Synthesis, Electric Transport, Mössbauer Spectroscopy, Specific Heat and Induction of Superconductivity in ReFeAsO (Re=La, Pr, Gd and Sm)[†]

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Abstract: We report an easy and versatile route of synthesis for ReFeAsO (Re = La, Gd, Pr and Sm) by both single step and precursor based double step solid-state reaction routes. The studied ground state compounds of the new FeAs based superconductor family crystallize in tetragonal $P4/nmm$ structure, with lattice parameters variation following their ionic radii. The resistivity measurements exhibit clearly the appearance of a metallic step below say 150-130 K, which is reminiscent of the *SDW* (Spin Density Wave) magnetic character. Also, It is observed that oxygen stoichiometric ReFeAsO is not formed and rather the same is slightly oxygen deficient. The Mössbauer spectroscopy (*MS*) carried out on some of them at 290 K and 90 K i.e. both above and below the *SDW* temperature exhibits the Fe ordered state at 90 K. Further the *MS* is proved to be the most efficient technique in picking up the FeAs based impurities in these materials. The heat capacity measurements on SmFeAsO, clearly demonstrates the *SDW* temperature with a hump in $C_p(T)$ at around 130 K. Further Sm spins are ordered anti-ferro-magnetically (*AFM*) at 4.5 K. Superconductivity is also induced in SmFeAsO with Co substitution at Fe site with T_c = 14 K. The general behavior of the ReFeAsO is discussed and it is concluded that (a) they can be synthesized by an easy and versatile methods, (b) their ground state is not oxygen stoichiometric, but deficient and (c) *MS* is the most efficient technique to pick up the Fe based impurities in these materials, that is yet rampant in this new class of superconductors.

Keywords: Iron oxypnictides, ReFeAsO, Mössbauer spectroscopy, Specific heat

INTRODUCTION

Although the ZrCuSiAs-type pnictide oxides including ReFeAsO with various Re (Re = rare earths) were known in literature from long back, see recent reviews [1, 2] and references there in. The same became very actively pursued hot materials after the invention of superconductivity in LaFeAs($O_{1-x}F_x$) at 26 K by Hosono's group [3, 4]. The oxygen stoichiometric ReFeAsO is seemingly a charge balanced compound with $Re^{3+}O^{2-}$ layer hole being compensated by the $Fe^{2+}As^{3-}$ electron. In fact very recent electronic structure calculations have revealed that the parent compound i.e., ReFeAsO is a bad metal and at the verge of the metal insulator transition [5]. Hosono's group doped mobile charge carriers in the parent LaFeAsO by replacing some of the O^{2-} ions by F^{-1} and discovered superconductivity in these compounds [3, 4]. Soon after, the effect of mechanical pressure was studied, which is a usual practice for any newly invented superconductor [6]. It was found that superconducting transition temperature (T_c) could yet be tuned to higher temperature with appropriate chemical pressure in the unit cell [6]. Interestingly, within a short span of time, T_c could be raised to 40-55 K on replacing the La ion by other rare-earth elements such as Ce, Nd, Pr, or Sm [7-10]. The change in ionic size and ensuing chemical pressure in the unit cell did the required job being predicted in Ref.6. Henceforth, it was clear for the first time that the scientific community has embarked on a new high T_c superconductor outside the so-called strong *BCS* limit, after the famous high T_c cuprate superconductors (*HTSc*) [11]. Curious and interesting commentaries were written by the Condensed matter physicists in scientific journals [12].

In these compounds with general chemical formula ReFeAsO (Re = La, Sm, Nd, Gd, Ce etc.), it is believed that doped ReO layers act as charge reservoirs for high mobility FeAs planes, making oxy-pnictides very similar to the layered structure of high-T_c cuprates [11]. At room temperature all the parent compounds crystallize in a tetragonal ZrCuSiAs-type structure (space group $P4/nmm$), which consists of alternate stacking of edge-sharing Fe_2As_2 tetrahedral layers and Re_2O_2 tetrahedral layers along *c*-axis. All the compounds undergo structural transition from the tetragonal high temperature phase to orthorhombic low temperature phase at around 150 K [1, 2, 9]. The magnetic phase for the Fe-based parent compounds is identified as a spin-density wave (*SDW*) ordering [9,13,14]. Superconductivity occurs in these Fe-based compounds when the anti-ferromagnetic instability or the *SDW* gets suppressed. Soon

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superconductivity could also be induced in other types of structure containing the same tetrahedrally coordinated Fe_2As_2 layers as in ReFeAsO compounds. The oxygen-free pnictide superconductors $(Ba,Sr)_{1-x}K_xFe_2As_2$ and $(Ba,Sr)Fe_{2-x}Co_xAs_2$ with T_c up to 38 K and 25 K [15-18] (so-called 122-compounds) have been discovered. It was proposed that these compounds have two-band structure and they do carry very high upper critical fields [6-10, 17-20]. In fact, their T_c decreases marginally with an applied field. This put these materials at forefront for practical applications.

Usually, two methods are followed for the preparation of these Fe-based oxypnictides; one is high-pressure high temperature (*HPHT*) [4, 7, 21] technique and another is in the presence of inert gas or in vacuum at ambient pressure [22, 23]. Besides Flourine doping [22, 23] and oxygen deficiency [4, 7, 21], superconductivity could also be introduced by Fe^{2+} site Co^{3+} substitution in the Fe-As layer, or hole doping by partial substitution of the rare- earth by strontium etc. [24-27]. Interestingly *HPHT* is not readily available in most laboratories and the fluorine corrodes with the quartz at high temperatures. Hence, in principle it is getting difficult for material scientists to synthesize these superconductors in abundance. This clarifies the situation that these interesting new superconductors are yet open to a few selected materials laboratories. Further the window of superconductivity in terms of the change in O^{2-}/F^{1-} or Fe^{2+}/Co^{3+} ensuing mobile carriers induction is very narrow [3, 4, 7-24]. The phase purity of the materials is also yet in question, often the samples are contaminated with small magnetically ordered FeAs, not seen by usual techniques such as powder *X*-ray diffraction (*XRD*) and is yet being mostly ignored. In this paper, we are discussing the synthesis, electric transport properties, Mössbauer spectroscopy (*MS*), specific heat and induction of superconductivity with Co substitution in ReFeAsO (Re=La, Pr, Gd & Sm) system. We followed the one-step and two-step solid-state reaction routes for synthesizing the samples at ambient pressure. We successfully synthesized the non-superconducting ground state of ReFeAsO (Re = La, Pr, Gd & Sm) in pure phase via these two synthesis routes. These samples exhibit a shallow metallic step below 130-150 K in $R(T)$ measurement. The shallow metallic step is an indication of the spin density wave (*SDW*) transition of the system. Based on the mössbauer spectroscopy (*MS*) characterization of our easy route synthesized phase pure ReFeAsO and some borrowed *HPHT* samples, we conclude that FeAs contamination in these materials is yet a real trouble. Further we propose that *MS* is the most efficient technique to pick up the Fe based impurities in these materials. Superconductivity is also introduced by Fe^{2+} site Co^{3+} substitution in SmFeAsO.

EXPERIMENTAL

One step method: The Fe, ReO, Re, and As were taken in stoichiometric ratio of ReFeAsO and sealed in an evacuated quartz tube followed by subsequent heating at 500, 850 and 1100^oC for 12, 12 and 33 hours respectively in a single step [28].

Two Step method: Polycrystalline samples with nominal composition ReFeAsO were synthesized by conventional solid state reaction route using high purity FeAs, which was prepared by using Fe and As chips. First the Fe and As chips were sealed in evacuated quartz tube and heat treated for 12 hours at 700^oC. As synthesized FeAs was ground with Re, ReO in stoichiometric ratio, palletized and subsequently vacuum-sealed in quartz tube. It was subsequently heat treated at 900^oC for 4 hours and later at 1100^oC for 15 hours respectively. We also tried to synthesize the ReFeAsO from ReAs instead of FeAs Precursor. The ReAs was prepared by taking Re and As chips in evacuated quartz tube, it was heat treated at 550^oC for 3 hours and then at 900^oC for 5 hours. After grinding in stoichiometric ratio of ReFeAsO with ingredients of ReAs, Fe_2O_3 and Fe, the resultant powder was again palletized and sealed in evacuated quartz tube. The sealed quartz tube was heated at 1160^oC for 48 hours followed by natural furnace cooling to room temperature.

The x-ray diffraction patterns of these compounds were taken on a Rigaku miniflex diffractometer using CuK_α radiation. The resistivity measurements were carried out by a four–probe method on a closed cycle refrigerator in the temperature range of 12 to 300 K. Heat capacity measurements were carried out on Quantum design *PPMS*. Zero-Field-Cooled (*ZFC*) and Field-Cooled-Cooling (*FCC*) dc magnetic measurements in the range of 5-300 K were performed on a commercial (Quantum Design) superconducting quantum interference device (*SQUID*) magnetometer. Mössbauer spectroscopy studies were performed by using a conventional constant acceleration drive and a 50 mCi ^{57}Co:Rh source. The velocity calibration was done at room temperature with a α-Fe absorber and the isomer shifts (*I.S.*) values are relative to that of iron. The observed spectra, measured at temperatures extending from 4.2 K to 300 K, were least square fitted by theoretical spectra including the full diagonalization (in the necessary cases) of the hyperfine interaction spin Hamiltonian, starting with hyperfine interaction parameters, corresponding to those of the assumed foreign phases [29-31].

RESULTS AND DISCUSSIONS

1. X-ray Diffraction Pattern Analysis

The room temperature powdered sample's x-ray diffraction (*XRD*) pattern and its Rietveld analysis are shown in Fig. (**la**) for ReFeAsO (Re = La, Pr & Gd), which are synthesized by one step and two step solid-state reaction method at ambient pressure. Inspection of the diffraction profiles at room temperature reveals that all the compounds possess the tetragonal unit cells with space group *P*4/*nmm*. It can also be seen from the figure that besides the majority phase (tetragonal *P*4/*nmm*), few impurity lines having very low intensity are also seen in the *XRD* pattern, which are marked by '*' in the figure. Rietveld analysis of the room temperature diffraction pattern proceeded smoothly. Re and As atoms are located at Wyckoff positions *2c*, O is situated at *2a* and Fe/Co are shared at site *2b*. Typical Rietveld refinement parameters for ReFeAsO (Re = La, Pr & Gd) are given in Table **1**. The Lattice parameters and volume of all studied samples are listed in Table 2. All the values are in well confirmation with literature [32-34]. The variation of lattice parameters and unit cell volume follows variation of the ionic radius i.e. these two quantity go on decreasing as the ionic size of rare-earth atom decreases. Both are

Table 1.   Rietveld Refined Parameters for ReFeAsO, Space Group: *P4/nmm*

Atom	Site	x	y	z (La)	z (Pr)	z (Gd)	z (Sm)
Re	2c	0.25	0.25	0.14240(35)	0.13720(81)	0.13747(71)	0.1356(8)
Fe	2b	0.75	0.25	0.5	0.5	0.5	0.5
As	2c	0.25	0.25	0.64993(60)	0.65378(41)	0.65705(32)	0.6514(15)
O	2a	0.75	0.25	0	0	0	0

maximum for Re = La and minimum for Gd (inset of Fig. (**1a**)).

Clearly our one/two step atmospheric pressure synthesized materials are as good as the samples prepared by *HPHT* method. In fact it has come to our notice that oxygen stoichiometric ReFeAsO is not the end product. Some oxygen of the compound is lost during baking of samples in quartz capsule. On the other hand, *HPHT* is a closed cell method hence neither the oxygen can come in nor it can go out. It is found repeatedly by some of us that oxygen

stoichiometric ReFeAsO being synthesized by *HPHT* is never a single phase compound, but accompanied with some impurity [35]. Ironically, yet there are no direct methods employed to know the exact oxygen content of ReFeAsO type compounds. Though our detailed *MS* results could provide only some indirect clues, that none of the as synthesized samples were oxygen stoichiometric and the loss of oxygen could be well up to 10-15% per unit or even more in some cases. Although in most of the literature yet available on ReFeAsO and its *SDW* character and good
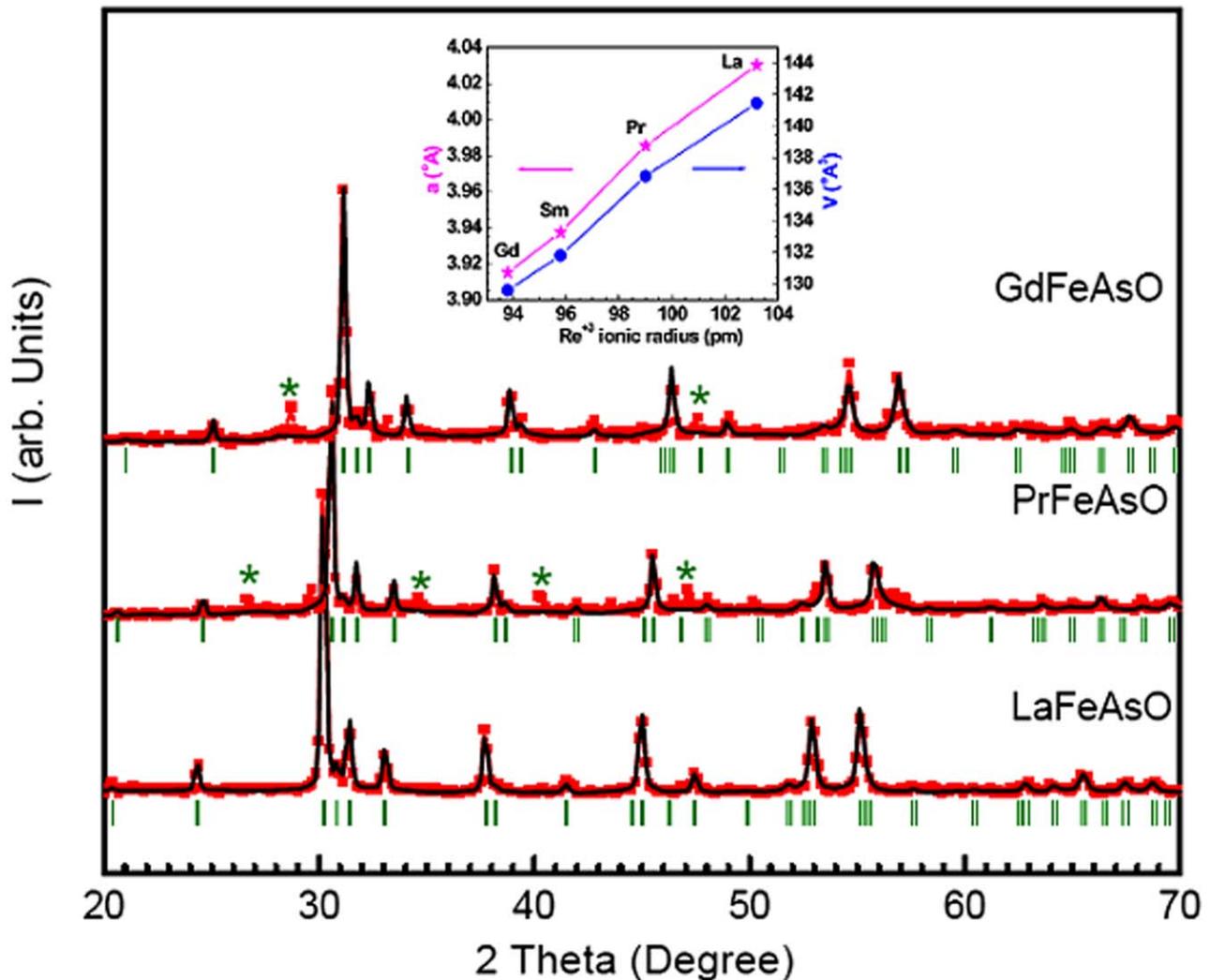
Fig. (1). (**a**) Room temperature XRD pattern of various ReFeAsO (Re = La, Pr, Gd) and Rietveld refinement of these patterns.
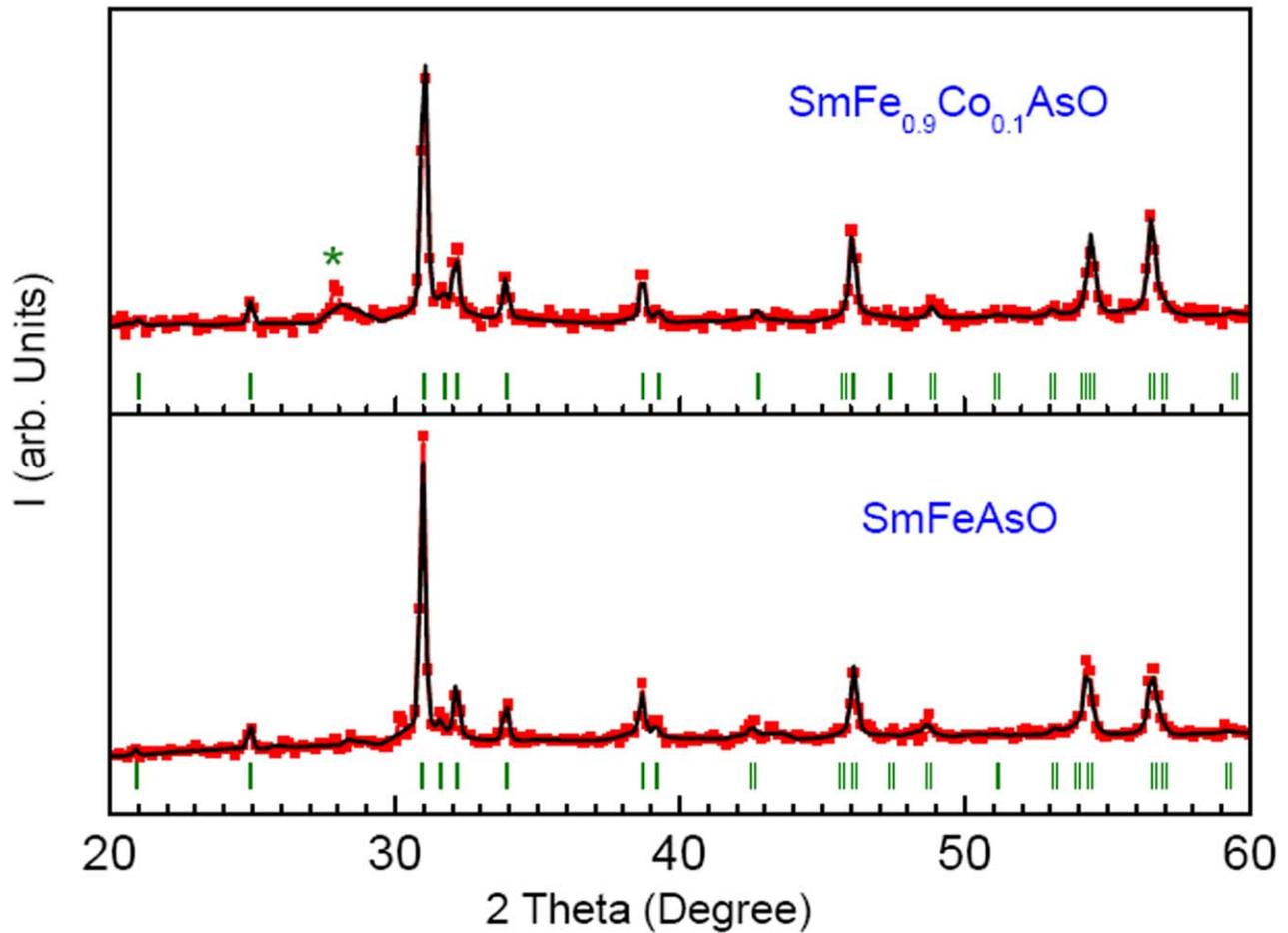
Fig. (1). (**b**) Fitted and observed room temperature X-ray diffraction patterns of SmFeAsO and SmFe$_{0.9}$Co$_{0.1}$AsO compounds.

metallic step, scientific community has presumed it to be oxygen stoichiometric [3, 4, 7-24], though it is not. This will be discussed more deliberately in our *MS* section.

Fig. (**1b**) shows the room temperature *XRD* patterns for SmFeAsO and SmFe$_{0.9}$Co$_{0.1}$AsO samples along with their Rietveld refinements. It is observed that all main peaks can be well indexed based on the basis of space group *P4/nmm*. Further, besides the majority phase (tetragonal *P4/nmm*) an extra peak at around 27.80 degree having low intensity

Table 2. **Lattice parameters and cell volume of ReFeAsO and Co doped SmFeAsO**

Sample	*a* (Å)	*c* (Å)	V (Å³)
LaFeAsO	4.0363(3)	8.7356(7)	142.322(11)
PrFeAsO	3.9855 (5)	8.6149 (1)	136.848 (31)
GdFeAsO	3.9152 (4)	8.4546 (1)	129.605 (30)
SmFeAsO	3.93726(33)	8.49802(07)	131.736(23)
SmFe$_{0.90}$Co$_{0.10}$AsO	3.9398 (7)	8.4639 (4)	131.386 (28)

(marked with *) is also seen in the XRD pattern of SmFe$_{0.9}$Co$_{0.1}$AsO sample. It is clear from the Table **2** that the *c* lattice parameter of undoped SmFeAsO decreases with Co doping, while no significant change in *a*-axis is noticed. Since the ionic size of Co^{3+} is smaller than Fe^{2+}, therefore decrease in *c* lattice parameter suggests that Co has gone in the tri-valence Co^{3+} state at the place of Fe^{2+}. This substitution of Co^{3+} at the site of Fe^{2+} increases electron carriers in Fe-As layer, which in turn induces the superconductivity in Co doped SmFeAsO, which will be discussed in the last section.

2. Resistivity Analysis

The resistance versus temperature (*R-T*) plots for different ReFeAsO is shown in Fig. (**2**). The resistance behavior is less metallic from room temperature to about 140-150 K, and later resistance drops abruptly. This is attributed to phase change anomaly in the compound at around 140-150 K [24, 36]. It also gives a clear indication of the spin density wave (*SDW*) transition of the system around 140-150 K [19, 24, 36]. It is noticed that T_{SDW} is slightly less for magnetic Re. For example the T_{SDW} is 150 K and 140K

respectively for the Re = La and Sm samples. All the samples have the same shape of $R(T)$ curve except as for LaFeAsO. Earlier Dong *et al.* [24] also got the same kind of $R(T)$ behavior for the LaFeAsO sample. The samples are non-superconducting but the *SDW* characteristic can be suppressed via induction of electrons or holes by fluorine doping or by creating oxygen deficiency and hence superconductivity can be introduced [3, 4, 5-9]. Metallic nature of prototype ReFeAsO system contrasts with insulating ground state of stoichiometric cuprates. After doping, e.g. by fluorine, the value of resistivity drops, its anomaly becomes less visible and disappears at higher doping resulting in the appearance of superconductivity. Appearance of superconductivity is usually connected with the breaking of "nesting" of the Fermi surfaces [37]. This behavior of resistivity is rather typical and is observed in all ReFeAsO systems [38], which are termed recently as 1111 – systems. However, as we discussed a short while ago in *XRD* section, the ReFeAsO are always slightly oxygen deficient, and hence possess good conductivity, against the electronic structure predictions [5]. Oxygen non-stoichiometry of these compounds will be more certain after the *MS* results.

parameters obtained from *CW* fitting are: $\chi_0 = 6.5 \times 10^{-6}$ emu/gOe, $C = 3.07 \times 10^{-4}$ emu K/gOe which yields a *PM* effective moment of $P_{eff} = 0.83$ μ_B and $\theta = -2.8$ K [39]. Presumably, this effective moment corresponds to divalent Fe ions since all other ions are non-magnetic. This P_{eff} is consistent with the low ordered moment (~0.25 μ_B) at the Fe site in LaFeAsO deduced from neutron diffraction (*ND*), μSR (muon spin resonance) and Mossbauer studies [40-41]. The multi step transitions are obtained in the *M-T* curve of PrFeAsO. Quite similar *M-T* behavior has earlier been reported by McGuire *et al.* [42] for PrFeAsO compound. Although it is not clear about how Pr^{3+} could possess so many multiple transitions that also ranging from 20 K to 50 K. These studied samples might though be single phase like in *XRD*, may still contain some Fe driven weakly ordered magnetic phases. This issue is not clarified in Ref. 42 neither at present we have any conclusive explanation for possible multiple magnetic orderings of Pr^{3+} spins. As far as SmFeAsO is concerned, curiously it's *M-T* is not Curie-Weiss like [43]. Infact, SmFeAsO exhibits Van-Vleck type magnetism [44].

Fig. (2). $R(T)$ Plots for various ReFeAsO (Re = La, Pr, Sm & Gd)).

3. Magnetization Studies

The temperature dependence of the magnetization in field cooled mode for LaFeAsO and PrFeAsO measured at 100 Oe and 10 Oe respectively is shown in Fig. (**3**). For LaFeAsO, the SDW features are not visible and the curve obtained has the typical paramagnetic (*PM*) shape and adheres closely to the Curie-Weiss (*CW*) law. The

Fig. (3). The temperature dependence of the Field cooled magnetization for LaFeAsO and PrFeAsO.

4. Mössbauer Spectroscopy

XRD measurements are not sensitive enough to disclose small amounts of foreign phases, in particular if they have *XRD* lines similar to those of the *SC* (superconducting) system. Since all these systems contain iron, and this is the only element, which can order magnetically at relatively high temperatures, then a small amount of iron compound, which orders magnetically, can contribute to the illusion that the superconducting materials exhibits magnetic order also.
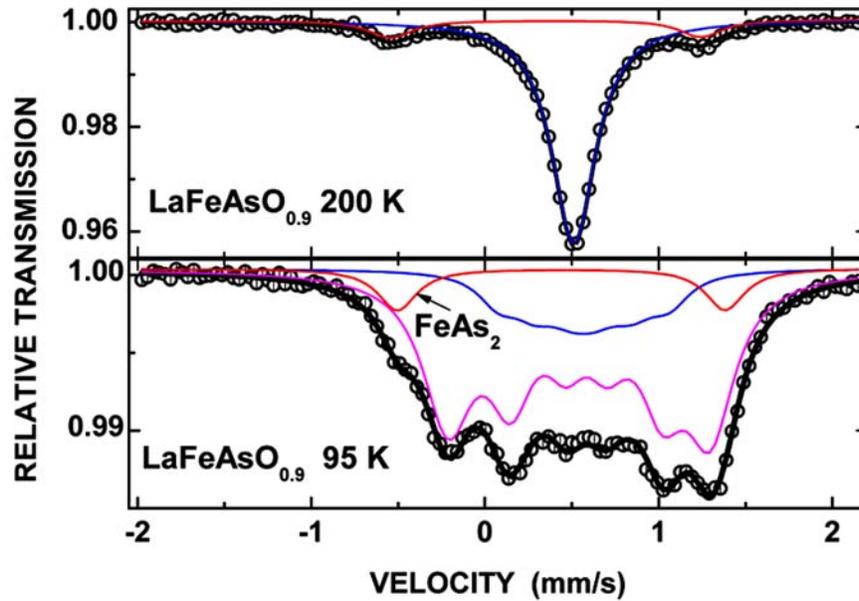
Fig. (4). The Mössbauer spectra of $LaFeAsO_{1-x}$ measured at 95 K and 200 K.

Generally speaking, all studied 1111 based materials, regardless of whether they are *SC* or *SDW* above their magnetic phase transition; their Mössbauer spectrum (*MS*) is composed of two sub-spectra. The intense sub-spectrum is a singlet with isomer shift (*IS*) of 0.55-0.59 mm/s, and corresponds to the iron nuclei of the main phase. Its relative intensity is sample dependent. The hyperfine parameters of this sub-spectrum do not change at T_c. In addition, almost all studied samples contained some amount of foreign Fe-As phases, thus a major consideration in analyzing the spectra is the amount of these extra phases present in the sample. These are most probably, Fe_2As (T_N=353 K), FeAs (T_M=77 K) and $FeAs_2$ (T_M< 5K) [6,45-46]. The percentages of the extra phases were evaluated as their relative sub-spectrum areas.

The *MS* spectra of $LaFeAsO_{0.9}$ measured below and above the magnetic phase transition are shown in Fig. (**4**). At 200 K one observes the central singlet absorption line corresponding to the iron in the sample, while the doublet (12%) is certainly due to an impurity of $FeAs_2$. The spectrum at 95 K was fitted with a superposition of commensurate (majority) and incommensurate spin density waves, as explained in [39]. The impurity subspectrum (~10%) is still a quadrupole doublet, since $FeAs_2$ orders magnetically at TM < 5 K.
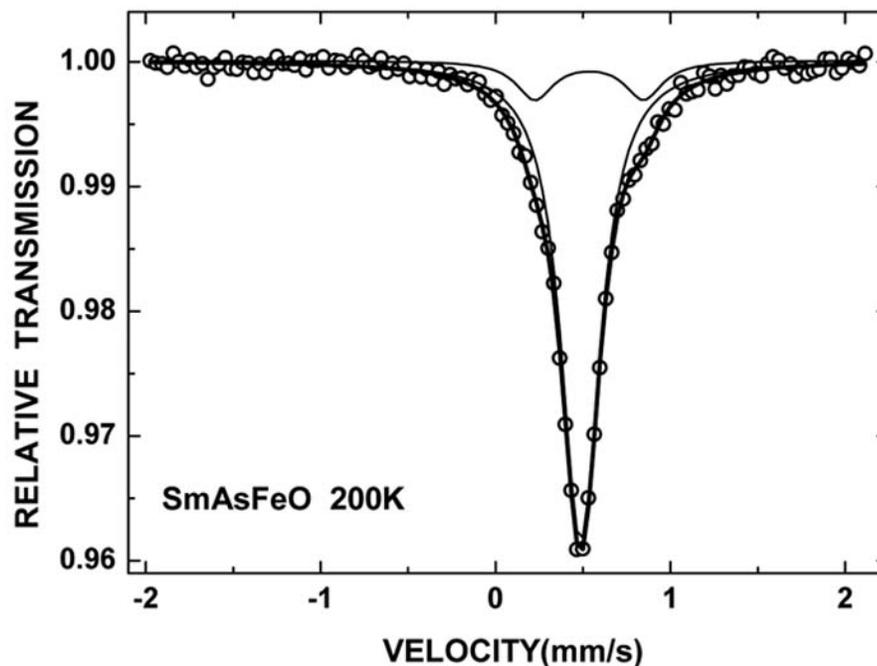
Fig. (5). The Mössbauer spectra of SmAsFeO below and above it's magnetic ordering temperature.

The Sm-Based samples reported here, were prepared under high pressure (6 *GPa*) at 1300°C [3]. SmFeAsO is a *SDW* system below 140 K. Above T_M, the Mössbauer spectrum in Fig. (**5**), shows the presence of a foreign phase of 13 ± 2 % intensity. This impurity quadrupole doublet (*IS* = 0.54(3) mm/s and *QS*=0.62(2) mm/s) can be identified with full certainty to be FeAs (T_M = 77 K).

The superconducting SmAsFeO$_{0.85}$ and SmAsFeO$_{0.9}$F$_{0.1}$ samples, possess their T_c = 52.6 K and 52 K respectively [46]. Their *MS* spectra are shown in Figs. (**6a**) and (**6b**). The doublet shown in Fig. (**6a**) & Fig. (**6b**) at 90 and 95 K respectively (*I.S.*= 0.60 mm/s and *QS*= 0.66 mm/s). The red lines assigned to Fe-As accounts for 15% and 50% for SmAsFeO$_{0.9}$F$_{0.1}$ and SmAsFeO$_{0.85}$ respectively. Both samples exhibit magnetic order at 4.2 K. Fe-As orders magnetically at T_N=77 K, thus the magnetic order in Figs. (**6a**) and (**6b**) is presumably due to Fe-As as an extra phase. This statement excludes the claim for coexistence of *SC* and

magnetic order in this material proposed by µ*SR* studies in SmAsFeO$_{0.82}$F$_{0.18}$, which observed complex magnetic correlations at low temperatures and relate them to the *SC* state [47].

The results reported here demonstrate that one has to be more careful in preparing polycrystalline materials of these superconducting-spin density wave materials. The amounts of impurities in the studied samples reached even 50%. The Fe-As as extra phases are obtained regardless the preparation method of the desired materials. Such materials may lead to wrong conclusions. Our research shows that Mössbauer spectroscopy of ^{57}Fe in these materials, even at room temperature, can easily discover the presence and amounts of Fe containing foreign phases.

5. Heat Capacity $C_P(T)$ Measurements

The resistance (*R-T*) measurements of ReFeAsO (Re = La, Pr, Sm & Gd) exhibited ground state spin-density-wave
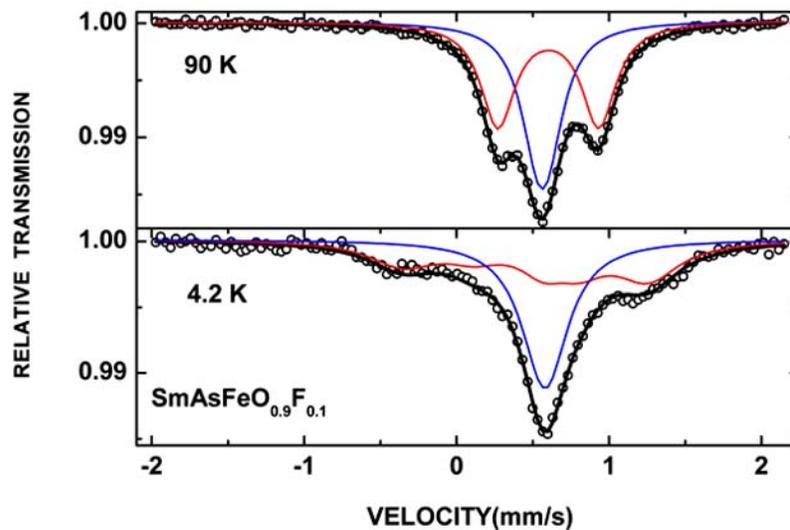
Fig. (6). (**a**) The Mössbauer spectra of SmAsFeO$_{0.9}$F$_{0.1}$ at 90 K and 4.2 K.
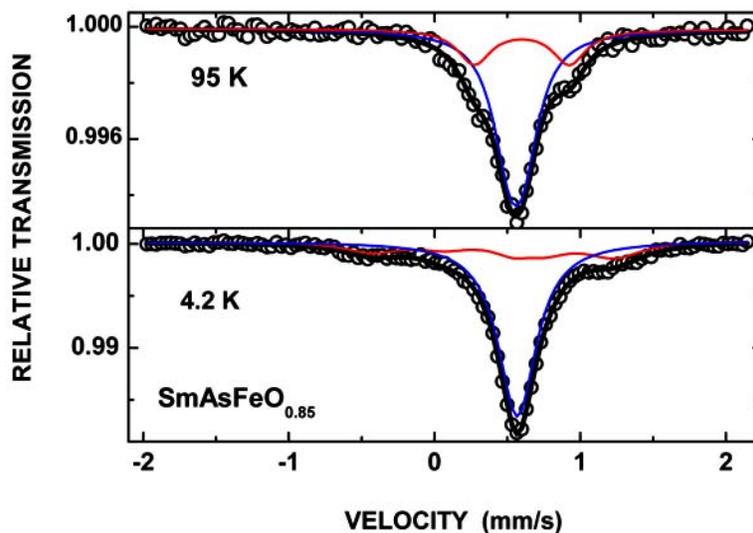
Fig. (6). (**b**) The Mössbauer spectra of SmAsFeO$_{0.85}$ at 95 K and 4.2 K.
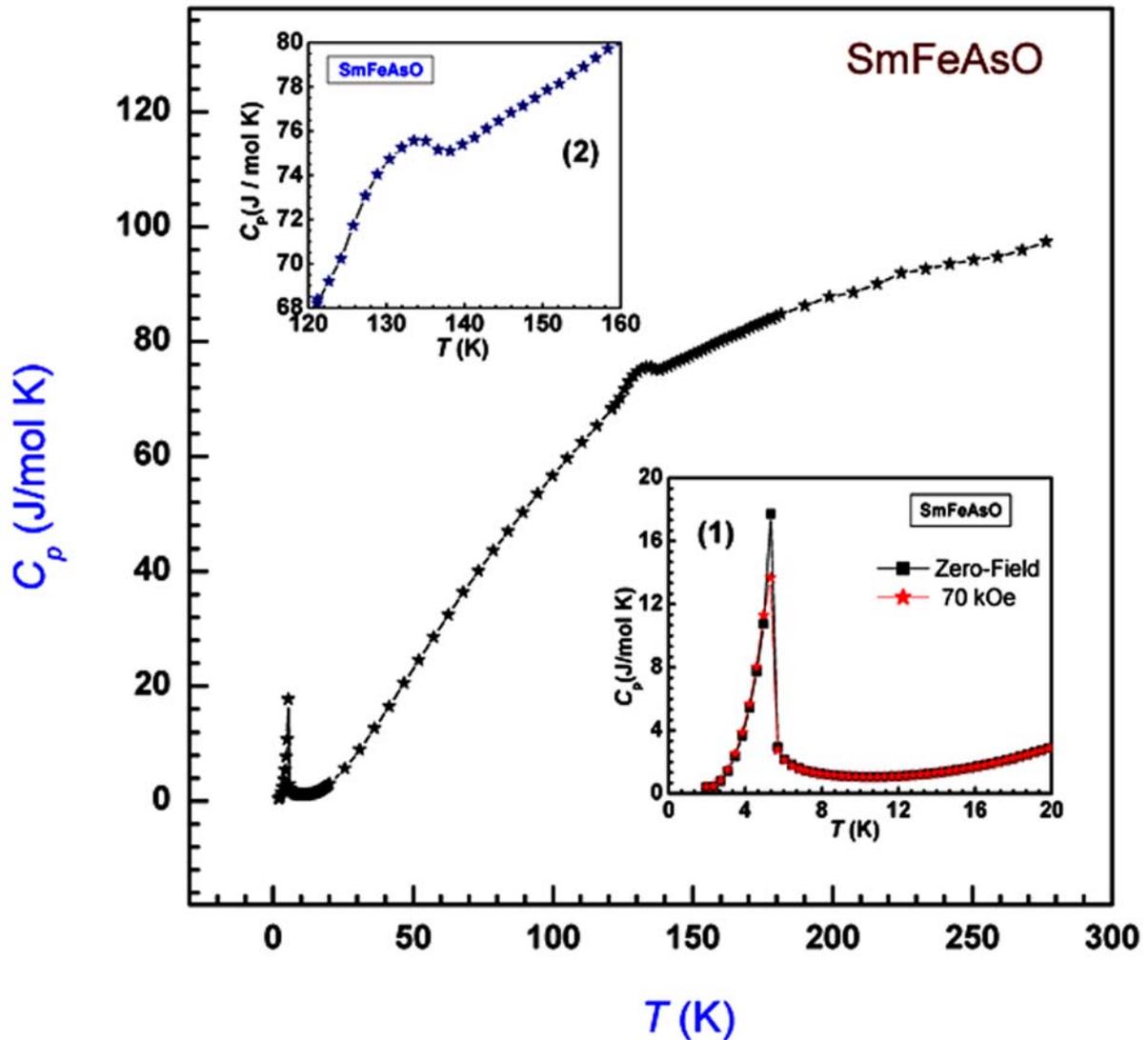
Fig. (7). Specific heat of SmFeAsO sample (main panel); Enlarged view of specific heat of SmFeAsO in the low temperature range at $H = 0$ and 70 kOe (inset 1) and Enlarged view of specific heat of SmFeAsO in the high temperature range (inset 2).

(*SDW*)-like metallic steps at around 140-150 K. Heat capacity $C_P(T)$ measurements on the SmFeAsO compound, showed an anomaly at around 140 K, which is reminiscent of the *SDW* ordering of the compound. Heat capacity (C_P) versus temperature plot for the SmFeAsO compound is shown in main panel of Fig. (**7**). The $C_p(T)$ measurements also exhibited a sharp peak at 4.5 K in addition to the shallow hump at around 140 K. The later is probably due to the *SDW* magnetic ordering and the structural phase transition and the former from *AFM* ordering of Sm^{3+} spins. To understand the nature of the observed two characteristic $C_P(T)$ peaks i.e., $C_P(140K)$ and $C_P(4.5K)$, the same are zoomed and shown in insets of Fig. (**7**). It is noted that sharp specific heat peak obtained at 4.5 K at zero magnetic field does shift anywhere at temperature scale on the application of 70 kOe magnetic field. These results are in well confirmation with other reports [14, 48-49]. Ding *et al.* [48] also observed a jump in specific heat at 130 K for parent SmFeAsO compound, but this jump disappears in the fluorine doped $SmFeAsO_{0.95}F_{0.05}$ sample indicating the suppression of the *SDW* order and structural distortion by

electron doping in the system. Simultaneously another sharp jump was found in heat capacity at 4.6 K and it shifts to 3.7 K upon electron doping in the sample [47].

After calculating the magnetic and non-magnetic contributions to C_p by fitting of data in temperature range 12 K $\leq T \leq$ 20 K [50], the temperature dependence of entropy associated with the magnetic transition was estimated from the C_p^{mag} (T). The magnetic entropy saturates at temperature above 4.5 K to a value $\approx$ 4.5 J/mole K.

6. Superconductivity in the $SmFe_{0.9}Co_{0.1}AsO$ System

It is clear from resistivity analysis Fig. (**2**) that the compound SmFeAsO is non-superconducting but shows the spin density wave (*SDW*) like anti-ferromagnetic ordering at around 140 K. In order to destroy the anti-ferromagnetic ordering and to induce the superconductivity in the parent system, the Fe^{2+} is substituted partially by Co^{3+} in $SmFe_{0.9}Co_{0.1}AsO$ sample. Superconductivity appears in $SmFe_{0.9}Co_{0.1}AsO$ system at around 14 K. The Co doping suppresses the *SDW* anomaly in the parent compound and
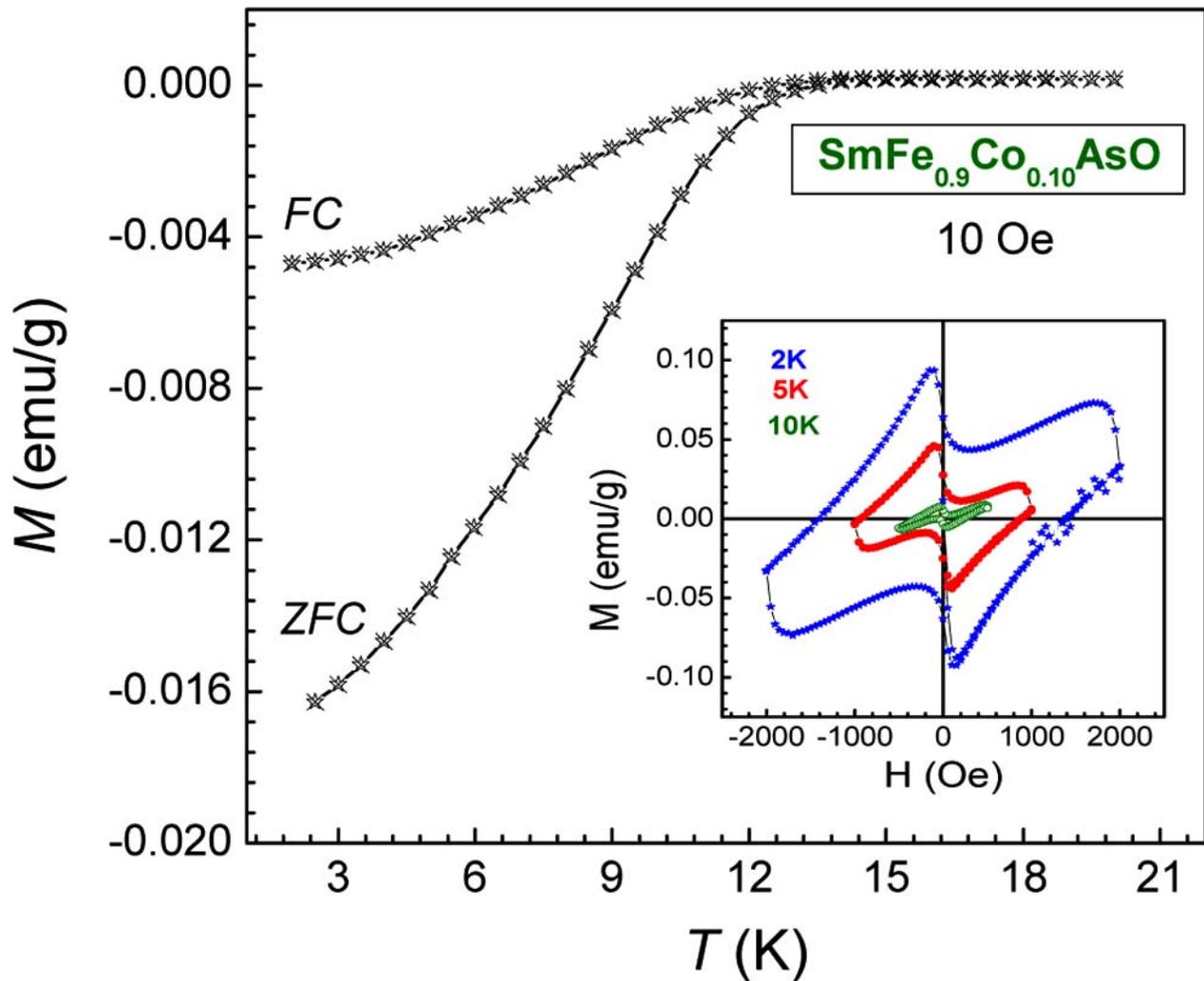
Fig. (8). Temperature variation of magnetic susceptibility $M(T)$ in *FC* and *ZFC* condition for studied SmFe$_{0.9}$Co$_{0.1}$AsO. Inset shows the complete magnetization loops $M(H)$ at 2 and 5 K for studied SmFe$_{0.9}$Co$_{0.1}$AsO.

induces the superconductivity. The structure of SmFeAsO and SmFe$_{0.9}$Co$_{0.1}$AsO at 300 K is refined with the tetragonal space group *P*4/*nmm* (Fig. (**1b**)).

The temperature dependence of magnetic susceptibility, measured in both zero-field-cooled (*ZFC*) and field-cooled (*FC*) conditions at 10 Oe for SmFe$_{0.9}$Co$_{0.1}$AsO is represented in Fig. (**8**). Although the transition is broad, both *ZFC* and *FC* clearly indicate the transition of the compound to a superconducting state below 14 K. The magnetic signal comes out to be negative below 14 K. The onset temperature of superconducting transition T_c^{dia} for SmFe$_{0.9}$Co$_{0.1}$AsO is hence considered at 14 K. The magnitude of the magnetic signal confirms the bulk superconductivity in our sample. The complete isothermal magnetization loops of the studied SmFe$_{0.9}$Co$_{0.1}$AsO at 2, 5 and 10 K are shown in inset of Fig. (**8**). The lower critical field values are seen at around 200, 150, 100 and 50 Oe at 2, 5, 7, and 9K respectively [51].

Hence we can say that Co doping is an alternate way to introduce the charge carriers in Fe-As layer without using the fluorine doping or creation of the oxygen vacancies in the charge reservoir Re-O layer. However, the challenge between competing direct carrier introduced (Fe^{2+}/Co^{3+})

superconductivity and the disorder thus created is yet to be resolved.

7. CONCLUSIONS

We have successfully synthesized the ground state of iron based ReFeAsO (Re =La, Gd, Pr and Sm) by both single step and precursor based double step solid-state reaction routes. The x-ray diffraction and Rietveld refinement confirm the formation of ReFeAsO phase along with minor impurity phases. The *SDW* magnetic character is obtained in the ground state of these compounds between 130-150 K confirmed by both, a metallic step in resistivity measurements and a hump in heat capacity measurements. Sm spins are ordered anti-ferro-magnetically (*AFM*) at 4.5 K in SmFeAsO. The Mössbauer Spectroscopy (*MS*) proved to be the most efficient technique in determining the FeAs based impurities in these materials, which are often not observed in x-ray diffraction. The FeAs extra phases are obtained regardless to the preparation method of the desired materials. Besides oxygen deficiency and fluorine doping, an alternative way of inducing superconductivity by Fe site Co substitution is proposed and superconductivity is obtained in SmFe$_{0.9}$Co$_{0.1}$AsO at 14 K.

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