JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

THE PROGRESS IN THE IRON PNICTIDES SUPERCONDUCTOR

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***Abstract** :*Superconductivity is remarkable phenomena in many materials at low temperature shows that the vanishing of electrical resistance and exclusion of magnetic field. Superconducting materials have important in power application due to high upper magnetic field and low anisotropic property. This article gives a brief overview of the development of iron based pnictide superconductors. It is based on the macroscopic quantum states of electron pairs. The report covers the advancement in the field that has been resulted in higher transition temperatures for superconductors in iron-based materials. The present report describe the crystal structure, classification of iron based superconductor and its superconducting properties.

Key word- Iron based superconductor, superconductivity, transition temperature

I. INTRODUCTION

Superconductivity is the most spectacular phenomenon in condensed matter physics, and realizing superconductivity at ambient temperature is the ultimate goal of researchers. Many metal and compounds exhibit a sudden decrease in resistivity when cooled to low temperature. This phenomena was called as superconductivity and first observed by Dutch scientist Kammerling Onnes in1908.In 1911 he discovered the phenomena of superconductivity while studying the properties of mercury especially resistivity at low temperature (T_c=4.2K) [1]. Next to vanishing of electrical resistance, another understanding of how matter behaves at extreme low temperature was occurred 1933 known as Meissner effect [2]. In 1934 Gorter and Casmir phenomenological understanding superconductivity by floating the two fluid model [3]. Below the superconducting transition temperature, the current flow is due to the superconducting electrons. In 1957 Bardeen, Cooper and Schrieffer (BCS) theory explained pairing interaction (electron pairing called Cooper Pair)originated from lattice vibration. In 1950's decade, Bernd Matthias assisted by John Hulm and Ted Geballe carried out a systematic crystallographic study of periodic table allowing the formulation and discovery of materials with critical temperature as high as 23 K. In 1986, a breakthrough discovery of brittle ceramic compound with composition $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$with transition temperature (T_c) above 30 K [4]. Cuprate superconductors by Bednorz and Muller triggered intensive research worldwide and the highest critical temperature was raised to 130 K in the HgBaCaCuO system at ambient pressure and increased to 164 K at high pressure 31 GPa in cuprate superconductors [5]. Further in 1994, discovery of intermetallic superconductors which incorporate borocarbides $RETm_2B_2C$ where R= Y,Er, Dy, Tm= Ni or Pd [6,7]. The main characteristic of these compounds are very high Tc among intermetallic.Since mercury was discovered to be superconductive, many more different types of superconducting materials have been identified. Based on their constituents and structure, superconductive materials can be classified into different categories as pure metals (mercury, niobium, lead), alloys (Nb-Ti, Nb-Ge), ceramic compounds ($PbMo_6S_8$) intermetallic compounds (Nb_3Sn, NB_3Al, MgB_2), copper based oxides (cuprates) etc. The cuprates have been studied carefully for two decades but still lack a complete understanding of how they work. The cuprate superconductor exhibits high anisotropy, a very short coherence length and is brittle, all of which make its large-scale applications difficult.

In 2006, Japanese group Y. Kamihara et.al at the Tokyo Institute of Technology discovered a new superconductor based on iron, LaFeOP can conduct electricity without resistance at 4 K [8]. When LaFe $[O_{1-x}F_x]$As was doped with fluorine, a large increase in T_c up to 26 K was found by the same Japanese group and reported in the Journal of American Society, 2008 [9]. Using external pressure of about 3 Gpa [10] or substituting La with other rare earth metals like Sm, it's been possible to get Tc above 55 K [11]. In 2008, the Hosono group at Tokyo Institute of Technology discovered a type of superconductor called an iron-based superconductor. This was the start of the "iron age" of high-temperature superconductors, which followed the "copper age" which was made up of cuprate superconductors. Depending on the chemical composition and crystal structure of the superconductor, it can be divided into different types, like the "1111" type (e.g., $LaFeAsO_{1-x}F_x$ and $SmFeAsO_{1-x}F_x$)[9,12], '122' type(e.g $Ba_{1-x}K_xFe_2As_2$ with Tc= 38 K[13], '111' type (e.g.,LiFeAs)[14,15,16]T_c up to 18 K and '11' type (e.g., FeSe, $FeSe_{1-x}Te_x$)Tc upto 27 K under pressure [17,18]. Just like cuprate basedsuperconductors, iron based superconductor's exhibit a layered crystal structure, small coherence length, and high upper critical fields as well as low anisotropic electromagnetic properties. Although the Tc values of iron (Tc = 38 K in the case of '122' system, 56 K in case of '1111' system) are lower than those of cuprate, the anisotropic properties of iron superconductors are remarkably low. Iron based superconductors are highly attractive for high field applications due to their high upper crtical field and low anisotropic which can operate upto range 20 K. This development of high temperature superconductivity over time is shown in figure 1.

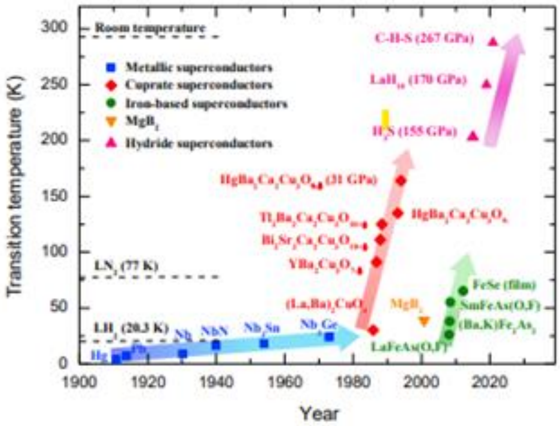

Fig. 1 Development of high temperature superconductivity over time

(Image source-https://en.wikipedia.org/wiki/Hightemperature_superconductivity)

Crystal structure of LaOFeAs :.

The LaFeAsO is the undoped parent compound of a superconductor and is part of the large family of LnTMPnO (where Ln=La,Ce, Po, Nd, Sm, Eu and Gdetc; M = Mn, Fe, CO and Ni etc; P = P and As etc). It is composed of four elements: Ln, representing (4f) rare earth element, TM- which is a transition metal with a shell that is more than half filled, and Pn – a pnicogen element. The origin of this type of material can be traced back in year 1995, when a german group fabricated a number of materials with same ZrCuSiAs type crystal structure. The LaOFeAs has layered crystal structure and a tetragonal $P_{4/nmm}$space group with lattice parameter a = 4.035 A and c = 8.7409 A [9]. Figure 2 shows the typical crystal structure of LaFeAsO .

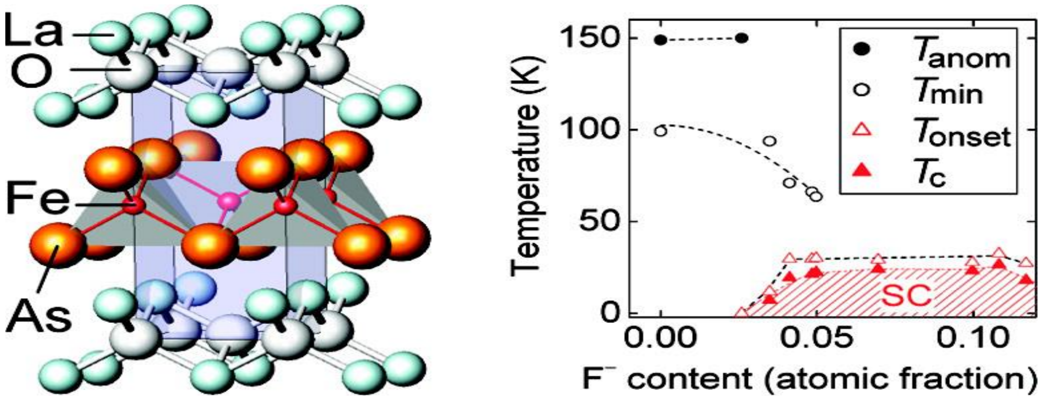

Fig. (2) *Crystal structure of LaOFeAs [33]*

Similar to high Tc cuprate superconductor iron pnictides are also layered structure. The LaOFeAs is composed of an alternate stack of (LaO) and (FeAs) layers where the Fe atoms are arranged in a simple square lattice. In a single cell there are two molecules of LaOFeAs are present and the valance of the cell s self balanced in its parent phase, whichis composed of charge of $(LaO)^{1+}$ and $(FeAs)^{1-}$. The Fe_2As_2 layer is sandwiched between the La_2O_2 layers acts as a charge reservoir [19, 20]. Thus, conduction carriers are two-dimensionally bonded in the Fe_2As_2 layer results in between interactions among the electrons. Further, the substituting F for O^{2-} or by oxygen deficiency in insulating La_2O_2 layer may introduce the electron carriers. Subsequently other series of Fe based analogous new compounds have been discovered including AFe_2As_2 (A is an alkali earth metal element such as Sr and Ba) [14,15] and LiFeAs [16]. Among them the observed lower T_c in LaFePO and LaNiP(As)O (T_c = 2–4 K) [18,19], strongly suggests that FeAs layers play an important role in the high T_c.

Synthesis Method of Pnictides:

Solid State Method: This method is carried out at high sintering temperatures in resistive heating box furnaces. Because of the air-sensitivity or toxicity of many of the reactants, the air exposure is minimal or avoided. For producing 1111 iron based superconductor, parent compound LaFePO can be chemically substituted for oxygen with fluorine and Phosphorous with Arsecnic $T_C \approx 26$ K was raised in $LaFeAsO_{1-x}F_x$ [9]. To synthesize polycrystalline sample LaOFeAs a mixture of precursor powders such as lanthanum arsenide, iron arsenide, and dehydrated La_2O_3 was filled in a silica tube heated at 1250 °C for 40 h with Ar gas. Other fluorine-doped 1111 polycrystalline superconductors, are discovered by replacement of La with other rare-earths in $SmFeAsO_{1-x}F_x$ and $NdFeAsO_{1-x}F_x$with T_C values as high as 55 K.

Synthesis of $SmFeAsO_{0.7}F_{0.3-\delta}$ (Sm-1111) superconducting wires by a one-step solid state reaction at temperatures 850–900 ◦C for 40 hr in Ar atmosphere was reported by Wang et.al [21]. The Tc critical transition temperature is strongly dependent on fluorine concentration in $SmFeAsO_{1-x}F_x$; suggest that the Sm1111 phase with a higher Tc can be produced at such low temperatures by reducing the volatility of fluorine.

High-pressure method: The high pressure method allows for considerably shortened reaction times and reduced evaporation of volatile elements. This method synthesis the metastable structures and produces materials with low oxidation states Shirage et.al reported a high pressure synthesis method used to prepare polycrystalline samples. The starting materials are La, As chips with particle diameter 1-4 nm, Fe powder and α Fe_2O_3 powder at molar ratio1:1:1:1-y. the oxygen content was controlled by changing ratio of Fe and Fe_2O_3. The powders were encapsulated into closed BN sleeve and then embedded into solid media, which transmit the pressure (typically 2 GPa) from surrounding anvil. Samples are heated at 1050- 1150 °C insitu using electrical heater that surround BN sleeve. Thus, prepared polycrystalline samples of LaFeAsO shows maximum Tc = 28 K. Introduction of oxygen vacancies results in decrease of lattice parameter [22].

Flux growth method at ambient pressure is used for synthesis of single crystals For growth of single crystals they used NaCl/KCl as flux. The single crystal of LnFeAsOF (where Ln = La, Nd, Ce, Pr, Sm and Gd) material have grown using flux NaCl/KCl a pressure of 3 GPa was applied and temperature of 1350-1450 °C maintained for 4-10 hr and decreased over 5-24 h to R.T. for crystal growth. The crystals obtained have maximum size of 300 µm [23]. PrFeAsO1-xFx have been grown from alkali metal chloride flux by sintering at 1250 ºC for 2 hrsand 6 GPa [24].

Powder in Tube method: Iron based superconducting wires and tapes are fabricated by the powder-in-tube (PIT) method. In this method precursor powders are put into metallic tube, swaged, drawn, and then annealed at temperature. Yanwei Ma etal reported the synthesis of $SmFeAsO_{0.8}F_{0.2}$ bulk samples. Precursor powders such as high-purity Sm, SmF_3, Fe and Fe_2O_3, were thoroughly mixed and put into a Ta tube with tightly close ends under an Ar atmosphere. The tubes were then swaged, welded into an Fe tube and annealed at a temperature of 1180 ºC for 45 hours under Ar. The samples sintered was extracted by breaking the Fe and sheath tubes The final Ta sheathed $SmFeAsO_{1-x}F_x$ wires of about 2.00 mm diameter drawn[25]. Fe sheathed $LaFeAsO_{0.9}F_{0.1}$ wires with Ti as a buffer were fabricated by Powder in tube (PIT) method and achieved transition temperature of around 25 K. the micrograph shows a homogenous microstructure with a grain size 1-3 µm [26]. Wang et al have systematically studied the influence of sintering temperature on the superconductivity of polycrystalline SmFeAsO0.8F0.2 [21], and found that samples sintered at a low temperature clearly show high Tc, as shown in figure 30, for example the Tc of the samples sintered at 850 ◦C is even above 53 K, and the samples prepared at 1000 ◦C display the highest Tc of 56.1 K reported so far.

Pulsed Laser Deposition: A high power pulsed laser beam is used to vaporize the target material. The wavelength, pulse laser ablation rate, target material -substrate condition, vacuum condition have influence on the nucleation and growth of the film. Iron based superconductor films has been synthesized with different laser sources of wavelength ArF (λ = 193 nm), KrF (λ = 248 nm), XeCl (λ = 308 nm) and Nd:YAG lasers (λ = 532 nm). The growth and anisotropy of pulsed laser deposited La(O,F)FeAs films reported by Backen et al. [27]. Haindl et al. reported in situ PLD growth of high-quality undoped and Fe-oxypnictide Sm(O,F)FeAs epitaxial films using a Nd:YAG laser (2ω) with laser repetition rate of 10 Hz and incident laser beam energy around 20–25 mJ. The high power laser system used to heat the CaF2(100) substrate 850-875°C under UHV environment (chamber base pressure $p = 5 \times 10^{-9}$ mbar)[28]

Superconducting properties of pnictides:

LaOFeAsoxypnictides are refered as 1111pnictides. At low temperatures iron based compounds of superconductors may exhibit either superconductivity or anti-magnetic properties which are undoped for example LaFePO, LiFeAs, or FeSe are non maganetic and superconducting. LaOFeP [20] has already been subjected to band structure calculation and is cabale of superconducting at a resolution of approximately 4K, demonstrating the metallic behavior up to a temperature of 300 K. However the temperatures dependent resistivity of this system is significantly lower than that of undoped LaOFeAs, with significant decrease in resistvity at temperature of approximately 150K [9] and a slight increase at a temperature of zero. The electrical resistivity of pure LeFePO reduces at 4 K, but that of F-doped LaFePO drops at higher temperatures, as illustrated in Figure.3. Magnetic susceptibility experiments for pure and F doped LaFePO confirmed superconducting transitions, as shown in Fig. 3(c). It's also important to note that resistivity in LaFePO starts at 10 K. On the other hand, LaFeAsO that's been undoped doesn't show any superconductivity. Doping with electrons or holes reduces the magnetic order and induces electrical conduction. LaFeAsO was found to undergo an irregular structural transition at 155 K by neutron scattering experiment [29].

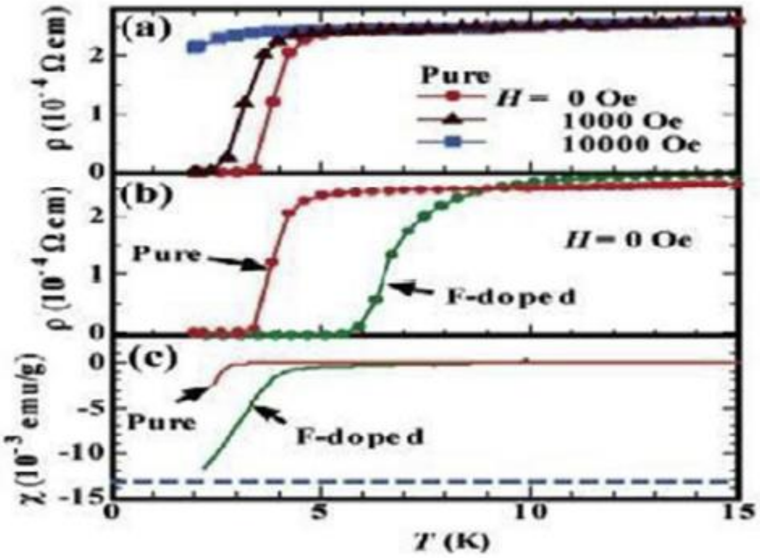

Figure. 3 Electrical resistivity, ρ vs. temperature, T, (a) for pure LaFePO at various magnetic field, H. (b) Electrical resistivity, ρ vs. temperature, T for pure and F doped LaFePO and (c) magnetic susceptibility, χ, vs T for pure and F doped LaFePO [32].

Shirge et al reported theY^{+3} (1.019 Å) substitution on the La^{+3} (1.16 Å) based iron oxypnictide superconductor LaFeAsO$_{0.6}$, 20 K class superconductor enhanced transition temperature_*Tc*_ up to 43.1 K . *Tc* increases and lattice parameters shrinks concomitantly with Y substitution on La. This fact shows that the internal chemical pressure caused by Y-La substitution is an important factor that improves *Tc.*

Mukuda et.al. reported the NMR studies on the oxygen deficient iron based oxypnictides superconductors LaFeAsO$_{0.6}$ with Tc=28 K along the results on LaFeAsO$_{0.75,}$ Tc=20 K and NdFeAsO$_{0.6}$ Tc=53K, enhancement of Tc in the Fe–oxypnictide superconductors is strongly related to the optimal local configuration of Fe and As atoms, and the optimal bandstructure derived from the hybridization between As 4p orbitals and Fe 3d orbitals [30,31]. A list of 1111 type iron based superconductors is given in table 1.

Table1: 1111 type iron based superconductors

Sr. No.	1111 type -Oxypnictide	Critical transition Temperaure (T_c)	Reference
1.	LaFePO	4 K	8
2.	$LaO_{0.89}F_{0.11}FeAs$	26K	9
3.	$LaFeAsO_{0.9}F_{0.1}$	25K	26
4.	$NdFeAsO_{0.6}$	53K	28
5.	$PrFeAsO_{0.89}F_{0.11}$	52 K	25
6.	$GdFeAsO_{1-y}$	55 K	28
7.	$CeFeAsO_{0.84}F_{0.16}$	41 K	33
8.	$SmFeAsO_{1-x}F_x$	58.1 K	32

The parent compounds of undoped iron based superconductors exhibit either superconductivity or antiferromagnetic at low temperatures for example undoped LaFePO, LiFeAs, are non magnetic and superconducting. On the other hand parent compound of LaFeAsO are non-superconducting antiferromagnetic metals.In the presence of electron or hole doping, the magnetic order is suppressed and superconductivity is induced**.** The pnictides of undoped 1111-type iron based superconductors show structural and magnetic phase transitions at slightly different temperatures. Neutron scattering experiments shows that LaFeAsO undergoes an sudden structural transition from tetragonal structure (space group P4/nmm), at high-temperature 155K to low-temperature monoclinic structure (space group P112/n).

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