MF</i>	<i>I mma</i>	5.42668 (13)	14.80042 (35)	5.60337 (13)
$\text{Ca}_{0.9}\text{Sr}_{0.1}\text{FeO}_{2.5}$	<i>SS</i>	<i>I mma</i>	5.43356 (9)	14.84005 (24)	5.61175 (10)
$\text{Ca}_{0.9}\text{Sr}_{0.1}\text{FeO}_{2.5}$	<i>MF</i>	<i>I mma</i>	5.43249 (4)	14.84468 (9)	5.60811 (4)

SS: solid solution method

MF: mirror furnace method

The unit cell volume of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ where $x \neq 0$ (Table 1) is larger than that of $\text{CaFeO}_{2.5}$ [6] and is monotonically increasing with the added amount of Sr due to the larger radius of Sr^{2+} compared to Ca^{2+} ($r(\text{Sr}^{2+}) = 1.44 \text{ \AA}$, $r(\text{Ca}^{2+}) = 1.34 \text{ \AA}$ [32]) in respect with Vegard's law (Fig. 3a and 3b).

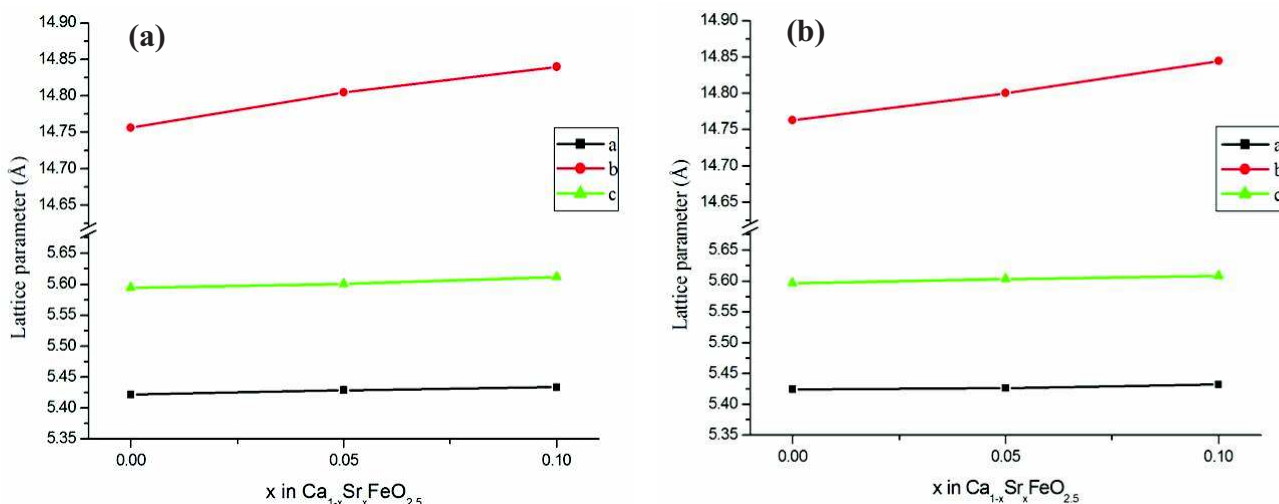


Fig. 3: The lattice parameters vs. composition of (a) SS and (b) MF samples

All peaks of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ [$x=0, 0.05$ (SS) and $x=0$ (MF)] samples can be refined on the brownmillerite structure $Pnma$ (Fig. 4a, 4b and 4c).

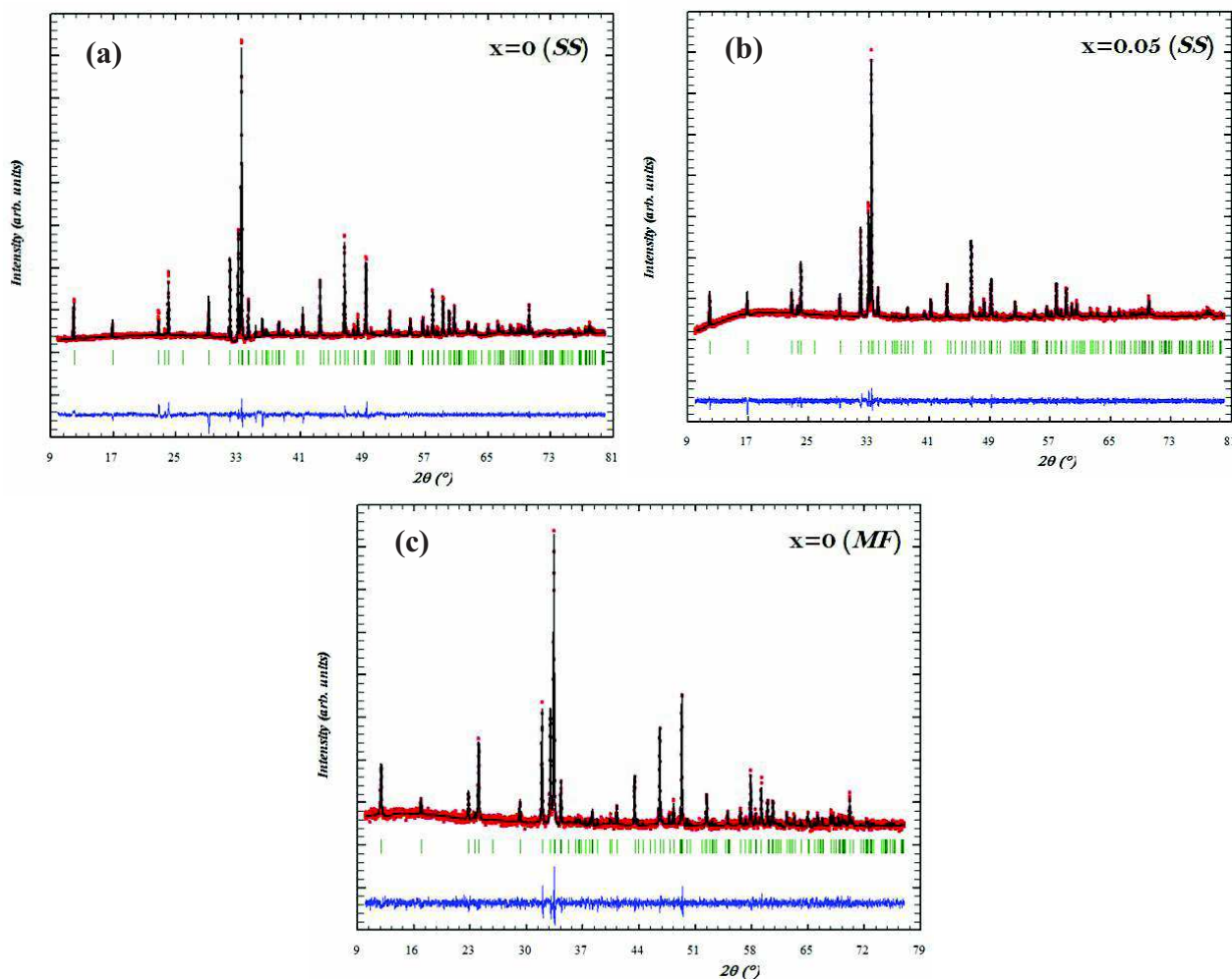


Fig. 4: Observed, calculated and difference XRD pattern of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ (a) $x=0$ (b) $x=0.05$ (SS) and (c) $x=0$ (MF) samples at room temperature refined in $Pnma$ space group

While, in the XRD pattern collected from the $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ [$x=0.1$ (SS) and $x=0.05, 0.1$ (MF)] samples, the (111), (131) and (151) reflections and all representative P lattice ($h+k+l=2n+1$) are

absent, indicating transition into a body-centered lattice (Fig. 5a, 5b and 5c). Also, it was noted previously that the $I2mb$ space group gave the same results as $Imma$ within the experimental error. In these types of structures, the general problem lies in the fact that only slight differences exist in the arrangement of the FeO_4 tetrahedral chains for these 3 space groups: ordered $Pnma$, $I2mb$ or disordered $Imma$.

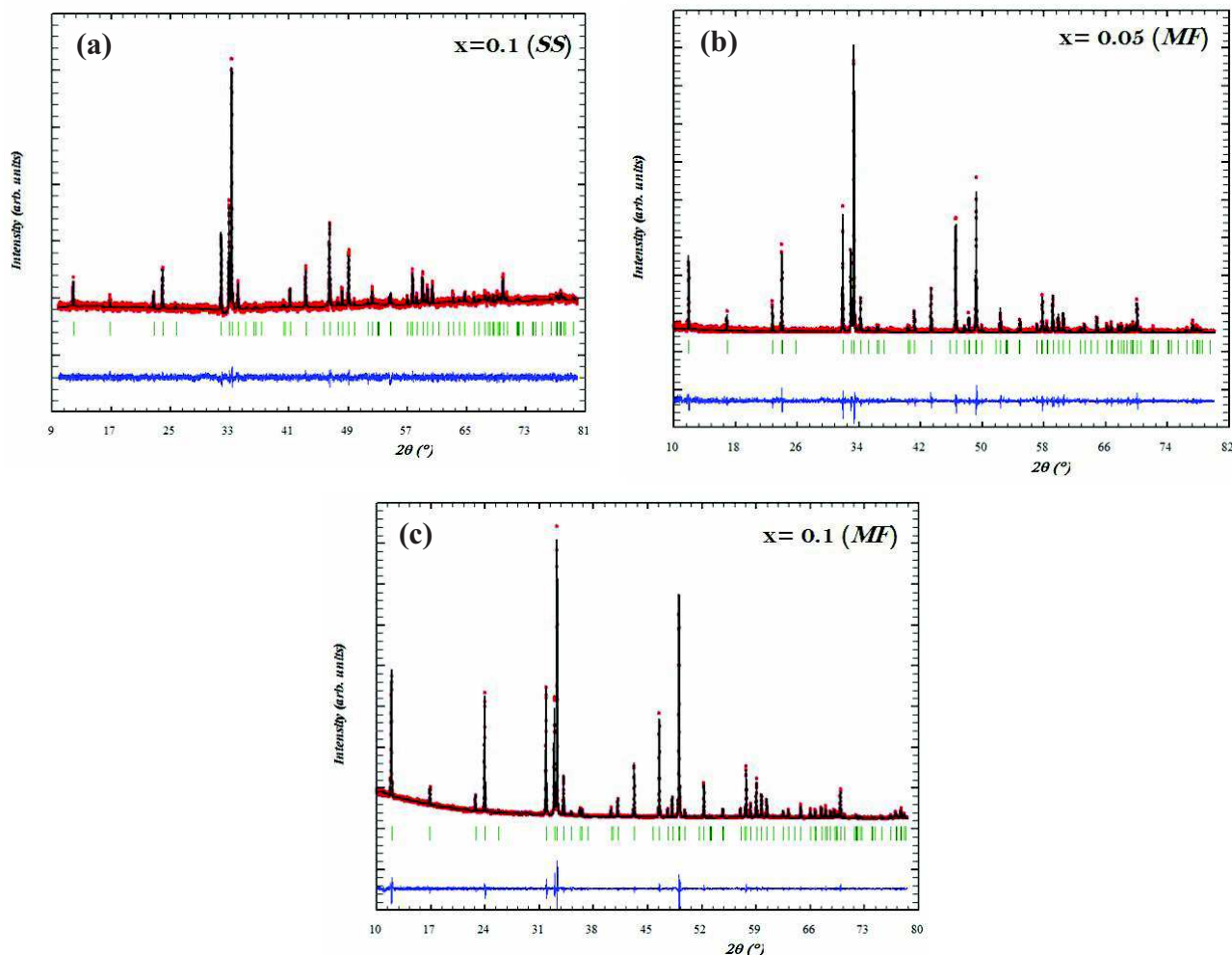


Fig. 5: Observed, calculated and difference XRD pattern of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ (a) $x=0.1$ (SS) (b) $x=0.05$ and (c) $x=0.1$ (MF) samples at room temperature refined in $Imma$ space group

We can explain this as the high temperature induces a change in displacements of the oxygen ions in the tetrahedra that build up the structure in alternating layers, and therefore transformation from $Pnma$ to $Imma$ or $I2mb$. This phase transformation was also observed about $\text{CaFeO}_{2.5}$ in the literature but in the range 950–1000 K [6, 9, 33]. Then, we can say that depending on the adopted synthesis method, the $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$ compound would show various structures under different formation mechanisms.

On the other hand, the average crystallite sizes of $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$ samples extracted from the (020), (200) and (002) reflections are varied from 83 nm to 120 nm for the sample obtained by SS method, and varied from 129 to 160 nm for the one obtained by MF method (Table 2).

Table 2: Crystallites average sizes in chosen orientations about $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$ compound

(h k l) peak	Synthesized method	2θ (°)	FWHM	Crystallites sizes (nm)
020	<i>SS</i>	11.95	0.0968 (25)	83 (2)
	<i>MF</i>	11.95	0.0619 (55)	129 (12)
002	<i>SS</i>	31.93	0.0772 (11)	107 (2)
	<i>MF</i>	31.92	0.0515 (34)	160 (11)
200	<i>SS</i>	32.97	0.0691 (8)	120 (1)
	<i>MF</i>	32.98	0.0554 (44)	150 (12)

SS: solid solution method

MF: mirror furnace method

Also, we can see the increase in peak intensities in the XRPD pattern of the second method which is due to the enhancement of the crystallinity and particle size during the synthesis process. In the general case, the growth of the grains supported by the thermal energy contribution is generally associated with the increasing of the temperature, which allows the interpretation of the increasing of crystallite sizes.

It is worth mentioning that $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$ sample prepared with the *MF* method can have a smaller value of full-width at half-maximum (FWHM) and higher peak intensities than the sample prepared with the *SS* method indicated the improvement of the crystallinity and particle size.

4. Conclusion

In summary, the influences of synthesis method on the structural behaviors of $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ [$x=0, 0.05$ and 1] compounds were investigated. The two synthesis methods studied lead to differences in the compounds, namely a different structure, which is a result of the higher temperature during preparation via the “mirror furnace method” based on melting zone technique. The high temperature during sample synthesis induces a change in displacements of the oxygen ions in the FeO_4 tetrahedra that build up the structure with the FeO_6 octahedra in alternating layers, and therefore from *Pnma* to body centered *Imma* or *I2mb* space group. We can also say that the critical value of x in the $\text{Ca}_{1-x}\text{Sr}_x\text{FeO}_{2.5}$ compounds governing the change of the *P* to *I* lattice is not stable but varies with the temperature ($x=0.1$ at $T=1473$ K and $x=0.05$ at $T\sim 1900$ K). Also, examination of the FWHM has shown that raising the synthesis temperature accompanies the increase of the crystallite size, in agreement with that the growth of the grains supported by the thermal energy contribution is generally associated with the increasing of the temperature. As a result, we can conclude that the preparation method for $\text{Ca}_{0.95}\text{Sr}_{0.05}\text{FeO}_{2.5}$ influences on the compound structure to a considerable extent and thereby in its physical properties.

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