Isovalent Substitution Effects of Arsenic on Structural and Electrical Properties of Iron-Based Superconductor NdFeAsO$_{0.8}$F$_{0.2}$

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Received: 9 January 2019 / Accepted: 3 July 2019

Abstract

We have studied the isovalent substitution of antimony (Sb) and phosphorus (P) for arsenic (As) in a nominal composition of NdFeAs$_{1-x}$M$_x$O$_{0.8}$F$_{0.2}$ (M = Sb and P) with $x = 0.0$, $0.05$. All samples were prepared by one-step solid-state reaction method. The structural, electrical, and morphological properties of samples were characterized through XRD pattern, 4-probe method, and SEM, respectively. The isovalent doping changed the lattice parameters, the $\alpha$ and $\beta$ bond angles, and Fe-As bond length of crystal structure based on the Rietveld refinement of XRD patterns of samples. The microstrain and crystalline size of samples were studied by the Williamson–Hall method. The FeAs$_4$ tetrahedron changed from a regular shape with the isovalent substitution and it effected on the superconducting critical temperature. The superconducting critical temperatures were attained at 56 K and 46 K for NdFeAsO$_{0.8}$F$_{0.2}$ and NdFeAs$_{0.95}$Sb$_{0.05}$O$_{0.8}$F$_{0.2}$ and it suppressed for the NdFeAs$_{0.95}$P$_{0.05}$O$_{0.8}$F$_{0.2}$, respectively. The flake type of grains was observed by SEM pictures of samples.

Keywords Iron-based superconductor · Isovalent doping · Crystal structure · Williamson–Hall method

1 Introduction

For the first time in 2006, superconducting transition temperature ($T_C$) was observed in a new category of superconductors called iron-based superconductors (IBs), in pure and fluorine-doped LaOFeP at $T_C = 3.2$ K [1]. After, the report of superconductivity at 26 K in fluorine-doped LaFeAsO was registered as high-transition superconductors in IBs [2]. Because of the existence of vortices and $T_C$ in IBs, they are in unconventional superconductors and high-temperature superconductors, respectively [3].

IBs have some of the most important and unique characteristics such as parent material: antiferromagnetic metal, impurity robust $T_C$, multi-band nature of Fe-3d, small anisotropy, large upper critical field, and advantageous grain boundary nature [4].
The effects of chemical pressures and bond covalency due to isovalent substitution of P/As in LaFeAs1–xPbxO were investigated by Wang et al. [31]. In ref. [32], superconductivity emerges in the region of 0.2 < x < 0.4 with the maximum transition temperature $T_C = 10.8$ K for $x = 0.25$. In 2010, Wang et al. [33] studied the co-doping of Sb and F on the structural and superconducting properties of LaFeAs1–xSbxO1–yFy. They result that the Sb doping hardly influences the spin density wave (SDW) anomaly. In 2014, Ji et al. [26] reported the enhancement of superconductivity by Sb doping in the hole-doped iron-pnictide superconductor Pr1–xSrxFeAsO. They obtained that the lattice constants remain almost unchanged and contracted when the Sb and P are doped in this structure. Wang et al. [31] investigated the effect of chemical pressures and bond covalency in LaFeAs1–xPbxO by the isovalent substitution of P/As. In this work, superconductivity emerges in the region of 0.2 < x < 0.4 with the maximum $T_C = 10.8$ K for $x = 0.25$. In 2010, Wang et al. [33] studied the co-doping of Sb and F on the structural and superconducting properties of LaFeAs1–xSbxO1–yFy. They result that the Sb doping hardly influences the SDW anomaly. In 2014, Ji et al. [26] reported the enhancement of superconductivity by Sb doping in the hole-doped iron-pnictide superconductor Pr1–xSrxFeAsO. They obtained that the lattice constants remain almost unchanged and contracted when the Sb and P are doped in this structure. Wang et al. [31] reported the enhancement of superconductivity by Sb doping in the hole-doped iron-pnictide superconductor Pr1–xSrxFeAsO. They obtained that the lattice constants remain almost unchanged and contracted when the Sb and P are doped in this structure. Wang et al. [31] investigated the effect of chemical pressures and bond covalency in LaFeAs1–xPbxO by the isovalent substitution of P/As. In this work, superconductivity emerges in the region of 0.2 < x < 0.4 with the maximum $T_C = 10.8$ K for $x = 0.25$. In 2010, Wang et al. [33] studied the co-doping of Sb and F on the structural and superconducting properties of LaFeAs1–xSbxO1–yFy. They result that the Sb doping hardly influences the SDW anomaly. In 2014, Ji et al. [26] reported the enhancement of superconductivity by Sb doping in the hole-doped iron-pnictide superconductor Pr1–xSrxFeAsO. They obtained that the lattice constants remain almost unchanged and contracted when the Sb and P are doped in this structure. Wang et al. [31] reported the enhancement of superconductivity by Sb doping in the hole-doped iron-pnictide superconductor Pr1–xSrxFeAsO. They obtained that the lattice constants remain almost unchanged and contracted when the Sb and P are doped in this structure. Wang et al. [31] investigated the effect of chemical pressures and bond covalency in LaFeAs1–xPbxO by the isovalent substitution of P/As. In this work, superconductivity emerges in the region of 0.2 < x < 0.4 with the maximum $T_C = 10.8$ K for $x = 0.25$. In 2010, Wang et al. [33] studied the co-doping of Sb and F on the structural and superconducting properties of LaFeAs1–xSbxO1–yFy. They result that the Sb doping hardly influences the SDW anomaly. In 2014, Ji et al. [26] reported the enhancement of superconductivity by Sb doping in the hole-doped iron-pnictide superconductor Pr1–xSrxFeAsO. They obtained that the lattice constants remain almost unchanged and contracted when the Sb and P are doped in this structure. Wang et al. [31] investigated the effect of chemical pressures and bond covalency in LaFeAs1–xPbxO by the isovalent substitution of P/As in the NdFeAs1–xSbxO material. They obtained that the lattice constants remain almost unchanged and contracted when the Sb and P are doped in this structure. In 2008, Ren et al. reported a new quaternary ironarsenide superconductor NdFeAsO1–xFy, with the onset resistivity transition at 51.9 K [15]. One of the major goals of the researchers is to achieve high-temperature superconductivity in these superconductors. To our knowledge, the highest $T_C$ transition in the NdFeAsO1–xFy material is obtained and reported at 55 K by controlling of As atmosphere in ambient pressure [34], at 54 K by oxygen-deficiency in fluorine-free of NdFeAsO1–y [16] and at 55.1 K by doping of chemical elements [29] so far. It can be concluded that the construction method and the doping of chemical elements are more effective in achieving higher transition temperatures. Motivated by this line of reasoning, we have tried to improve the synthesis method and to get a higher superconductivity transition temperature. For this purpose, we have synthesized a series of NdFeAsO0.8F0.2 samples using solid-state reaction technique. In our previous work, the construction method improved by thermogravimetric analysis (TGA) and we were able to record the highest transition superconductivity temperature for this nominal composition NdFeAsO0.8F0.2 at 56 K [14].

In the following, our goal is to focus on the effect of the isovalent substitution for arsenic in this nominal composition. For this purpose, the influence of isovalent substitution of phosphorus (P) and antimony (Sb) for arsenic (As) on the structural and electrical properties of nominal composition of NdFeAs1–xMxO0.8F0.2 (M = P, Sb) is investigated by using X-ray powder diffraction for structural properties along with the 4-probe method for electrical measurement. We study the XRD patterns for calculation of crystal structure parameters such as occupancy, bond length, bond angle, microstrain, and crystalline size which is determined by Rietveld refinement by materials analysis using diffraction (MAUD) software [35]. The surface morphology of grains will be studied by scanning electron microscopy (SEM).

### 2 Materials and Method

Samples with nominal compositions of NdFeAs1–xMxO0.8F0.2 (M = P, Sb) with $x = 0.0, 0.05$, labeled as Nd-1111, Nd-P0.05, and Nd-Sb0.05, respectively, were synthesized by one-step solid-state reaction method. At first, the stoichiometric amounts of Nd (99.99%), As (99.99%), FeO3 (99.9%), Fe (99.9%), FeF3, and red phosphorus P (99.99%), or antimony Sb (99.5%) powders were mixed according to Eq. (1):

$$\text{Nd} + (1-x)\text{As}_{1-x} + x\text{M} + \frac{6}{15}\text{Fe} + \frac{4}{15}\text{Fe}_{2}\text{O}_{3} + \frac{1}{15}\text{Fe}_{3}\text{F}_3 \rightarrow \text{NdFeAs}_{1-x}\text{M}_x\text{O}_{0.8}\text{F}_{0.2}$$  \hspace{1cm} (1)

The mixed powder was pressed to 45 kg/cm² and further encapsulated in an evacuated quartz tube. All stages of procedure were performed in a glove box in the nitrogen atmosphere. Then, the sealed and evacuated quartz tube was heated with a slow heating rate through 4 stages: (i) 5 h at 350 °C, (ii) 14 h at 640 °C, (iii) 20 h at 880 °C, and (iv) 20 h at 1150 °C. After the heat treatment, the sample comes in powder form in the quartz tube. Again, the powder was pressed and was encapsulated in an evacuated quartz tube. The heat treatment was repeated. Then furnace was cooled slowly down to room temperature. After this stage, the obtained compound was hard and in black color. In the structure of NdFeAsO0.8F0.2, formation of the NdO and FeAs layers is very important, because of this, we used thermogravimetric analysis of NdAs to determine the correct thermal process [14] (see Fig. 1). Due to the thermogravimetric analysis of NdAs and negligible effect of amount of phosphorus and antimony in thermogravimetric

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** Thermogravimetric and differential thermal analysis of NdFeAsO0.8F0.2 [14]
analysis of this compound, the heat treatment was repeated again. After two stages of heat treatment, we got the black pill for these two compounds.

3 Results and Discussion

X-ray crystallography is a technique used for determining the crystal structure of sample. X-ray powder diffraction patterns were measured using an X’Pert PRO MPD, PANalytical Company (Netherlands, for Cu-Kα (λ = 0.15406 nm) with a step size of 0.0260°.

The XRD patterns of the Nd-1111, Nd-Sb0.05, and Nd-P0.05 are shown in Fig. 2. The existence of the (101), (102), (003), (110), (111), (112), (103), (004), (200), (104), (211), (114), (121), (213), (204), (006), (220), (214), (106), (205), (302), (310), (311), and (312) major Bragg peaks in the XRD patterns confirms the formation of tetragonal structure with the p4/nmm:2 space group in the Nd-1111 sample. It indicates that almost any impurity phase is in this sample.

Figure 3 shows the enlarged view of XRD patterns of the main peak (102) of the Nd-P0.05 and Nd-Sb0.05 samples keeping Nd-1111 as a reference pattern. It is observed that the main peak of P- and Sb-doped samples shifts towards the right. In order to understand the effect of P and Sb substitution on the crystal lattice of Nd-1111 system, the lattice parameters of all the samples were calculated using the Rietveld refinement of XRD data by using MAUD software.

Rietveld analysis of the X-ray diffraction data of the Nd-1111, Nd-Sb0.05, and Nd-P0.05 samples shows that the structure of samples is tetragonal with space group P4/nmm:2. This type of IBs has a two-dimensional layer of Fe (Pn/Ch) tetrahedra, and there are two angles in tetrahedra that they indicated by α and β (see Fig. 4). The β angle and its bond length of the Fe (Pn/Ch) in the tetrahedra are related to superconductivity transition temperature $T_C$ [16, 24, 32, 36].

The $S$ parameter ($S = R_{wp}/R_{exp}$) describes the fit quality that $R_{wp}$ and $R_{exp}$ are the residual error and the expected error, respectively. Since the antimony atom can react with two oxidation states of +3 and +5, we consider all cases in Rietveld analysis for Nd-Sb0.05. Samples with nominal compositions of NdFeAs$_{0.95}$Sb$_{0.05}$O$_{0.8}$F$_{0.2}$ for Sb with +3 and +5 oxidation states are labeled as Nd-Sb(+3)0.05 and Nd-Sb(+5)0.05, respectively. All MAUD analyzed patterns of these samples are shown in Fig. 5(a–c). Since we want to investigate the isovalent substitution effect of the Sb/As and P/As on the
Nd-1111 structure, we consider the occupancy number of As, P, and Sb is float (i.e., the isovalent substituted atoms) in all Rietveld analysis. The Rietveld results of before and after refinement are listed in Table 1. Based on the Rietveld analysis of X-ray refinement are listed in Table 1. Rietveld analysis. The Rietveld results of before and after refinement have been included 1.5 wt% NdF$_2$, 0.5 wt% Sb in the Nd-Sb0.05 sample and 0.99 wt% NdF$_2$, 0.4 wt% P in the Nd-P0.05 sample.

The crystal structure parameters including exact atoms position and occupancy number in unit cell for our sample were refined by MAUD software (see Table 1).

The occupancy of As, P, and Sb for after refinement has less amount than the considered value, since these materials are evaporated during the synthesis. In many research works, in order to compensate for the loss of As element during the synthesis, the precursor As has 5–15% more than stoichiometric value of it [40, 41].

Table 1 presents the crystal structure parameters of unit cell for three samples. (i) For N-d1111, $a = 0.3967$ nm and $c = 0.8596$ nm. Substitution of P/As and Sb/As for content $x = 0.05$ has been affected on crystal structure parameters. (ii) For Nd-P0.05, $a = 0.3968$ nm and $c = 0.8582$ nm and (iii) for Nd-Sb0.05, $a = 0.3962$ nm and $c = 0.8560$ nm. Figure 4 presents the schematic picture of unit cell in tetragonal structure with space group of p4/nmm2. Rietveld analysis represents the "$a_{\text{Nd-P0.05}}$" > "$a_{\text{Nd-1111}}$" > "$a_{\text{Nd-Sb0.05}}$" and $c_{\text{Nd-1111}}$ > $c_{\text{Nd-Sb0.05}}$ > $c_{\text{Nd-P0.05}}$. It can be anticipated that with the increase of crystal structure parameter $c$ of the unit cell, the superconductivity transition temperature increases based on the results of other researchers for Nd-1111 structure [42]. Decreasing of the "$c$" parameters can be related to the electronegativity [43] of isovalent atoms. Based on our results in Table 1, in comparison of Nd-Sb0.05 with pure sample of Nd-1111, we have $Z_{\text{Sb}}(0.6563c) < Z_{\text{Nd}}(0.6580c)$. Moreover, the electronegativity of Sb ion (2.05) is smaller than to the electronegativity of As ion (2.18) causes the bond length of Fe-As/Sb is less than Fe-As and then $\alpha$ angle increases and $\beta$ angle decreases. The $\beta$ angle for our samples versus the $\beta$ angle for regular FeAs$_4$ tetrahedron is:

\[
\beta_{\text{regular FeAs}_4-\text{tetrahedron}}(109.47^\circ) > \beta_{\text{Nd-1111}}(108.61^\circ) > \beta_{\text{Nd-Sb0.05}}(108.26^\circ) > \beta_{\text{Nd-P0.05}}(107.3^\circ)
\]

The effect of structural parameters on superconductivity in 1111-type IBs was investigated by Lee et al. [44]. They claimed that superconducting transition temperatures seem to attain maximum values for regular FeAs$_4$ tetrahedrons. Then, it can be expected that the superconductivity transition temperature for our pure sample is greater than the Sb-doped sample.
In cuprates, the highest superconductivity transition temperature is observed for flat and square CuO$_2$ planes in the tetragonal structure and it is decreased by the structural distortions of the CuO$_2$ planes in the orthorhombic structure [45–48]. The 1111-type of IBs has a layered structure such as cuprates and also the effect of tetrahedral distortion has been studied on superconducting transition temperature. In this type of IBs, as much as the As-Fe-As tetrahedral angle is closer to the regular tetrahedral angle (109.47°), the higher transition temperature expects for sample. Moreover, the DOS of superconducting layers in IBs that correspond to CuO$_2$ plane in cuprate superconductors is maximum for these angles [49–51]. These results indicate a relevant approach of superconducting layers for IBs and cuprate superconductors.

| Sample          | Before refinement | After refinement |
|-----------------|-------------------|------------------|
|                | $a$ (nm)  | $c$ (nm)  | $V$ (nm$^3$) | Space group | $x/a$  | $y/b$  | $z/c$  | Occupancy | $x/a$  | $y/b$  | $z/c$  | Occupancy |
| Nd-1111         | 0.3967    | 0.8596   | 0.135276    | P4/nmm:2  | Nd$^{4+}$ | 0.25  | 0.25  | 0.1394 | 1  | Nd$^{3+}$ | 0.25  | 0.25  | 0.1392 | 1  |
| Nd-P0.05        | 0.3967    | 0.8596   | 0.135276    | P4/nmm:2  | Fe$^{3+}$ | 0.75  | 0.25  | 0.5    | 1  | Fe$^{2+}$ | 0.75  | 0.25  | 0.5    | 1  |
| Nd-Sb0.05       | 0.3967    | 0.8596   | 0.135276    | P4/nmm:2  | As  | 0.25  | 0.25  | 0.6579 | 1  | As  | 0.25  | 0.25  | 0.6580 | 0.96 |
| Nd-(Sb + 3)0.05 | 1.162     | 4.553    | 3.480       | 3.918     | F$^{1-}$ | 0.75  | 0.25  | 0.0    | 0.2 | F$^{1-}$ | 0.75  | 0.25  | 0.0    | 0.2 |
| Nd-(Sb + 5)0.05 | 1.162     | 4.553    | 3.480       | 3.918     | F$^{1-}$ | 0.75  | 0.25  | 0.0    | 0.2 | F$^{1-}$ | 0.75  | 0.25  | 0.0    | 0.2 |

Table 1: Refined crystal structure parameters of Nd-1111, Nd-P0.05, Nd-Sb0.05, Nd-Sb(+ 3)0.05, and Nd-Sb(+ 5)0.05 by MAUD analysis in before and after refinements.
About the replacement of major Bragg peak (102) based on the refinement of XRD data, all diffraction peaks clearly shift to higher angles with increasing of \( a \) unit cell parameter. Our result confirmed the consistency of dopant value of isovalent atom with their occupancy number and the replacement of origin peaks in XRD pattern of samples.

As you know that the integral breadth of the diffraction peaks can be linked to the apparent size of the crystals and to their microstrains. The Williamson and Hall method has suggested a simple method for solving this problem. It works by considering that both the limited size of the crystals and the presence of crystallographic distortions lead to Lorentzian intensity distributions. If we denote by \( \beta_p \) the pure breadth and by \( \beta^T \) and \( \beta^D \) the breadths related to size and microstrains, respectively, then we obtain:

\[
\beta_p = \beta^T + \beta^D
\]

and therefore:

\[
\beta \cos \theta / \lambda = K / D + \eta \sin \theta / \lambda \quad (3)
\]

where \( K \) is Scherrer’s constant and \( \beta \) and \( \theta \) are full width at half maximum and diffraction degree for each peak, respectively \([52]\). If we plot \((\beta \cos \theta) / \lambda\) according to \((\sin \theta) / \lambda\), we get a straight line with a \( y \)-intercept equal to the inverse of the size and a slope equal to the value of the microstrains \( \eta \) (see Fig. 6).

The results of this computation for three samples are given in Table 3.

According to the results of Table 2 and Table 3, microstrain \( \eta \) is equal to 0.43\% for the Nd-1111 sample which the volume of its unit cell is 0.135276 \( \text{nm}^3 \). For the Nd-P0.05 sample, since the phosphorus atom has an electron layer less than arsenic atom, also the volume of its unit cell is 0.133635 \( \text{nm}^3 \); therefore, the lattice becomes shrinking and its microstrain increasing to 0.53\%. For the Nd-Sb0.05 sample, the antimony atom has an electron layer more than arsenic and also the volume of its unit cell is 0.134370 \( \text{nm}^3 \), so again, the lattice will shrink fewer than the unit cell of Nd-P0.05 and it results in fewer microstrain than this sample.

As shown in Table 3, the crystalline size of samples increases for Nd-Sb0.05 and Nd-P0.05 with respect to the Nd-1111 sample, respectively. The greater microstrain in the Nd-P0.05 can be due to the smaller size of the phosphorus atom than antimony and arsenic atoms. This causes to more distortion of the unit cell.

We used the 4-probe contact method for obtaining superconductivity parameters of our samples. The 20 K Closed Cycle Cryostat (QCS 101), ZSP Croygenics Technology (Iran), was used for measurement of superconductivity behavior of samples. The normalized resistivity as a function of temperature is shown in Fig. 6. For the Nd-1111 sample, the electrical resistivity gradually decreases by cooling and the onset of the resistive transition is 62 K, and finally, it reaches to zero at \( T_{\text{offset}} = 50 \) K. The \( T_c \) was obtained at 56 K for this sample \([14]\). This sample exhibits as a metallic behavior in the normal state. It was observed that by substitution of P in Nd-1111, the superconductivity state eliminates and the structural transition temperature appears at 140 K (Fig. 7).

At a higher temperature than the structural transition temperature, the behavior of the Nd-P0.05 sample is similar to the insulator. It can be due to the phosphorus atom. It is the only element in the fifteenth group of periodic tables that has

![Fig. 6 Williamson–Hall plot of Nd-1111 (blue diamond dots), Nd-Sb0.05 (red square dots), and Nd-P0.05 (green circle dots)]](image)

Table 2 The bond length, bond angle, and thickness of layer of NdFeAsO0.8F0.2 unit cell

| Sample      | Nd-P 0.05 | Nd-1111 | Nd-Sb 0.05 | Nd-Sb+0.05, Nd-Sb+0.05 |
|-------------|-----------|---------|------------|------------------------|
| Bond angle  | \( \alpha \): As-Fe-As (deg.) | 112.59 (11) | 111.20 (11) | 111.93 (11) | 111.93 (11) |
|             | \( \beta \): As-Fe-As (deg.) | 107.93 (6)  | 108.61 (6)  | 108.26 (6)  | 108.26 (6)  |
|             | \( \eta \): (O, F)-Nd-(O, F) (deg.) | 117.5 (2)  | 117.8 (2)  | 115.6 (2)  | 115.6 (2)  |
| Bond length | \( t \): Fe-As (nm) | 0.2385 (3)  | 0.2404 (3)  | 0.2390 (3)  | 0.2390 (3)  |
|             | \( y \): Nd-O (nm) | 0.2321 (4)  | 0.2316 (4)  | 0.2340 (4)  | 0.2340 (4)  |
|             | 2d: thickness of Fe-As layer (nm) | 0.2646 (7) | 0.2716 (3) | 0.2675 (8) | 0.2675 (8) |
|             | 2h: thickness of Nd-O layer (nm) | 0.2408 (1) | 0.2393 (1) | 0.2492 (7) | 0.2492 (7) |
|             | \( F \): distance of Fe-As and Nd-O layers (nm) | 0.1763 (6) | 0.1743 (2) | 0.1695 (7) | 0.1694 (8) |
insulating behavior. For the Nd-Sb0.05 sample, the electrical resistivity decreases by cooling and then rapidly drops at $T_{\text{onset}} = 48$ K, and finally, it reaches to zero at $T_{\text{offset}} = 44$ K. The critical temperature was obtained at 46 K for this sample.

The shape of the FeAs$_4$ tetrahedron seems to play a conclusive role with, in particular, the Fe-As bond length having a robust effect on the transition temperature superconductivity [12, 20, 22, 24, 36, 53, 54]. The bond length of Fe-As in the Nd-1111 sample is 0.2404 nm and it decreases by substitution of P/As and Sb/As. It was observed that the bond length of Fe-As, the $\beta$ bond angle in this structure, and the thickness of Fe-As layer increase by the increasing the transition temperature superconductivity. Our work confirms other research works for this claim [22, 24, 55].

The surface morphology and the grain connectivity of the all samples have been determined using scanning electron microscopy (SEM). These three samples imaged with the TESCAN VEGA3 LMU with magnification 60.000e3. The SEM images are illustrated in Fig. 8(a–c) for the Nd-1111, Nd-Sb0.05, and Nd-P0.05.

The SEM images clearly represent the crystalline morphology of sample. Since the edges of the crystal grains are sharp (see Fig. 8(a–c)), the temperatures selected in the manufacturing method are well chosen and implying the correct preparation method. The surface morphology of these samples is the mixture of flake-type and nodule-type grains and the grains are

| Sample   | Williamson–Hall equation | Microstrain $\eta$ (%) | Crystalline size D (nm) |
|----------|--------------------------|------------------------|-------------------------|
| Nd-P0.05 | $y = 0.0053x + 0.0043$    | 0.53                   | 232.55                  |
| Nd-1111  | $y = 0.0043x + 0.0079$    | 0.43                   | 126.58                  |
| Nd-Sb0.05| $y = 0.0046x + 0.0047$    | 0.46                   | 212.77                  |

Fig. 7 The normalized resistivity of Nd-1111(square blue dots), Nd-P0.05 (circle green dots), and Nd-Sb0.05 (diamond red dots)

Fig. 8 SEM image for (a) the Nd-1111, (b) Nd-Sb0.05, and (c) Nd-P0.05 samples
Fig. 9  EDS measurements for (a) the Nd-1111, (b) Nd-Sb0.05, and (c) Nd-P0.05 samples
distributed randomly with the grain size between 39 nm and more than 100 nm for Nd-1111, 40 nm and more than 300 nm for Nd-Sb0.05, and 34 nm and more than 250 nm for Nd-P0.05. The apparent shape of grain for all samples can also be confirmed by the sample manufacturing method.

The composition of samples was determined by multi-point energy dispersive X-ray spectral (EDS) measurements. EDS measurements are shown in Fig. 9(a–c).

Figure 9 (b and c) show the existence of isovalent atoms of Sb and P in substituted Sb/As and P/As samples, respectively. These results confirm the actual composition of our samples. It is noticeable that our samples were coated with a thin layer of gold in the EDS measurements and were observed in EDS results.

4 Conclusion

In summary, based on Rietveld refinement of XRD patterns of samples, it was shown that all the samples have similar structural properties as tetragonal crystal structure with P4/nmm:2 space group with different unit cell parameters. The “α” unit cell parameter of samples increases by substitution of P/As to Nb/As. The “c” unit cell parameter of samples due to the electronegativity of isovalent atoms increases from Nd-P0.05, Nd-Sb0.05, and Nd-1111, respectively. Our results show that the arsenic isovalent doping increased the α angle and decreased the β angle, bond length of the Fe-As, and the thickness of Fe-As layer. The substitution of P/As in nominal composition of Nd-1111 suppressed the superconductivity. We have observed a structural phase transition at 140 K in Nd-P0.05. Also, the Tc of samples has increased from 56 to 46 K in Nd-Sb0.05 by substitution of Sb/As in nominal composition of Nd-1111. The microstrain of Nd-1111 has been increased by substitution of P/As more than Sb/As. It seems that the lattice shrinkage can be related with the Tc and it becomes maximum when the FeAs4 tetrahedron of lattices is close to the regular tetrahedron.

Acknowledgments We are grateful to Prof. M. Akhavan (Sharif university of Technology, Tehran, Iran) for his help with the measurement set up laboratory. Also, we acknowledge the Vice Chancellor Research and Technology of Alzahra University (Tehran, Iran).

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