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Magnetic, gas sensing properties, and structural parameters of barium–calcium hexaferrite synthesized by sol-gel auto combustion method

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Abstract

Sol-gel combustion method has been used to obtain nano-sized particles of barium–calcium hexaferrite $\text{Ba}_{1-x}\text{Ca}_x\text{Fe}_{12}\text{O}_{19}$ ($0 \leq x \leq 1$). The dried gel samples were calcined at 950°C for 4.5 hr. The phase evaluation and microstructure of calcined samples were investigated by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) techniques, respectively. The result revealed the formation of barium–calcium hexaferrite phase with a small amount of hematite as a secondary phase. There is a variation of particle size from 20 to 500 nm and a combination of plates-like hexagonal and spherical morphology of particles for synthesized samples. The measured magnetic properties of synthesized samples, using a vibrating sample magnetometer (VSM), revealed that the sample synthesized with $x = 0.4$ exhibited the lowest level of magnetization saturation in comparison with others, which can be due to the heterogeneity of the structure and the presence of nonmagnetic phases such as BaFe_2O_4 and Fe_2O_3 . The obtained results of sensory tests in acetone gas showed that the barium–calcium hexaferrite sample with $x = 0.2$ exhibits the highest sensitivity ($S = 0.57$) and shortest response time ($t_r = 20$ s) under the conditions of 900 ppm of concentration and 300°C of temperature, although the recovery time is long.

KEYWORDS

barium-calcium hexaferrite, gas sensor, sol-gel auto combustion

1 | INTRODUCTION

Various oxide semiconductor-based gas sensors have been used to detect harmful and toxic gases such as methane, ethane, and hydrogen sulfide.^[1] Metal organic frameworks (MOFs) are another promising materials with unique properties, such as large specific surface area, high porosity, adjustable pore sizes, and excellent flexibility. MOFs have potential application prospects in various fields, such as gas storage and separation,

chemical sensing, catalysis, adsorption, and biomedicine.^[2] The most common conventional sensor materials, that have been widely explored to find new functionalities of relationship between electrical resistance and change in chemical composition,^[3] are SnO_2 , ZnO , TiO_2 ,^[4] WO_3 ,^[5] In_2O_3 ,^[6] and Fe_2O_3 exhibiting n-type oxide semi conductivity. Owing to the significance of gas sensing of non-conventional sensors, various complex oxide-based (e.g., spinel ferrite, perovskite, etc.) sensors have been studied in last few years.^[1] These types of sensors have

the ability to adjust the electrical resistance value and the type of conductivity (n and p) by changing the cation composition, stoichiometry, and annealing conditions. In recent years, due to environmental pollution and health concerns, extensive research activities are devoted toward finding newer, more efficient, and low-cost sensing techniques for detecting specific gases/vapors. Recently, hard and soft ferrites and their composites with significant potential applications in gas and humidity sensors have been developed.^[3] These sensors are inexpensive and very sensitive to a wide range of reducing gases, but the majority of them suffer from disadvantages such as lack of selectivity for a particular gas in the mixture of gases and limited detection capability in high concentration ranges.^[7,8] Ferrite sensors based on BaFe₁₂O₁₉, BaFe₂O₄, CaFe₂O₄, LaFeO₃, GdFeO₃, and NiFe₂O₄ are more sensitive to a specific gas (both toxic and flammable gases).^[9–15] Hexaferrites such as BaFe₁₂O₁₉ are ferromagnetic compounds with a magnetoplumbite structure, crystalline anisotropy along the c-axis, high coercive force, excellent chemical stability, and high corrosion resistance.^[4] Barium ferrites play an important role in such applications as high-density recording media, ferro-fluids, catalysts, microwave devices, and gas sensors. There are various methods for the synthesis of hexaferrites including hydrothermal,^[16] co-precipitation,^[17] molten salt,^[18] sol-gel,^[19–23] self-combustion sol-gel,^[24–27] and solid-state reaction processes.^[11,15,28] Among these, the self-combustion sol-gel method has the advantages of the product with high purity, small particle size, and high homogeneity, as well as the ability to control the chemical and phase composition.

In studies of the synthesis of barium hexaferrites by combustion sol-gel method, the effects of various parameters including molar ratio of citric acid to nitrate (barium nitrate + iron nitrate + metal nitrate related to alternative cation),^[29] pH changes,^[3] sintering temperature,^[30] the molar ratio of iron to barium,^[31] and the substitution of barium cations with different cations such as La, Pr, Ti, Co, Bi, Ni, Cr, Cs, Mg, Zn, and Sn^[32–34] on physical, magnetic, and sensing properties have been investigated. However, limited studies have been performed on the substitution of barium cation in barium hexaferrite with calcium and its effect on changes in magnetic and especially in gas sensing properties.^[19,23,24] The aim of this study is to investigate the effect of Ca²⁺ cation substitution in different ratios ($0 \leq x \leq 1$) in barium-calcium hexaferrite Ba_{1-x}Ca_xFe₁₂O₁₉ structure by self-combustion sol-gel method on phase composition, microstructure, magnetic properties, and gas sensing properties.

2 | EXPERIMENTAL PROCEDURE

2.1 | Materials and synthesis

In this study, the raw materials including iron nitrate (Fe(NO₃)₃·9H₂O ≥ 99%), barium nitrate (Ba(NO₃)₂ ≥ 99%), calcium nitrite (Ca(NO₃)₂·4H₂O ≥ 99%), citric acid (C₆H₈O₇ ≥ 99%), and ammonia solution (NH₄OH ≥ 99%) were acquired from Merck company. To investigate the effects of doped calcium on structural parameters and magnetic and gas sensing properties of barium hexaferrite, the barium-calcium hexaferrite combination with the Ba_{1-x}Ca_xFe₁₂O₁₉ composition, where x = 0, 0.2, 0.4, 1 in molar ratio, were prepared by the sol-gel auto combustion method as presented in Table 1.

At the first stage, stoichiometric amounts of nitrate precursors were dissolved together in an appropriate amount of distilled water at 50°C under stirring to obtain a clear solution. Then, citric acid, with the molar ratio of total metal salts and citric acid equal to 1:1, was added to the resulting solution. In order to adjust the pH at 7, ammonia was slowly added to this solution. While the solution is stirred, it was heated at 80°C for about 2 hr until a reddish-brown gel was formed. The obtained gel was heated at 120°C for 20 hr to evaporate the solvent water. The dried gel was ignited (self-combustion process) by increasing the temperature up to 330°C to form a puffy brown powder. Ignited powder was calcined at 950°C during 4.5 hr to form the desired phase of barium-calcium hexaferrite. The sequence of synthesis steps is illustrated in Figure 1.

2.2 | Characterization

The phase identification of calcined gel was performed using X-ray diffraction (XRD-Aw-Xdm300, λ_{Cu} Kα = 1.5406 Å, 2θ = 20–90). The relative abundance of phases, the average crystallite size, and change in particle size and lattice parameter by replacing barium with calcium cations were obtained by XRD data and the Williamson-Hall formula Equation (1).

$$\beta \cos \theta = (0.89 \lambda / d + a \sin \theta) \quad (1)$$

In the above equation, λ: the radiation X-ray wavelength, d: the size of the crystal grain, β: the peak width at its half-height (in radian), and θ: the Bragg angle. Field-emission scanning electron microscopy, FE-SEM (Tescan, MiraIII, 20Kv, Czech), is used for microstructural observation. Magnetic properties were measured by a vibrating sample magnetometer (VSM, Magnetic

TABLE 1 Raw materials used in preparing 5 g batches with specified values of x

Sample no.	Starting material	$\text{BaFe}_{12}\text{O}_{19}$	$\text{Ca}_{0.2}\text{Ba}_{0.8}\text{Fe}_{12}\text{O}_{19}$	$\text{Ca}_{0.4}\text{Ba}_{0.6}\text{Fe}_{12}\text{O}_{19}$	$\text{CaFe}_{12}\text{O}_{19}$
		x = 0	x = 0.2	x = 0.4	x = 1
1	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	21.77	22.14	22.55	23.85
2	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	-	0.21	0.436	4.97
3	$\text{Ba}(\text{NO}_3)_2$	1.17	0.995	0.72	-
4	$\text{C}_6\text{H}_8\text{O}_7$	11.13	11.328	11.52	15.36

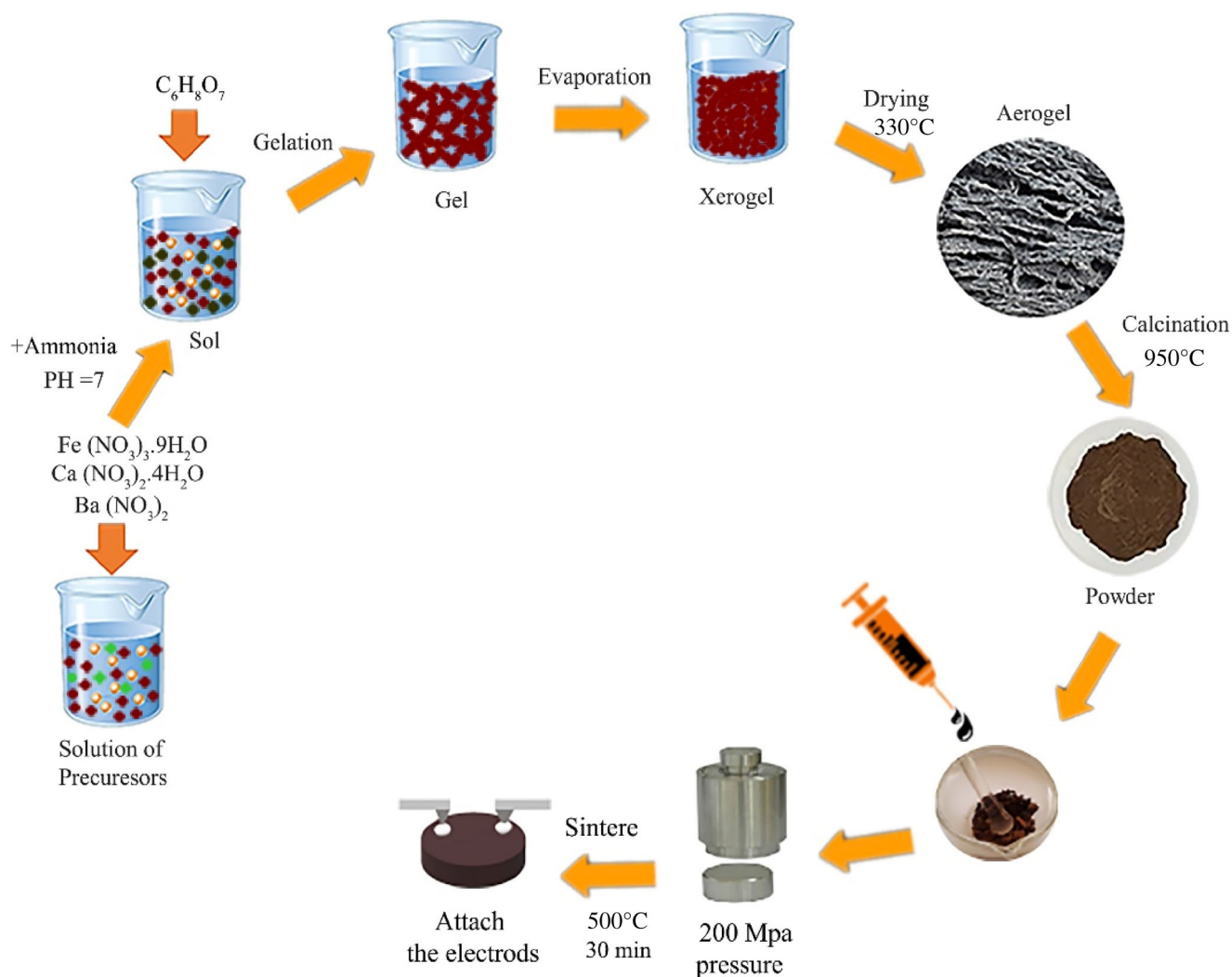


FIGURE 1 Schematic representation of the sol-gel synthesis process used in this study

Daghigh Danesh pajouh, Iran) with a maximum applied magnetic field of 1.5 T. Temperatures of physical and chemical changes performed in the dried gel during heat treatment up to 1,200°C with heating rate of 20°C/min under air atmosphere were determined by simultaneous thermogravimetry/differential thermal analysis technique (DTA, STA504, Bahr, Germany, 1,700°C).

2.3 | Gas sensor tests

The synthesized powders with required amount of glycine were mixed and pressed under pressure 200 MPa to form a disk with a diameter of 11 mm and a thickness of 2 mm. The discs were sintered at 500°C for 30 min. Using pure silver paint, the copper electrodes

were placed on the disc surface at a distance of 0.5 cm. In order to establish a good electrical connection of the electrodes, the sensor specimens were annealed for 15 min at 300°C. The sensor specimen was inserted inside the device chamber (designed by the researchers of this study) at room temperature with an atmosphere of air. The measurements were performed using a gaseous mixture of acetone and argon with a desired concentration of acetone (450–1,350 ppm) at different temperatures of 200–300°C. Due to the reaction between the sample surface and the test gas, the electrical resistance of the sensor specimen is changed. This change in electrical resistance, considered as the sensor response, is measured by an electrical circuit (Fluke 289 digital multimeter). The sensitivity of the sample to acetone gas was calculated using Equation (2), where R_a is the sensor electrical resistance in air and R_g is the sensor electrical resistance in acetone gas.

$$S = 100 \times (R_a - R_g) / R_a \quad (2)$$

3 | RESULTS AND DISCUSSION

3.1 | DTA analysis

The thermal analysis curve (DTA) for combusted gels of $Ba_{1-x}Ca_xFe_{12}O_{19}$ with $x = 0, 0.2, 0.4, 1$ is shown in Figure 2. The DTA results for $x = 0$ show an endothermic peak at around 100°C associated with weight loss of the sample that could be attributed to the dehydration of the absorbed water.^[27] The positive slope of the DTA curve in the temperature range 150–550°C is related to the continued combustion of citric acid.^[3] For samples from $x = 0$ to $x = 0.4$, in the temperature range 600–800°C, an endothermic peak is observed that is related to the formation of barium–calcium spinel ferrite as a result of the diffusion phenomenon of iron and barium cations into oxide structures.^[3] As the percentage of doped calcium increases, the formation temperature of calcium–barium spinel ferrite is increased from 600°C for $x = 0$ to 1, 150°C for $x = 1$ indicating a harder diffusion conditions of three cations Ca^{2+} , Ba^{2+} , and Fe^{3+} for formation of double spinel of barium–calcium ferrite compared

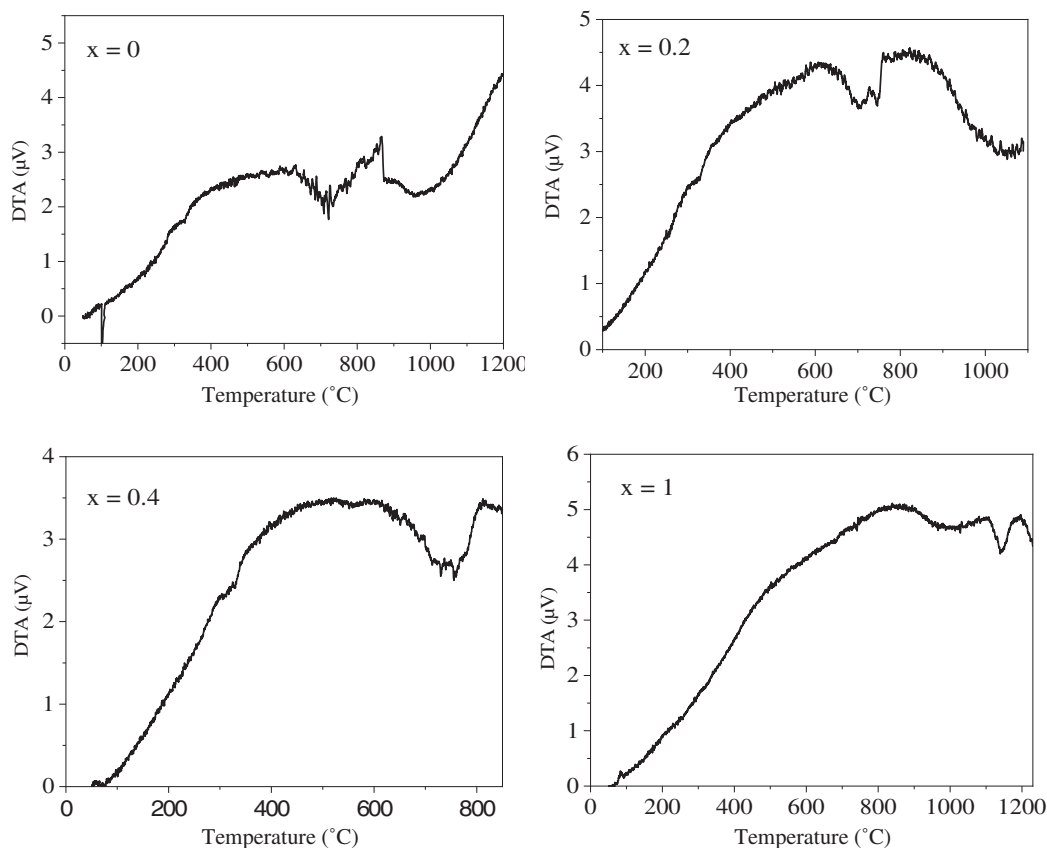


FIGURE 2 Differential thermal analysis (DTA) versus temperature for $Ba_{1-x}Ca_xFe_{12}O_{19}$ ($0 \leq x \leq 1$) samples

to barium hexaferrite.^[24] On the other hand, with increasing the percentage of calcium, the depth of peaks related to spinel formation decreases indicating less formation of barium–calcium hexaferrite and gradual appearance of independent calcium ferrite compounds as shown by the results of X-ray diffraction (Figure 3, $x = 1$). For the sample with $x = 1$, calcium hexaferrite, $\text{Ca}_2\text{Fe}_7\text{O}_{11}$, is one of the most important phases corresponding to endothermic peak at temperature of $1,100^\circ\text{C}$ (Figure 3, $x = 1$). However, various compounds of calcium ferrite were appeared; the most important phase is CaFe_2O_4 corresponding to a large exothermic peak with relatively high intensity at 900°C (Figure 3, $x = 1$).

3.2 | XRD analysis

Figure 3 shows the XRD patterns of calcined powders at 950°C for 4.5 hr. The results of XRD analysis reveal the existence of Fe_2O_3 , CaFe_2O_4 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, BaFe_2O_4 , and

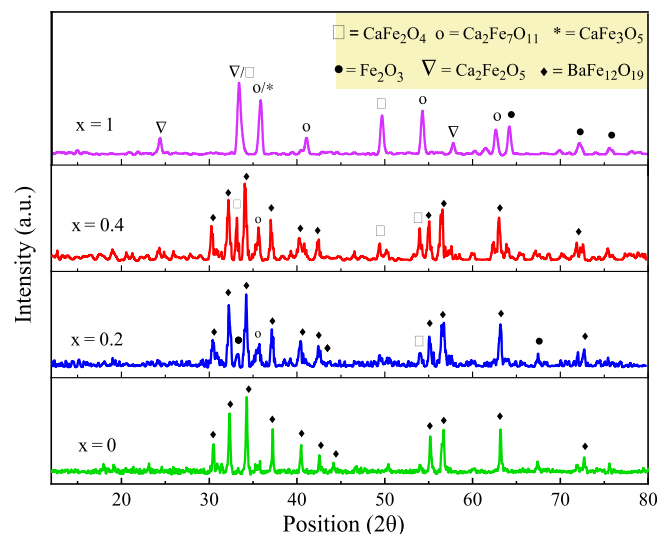


FIGURE 3 X-ray diffraction (XRD) patterns of the calcined samples

$\text{BaFe}_{12}\text{O}_{19}$ phases for different synthesized samples of $\text{Ba}_{1-x}\text{Ca}_x\text{Fe}_{12}\text{O}_{19}$ (From $x = 0$ to $x = 1$). The presence of small amounts of impurity phases such as Fe_2O_3 and $\text{Ca}_2\text{Fe}_2\text{O}_5$ for samples from $x = 0$ to $x = 0.4$ indicates the optimal formation of barium spinel ferrite and calcium–barium spinel ferrite. Most of the diffracted peaks in these samples are similar to the barium hexaferrite sample except that, diffracted angles have a slight deviation, and all of the peaks are slightly shifted to the right. It should be noted that the ionic radius of calcium is less than barium, so the substitution of barium with calcium cations reduces the distance between the atomic plates. Therefore, according to the Bragg relation, $2d\sin\theta = \lambda$, by decreasing the distance between the atomic plates (d), we will have an increase in the angle of diffraction (θ) resulting a displacement and shift of the peaks to the right. Moreover, by substituting barium with calcium cations, a shrinkage strain is created in the crystal lattice by cooling the sample from the sintering temperature, and it increases from $x = 0$ to $x = 0.4$. The parameters and volume of lattice for all samples from $x = 0$ to $x = 0.4$ are given in Table 2. According to the results in Table 2, by substitution of barium with calcium, the lattice parameter “ a ” remains nearly constant, while the lattice parameter “ c ” is decreased due to the smaller ion radius of calcium ($0.99 \text{ \AA}$) in comparison with the barium ion radius ($1.34 \text{ \AA}$) and thus resulting in reduction of unit cell volume. As a result, the reduction of the lattice parameter and the volume of cell in conjunction with the deviation of the scattering angles indicate doping of calcium ions into the barium hexaferrite lattice which has been confirmed in another research work.^[29] Furthermore, according to the Table 2, by increasing the amount of calcium cations in the barium ferrite lattice, the crystalline grains size is decreased. As you can see in X-ray diffraction graph (Figure 3), by increasing the calcium concentration, the solubility of Ca ions into the hexagonal lattice was reduced resulting, the appearance of second phases and prohibiting the grain growth.^[20]

According to the results of X-ray diffraction (Figure 3), for the sample with $x = 1$, calcium ferrite

TABLE 2 - Lattice parameters for $\text{Ba}_{1-x}\text{Ca}_x\text{Fe}_{12}\text{O}_{19}$ with $x = 0, 0.2, 0.4$

Sample	Chemical composition	Lattice parameter ($\text{\AA}$)		Volume ($\text{\AA}^3$)	Crystallite size (nm)
		c ($\text{\AA}$)	a ($\text{\AA}$)		FE-SEM
-	$\text{BaFe}_{12}\text{O}_{19}$ JCPDS reference card #078-0133	5.8650	23.000	688.11	-
$x = 0$	$\text{BaFe}_{12}\text{O}_{19}$	5.8739	23.0520	689.4739	80.33
$x = 0.2$	$\text{Ba}_{0.8}\text{Ca}_{0.2}\text{Fe}_{12}\text{O}_{19}$	5.8772	23.0469	687.62	69.39
$x = 0.4$	$\text{Ba}_{0.6}\text{Ca}_{0.4}\text{Fe}_{12}\text{O}_{19}$	5.6734	23.0386	694.74	66.53

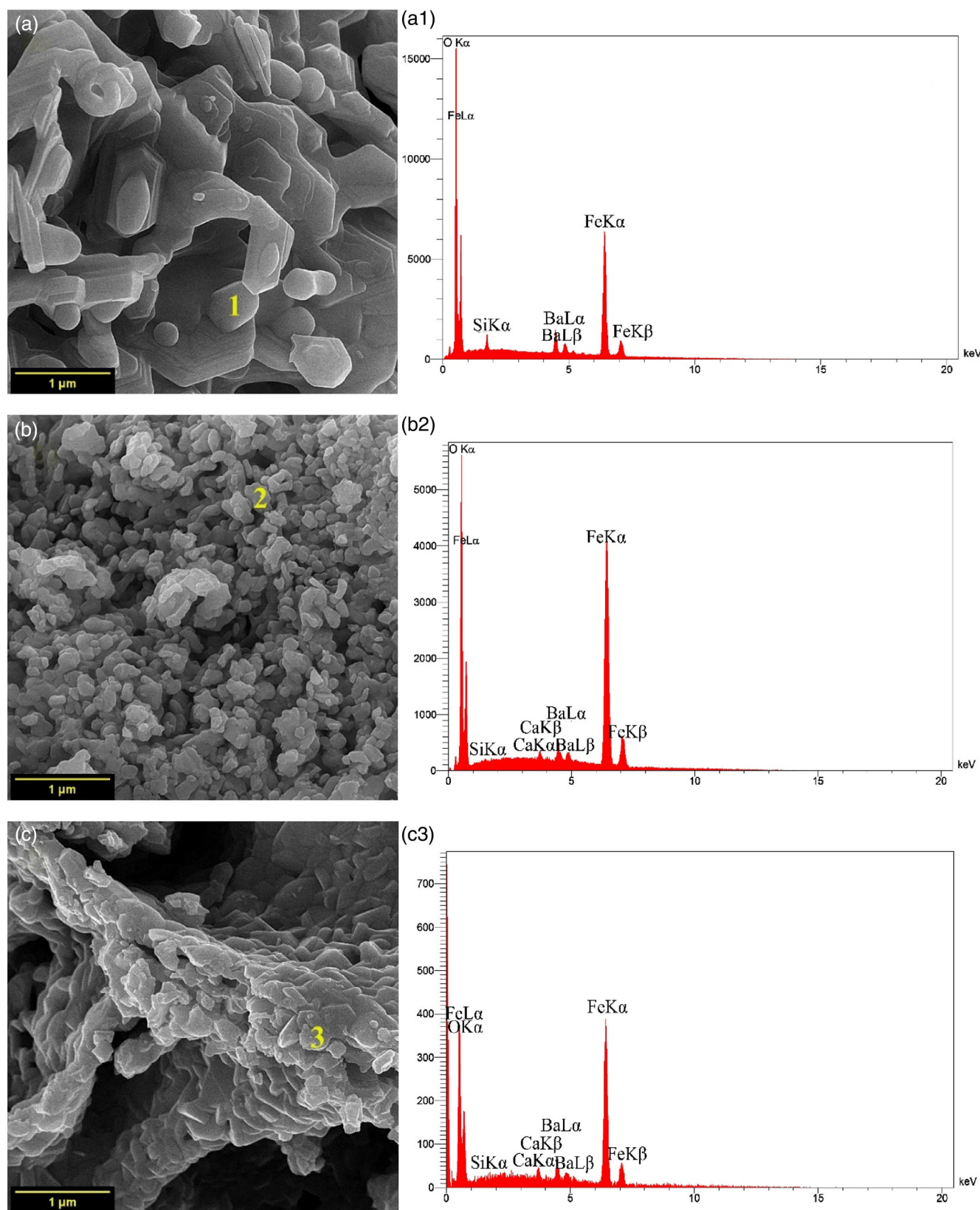


FIGURE 4 Field-emission scanning electron microscopy (FE-SEM) images and energy-dispersive X-ray spectroscopy (EDS) pattern for samples of synthesized barium-calcium ferrite ($\text{Ba}_{1-x}\text{Ca}_x\text{Fe}_{12}\text{O}_{19}$) where (a) $x = 0$, (b) $x = 0.2$, and (c) $x = 0.4$

Elemental composition evaluated from (molar ratio percentage)	Fe	Ba	Ca
Stoichiometry composition			
Ba Fe ₁₂ O ₁₉	37.5	3.12	-
Ba _{0.8} Ca _{0.2} Fe ₁₂ O ₁₉	37.5	2.5	0.62
Ba _{0.6} Ca _{0.4} Fe ₁₂ O ₁₉	37.5	1.87	1.25
EDS			
Point1	32.28	2.46	-
Point2	46.08	1.98	0.63
Point3	38.69	2.06	0.97

TABLE 3 Elemental composition of synthesized nanoparticles Ba_{1-x}Ca_xFe₁₂O₁₉ with x = 0, 0.2, 0.4 as evaluated from stoichiometry composition and energy-dispersive X-ray spectroscopy (EDS)

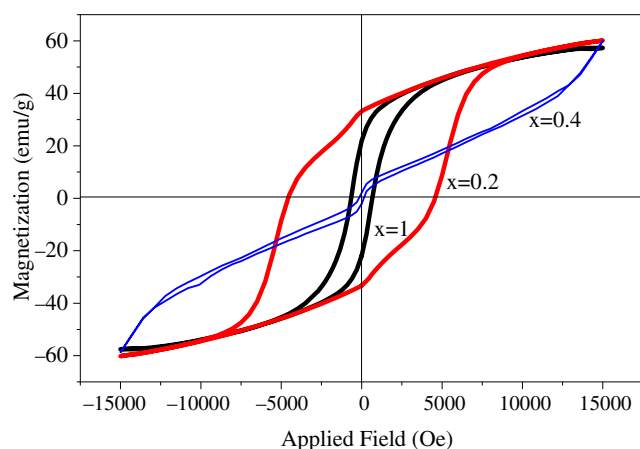


FIGURE 5 Hysteresis loops for compositions Ba_{1-x}Ca_xFe₁₂O₁₉, with x = 0, 0.2, 0.4 at room temperature

TABLE 4 Magnetic properties of Ba_{1-x}Ca_xFe₁₂O₁₉ with x = 0, 0.2, 0.4

Sample	M _s (emu/g)	M _r (emu/g)	H _c (Oe)	M _r /M _s
x = 0	60.1	33.3	45,000	0.55
x = 0.2	57.3	21.8	450	0.38
x = 0.4	1.07	0.09	100	0.08

spinel's of CaFe₂O₄, CaFe₃O₅, Ca₂Fe₇O₁₁, and CaFe₃O₅ with some hematite phases are observed as impurities, while the calcium hexaferrite compound (CaFe₁₂O₁₉) should be formed. In other words, calcium and iron oxides are not able to form M-type calcium hexaferrite spinel, which can be due to differences in the parameters of their crystal structures. It should be noted that the formation temperature of calcium hexaferrite is higher than 1,150°C (Figures 3 and 4). Some research results have shown that the presence of lanthanum oxide facilitates the formation of calcium hexaferrite at lower temperatures and stabilizes it.^[24]

3.3 | Microstructural observations

Figure 4 illustrates the FE-SEM images for samples of synthesized barium-calcium ferrite (Ba_{1-x}Ca_xFe₁₂O₁₉, x = 0, 0.2, 0.4). It is observed that for all samples, there is a variation of particle size from 20 to 500 nm and a combination of hexagonal and spherical morphology of particles (Figure 4a-c). For x = 0 sample, the presence of plates-like hexagonal grains with sharp edges is more obvious relating to M-type ferrite (Figure 4a). For calcium-doped specimens, a distribution of spherical and fine particles is predominant (Figure 4b,c). It should be mentioned that during the combustion process, a large amount of gaseous material is formed leading to the microporous agglomerates. Indeed, the high specific surface area of the synthesized powder causes agglomeration of the powder. The result of energy-dispersive X-ray spectroscopy (EDS) analysis for different ferrite samples shows that, the atomic ratio of iron, barium, and oxygen for the sample of x = 0 has a good approximate correspondence with compound BaFe₁₂O₁₉ (point 1) and the atomic ratio of iron, barium, calcium, and oxygen for the sample of x = 0.2 and 0.4 have a good approximate correspondence with compounds of Ba_{0.8}Ca_{0.2}Fe₁₂O₁₉ (point 2) and Ba_{0.6}Ca_{0.4}Fe₁₂O₁₉ (point 3), respectively (Table 3).

3.4 | VSM measurements

The magnetic characteristics of Ba_{1-x}Ca_xFe₁₂O₁₉ (where x = 0, 0.2, 0.4) compounds were recorded at room temperature using a VSM at maximum magnetic field of 1.5 T. The magnetic hysteresis loops are shown in Figure 5. Magnetic characteristics including saturation magnetization (M_s), coercivity (H_c), and remnant magnetization (M_r) for all synthesized samples are extracted from the hysteresis loops and are summarized in Table 4. Saturation magnetization is influenced by different factors such as level of impurity phases (BaO, BaFe₂O₄,

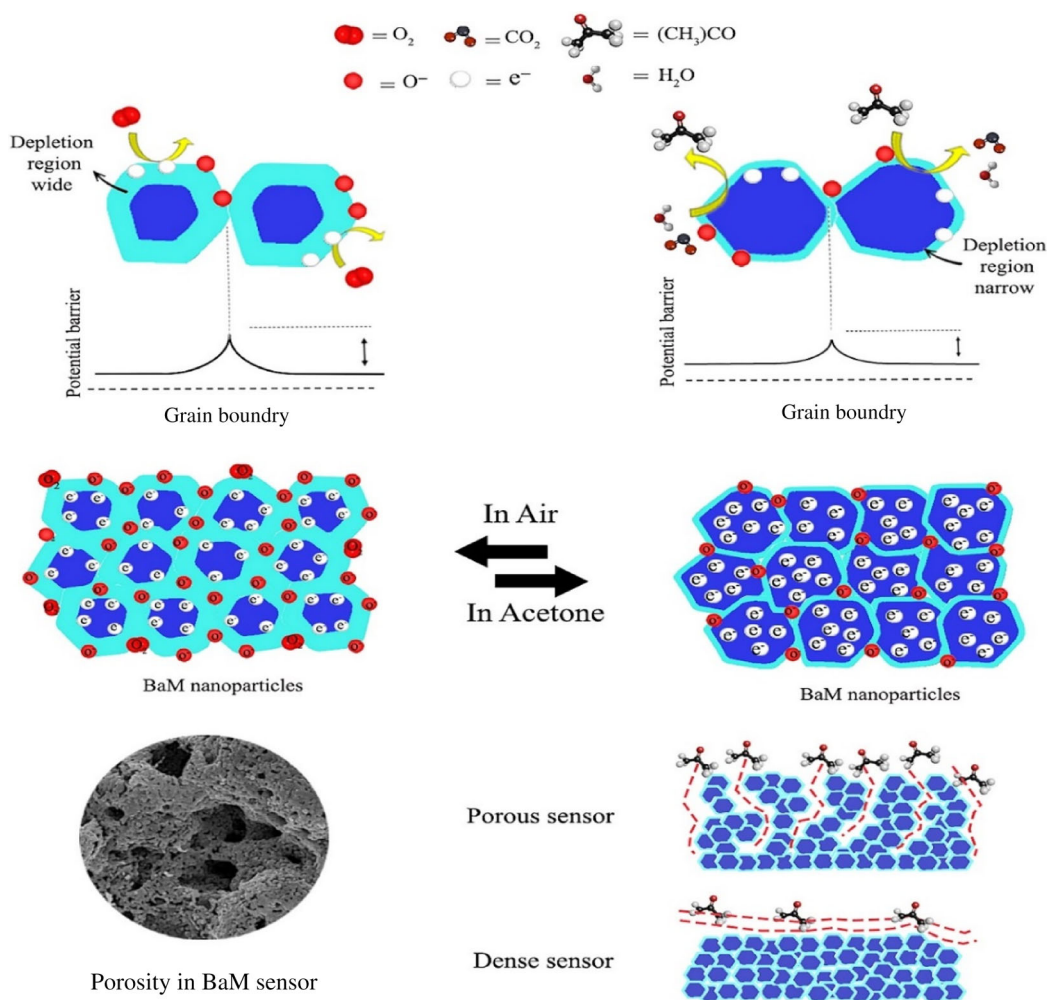


FIGURE 6 Schematic mechanism for the sensing of acetone over chemi-resistive semiconducting metal oxide-based sensors

$\alpha\text{-Fe}_2\text{O}_3$, CaFe_2O_4 , ...),^[3] type of bond between particles or agglomerates,^[16] degree of homogeneity or heterogeneity, particle distribution,^[30] crystal grain size, and replacement of Fe or Ba ions with impurity cations.^[28] The results of the magnetic data show that the saturation magnetization (M_s) increases with higher level of the spinel phase of barium ferrite and decreases with higher level of barium–calcium ferrite spinel and particularly, nonspinel compounds such as BaFe_2O_4 , $\alpha\text{-Fe}_2\text{O}_3$, and CaFe_2O_4 . Therefore, for the sample with $x = 0$ with the presence of 100% BaM phase, the highest value of M_s is obtained (Table 4 and Figure 5). On the other hand, increasing the value of x decreases the saturation magnetization due to the placement of calcium ions in places 2b and the lack of displacement of the walls of the magnetic fields in the direction of the applied field.^[19] Furthermore, increasing the amount of calcium (increasing the amount of x) increases the possibility of formation of

calcium ferrite compounds such as CaFe_2O_4 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, and CaFe_3O_5 , which are nonmagnetic and, for this reason, M_s for samples with $x = 1$ is the lowest, so that M_s is not even measurable. However, the amount of calcium compounds for the samples $x = 0.2$ and 0.4 is below 5% and does not appear in the XRD spectrum. Furthermore, substitution of barium ions with calcium ions reduces the super-exchange interactions of $\text{Fe}^{3+}\text{-O-Fe}^{3+}$, which in turn leads to a decrease in saturation magnetization.^[34] In fact, by substituting barium ions in barium hexaferrite with calcium ions, number of calcium ions occupy the positions of Fe^{3+} cations.^[35] Each trivalent iron ion has 5 unpaired electrons in its 3d orbital (5 μB magnetic moment), while calcium cations are nonmagnetic (0 μB), as a result, with the entry of calcium ions, the total number of single-electron spins upward and in the same direction decreases, and the interaction strength of the exchange cloud between Fe^{3+} and O^{2-} is decreased.

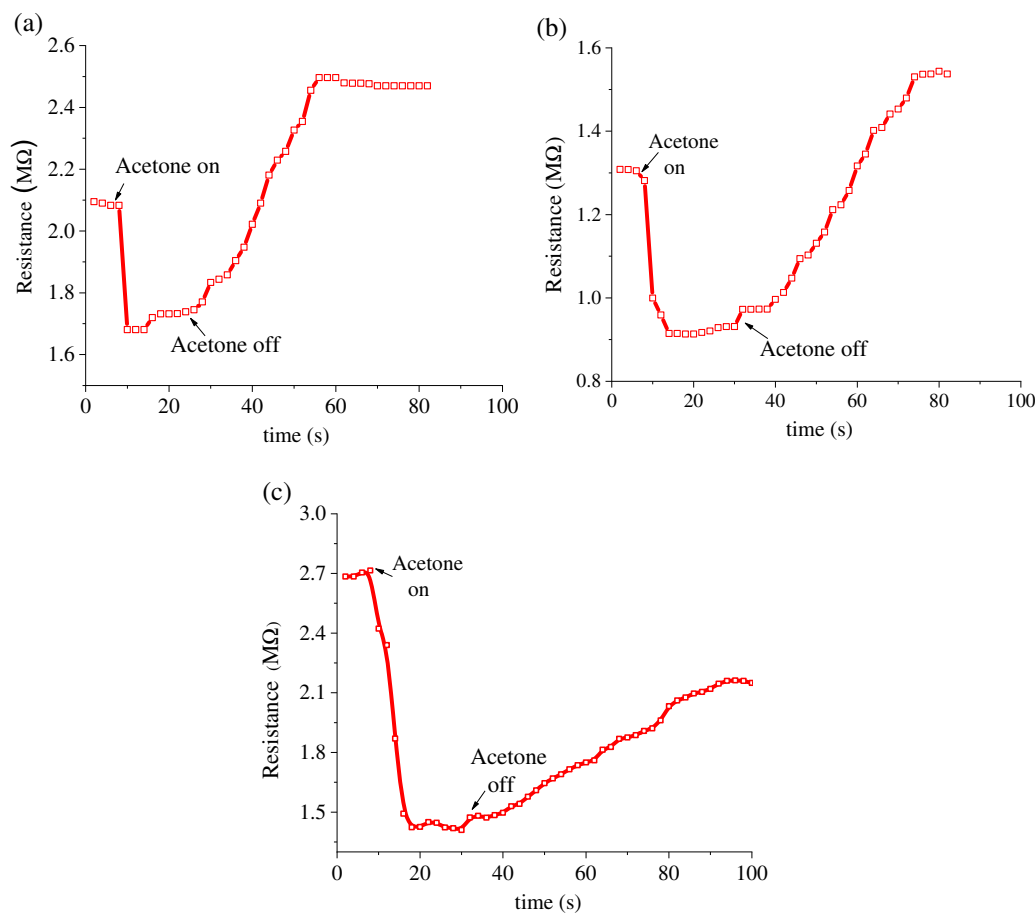
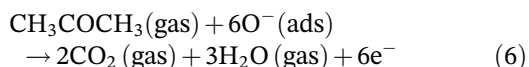
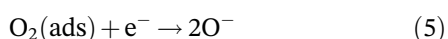
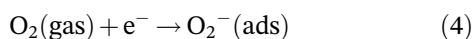
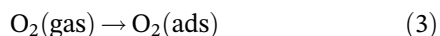


FIGURE 7 Response of barium ferrite sensor ($x = 0$) against acetone gas at 300°C with a concentration of (a) 450 ppm, (b) 900 ppm, and (c) 1,350 ppm

3.5 | Gas sensing mechanism

When the sensing elements are kept in air at elevated temperature, oxygen is chemi-adsorbed by accumulating electrons from the sensor surface. Reducing gases in contact to the surface containing chemisorbed oxygen (O^- , O_2^- , $\text{O}_2^{\cdot-}$) anions is oxidized and leaving the electron to the conduction band of the sensing material resulting in an increase in electrical resistance of the sensor. Acetone oxidized into carbon monoxide or carbon dioxide and leave the sensor surface during recovery. Thus, resistance of the sensors changed and the sensors responded to the target gas. The following equations (3)–(6) describe the reactions:



The good conductivity of sensor depends on porous nanostructure observed here that is likely to be the result of two factors. The porous structure promotes the diffusion of gas molecules from outside to the internal and made them efficiently react with the absorbed oxygen species. Furthermore, the crystalline size is very important to sensing gas when crystalline size is small the surface of crystalline become significantly more active and likely to absorb oxygen and form ionized oxygen species. The sequential sensing phenomenon and the corresponding change of sensor resistance during detection of acetone over chemi-resistive type Sensors have been illustrated schematically in Figure 6.

3.6 | Gas sensing properties

The sensor characteristics of $\text{Ba}_{1-x}\text{Ca}_x\text{Fe}_{12}\text{O}_{19}$ ($x = 0, 0.2, 0.4$) at different concentrations (450, 900, 1,350 ppm) and different temperatures ($200, 300^{\circ}\text{C}$) were tested upon exposure to acetone gas.

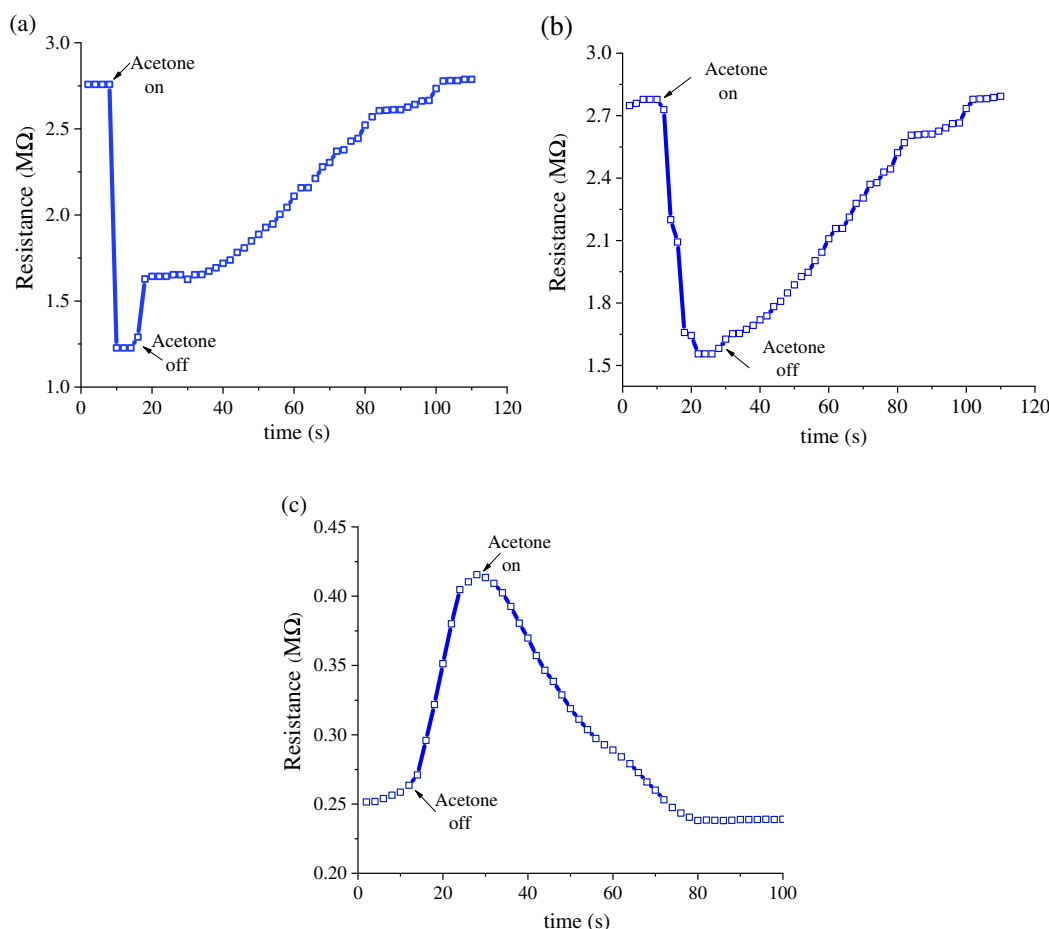


FIGURE 8 Response of calcium-barium ferrite sensor ($x = 0.2$) against acetone gas at 200°C with a concentration of (a) 450 ppm, (b) 900 ppm, and at 300°C with concentration of (c) 900 ppm

TABLE 5 Gas sensing parameters for $\text{Ba}_{1-x}\text{Ca}_x\text{Fe}_{12}\text{O}_{19}$ samples with different values of x

Sample	Temp ($^{\circ}\text{C}$)	Sensitivity	Response time (s)	Concentration (ppm)	Recovery time (s)	Crystallite size (nm)
$x = 0$	300	0.13	8	450	29	80.33
	300	0.307	24	900	33	
	300	0.481	22	1,350	56	
$x = 0.2$	200	0.53	2	450	80	69.39
	200	0.28	11	900	75	
	300	0.57	15	900	43	
$x = 0.4$	200	-	-	450	-	66.53
	300	-	-	900	-	

The results show that the sample with $x = 0$ sensory sample at temperature 200°C does not show any response in the presence of acetone gas for any of the concentration values from 450 to 1,350 ppm due to insufficient temperature for acetone gas molecules to react with the sensor surface. The gas molecules at a temperatures below a critical limit do not have enough thermal energy

to produce the chemi-adsorbed oxygen species O_2 on the surface of sensor material decreasing the adsorption-desorption surface reaction rate and resulting in a lower sensory response.^[36]

At temperature of 300°C and a concentration of 450–1,350 ppm (Figure 7a–c), the $x = 0$ sample shows good reversibility, which indicates the physical adsorption of

TABLE 6 Comparison for the gas sensing characteristics of synthesized barium calcium hexaferrite sensing elements with other reported sensors

Sensing material	Vapor	Temp (°C)	Sensitivity %	Response time (s)	Concentration (ppm)	Recovery time (s)	References
BaO ₆ Fe ₂ O ₃	Acetone	325	19	□26	20	□80	[37]
	Ethanol	375	35	□37	20	□130	
BaCa ₂ Fe ₁₆ O ₂₇	Ethanol	300	55	-	100	150	[22]
CaFe ₂ O ₄	Ethanol	200	41.3	240	100	1800	[12]
Gd _{0.9} Ca _{0.1} FeO ₃	Ethanol	260	117	48	600	66	[9]
Ca _{0.2} Ba _{0.8} Fe ₁₂ O ₁₉	Ethanol	300	0.57	15	900	43	This work

gas molecules on the sensor surface. Hence, after removing the gas, weak bonds are easily broken and the electrical resistance of sensor returns to its base state. For the $x = 0.2$ sample (Figure 8a–c), the sensor behavior at 200°C in concentration of 450 ppm (Figure 8a) shows lowest response time with good reversibility, which is different by 300°C for a concentration of 900 ppm (Figure 8c) of acetone gas. The sensor surface of $x = 0.2$ sample at 300°C and 900 ppm in the presence of acetone gas (Figure 8c) shows an increased electrical resistance and exhibits a p-type semiconductor behavior.^[11] In fact, the absorption of gas increases the functional groups on the surface of the sensor (OH, O₂, NH, and CH) as a result of the interaction of the sensor surface with oxygen and nitrogen in the air and act as electron donors.^[14] While at 200°C, the sensor behaves as n-type, and its electrical resistance decreases during sensor testing. For $x = 0.2$ and concentration of 900 ppm, the level of electrical resistance values at 300°C is lower resulting a higher electrical conductivity in comparison with 200°C. Therefore, the response time of the sensor for the sample $x = 0.2$ at 300°C (40 s) is significantly shorter than 200°C (20 s), (Figure 8a,b) also the recovery time at 200°C is relatively longer (75 s) in comparison with 300°C (43 s). Owing to smaller size of crystallites gives and therefore the larger surface area for the $x = 0.2$ sample Compared to the $x = 0$ sample, there is a more chemi-adsorbed oxygen and a stronger oxidizing of acetone to water vapor and CO₂.^[36] Thus, the barium–calcium ferrite sample ($x = 0.2$) shows a relatively shorter response time than the barium ferrite sample under similar conditions. The results of sensory analysis of samples with different values of x are given in Table 5.

According to the results of sensory analysis of samples with different values of x (Table 5), with increasing the amount of calcium to $x = 0.2$, the sensitivity of the sensor is increased. For the sensor sample with $x = 0.4$, despite the smaller size of the crystals, there is not any response and any electrical resistance variation in all test conditions.

As mentioned before, by increasing the amount of calcium (increasing the amount of x), the possibility of formation of calcium ferrite compounds such as CaFe₂O₄, Ca₂Fe₂O₅, and CaFe₃O₅ is increased although, the X-ray spectrum does not show them (the values of the compounds are less than the detection limit). The research results have shown that the sensory property of hexaferrites is significantly reduced by the above compounds and weakening of hexaferrite structure.^[22] The acetone and ethanol sensing characteristics include sensitivity, response, and recovery time, operating temperature, and optimum ppm concentration for Barium calcium hexaferrite (current work) have been compared with a few other materials obtained previous works (Table 6). As you see in this table barium–calcium hexaferrite has lowest response and recovery time in comparison with other elements.

4 | CONCLUSIONS

1. For all samples of Ba_{1-x}Ca_xFe₁₂O₁₉, except $x = 1$, the barium hexaferrite phase is the main phase and with increasing the amount of calcium, the diffraction angles in the XRD spectrum shift slightly to the right.
2. With increasing the value of x in Ba_{1-x}Ca_xFe₁₂O₁₉, the formation temperature of spinel phase (type M) increases from 600°C for $x = 0$ to 1,150°C for $x = 1$.
3. For $x = 1$ sample, the spinel phase of calcium–barium hexaferrite is slightly formed and the main phases are CaFe₂O₄, CaFe₃O₅, and Ca₂Fe₂O₅. In other words, calcium and iron oxides are not able to form M-type calcium hexaferrite.
4. The formation of BaFe₁₂O₁₉Ba_{0.8}, Ca_{0.2}Fe₁₂O₁₉, and Ba_{0.6}Ca_{0.4}Fe₁₂O₁₉ as a type M hexaferrite is confirmed by the result of EDS analysis.
5. Microstructural observations show a variation of particle size from 20 to 500 nm and a combination of plate-like hexagonal and spherical morphology of particles. Increasing the molar ratio of calcium from

$x = 0$ to $x = 0.4$, the presence of plate-like hexagonal grains is reduced.

6. By increasing the molar ratio of calcium from $x = 0$ to $x = 0.4$ in barium–calcium hexaferrite sample, the saturation magnetization (M_s) is decreased from 60.1 to 1.07 emu/g, the residual magnetization (M_r) from 33.3 to 0.09 emu/g, and the coercive force (H_c) from 4,500 to 100 Oe. For the sample with $x = 1$, the magnetic response is so weak that M_s cannot be measured.
7. For similar conditions, the barium–calcium ferrite sample ($x = 0.2$) shows the shortest response time (20 s) and highest sensitivity ($S = 0.57$) against acetone gas with a concentration of 900 ppm at a temperature of 300°C; for this sensory sample, the response time of the sensor is increased to 40 s, and sensitivity is decreased to 0.28 by decreasing of temperature to 200°C.

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