

The Phase Transformation and Crystal Structure Studies of Strontium Substituted Barium Monoferrite

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Abstract. Unlike other AFe_2O_4 ferrite materials, Barium Monoferrite (BaFe_2O_4) have an orthorhombic structure which is very interesting to further study the crystal structure and phase formation. In this study, Strontium substituted Barium Monoferrite in the form of $\text{Ba}_{(1-x)}\text{Sr}_x\text{Fe}_2\text{O}_4$ has successfully been synthesized through solid state reaction method which includes BaCO_3 , SrCO_3 , and Fe_2O_3 as starting materials. $\text{Ba}_{(1-x)}\text{Sr}_x\text{Fe}_2\text{O}_4$ was made by varying the dopant composition of Strontium (Sr^{2+}) from $x = 0, 0.1, 0.3$, and 0.5 . Each composition was assisted by ethanol and continued to the milling process for 5 hours then followed by sintering process at 900°C for 5 hours. The phase transformation was studied by using X-ray diffractometer (XRD) and Rietveld refinement using General Structure Analysis System (GSAS) also 3D crystal visualization using VESTA. Referring to the refinement results, a single phase of BaFe_2O_4 was formed in $x = 0$ and 0.1 . The composition has orthorhombic structure, space group B $b21m$, and lattice parameters of $a = 19.0229$, $b = 5.3814$ $c = 8.4524$ Å, $\alpha = \beta = \gamma = 90^\circ$ and $a = 18.9978$, $b = 5.3802$ $c = 8.4385$ Å, $\alpha = \beta = \gamma = 90^\circ$ respectively. In the composition of $x = 0.3$ it was found that the phase of $\text{BaSrFe}_4\text{O}_8$ begin to form due to the overload expansion of the Sr^{2+} occupancy which made the distortion of the initial lattice parameters and finally in the $x = 0.5$ composition the single phase of $\text{BaSrFe}_4\text{O}_8$ was clearly formed. Energy Dispersive Spectroscopy (EDS) was used to confirm the change of the material structure by measuring the elemental compound composition ratio. The result of EDS spectra clearly exhibited the dominant elements were Barium (Ba), Strontium (Sr), Iron (Fe), and Oxygen (O) with the compound ratio (Atomic percentage and mass percentage) correspond to the BaFe_2O_4 and $\text{BaSrFe}_4\text{O}_8$ phase.

Keywords : Barium Monoferrite; Solid State Reaction; Strontium Substitution; Crystal Structure, Phase Transformation, Atomic Structure Simulation

1. Introduction

Ferrite magnetic materials is either in the form of soft magnetic or hard magnetic have been applied in such a wide technology application area. Spinel magnetic materials with the general formula $\text{M}^{2+}\text{Fe}_2\text{O}_4$ (divalent ion metal, $\text{M} = \text{Ni}, \text{Co}, \text{Mn}, \text{Zn}, \text{Mg}, \text{Fe}$, etc) were highly studied due to the unique magnetic and electric properties which very appropriate to be applied as sensor materials, nano devices, microwave devices, etc[1]



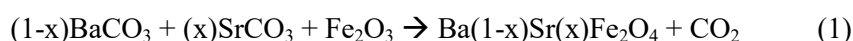
Unlike the usual $M^{2+}Fe_2O_4$ ferrite which exhibits spinel structure, Barium Monoferrite ($Ba^{2+}Fe_2O_4$) have an orthorhombic structure where the Fe^{3+} is bonded tetrahedrally with O^{2-} cations. These type ferrite material are less studied compared to the spinel ferrite type due to the assumption only as a coexisting phase into the M-type Barium Hexaferrite ($BaFe_{12}O_{19}$) along with the Fe_2O_3 [2]. $BaFe_2O_4$ has several advantages compared to the spinel ferrite such as high capacity of magnetization, high coercivity, highly stable, high permittivity, low-band-gap ferrite material [3]. Due to the low band gap properties, Barium Monoferrite oftenly only used as an important candidate for visible light photo-catalysis material and ceramic pigment[4] (1). Another beneficial properties of $BaFe_2O_4$ such high permittivity are rarely studied. The development of microwave and radar absorber materials (M-RAM) are growing rapidly to be applied in the military application and information technology. The candidate material which would be applied as M-RAM materials should have high permittivity and permeability values [5]. The high permittivity of the $BaFe_2O_4$ will make this ferrite material as a good candidate to be applied as M-RAM materials. In this work, the low permeability properties of the $BaFe_2O_4$ will be improved by substituting the Sr^{3+} cation into the $BaFe_2O_4$ structure in the form of $Ba_{(1-x)}Sr_xFe_2O_4$.

There are several methods that have been conducted to synthesize ferrite magnetic materials such as combustion method, solid state reaction method, glass crystallization method [6-8]. In this study, in order to improve the permeability value, the Sr^{3+} cations were substituted into $BaFe_2O_4$ by using solid state reaction method with High Energy Milling machine. This technique was used due to the simplicity and efficiency for preparing the fine powder of the $Ba_{(1-x)}Sr_xFe_2O_4$ powder. In this regards, The aim of this study is to understand the mechanism of the phase transformation when the $BaFe_2O_4$ structure was substituted by Sr^{3+} cations which are never studied before, as far the literature research by the author.

2. Experimental Procedure

2.1 Sample preparation

The starting materials which employed to synthesize substituted Strontium to Barium Monoferrite, in the form of $Ba_{(1-x)}Sr_xFe_2O_4$, are Barium Carbonate powder ($BaCO_3$, Merck), Strontium Carbonate powder ($SrCO_3$, Merck), and Iron (III) Oxide powder (Fe_2O_3 , Sigma Aldrich). All of the Barium Strontium Monoferrite (BSMFO) samples were made by varying the Strontium (Sr) substitution to Barium Monoferrite ($BaFe_2O_4$) in the range of $x = 0, 0.1, 0.3$, and 0.5 respectively, with the chemical reaction are shown as below:



The BSMFO compositions have been synthesized by using solid state reaction method. The synthesize process was started by mixing all the compound materials in stainless steel vial and assisted by ethanol then being milled for 5 hours. After the milling process, the raw BSMFO compositions were heated in the oven to evaporate the ethanol and followed by sintering process in furnace at $900^\circ C$ in ambient condition for 5 hours, all samples were finally grinded by using Agate mortar until fine powder of BSMFO were formed.

2.2 Characterization technique

In order to confirm the phase composition to all of the BSMFO samples, the X-ray diffraction pattern was carried out by using X-ray Diffractometer Panalytical Phillips with $Cu K\alpha$ radiation ($\lambda=0.15406$ nm), with the range of the 2θ angles started from 10° to 80° with the scan step 0.0263° per second. The elemental compound ratio (atomic percentage and mass percentage) was measured by using Energy Dispersive Spectroscopy (EDS) at 20 kV which attached in Scanning Electron Microscope (SEM) JEOL JSM-6510 LA.

3. Results and Discussion

The x-ray diffraction patterns of all BSMFO composition ($x = 0, 0.1, 0.3$, and 0.5) are shown in figure 1. In order to identify the phase that have been formed in the composition, all diffraction peaks were firstly confirmed by using Match! ver.3.1 software which referred to the Crystallography Open Database (COD). The BaFe_2O_4 phase was identified by the COD number 96-430-9916 and the $\text{BaSrFe}_4\text{O}_8$ was identified by the COD number 96-210-6519. Referring to all diffraction peaks, it was known that the single phase of BaFe_2O_4 has been formed in the composition of $x = 0$ and 0.1 , the most intense peak of the BaFe_2O_4 phase was indexed to (212) crystal plane. In both composition the single phase formation of BaFe_2O_4 were formed without the presence of any secondary phases such as Fe_2O_3 , Fe_3O_4 , or even the residual of BaCO_3 and SrCO_3 which oftenly formed through the crystallization process of BaFe_2O_4 . Silvana da Silva et al also tried to synthesize BaFe_2O_4 by using combustion method which reported the presence of Fe_2O_3 and Fe_3O_4 as secondary phase until 1000°C [4]. According to the inset figure 1.(b) and 1.(c), even though the single phase of BaFe_2O_4 was successfully formed in the composition of $x = 0$ and 0.1 , the dominant diffraction pattern of $x = 0.1$ composition were slight changed, it happened due to the occupation of the Sr^{2+} to the initial lattice of BaFe_2O_4 . This phenomenon became cleared when the Strontium substitution was increased in the composition of $x = 0.3$ in which the diffraction pattern clearly exhibited the phase transformation from BaFe_2O_4 to $\text{BaSrFe}_4\text{O}_8$. In the composition of $x = 0.5$ the crystal structure have completely transformed into a single phase of $\text{BaSrFe}_4\text{O}_8$, it has two dominant peaks which indexed to (102) and (110) crystal plane. The phase confirmation process then continued to the refinement process by using General Structure Analysis System (GSAS) software with Rietveld analyze method to further study the effect of the Strontium substitution to the initial lattice of BaFe_2O_4 . The detailed refinement graphics, lattice parameters, density, volume of unit cell, and the phase fraction were shown in table 1 and figure 2.

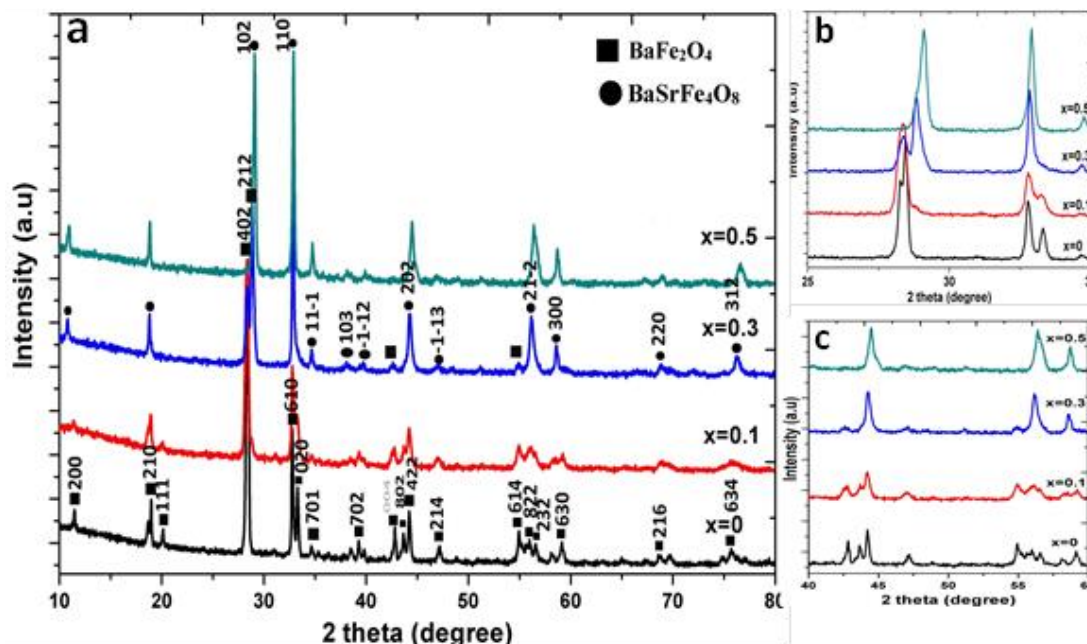
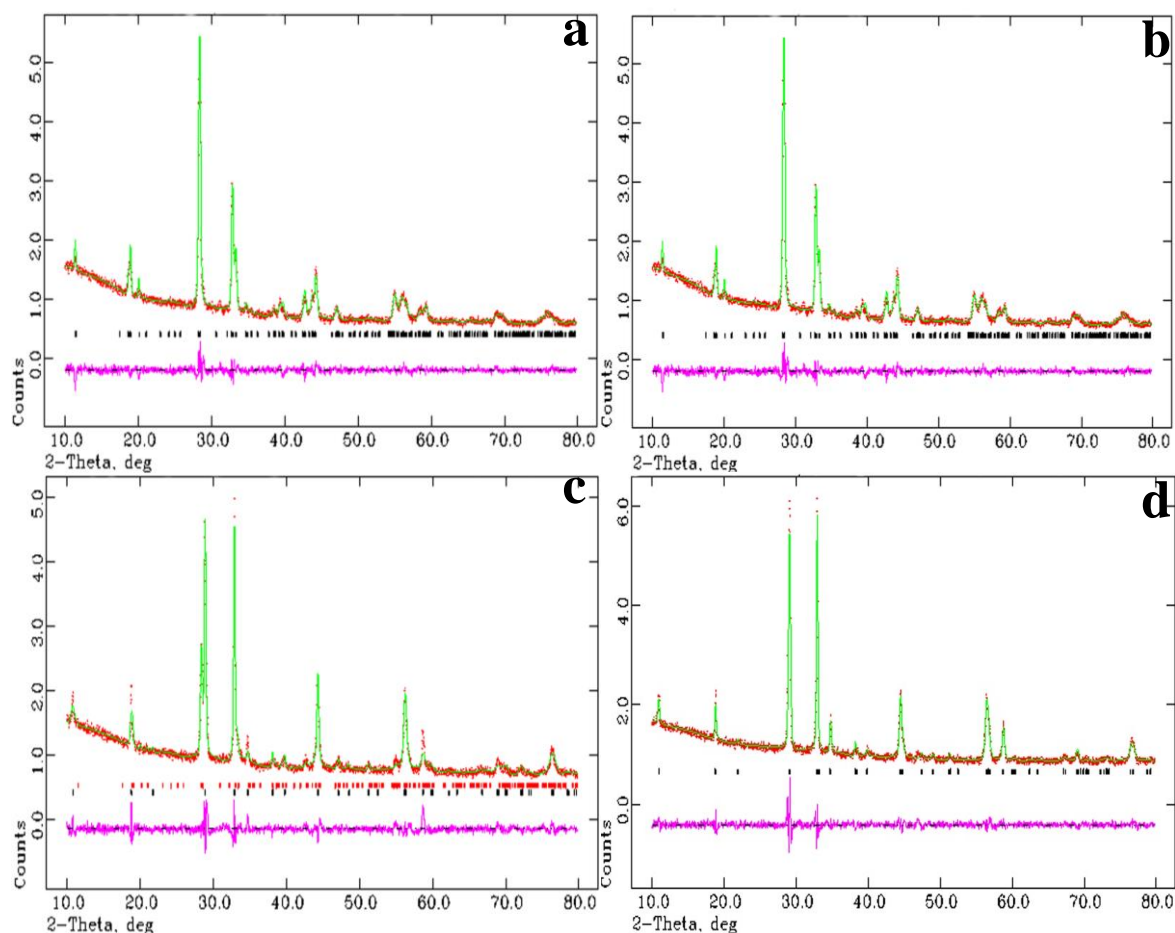


Figure 1. (a) X-ray diffraction pattern of all BSMFO compositions (Strontium substitution, $x = 0, 0.1, 0.3$, and 0.5), (b) inset figure of diffraction pattern from $2\Theta = 25$ to 35° , (c) inset figure of diffraction pattern from $2\Theta = 40$ to 60° .

Table 1. Refinement result from GSAS software for all of the BSMFO compositions (Strontium substitution, $x = 0, 0.1, 0.3$, and 0.5).

Sample (x)	Phase	Lattice parameter (\AA)			V (\AA^3)	ρ (g/cm^3)	Fraction wt%	R_{wp} (%)	χ^2
		a	b	c					
0	BaFe ₂ O ₄	19.023	5.382	8.452	865.279	4.806	100	4.900	1.292
0.1	BaFe ₂ O ₄	18.964	5.381	8.465	863.744	4.738	100	4.510	1.846
0.3	BaFe ₂ O ₄	18.383	5.360	8.443	852.434	2.575	28.882	4.900	2.403
	BaSrFe ₄ O ₈	5.446	5.446	8.185	210.217	4.482	71.185		
0.5	BaSrFe ₄ O ₈	5.445	5.445	8.102	207.998	4.733	100	4.500	2.300

**Figure 2.** The refinement graphics to all of the BSMFO compositions as the output of the GSAS software (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.3$, and (d) $x = 0.5$

The obtained lattice parameters for both phase of BaFe₂O₄ and BaSrFe₄O₈ in all BSMFO composition showed a good suitability to the COD database, BaFe₂O₄ phase have the orthorhombic crystal structure with space group $Cmcm$ 21 and detailed lattice parameter is $a = 19.04 \pm 2^0$, $b = 5.3826 \pm 2^0$, $c = 8.4538 \pm 2^0$ and $\alpha = \beta = \gamma = 90^0$, in other side BaSrFe₄O₈ have the trigonal crystal structure with space group $P\bar{3}1m$ and detailed the lattice parameter is $a = b = 5.45 \pm 2^0$, $c = 8.10 \pm 2^0$ and $\alpha = \beta = 90^0$, $\gamma = 120^0$. The lattice parameters and the 2θ diffraction angles of this experiment also correspond to another experiment results[2,3].

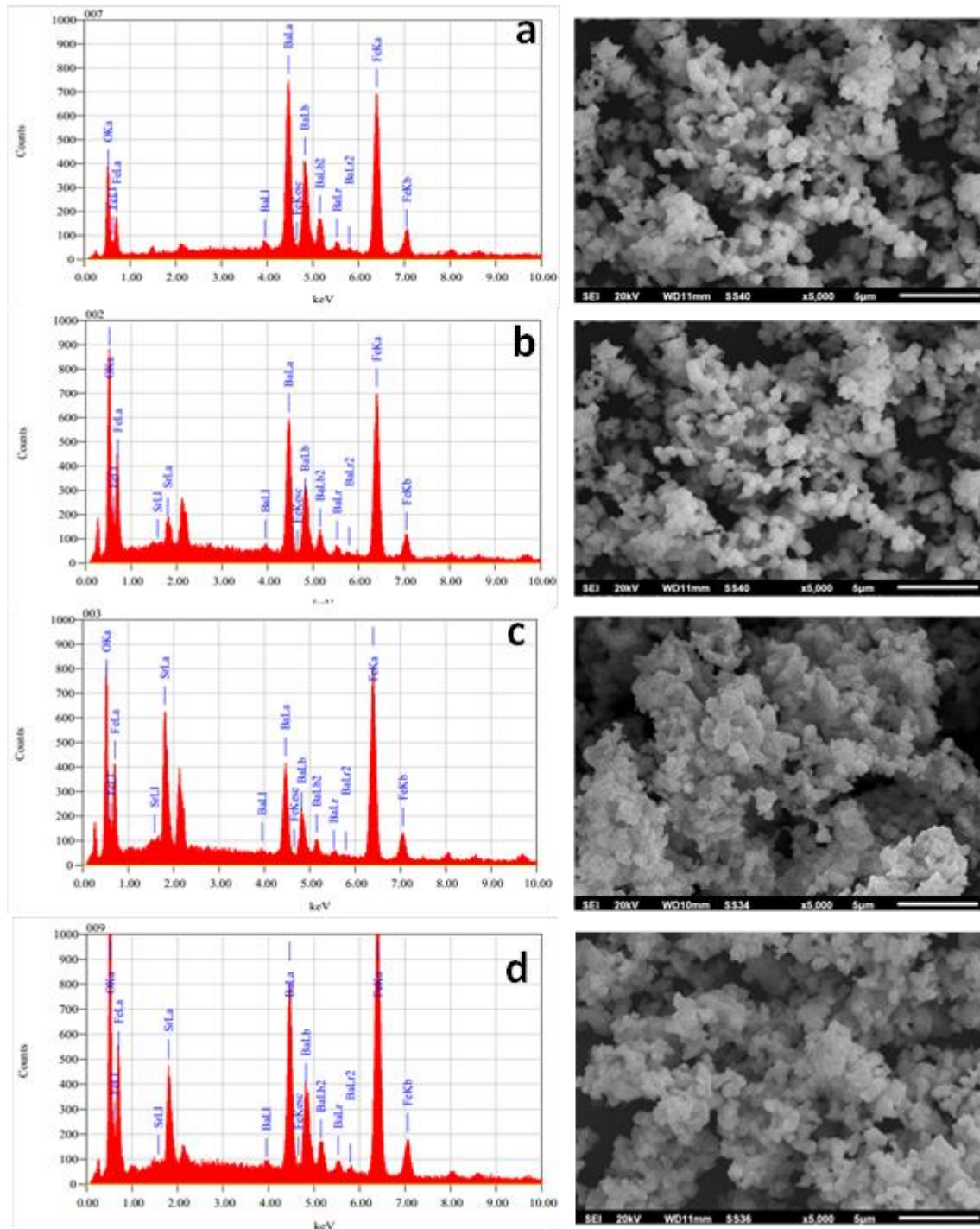


Figure 3. The Energy Dispersive Spectroscopy (EDS) and microstructure images of all BSMFO compositions; (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.3$, and (d) $x = 0.5$

As shown in table 1, there was a gradual decrease for lattice parameters of BaFe_2O_4 phase align with the increasing contain of Strontium (Sr^{2+}) which influenced the value of the cell volume and the density. This phenomenon happened due to the replacement of Ba^{2+} by the Sr^{2+} cation, Sr^{2+} have a lower ionic radius with the value of 2.15\AA rather than Ba^{2+} cation with the

value of 2.24Å. In the composition of $x = 0.1$ the Sr^{2+} cation were perfectly substitute the position of the Ba^{2+} and made the crystal structure to be a bit more shrinkage compared to the initial lattice in the composition of $x = 0$. The same conclusion was also gained to another related research by M.Ait Haddouch, et al who tried to synthesize the $\text{Ba}_{(1-x)}\text{Sr}_x\text{WO}_4$ ceramics who also found that the substitution of the Sr^{2+} will decrease the lattice parameters and influenced the cell volume [9]. In the composition of $x = 0.3$, the abundance of the Sr^{2+} created an overload expansion to the initial lattice which had an orthorhombic crystal structure, this made a great distortion in the lattice and finally created another phase; $\text{BaSrFe}_4\text{O}_8$ which had a trigonal crystal structure with weight fraction 28.882% for BaFe_2O_4 and 71.185% for $\text{BaSrFe}_4\text{O}_8$. The trigonal structure have been fully formed in the composition of $x = 0.5$ due to the value of lattice parameters database, it made the cell volume were slightly different compared to the composition of $x=0.3$ which still affected by the BaFe_2O_4 .

The characterization process using Energy Dispersive Spectroscopy (EDS) is a powerful tool to determine the relative elemental compound ratio (in mass percentage and atomic percentage) which directly correspond to the phase that have been formed in the composition. The relative elemental compound ratio, microstructure images, and EDS graphics were shown in the table 1 and figure 3. Scanning electron microscope (SEM) images were taken at 5000x magnification. Referring to the SEM images from figure 3, it can be noticed that the particle have homogenous size distribution with low degree of agglomeration. The EDS spectra images of all BSMFO compositions also shown in figure 3. The result for all of the BSMFO compositions clearly exhibited the dominant elements of Barium (Ba), Strontium (Sr), Iron (Fe), and Oxygen (O). Referring to the atomic percentage in the table 2, the quantification ratio of each elemental compound showed a good agreement to the BaFe_2O_4 and $\text{BaSrFe}_4\text{O}_8$ phase with an error less than 0.4%. In the composition of $x = 0$, the quantification ratio between Ba : Fe were in the range of 1 : 2 which correspond to the phase of BaFe_2O_4 . The same quantification ratio was also found in the composition of $x = 0.1$, which related to the phase of BaFe_2O_4 , the amount of Sr which detected in this composition have confirmed that the Sr^{2+} were successfully replaced the Ba^{2+} cation in the lattice. The unusual quantification result in the composition of $x = 0.3$ were likely caused by the mixed composition between the BaFe_2O_4 and $\text{BaSrFe}_4\text{O}_8$. The quantification ratio in the composition of $x = 0.5$ between Ba : Sr : Fe showed a good agreement to the phase of $\text{BaSrFe}_4\text{O}_8$ with the value of 1 : 1 : 4. All of the quantification ratio was well correspond to the x-ray diffraction pattern.

Table 2. EDS results of all BSMFO compositions (Strontium substitution, $x = 0, 0.1, 0.3$, and 0.5).

Strontium substitution (x)	Elemental Compound							
	Atomic Percentage (%)				Mass Percentage (%)			
	Ba	Sr	Fe	O	Ba	Sr	Fe	O
0	22.46	-	41.03	36.52	51.75	-	38.44	9.80
0.1	12.08	1.98	27.47	58.47	38.57	4.03	35.65	21.74
0.3	10.37	4.09	28.33	57.21	33.28	8.38	36.96	21.38
0.5	7.08	7.28	27.19	58.45	23.93	15.70	37.36	23.01

Table 3. Selected inter-atomic distances (Å) for all BSMFO compositions (Strontium substitution, $x = 0, 0.1, 0.3$, and 0.5).

Composition	$x = 0$ (Å)	$x = 0.1$ (Å)	$x = 0.3$ (Å)	$x = 0.5$ (Å)
Ba-O	2.7430	2.8163	2.8573	2.9307
Sr-O	-	-	2.60629	2.49926
Fe-O	1.8842	1.8791	1.8444	1.8136

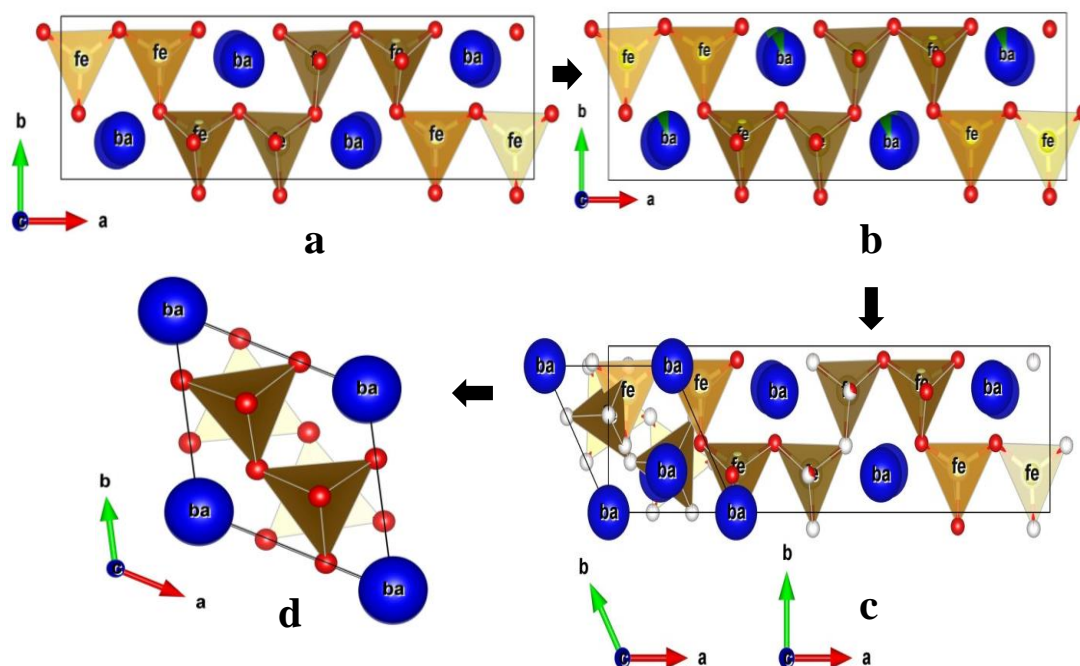


Figure 4. The gradual changes of the crystal structure from orthorhombic (space group $Cm\bar{c}21$) into trigonal (space group $P\bar{3}1m$) in 2-dimensional form; (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.3$, and (d) $x = 0.5$

The visualization of the atomic structure in order to clarify the gradual changes of the crystal structure of each composition were carried out by using vesta software. The gradual changes were shown in the 2-dimensional figure (figure 4) and 3-dimensional form (figure 5). The orthorhombic unit cell of $BaFe_2O_4$ phase was outlined by the solid black lines in the composition of $x = 0$ and 0.1 , which based on the X-ray diffraction pattern had a single phase of $BaFe_2O_4$. The orthorhombic unit cell was built by the two type of cations Ba^{2+} and Fe^{3+} (12 Ba atom and 16 Fe atom) and the Oxygen anions (36 atom). In the composition of $x = 0$, the Ba^{2+} , Fe^{3+} , and O^{2-} were located in the 4a and 8b sites in which the Fe atom were tetragonally bonded with the Oxygen as shown in the figure 4(a) and 5(a). The perfect substitution of the Sr^{2+} into the initial lattice of the was shown in the figure 4(b) and 5(b) represented by a slight green colour decorated the spherical Barium atom,. It can be noticed that the occupancy of the Sr^{2+} was not disturbing the form of the initial lattice however with decreasing the cation size (substituted by the Sr^{2+}), it affected the inter-atomic distances either for Ba-O or Sr-O in this composition which it became greater than the initial lattice in the composition of $x = 0$ (table 1). The overload expansion of Sr^{2+} in the composition of $x = 0.3$ which have made a great distortion in the initial lattice and transformed into $BaSrFe_4O_8$ was clearly shown in the figure 4(c) and 5(c) where the Sr^{2+} were entirely moved into the 1b site and made the distance even smaller. The greatest

distance between Ba-O was known in the composition of $x = 0.5$ due to the great distortion which made the phase fully transformed into a complete phase of $\text{BaSrFe}_4\text{O}_8$ in which the Fe^{3+} still bonded tetragonally into the Oxygen anions but the Ba^{2+} was moved into the corner of the site as shown in the figure 4(d) and 5(d).

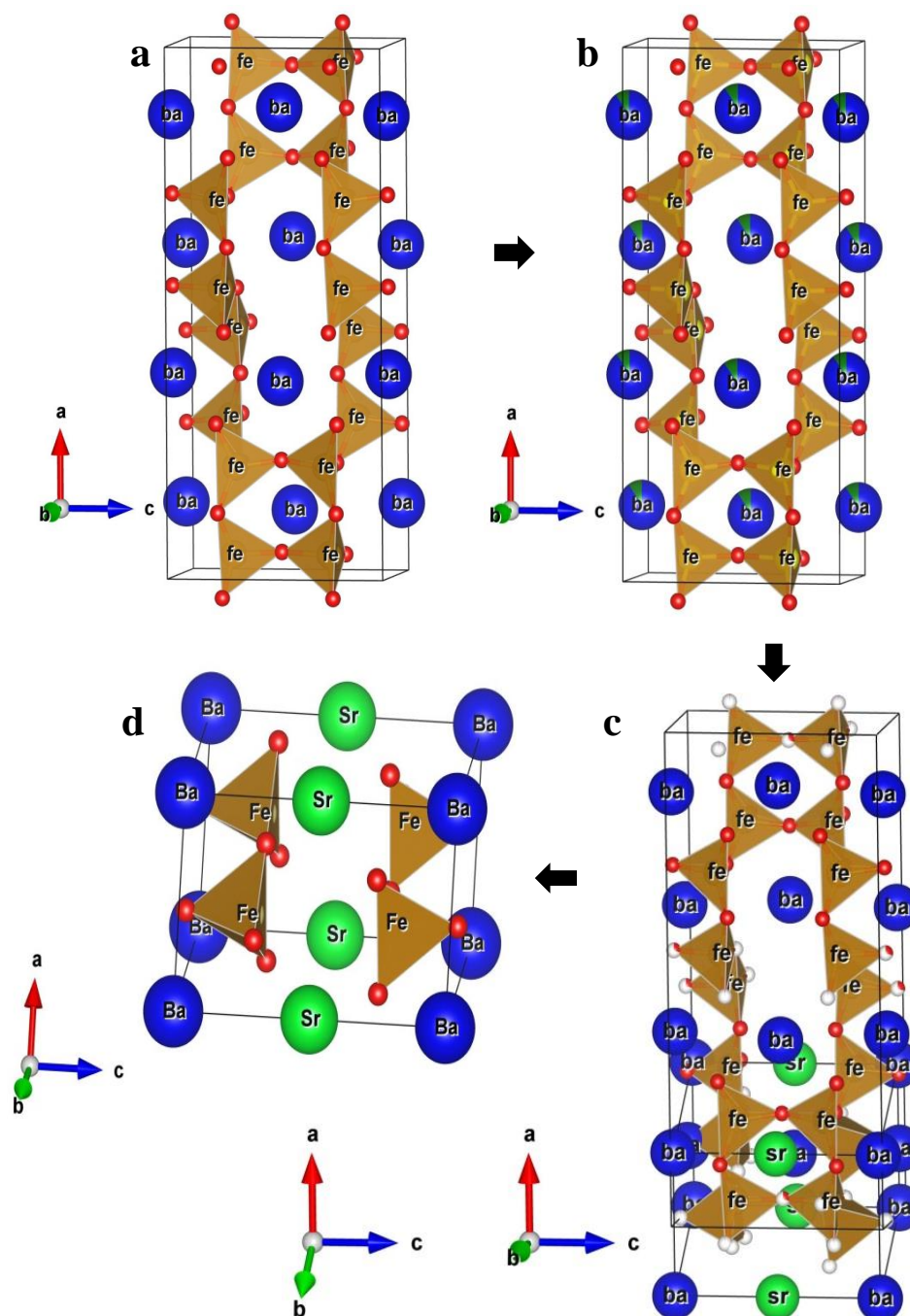


Figure 5. The gradual changes of the crystal structure from orthorhombic (space group $C m c 21$) into trigonal (space group $P -3 1 m$) in 3-dimensional form; (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.3$, and (d) $x = 0.5$

4. Conclusion

Referring to the the result of the X-ray diffraction pattern, it was known that the single phase of BaFe_2O_4 were successfully made by using solid state reaction method with High Energy Milling in the composition of $x = 0$ and 0.1 . Due to the Rietveld refinements using GSAS software, it was observed that there was a gradual decrease for lattice parameters of BaFe_2O_4 phase align with the increasing contain of Strontium (Sr^{2+}) which influenced the value of the cell volume and the density. It was also found that in the composition of x 0.3 the presence of $\text{BaSrFe}_4\text{O}_8$ phase was begin to form due to to the overload expansion of the Sr^{3+} cations and fully formed in the composition of $x = 0.5$.

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