SYNTHESIS AND STRUCTURE REFINEMENT OF $Ca_{0.5}Sr_{0.5}FeO_2$ SOLID SOLUTION

Soria ZEROUAL[1], Mohammed Sadok MAHBOUB[2], Ali BOUDJADA[3]

*$Ca_{0.5}Sr_{0.5}FeO_2$ solid solution has been prepared by the reacting of $Ca_{0.5}Sr_{0.5}FeO_{2.5}$ brownmillerite with CaH_2 at 553 K. The crystal structure of $Ca_{0.5}Sr_{0.5}FeO_2$ phase has been refined by the Rietveld method from X-ray powder diffraction data. In the present study, we have successfully synthesized a stable Oxoferrate $Ca_{0.5}Sr_{0.5}FeO_2$ phase, where no phase separation was observed. The structure is tetragonal, space group P4/mmm, a=3.95718 (9) Å and c=3.39839 (13) Å. The Final structure refinement values of the Rietveld parameters are: R_p=1.15%, R_{wp}=1.75% and χ^2=2.72. The structure of $Ca_{0.5}Sr_{0.5}FeO_2$ consists of a stacking sequence of infinite FeO_2 layers with square-planar coordinated iron (II) lattices separated by alternating Ca/Sr atoms in the **c** direction. This structure might be promising candidates for applications as membrane in solid oxide fuel cells (SOFC).*

Keywords: Calcium strontium oxoferrate, Crystal structure, Infinite layer, X-ray Powder diffraction, Rietveld refinement

1. Introduction

Among candidate for the ionic conductor materials we can quote $SrFeO_{2.5}$ compound exhibit fast oxygen transport and high electron conductivity even at low temperatures [1-5]. It became an interesting field of research, such as: ceramic membranes for oxygen separation and electrodes of solid oxide fuel cells (SOFCs), electrocatalysis, battery electrodes and sensor materials [6-13]. Controversy, the isomorphic $CaFeO_{2.5}$ unlike $SrFeO_{2.5}$ compound shows inability to the electrochemical intercalation of oxygens [2,14-17]. 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.* [18]. Deepened study of $Ca_{1-x}Sr_xFeO_{2.5}$ is required, considering their important function as a key to better understanding of the ionic conduction mechanism in perovskite-related oxides. A few years ago, Tsujimoto *et al.* [19] reported on the synthesis of the first ternary earth alkaline oxoferrate (II), $SrFeO_2$, by the reduction of perovskite-related $SrFeO_{2.875}$ precursor at 553 K with CaH_2. In their study, Tassel *et al.* [20] have observed that the $Ca_{1-x}Sr_xFeO_2$-phases persists up to 960 K for $SrFeO_2$ and

[1] PhD Researcher, LEVRES Laboratory, Department of Physics, Faculty of Exact Sciences, University of El-Oued, Algeria, e-mail: zersoraya@yahoo.com
[2] PhD Researcher, LEVRES Laboratory, Department of Physics, Faculty of Exact Sciences, University of El-Oued, Algeria, Corresponding author, e-mail: mmsad1@yahoo.fr
[3] Professor, Laboratoire de Cristallographie, Unité de Recherche de Physique, Faculté des Sciences Exactes, Université Constantine 1, Algeria, e-mail: boudjada_ali@yahoo.fr

630 K at least for $CaFeO_2$. They have concluded that the infinite layer (IL) iron oxide is thermodynamically stable against substitution as well as temperature. Recently, we have reported for the first time a new synthesis method using a mirror furnace (*MF*) for pure $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$ compound [21]. Based on the relationship between structure and physical properties, we will report in this contribution the synthesis and structural characterization of $Ca_{0.5}Sr_{0.5}FeO_2$ obtained by X Ray Powder Diffraction (XRPD) in order to check the stability of our sample synthesized by a new technique so-called "mirror furnace method".

2. Experimental

2. 1. Synthesis method

$Ca_{0.5}Sr_{0.5}FeO_2$ powder was obtained by a solid state reaction through mixing $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$ prepared according to [21] and CaH_2 in a 1:2 molar ratio, ground inside an argon-filled glovebox. The mixture was inserted into a Pyrex tube. The sealed tube was inserted in a furnace for 6 days at 553 K. The unreacted CaH_2 and byproduct CaO were removed from the product by washed it in a solution of methanol and 0.1 M of NH_4Cl.

2. 2. X-ray Powder diffraction

Powder X-ray diffraction data were performed at room temperature on a Brucker D8 Advance diffractometer (Bragg–Brentano configuration) equipped with Johanson Ge (111) monochromator and a LynxEye position sensitive detector. The datasets were collected in the range of $20° \leq 2\theta < 120°$ using $CuK_{\alpha 1}$ radiation at step size of $2\theta = 0.016°$ and a fixed counting time of 15 s/step.

2. 3. EDS spectroscopy

The energy dispersive X-ray spectroscopy (EDS) analysis was carried out for $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$ sample using a JEOL (JSM-6400) scanning electron microscope equipped with an EDAX (Oxford Link INCA) micro-analytical system, intended for the observation of dry and conducting samples.

3. Result and discussion

A quantitative analysis of the precursor $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$ by the energy dispersive X-ray spectroscopy (EDS) analysis was used to check the chemical composition. Small amount of the sample's size is observed on a holey carbon film supported by a copper grid. EDS analysis indicates a Ca:Sr ratio of 0.5:0.5 in $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$, which is consistent with the expected stoichiometry, within the limit of experimental error (Table 1).

The EDS spectrum confirms the desired compound (Fig. 1). XRD powder pattern of the final product $Ca_{0.5}Sr_{0.5}FeO_2$, is isomorphic to those of the parent

structure for $SrFeO_2$ [19]. An additional peak was detected at $2\theta = 32.7°$, thus indicating the presence of a small amount of unreacted phase.

Table 1

Compositions of $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$ extracted by theoretical calculation and EDS analysis

Element	Ca	Sr	Fe
Theoretical composition (% wt.)	12.55	27.43	34.97
Experimental sample composition (% wt.)	12.86	28.04	36.82

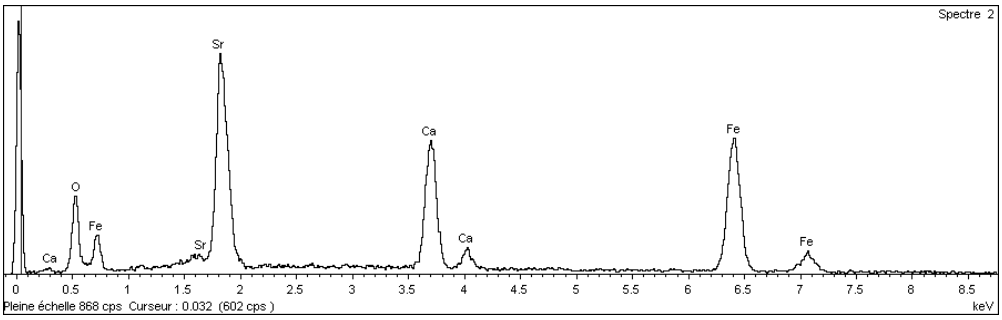

Fig. 1. EDS analysis of initial product $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$

We have found that this peak corresponds to the (141) more intense reflection of the starting Brownmillerite $Ca_{0.5}Sr_{0.5}FeO_{2.5}$ not reacted. The Rietveld refinement of the XRD data was carried out with *FULLPROF* [22] in the *P*4/*mmm* space group. The background in rietveld refinement was fitted with a linear interpolation function, and pseudo-voight function was employed to model the peak shapes. No splitting peaks were observed, which allowed to us indexing the diffraction pattern in this tetragonal space group. This situation indicates that a no phase separation takes place and the ‘‘miscibility gap’’ problem resolved in $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$ solid solution [21] does not arise again. There is no decomposition to form Ca- and Sr-enriched microdomains. We started the refinement with the lattice parameters and initial atomic positions, referring to those quoted by Tassel *et al.* [20]. After careful treatment, the structure refinement leads to rather good match between the experimental and calculated XRD pattern (Fig. 2). The Rietveld refinement leads to confidence reliability factors quite satisfactory. The refinement parameters are listed in Table 2.

Final atomic positions, isotropic displacement factors are given in Table 3 and interatomic distances in Table 4. A possibility of disorder for Ca (Sr) atom was checked.

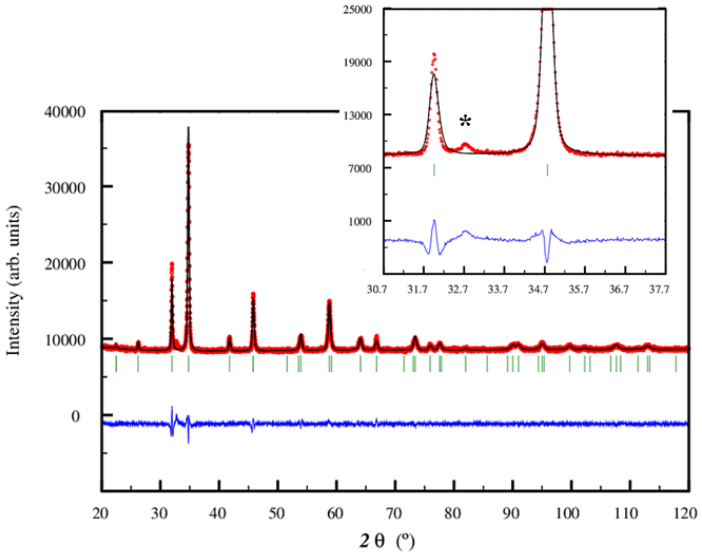

Fig. 2. Observed, calculated and difference X-ray diffraction plots for $Ca_{0.5}Sr_{0.5}FeO_2$. The intense reflection of unreacted $Ca_{0.5}Sr_{0.5}FeO_{2.5}$ is marked is marked

Table 2

Crystallographic data for $Ca_{0.5}Sr_{0.5}FeO_2$

System	*Tetragonal*
Space group	*P*4/mmm
Lattice parameters	a= 3.95718 (9) Å
	c = 3.39839 (13) Å
Volume of unit cell	53.216 (1) Å^3
Z	1
D_x	4.72 (1) Mg m^{-3}
λ	1.54056 Å
R_p (%)	1.15
R_{wp} (%)	1.75
R_{exp} (%)	1.06
χ^2	2.72
N^o of parameters refined	45

where:

$$R_p = \frac{\sum \boldsymbol{y_i(obs) - y_i(cal)}}{\sum \boldsymbol{y_i(obs)}} \quad (1)$$

$$R_{wp} = \left\{\frac{\sum \boldsymbol{w_i(y_i(obs) - y_i(cal))^2}}{\sum \boldsymbol{w_i(y_i(obs))^2}}\right\} \quad (2)$$

$$R_{exp} = [(N - P)/\sum w_i y_{oi}^2]^{\mathbf{1/2}} \quad (3)$$

$$\chi^2 = {R_{wp}}/{R_{exp}} \quad (4)$$

Refining both the atomic occupation number and displacement parameters revealed that the ratio of Ca:Sr = 0.51: 0.49. Refinement in both possible tetragonal space groups $P42_12$ and $P\text{-}42_1m$ not successful.

Table 3

Atomic coordinates, isotropic displacement parameters and BVS of $Ca_{0.5}Sr_{0.5}FeO_2$

Atom	*x*	*y*	*z*	*U*iso*/Ueq (Å^2)	Occ.	BVS
Ca	1/2	1/2	1/2	0.0056 (8)	0.512	2.127
Sr	1/2	1/2	1/2	0.0056 (8)	0.488	2.127
Fe	0	0	0	0.0122 (11)	1.000	2.065
O	1/2	0	0	0.0148 (18)	1.000	2.096

Table 4

Interatomic Distances and Torsion angles for $Ca_{0.5}Sr_{0.5}FeO_2$ (Å, °)

Fe - O x 4	1.9786(6)	O – Fe - O x 2	180.00
(Ca, Sr) - O x 6	2.6081(8)	O – Fe - O x 4	90.00

We note that the mean Fe-O distance in the structure of $Ca_{0.5}Sr_{0.5}FeO_2$ solid solution is 1.98 Å, which is comparable with the mean Fe-O (octahedral site) distance of 1.97 Å in $CaFeO_{2.5}$ [23-24], and 2.06 Å in $SrFeO_{2.5}$ [25], due to the effect of the partial replacement of Ca by Sr in the crystal structure. On the other hand, the mean (Ca, Sr)-O distance in the title structure is 2.61 Å which are significantly larger than the Ca-O bond value of 2.55 Å in $CaFeO_{2.5}$ [23] and 2.59 Å in $CaFeO_2$ [20], but smaller than the bond values of 2.63 Å [25] or 2.65 Å [23] for Sr-O bond in $SrFeO_{2.5}$ and 2.65 Å in $SrFeO_2$ [19], indicating that calcium and strontium occupy the same position (static disorder). In this structure, the Fe^{2+} ions are fourfold coordinated by oxygen in the planes, and no apical oxygen are present. The Fe atoms with their immediate environment consisting of Oxygen atoms form square planes that are repeated in an infinite way on both *a* and *b* directions to form infinite $(FeO_2)_\infty$ layers (Fig. 3a). These layers are separated by A = ($Ca_{0.5}Sr_{0.5}$) atoms (Fig. 3b).

Therefore, the structure consists of a stacking sequence of these infinite layers (IL) of square lattices FeO_2 in the ***c*** direction (Fig. 4). Four equal Fe–O distances form a perfect square planes, because all atoms situated in special position. In this new architecture all of the apical O atoms have been selectively removed upon reduction. We are therefore facing a new phase "$Ca_{0.5}Sr_{0.5}FeO_2$" with an unusual coordination in this type of oxides formed by square planes around the iron to form infinite $(FeO_2)_\infty$ layers. In other hand, the very small U_{iso} values of all atoms indicates the stability of this structure. It is isostructural with the superconducting copper oxide $SrCuO_2$ [26]. The structure is plotted using Balls & Sticks -1.80beta structural visualization program [27].

The calculated Bond Valence Sum (BVS) of each ion [28-29] [Sr/Ca: 2.127, Fe: 2.065, O: 2.096] are in agreement with the expected valence state of Sr/Ca $^{2+}$, Fe^{2+} and O^{2-} respectively. Likewise, the perfect square planes formed by

four equal Fe-O bond mentioned above might contribute to the fact that the BVS value of the Ca^{2+}, Sr^{2+}, Fe^{2+} and O^{2-} ions given in Table 3 with values very close to the expected formal oxidation states of each ion.

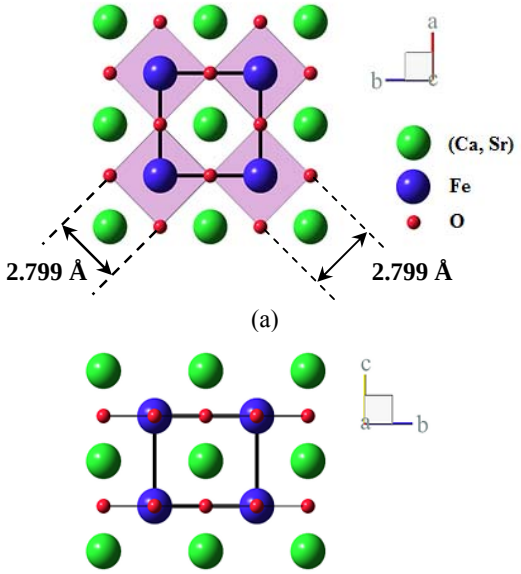

Fig. 3. Structure view of $Ca_{0.5}Sr_{0.5}FeO_2$ at: (a) c axis (b) a axis

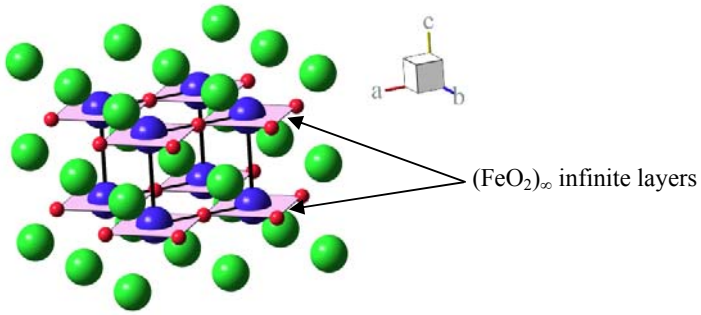

Fig. 4. Perspective view of the crystal structure $Ca_{0.5}Sr_{0.5}FeO_2$

Crystallographic data for the structure reported here have been deposited under FIZ Deposition No. CSD- 430786. These data can be obtained free of charge from FIZ Karlsruhe, D-76344, Eggenstein-Leopoldshafen, Germany, E-mail: crysdata@fiz-karlsruhe.de.

4. Conclusions

The influences of reduction of homogenous $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$ brownmillerite prepared by a mirror furnace technique were investigated. Synthesis and structure refinement of Oxoferrate $Ca_{0.5}Sr_{0.5}FeO_2$ phase have been reported here. The sample was characterized by powder X-ray diffraction. A stable structure of $Ca_{0.5}Sr_{0.5}FeO_2$ consists of a stacking sequence of infinite FeO_2 layers with square-planar coordinated iron (II) lattices separated by alternating Ca/Sr atoms in the ***c*** direction. There is no decomposition to form Ca- and Sr-enriched microdomains. Calculated Bond Valence Sum (BVS) of Sr/Ca $^{2+}$, Fe^{2+} and O^{2-} ions are in agreement with the expected valence state. This compound might be promising candidate for important technological applications such as membrane in solid oxide fuel cells. So, further studies are needed to investigate the ionic diffusion in this type of structure.

Acknowledgments

This work was supported by the Ministry of Higher Education and Scientific Research of Algeria. The authors thank Prof. W. PAULUS, Dr. M. CERETTI (Institut Charles Gerhardt de Montpellier - FRANCE*)* and Dr. O. HERNANDEZ (Institut des Sciences Chimiques de Rennes - FRANCE) for their help.

R E F E R E N C E S

[1]. *M.V. Patrakeev, I.A. Leonidov, V.L. Kozhevnikov, & V.V. Kharton*, Ion–electron transport in strontium ferrites: relationships with structural features and stability, Solid State Sci., **vol. 6**, no. 9, 2004, pp. 907-913.

[2]. *A. Nemudry, M. Weiss, I. Gainutdinov, V. Boldyrev, & R. Schöllhorn*, Room Temperature Electrochemical Redox Reactions of the Defect Perovskite $SrFeO_{2.5+x}$, Chem. Mater., **vol. 10**, no. 9, 1998, pp. 2403-2411.

[3]. *C. Haavik, E. Bakken, T. Norby, S. Stølen, T. Atake, & T. Tojo*, Heat capacity of $SrFeO_{3-\delta}$; δ= 0.50, 0.25 and 0.15 - configurational entropy of structural entities in grossly non-stoichiometric oxides, Dalton trans. 2003, no. 3, pp. 361-368.

[4]. *C.A.J. Fisher, M. Saiful Islam*, Mixed ionic/electronic conductors $Sr_2Fe_2O_5$ and $Sr_4Fe_6O_{13}$: atomic-scale studies of defects and ion migration, J. Mater. Chem., **vol. 15**, no. 31, 2005, pp. 3200-3207.

[5]. *H. D'Hondt, A.M. Abakumov, J. Hadermann, A.S. Kalyuzhnaya, M.G. Rozova, E.V. Antipov, & G. Van Tendeloo*, Tetrahedral Chain Order in the $Sr_2Fe_2O_5$ Brownmillerite, Chem. Mater., **vol. 20**, no. 22, 2008, pp. 7188-7194.

[6]. *H.J.M. Bouwmeester, A.J. Burggraaf*, In Fundamentals of Inorganic Membrane Science and Technology; Burggraaf, A.J.L. Cot (Eds.), Elsevier: Amsterdam, 1996, pp. 435.

[7]. *C.H. Chen, H.J.M. Bouwmeester, R.H.E. van Doorn, H. Kruidhof, & A.J. Burggraaf*, Oxygen permeation of $La_{0.3}Sr_{0.7}CoO_{3-\delta}$, Solid State Ionics, **vol. 98**, no. 1-2, 1997, pp. 7-13.

[8]. *S.P.S. Badwal, F.T. Ciacchi*, Ceramic Membrane Technologies for Oxygen Separation, Adv. Mater., **vol. 13**, no. 12-13, 2001, pp. 993-996.

[9]. *J.P.P. Huijsmans*, Ceramics in solid oxide fuel cells, Curr. Opin. Solid State Mater. Sci., **vol. 5**, no. 4, 2001, pp. 317-323.

[10]. *P.V. Hendriksen, P.H. Larsen, M. Mogensen, F.W. Poulsen, & K. Wiik*, Prospects and problems of dense oxygen permeable membranes, Catal. Today, **vol. 56**, no. 1-3, 2000, pp. 283-295.
[11]. *A.F. Sammells, M. Schwartz, R.A. Mackay, T.F. Barton, & D.R. Peterson*, Catalytic membrane reactors for spontaneous synthesis gas production, Catal. Today, **vol. 56**, no. 1-3, 2000, pp. 325-328.
[12]. *B.C.H. Steele*, Oxygen ion conductors and their technological applications, Mater. Sci. Eng. B, **vol.13**, no. 2, 1992, pp. 79-87.
[13]. *H.Y. Tu, Y. Takeda, N. Imanishi, & O. Yamamoto*, $Ln_{1-x}Sr_xCoO_3$(Ln = Sm, Dy) for the electrode of solid oxide fuel cells, Solid State Ionics, **vol. 100**, no. 3-4, 1997, pp. 283-288.
[14]. *E. Goldberg, A. Nemudry, V. Boldyrev, & R. Schöllhorn*, Model for anomalous transport of oxygen in nonstoichiometric perovskites: 1. General formulation of the problem, Solid State Ionics, **vol. 110**, 1998, no. 3-4, pp. 223-233.
[15]. *A. Nemudry, A. Rogatchev, I. Gainutdinov & R. Schöllhorn*, Reactivity of the perovskite system $Ca_{1-x}Sr_xFeO_{2.5}$ in topotactic electrochemical oxidation at ambient temperature, J. Solid State Electrochem. , **vol. 5**, no. 7-8, 2001, pp. 450-458.
[16]. *A. Wattiaux, L. Fournès, A. Demourgues, N. Bernaben, J.C. Grenier & M. Pouchard*, A novel preparation method of the $SrFeO_3$ cubic perovskite by electrochemical means, Solid State Commun., **vol. 77**, no. 7, 1991, pp. 489-493.
[17]. *A. Piovano, G. Agostini, A.I. Frenkel, T. Bertier, C. Prestipino, M. Ceretti, W. Paulus, & C. Lamberti*, Time Resolved in Situ XAFS Study of the Electrochemical Oxygen Intercalation in $SrFeO_{2.5}$ Brownmillerite Structure: Comparison with the Homologous $SrCoO_{2.5}$ System, J. Phys. Chem. C, **vol. 115**, no. 4, 2011, pp. 1311-1322.
[18]. *W. Paulus, H. Schober, S. Eibl, M. Johnson, T. Berthier, O. Hernandez, M. Ceretti, M. Plazanet, K. Conder, & C. Lamberti*, Lattice Dynamics To Trigger Low Temperature Oxygen Mobility in Solid Oxide Ion Conductors, J. Am. Chem. Soc., **vol. 130**, no. 47, 2008, pp. 16080-16085.
[19]. *Y. Tsujimoto, C. Tassel, N. Hayashi, T. Watanabe, H. Kageyama, K. Yoshimura, M. Takano, M. Ceretti, C. Ritter & W. Paulus*, Infinite-layer iron oxide with a square-planar coordination, Nature, **vol. 450**, no. 7172, 2007, pp. 1062-1065.
[20]. *C. Tassel, T. Watanabe, Y. Tsujimoto, N. Hayashi, A. Kitada, Y. Sumida, T. Yamamoto, H. Kageyama, M. Takano, & K. Yoshimura*, Stability of the Infinite Layer Structure with Iron Square Planar Coordination, J. Am. Chem. Soc., **vol. 130**, no. 12, 2008, pp. 3764-3765.
[21]. *M.S. Mahboub, S. Zeroual, & A. Boudjada*, Synthesis of homogeneous $Ca_{0.5}Sr_{0.5}FeO_{2.5+\delta}$ compound using a mirror furnace method, Mater. Res. Bull., **vol. 47**, no. 2, 2012, pp. 370-374.
[22]. *J. Rodriguez-Carvajal*, FULLPROF: http://www.ill.eu/ sites/fullprof/, (2001).
[23]. *P. Berastegui, S-G. Eriksson, & S. Hull*, A neutron diffraction study of the temperature dependence of $Ca_2Fe_2O_5$, Mater. Res. Bull., **vol. 34**, no. 2, 1999, pp. 303-314.
[24]. *E.F. Bertaut, P. Blum, & A. Sagnières*, Structure du Ferrite Bicalcique et de la Brownmillerite, Acta Cryst., **vol. 12**, no. 2, 1959, pp. 149.
[25]. *C. Greaves, A.J. Jacobson, B.C. Tofield & B.E.F. Fender*, A Powder Neutron Diffraction Investigation of the Nuclear and Magnetic Structure of $Sr_2Fe_2O_5$, Acta Cryst. B, **vol. 31**, no. 3, 1975, pp. 641-646.
[26]. *X. Zhou, C. Dong, F. Wu, H. Chen, G. Che, Y. Yao, & Z. Zhao*, High-Temperature X-Ray Diffraction Study on Stability of the Infinite-Layer $SrCuO_2$, J. Solid State Chem., **vol. 112**, no. 1, 1994, pp. 211-213.
[27]. *T.C. Ozawa, S.J. Kang*, "Balls & Sticks: Easy-to-Use Structure Visualization and Animation Creating Program", J. Appl. Cryst., **vol. 37**, no. 4, 2004, pp. 679.
[28]. *N.E. Brese, M. O'Keeffe*, Bond-valence parameters for solids, Acta Cryst. B, **vol. 47**, no. 2, 1991, pp. 192–197.
[29]. *I.D. Brown, D. Altermatt*, Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database, Acta Cryst. B, **vol. 41**, no. 4, 1985, pp. 244–247.