# The Continuing Quest for High Tc – Superconductors: A Review

# ABSTRACT

Superconductors, perhaps a mirage in the eyes of most chemists for many years, was pushed to the forefront of chemical interest with the synthesis and characterization of the first "high - temperature" superconductor (Sr-doped La<sub>2</sub>CuO<sub>4</sub> or 2-1-4) in 1986 [1]. The first superconductor with a Tc above the boiling point of liquid nitrogen (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> which is often referred to as "1-2-3" compound because of Y: Ba: Cu stoichiometry) was synthesized a year later [2]. This was a time in which superconducting materials created unprecedented excitement in scientific community; it was a year in which the public was captivated by new vistas in technology. The title of the article reflects that there is a crave for superconductors and reflects the notation that chemistry can have a positive impact upon our lives. Firstly, the historical background of superconductivity is presented then the theory of superconductivity and the description of physical and chemical principles upon which it rests is given. Finally, some prospects for the future applications of these new materials are discussed.

#### 10 Keywords: High Tc superconductor, 1, 2, 3, compound; liquid nitrogen; Y:Ba:Cu; Phonons

# 11

# 12 **1. INTRODUCTION**

Superconductivity is the ability of certain metals, alloys and ceramic materials to let electrical current flow with no electrical resistance and energy dissipation. A superconductor is generally considered as a conventional superconductor if it can be explained by BCS theory. Conventional superconductors can be either type-I or type-II. Most of the elemental superconductors are conventional except Niobium and Vanadium which are type-II. While other elemental superconductors are type-I but the recently advanced high temperature superconductors are type II or unconventional [3].

20 Since the initial discovery of superconductivity in 1911 by KamerlinghOnnes [4], great 21 advances have been made in both the understanding of the phenomenon and the materials 22 which exhibit it. The materials which exhibit superconductivity have steadily grown in number and variety, but the number used in practical, commercial applications is still rather small. 23 24 Even though few theories have been developed and widely accepted, extensive researches are underway regarding the deep understanding of the concept of superconductivity, the 25 26 chemical composition of different superconductors, and to use them as a substitute of the 27 normal conductors in the commercial world. But Understanding the mechanism of high-28 temperature super-conductivity has remained a subject of much interest since its 29 experimental discovery in the cuprates in 1986 [5].

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The most important characteristic of any superconductor, from the viewpoint of practical applications, is the maximum electrical transport current density that the superconductor is able to maintain without resistance. This statement is equally true for large-scale applications, such as power transmission lines, electromagnets, transformers, fault-current limiters and rotating machines, as well as for small-scale electronic applications [6].

Therefore in this review, the events in the historical developments of superconductivity including the theories, physical and chemical properties which describe the nature of superconductors, the recent advancement and challenges in the application of HTSC and the future perspectives of high temperature superconductors will be discussed in detail.

# 39 2. HISTORY OF SUPERCONDUCTIVITY

40 The history of superconductivity as a phenomenon is very rich, consisting of many events 41 and discoveries. The first phenomenon of superconductivity was discovered in 1911 by the Dutch physicist H. KamerlinghOnnes and his assistant Gilles Holst in Leiden. They found 42 43 that dc resistivity of mercury suddenly drops to zero below 4.2K [7]. In their subsequent 44 experiment they cooled a mercury sample to 3K and again observed that the resistance was 45 "practically zero". As the temperature of the sample was slowly raised, near 4K, the 46 resistance abruptly increased, by more than three orders of magnitude over a temperature 47 interval much less than 0.1K.

48 Soon after two decades of the discovery of superconductivity, in 1933, W. Meissner and R. 49 Ochsenfeld discovered in Berlin one of the most fundamental properties of superconductors: 50 perfect diamagnetism. The applied magnetic field, below transition temperature, gets to 51 magnetize the substance in an opposite direction, so it shows a negative magnetic 52 susceptibility. They found that the magnetic flux is expelled from the interior of the sample 53 that is cooled below its critical temperature in weak external magnetic fields. Thus, they found that no applied magnetic field is allowed inside a metal when it becomes 54 superconducting. This phenomenon is known today as the Meissner effect [6, 7]. 55

56 Following the discovery of the expulsion of magnetic flux by a superconductor (the Meissner 57 effect) the brothers F. and H. London together proposed in 1935 two equations to govern the 58 microscopic (local) electric and magnetic fields. These two equations provided a description 59 of diamagnetism of superconductors in a weak external field. In the framework of the two-60 fluid model, the London equations, together with the Maxwell equations describe the 61 behavior of superconducting electrons. The London equations explained not only the Meissner effect, but also provided an expression for the first characteristic length of 62 superconductivity, namely what became known as the London penetration depth  $\lambda L$ [7, 9]. 63

64 Also in 1950, V. Ginzburg and L. Landau proposed an intuitive, phenomenological theory of 65 superconductivity. The equations derived from the theory are highly non-trivial, and their validity was proven later on the basis of the microscopic theory. The Ginzburg-Landau 66 67 theory played an important role in understanding the physics of the superconducting state. 68 This theory is able to describe the behavior of superconductors (both conventional and 69 unconventional) in strong magnetic fields. The Ginzburg-Landau theory provided the same 70 expression for the penetration depth as the London equations and also an expression for the 71 second characteristic length  $\xi$  GL, called the coherence length [7, 9, 10].

The first widely-accepted theoretical understanding of superconductivity was advanced in 1957 by American physicists John Bardeen, Leon Cooper, and John Schrieffer which is called the "BCS theory". They described, in great detail, the unique electrical and thermal properties of the superconducting state. The central concept in the BCS theory are the 76 cooper pair of electrons in which such electrons pass through a crystal lattice, the lattice 77 deforms inward towards the electrons generating sound packets known as "phonons". These 78 phonons produce a trough of positive charge in the area of deformation that assists 79 subsequent electrons in passing through the same region in a process known as phonon-80 mediated coupling. For their pioneering work in developing their theory, they received the 81 Nobel Prize in Physics in 1972 [6, 8, 9].

 Quantum-mechanical tunneling of Cooper pairs through a thin insulating barrier (of the order of a few nanometers thick) between two superconductors was theoretically predicted by B.
 D. Josephson in 1962. The DC Josephson effect and AC Josephson effect collectively called the Josephson effects of mathematical predictions were later experimentally approved and played a special role in superconducting applications. [7, 11].

87 During the first 75 years after the discovery of superconductivity in mercury, more than 5,000 88 elements, compounds and alloys were discovered to exhibit superconductivity at a 89 temperatures below about 23 K [8]. But the idea of High-Temperature Superconductivity was 90 not still developed. In 1964 Little hypothesized that high-temperature super- conductivity can 91 be realized in one-dimensional structures on the basis of the exciton mechanism. According 92 to his hypothesis, the system should contain long linear conducting molecules(polyenes or 93 polymers with metallic atoms in an organic matrix), and on each side of these molecules 94 groups of atoms with a high electronic polarizability should be located. These side branches 95 should guarantee the mutual attraction of the conducting electrons as a result of the 96 exchange of molecular excitations of the electronic type [12].

97 The notable events in this regard were the discovery of  $Nb_3Sn$  in 1954 and its wire 98 development in 1961. They were followed quickly the discovery of other A15 materials and 99 NbTi, the currently most-used material. These enabled the construction of electromagnets 100 which can produce much higher magnetic fields than conventional copper-wire 101 electromagnets [13].

102 In 1977, Ginzburg and coworkers at the P. N. Lebedev Physical Institute in Moscow 103 published a book entitled "High-Temperature Superconductivity". In this book, they 104 discussed the possibility of high-temperature superconductivity in many types of materials, 105 including quasi-one and- two-dimensional materials. The appearance of this book excited 106 scientists in many countries and the discovery of HTS materials aroused tremendous 107 excitement, because many of them are superconducting and carry significant current above 108 the boiling point of liquid nitrogen at 77.4 K (-196  $^{\circ}$ C) [12,14].

109 The true history of high Tc superconductors was began in 1986 with the discovery of superconductors on the system Ba-La-Cu-O having the critical temperature 36K by Karl 110 111 Muller and Johannes Bednorz in IBM research laboratory. They studied the phenomenon of 112 high-temperature superconductivity in the cuprateperovskites materials and they proposed 113 high-Tc superconductivity is achieved when a moderate density of electrons or holes is 114 introduced into the parent antiferromagnetic phases of the cuprate. This opened a new branch of high Tcsuperconductivity namely "High Tc superconductivity" [15,16]. Soon after 115 116 this many other oxide based superconductors were discovered having transition 117 temperatures (Tc) up to 138 K (164 K under pressure) [4].

In 1987, the groups at the Universities of Alabama and Houston under the direction of M. K.
 Wu and P. W. Chu, respectively, jointly announced the discovery of the 93 K superconductor
 Y-Ba-Cu-O. Electron-doped high-Tc cuprates were also first discovered by Tokura et al. in
 1989 [7]. Pronounced features different from those in the hole-doped cupratesis not only the

electron carrier, but also the reduction annealing, which is absolutely essential to obtain thesuperconductivity in the electron-doped cuprates [17].

124 In 1990, A. S. Davydov presented a theory of high-Tc superconductivity based on the 125 concept of a moderately strong electron-phonon coupling which results in perturbation theory 126 being invalid [7]. The theory utilizes the concept of bisolitons, or electron (or hole) pairs 127 coupled in a singlet state due to local deformation of the -O-Cu-O-Cu- chain in the CuO<sub>2</sub> 128 planes.

129 In 2005, a surprising result was obtained in thin films of the electron-doped cuprates with the 130  $Nd_2CuO_4$ -type structure (the so-called T' structure), in which the superconductivity appears 131 without electron doping. Following observations of the undoped (Ce-free) superconductivity 132 in the parent compounds and the suggestion of a new phase diagram opened a new era of 133 research in the high-Tc superconductivity. Yet to date, the mechanism of the undoped 134 superconductivity is unclear [17].

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# 136 **3. THEORY OF SUPERCONDUCTIVITY**

Superconductivity is not a universal phenomenon. It shows up in materials in which the electron attraction overcomes the repulsion [7]. Even though the core concept of superconductivity is the above phenomenon, there are different theories regarding the nature, physics of conductivity, type of conductors, physical state of the superconductors etc.

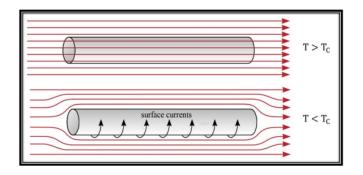
# 141 **3.1. London Theory**

142 In 1935 F. London and H. London described the Meissner effect and zero resistivity of the 143 superconducting material by taking E= 0 and B = 0 in the Maxwell's electromagnetic 144 equation.

145 
$$B(x)=B_0exp(-x/\lambda_L)$$

This first London equation is consequence of the perfect magnetism [18]. According to this,
the applied field does not suddenly drop to zero at the surface of the superconductor but
decay exponentially according to the equation.

According to this theory a magnetic flux penetrating through a superconducting ring or a hollow superconducting cylinder can have values equal to nh/e, where n is an integer. The flux quantization has been confirmed experimentally, but the quantum of flux has been found to be h/2e rather than h/e. This unit of flux is called a fluxoid [16].



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Fig.1. Meissner effect later approved by London theory [40]

#### 155 **3.2. Ginzburg - Landau Theory**

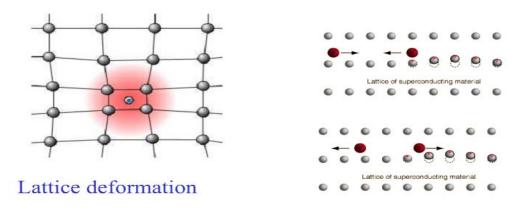
156 In 1950, seven years before the microscopic theory of Bardeen, Cooper and Schrieer (BCS) 157 was published, Ginzburg and Landau proposed a macroscopic, phenomenological theory of 158 superconductivity to describe the properties of superconductors for temperatures near the 159 critical temperature. There is no concept of the coherence length  $\xi$  in the London equation. 160 Ginzburg and Landau proposed the phenomenological theory of the superconductor by using the order parameter  $\psi = |\psi_0| \exp(i\theta)$  [6,18]. According to the Ginzburg–Landau theory, 161 when  $\psi$  is small, the Helmholtz free energy per unit volume of the superconductor is 162 expanded as a Taylor series of  $|\psi|^2$ . Thus we have 163

164 
$$F_s = F_n + \alpha |\psi_0|^2 + (\beta/2) |\psi_0|^2$$

165 Where  $F_s$  and  $F_n$  are the Helmholtz free energies for the superconducting state and the 166 normal conducting state, respectively, and  $\alpha$  and  $\beta$  are the expansion coefficients.

#### 167 **3.3. BCS Theory**

168 The first widely-accepted theory to explain superconductivity put forth in 1957 by John 169 Bardeen, Leon Cooper, and John Schreiffer. The theory asserts that, as electrons pass 170 through a crystal lattice, the lattice deforms inward towards the electrons generating sound packets known as "phonons". These phonons produce a trough of positive charge in the 171 172 area of deformation that assists subsequent electrons in passing through the same region in 173 a process known as phonon-mediated coupling. The consequence is an attractive interaction 174 between the two electrons. Now, the correlated pair of electrons is referred to as a Cooper 175 pair. Cooper pairs occupy a collective state and move through the crystal lattice unimpeded 176 [6,9, 16].



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#### 178 Fig.2. Schematic representation of phonon-electron attraction in a lattice [9]

179 When sufficient energy is supplied to Cooper pairs, they will decouple and the 180 superconducting state ceases. Since the momentum is proportional to current density, the 181 energy required to break Cooper pairs implies the existence of a critical current density Jc 182 [20]. When Jc is exceeded, the Cooper pairs are destroyed. The energy required to break 183 Cooper pairs also comes in the form of thermal energy from the vibrations of the crystal lattice and magnetic energy from magnetic fields. The former implies the existence of a 184 185 critical temperature Tc, mentioned above, while the latter suggests the existence of a critical magnetic field H<sub>c</sub>. The critical field depends on material and is temperature dependent 186 187 according to the following equation

 $H_c = H_0 [1 - (T/T_c)]^2$ 

189 Where  $H_0$  is the value of the critical field strength as  $T \rightarrow 0$ .

190 The BCS theory in its original form cannot be applied to the high temperature 191 superconductors because the BCS predicted temperature are too low and because of non 192 occurrence of the BCS predicted isotope effect [9,18].

# 193 3.4. Possible mechanism of conductivity in HTSC

194 Until Fe-based superconductors were discovered in 2008, the term high-temperature 195 superconductor was used interchangeably with cuprate superconductor for compounds such 196 as bismuth strontium calcium copper oxide (BSCCO) and yttrium barium copper oxide 197 (YBCO) [19].

The question of how superconductivity arises in high-temperature superconductors is one of the major unsolved problems of theoretical condensed matter physics as of 2010 [9, 14]. The mechanism that causes the electrons in these crystals to form pairs is not known [7]. Despite intensive research and many promising leads, an explanation has so far eluded scientists. One reason for this is that the materials in question are generally very complex, multilayered crystals (for example, BSCCO), making theoretical modeling difficult.

204 There have been two representative theories for HTS. Firstly, it has been suggested that the 205 HTS emerges from antiferromagnetic spin fluctuations in a doped system [21]. According to 206 this theory, the pairing wave function of the cuprate HTS should have a  $d_x^2$ -y<sup>2</sup> symmetry [50]. Thus, determining whether the pairing wave function has d-wave symmetry is essential to 207 208 test the spin fluctuation mechanism. That is, if the HTS order parameter (pairing wave 209 function) does not have d-wave symmetry, and then a pairing mechanism related to spin 210 fluctuations can be ruled out. Secondly, there was the interlayer coupling model, according 211 to which a layered structure consisting of BCS-type (s-wave symmetry) superconductors can 212 enhance the superconductivity by itself. By introducing an additional tunneling interaction 213 between each layer, this model successfully explained the anisotropic symmetry of the order 214 parameter as well as the emergence of the HTS [7, 9, 22, 23]. 215

# 216 4. PROPERTIES OF SUPERCONDUCTING STATES

Among the many superconducting properties some basic and significant physical and chemical properties are discussed. Along with those properties, the superconducting property of cuprates particularly YBCO is presented.

#### 220 **4.1. Critical temperature**

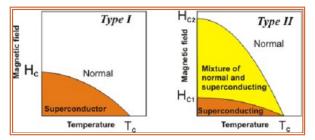
221 The most commonly known property of the superconducting state is that a superconductor is 222 characterized by a critical temperature, below which the material exhibits "zero" resistance 223 [8]. The critical temperature is mainly determined by chemical composition and structure, 224 [24].Superconducting cuprate materials have higher transition temperatures. YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> 225 (YBCO) has a Tc of 93 K which is significant because it is greater than the boiling point of 226 liquid nitrogen at atmospheric pressure. Bi-Sr-Ca-Cu-O, TI-Ba-Ca-Cu-O, Hg-Ba-Ca-Cu-O 227 and Hg-TI-Ba-Ca-Cu-O compounds have higher critical temperatures as shown in the table 228 [25]. All these high temperature superconductors have highly anisotropic crystal structures, 229 containing layered CuO<sub>2</sub> planes in which the superconducting charge carriers are thought to 230 be localized.

Compounds	тс к	Compounds	ТС К
YBA <sub>2</sub> CU <sub>3</sub> O <sub>7</sub>	93	TL <sub>2</sub> CABA <sub>2</sub> CU <sub>2</sub> O <sub>8</sub>	119
YBA <sub>2</sub> CU <sub>4</sub> O <sub>8</sub>	80	TL <sub>2</sub> CABA <sub>2</sub> CU <sub>2</sub> O <sub>10</sub>	128
Y <sub>2</sub> BA <sub>4</sub> CU <sub>7</sub> O <sub>15</sub>	93	TLCABA <sub>2</sub> CU <sub>2</sub> O <sub>7</sub>	103
BI <sub>2</sub> CASR <sub>2</sub> CU <sub>2</sub> O <sub>8</sub>	92	TLCA <sub>2</sub> BA <sub>2</sub> CU <sub>3</sub> O <sub>8</sub>	110
BI <sub>2</sub> CA <sub>2</sub> SR <sub>2</sub> CU <sub>3</sub> O <sub>10</sub>	110	$TL_{0.5}PB_{0.5}CA_2SR_2CU_3O_9$	120
HGBA <sub>2</sub> CA <sub>2</sub> CU <sub>3</sub> O <sub>8</sub>	135	HG <sub>0.8</sub> TL <sub>0.2</sub> BA <sub>2</sub> CA <sub>2</sub> CU <sub>3</sub> O <sub>8.33</sub>	138

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#### 233 **4.2. Critical magnetic fields**

234 Superconducting state can be destroyed by a sufficiently strong magnetic fields. But for type-Il superconductor, there are two critical fields, the lower critical field H<sub>c1</sub> and the upper critical 235 236 field H<sub>c2</sub>. In applied fields less than Hc<sub>1</sub>, the superconductor completely expels the field, just as a type-I superconductor does below H<sub>c</sub>. At fields just above H<sub>c1</sub>, flux, however, begins to 237 penetrate the superconductor.Type II superconductors are the most technologically useful 238 239 because the second critical field can be quite high, enabling high field electromagnets to be 240 made out of superconducting wire. Wires made from say niobium-tin (Nb<sub>3</sub>Sn) have a  $H_{c2}$  as 241 high as 24.5 Tesla - in practice it is lower. This makes them useful for applications requiring high magnetic fields, such as Magnetic Resonance Imaging (MRI) machines, [7]. 242



- Fig. 3. Schematic plot of magnetic field vs temperature to type-I and type-II
   supercoductor.[40]
- 246 **4.3. Critical current**

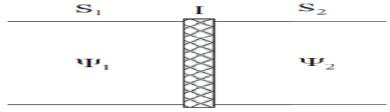
247 Another important characteristic of a superconductor is the maximum transport current which 248 can flow without dissipation. This is called the critical current,  $I_{c}$ . Its value is very sample 249 dependent and can be affected by the sample shape and material quality. There is a 250 criterion that says a superconductor loses its zero resistance when, at any point on the 251 surface, the total magnetic field strength, due to the transport current and applied magnetic 252 field, exceeds the critical field strength H<sub>c</sub>. This quantity, I<sub>C</sub>, is called the critical current. Icdepends on the external magnetic field experienced by the superconductor and has typical 253 values of the order of  $10^6 - 10^8$  Å cm<sup>-2</sup> depending on the sample temperature [26]. 254

# 255 **4.4. Zero resistance**

256 Every superconductor has zero resistivity, i.e. infinite conductivity, for a small-amplitude dc current at any temperature below T<sub>c</sub>. This property of the superconducting state was 257 258 demonstrated by inducing a small-amplitude dc current around a closed ring of a 259 conventional superconductor. The experiment continued over two and a half years-there 260 was no measurable decay of the current. This means that the resistivity of a superconductor is smaller than  $10^{-24}$  Ωm. This value is 18 orders of magnitude smaller than the resistivity of 261 copper (1.7x10<sup>-6</sup>) at room temperature. Such a value of resistivity in a superconductor 262 implies that the current lifetime in a super-conducting ring in zero magnetic field is not less 263 264 than 10<sup>5</sup> years [7, 26].

# 265 **4.5. Josephson Effects**

As with semiconductor and thermocouple devices, there is the concept of a junction in a superconductor when it joins with an insulator. Two superconductors are separated by a thin insulating layer whose thickness is so small that Cooper pairs can pass through by the tunneling effect. This geometry is called the Josephson junction.



# Fig. 4.Geometry of Josephson junction (where s<sub>1</sub> and s<sub>2</sub> are two kinds of Superconductors, I is thin insulating layer)

The Josephson Effect is the phenomenon of super current (A current that flows indefinitely long without any voltage applied) across a device which is known as Josephson junction. The Josephson Effect is an important basis of superconducting electronics applications and has widespread applications in many instruments such as voltage reference, superconducting cavities, superconducting filters and Superconducting Quantum Interference Devices (SQUIDs )[3].

#### 279 **4.6. Thermal property**

#### 280 **4.6.1 Entropy**

A marked decrease in entropy is observed during normal to superconductivity transition near the critical temperature; which indicates that the superconducting state is more ordered than normal state.

#### 284 **4.6.2 Specific heat**

From the specific heat study of superconductor we can get the information about the existence of the band gap in superconductors. As we know specific heat of normal metal,

 $287 C_n = \gamma T + \beta T^3$ 

288 Where, γT=specific heat term

289  $\beta T^3$ =contribution of lattice vibration at low temp

290 Specific heat of superconductor shows a jump at Tc since the superconductivity affects 291 electron mainly. So, the lattice vibration part remains unaffected. By this substitution the 292 electronic specific heat Ces shows the exponential curve.

And this indicates the existence of finite gap in the superconductor [16].

# 295 4.7. Superconducting Energy Gap

According to the BCS theory, the Cooper pairs are bound together with an energy E given by the relationship

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$$E = hv = 3.52k_BT_c$$

Where h is Planck's constant (h =  $6.6262 \times 10^{-34}$  Joule-sec), is the frequency, k<sub>B</sub> is Boltzmann constant (k<sub>B</sub> =  $1.3806 \times 10^{23}$  Joules/Kelvin) and T<sub>c</sub> is the superconducting transition 299 300 temperature. The photon frequency corresponding to the energy gap of a superconductor 301 302 with a  $T_c$  = 1 K is about 73 GHz. Thus the energy gap of most superconductors corresponds 303 to photons in the terahertz or far infrared frequency regions of the spectrum [8]. Absorption 304 of energy in that region may cause promotion of electron from supper conducting state to 305 metallic state. Additional evidence for reduced free energy in supper conducting state comes 306 from heat capacity measurements. These show the superconducting state to have lower 307 entropy and hence to be more ordered than the metallic state [27].

# 308 5. SUPERCONDUCTIVITY IN CUPRATE OXIDES

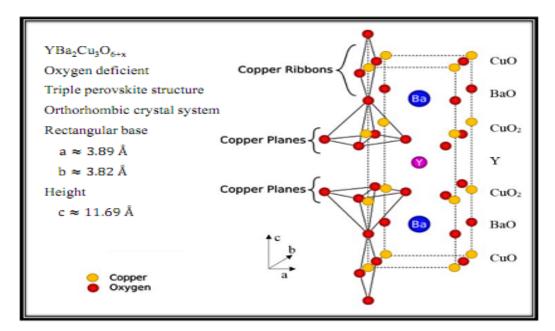
Since 1987, cuprate superconductors with Tc > 77K have been the centre of intense interest. One of the first to be discovered was  $YBa_2Cu_3O_7$  made by reaction given below. The oxygen content of the final material depends on reaction conditions (e.g. temperature and pressure).

314 It is related to the perovskite structure as follows: by tripling the perovskite (ABO<sub>3</sub>) unit 315 cell and substituing one yttrium atom for every third barium atom, the formula  $Y_1Ba_2Cu_3O_9$ 316 results. Hovewer, a little more than two oxygen vacancies are required for 317 superconductivitythere are position of nine atoms of O in the unit cell but only 7 are occupied 318 [29,30].

There are systematic oxygen atom vacancies in the unit cell compared to stack of simple perovskite unit cells. These occur between adjacent copper atoms along the caxis. The vacancies are in the yittruim atom plan. There are also vacancies between copper atoms along the a axis in the copper-and-oxygen planes that lie between the planes of barium 323 atoms [28]. This non-stoichiometry is denoted by the x in the chemical formula  $YBa_2Cu_3O_{7-x}$ . 324 When x = 1, the O(1) sites in the Cu(1) layer are vacant and the structure is tetragonal. The 325 tetragonal form of YBCO is insulating and does not superconduct. Increasing the oxygen 326 content slightly causes more of the O(1) sites to become occupied. For x< 0.65, Cu-O chains 327 along the b axis of the crystal are formed. Elongation of the b axis changes the structure to 328 orthorhombic, with lattice parameters of a = 3.82, b = 3.89, and c = 11.68 Å. Optimum 329 superconducting properties occur when  $x \approx 0.07$ , i.e., almost all of the O(1) sites are 330 occupied, with few vacancies.

331 In experiments where other elements are substituted on the Cu and Ba sites, evidence has 332 shown that conduction occurs in the Cu(2)O planes while the Cu(1)O(1) chains act as 333 charge reservoirs, which provide carriers to the CuO planes. However, this model fails to address superconductivity in the homologue Pr123 (praseodymium instead of yttrium). This 334 335 (conduction in the copper planes) confines conductivity to the a-b planes and a large anisotropy in transport properties is observed. Along the c axis, normal conductivity is 10 336 337 times smaller than in the *a-b* plane. For other cuprates in the same general class, the 338 anisotropy is even greater and inter-plane transport is highly restricted [31].

The oxidation state of copper in  $Y_1Ba_2Cu_3O_7$  is unusual .If we assume that Y,Ba and O have their usual oxidation state +3,+2 and -2 respectively,for charge balance,the copper must have an average of +2.33.This may be rationalized interms of one third of the copper is Cu<sup>3+</sup> and the remainder is Cu<sup>2+</sup> [3,25,27,28,30].



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344

#### Fig. 5. The crystal structure of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> oxygen deficient [ 40]

#### 345 6. APPLICATION OF SUPERCONDUCTORS

346 Due to the unique properties of high temperature superconducting materials, their 347 applications are becoming attractive continuously with the improvement in properties of 348 superconductors. The search for applications has always been a driving force for 349 superconductor material science. Right from the discovery, it had been envisioned that superconducting coils with high persistent current might be used to produce strong magneticfield.

352 In the last 20 years, many applications of high temperature superconductors have been 353 developed in very diverse fields. Applications of superconductivity can be found in 354 transportation (maglev trains), marine and military (propulsion motors, degaussing systems 355 and EMP weapons), particle research (large hadron collider, proton-antiproton collider and 356 electron proton collider etc.), power generation and distribution (fault current limiters, superconducting wires, superconducting magnetic energy storage systems and 357 358 superconducting transformers etc.), information technology & computing (quantum 359 computers, quantum cryptography and high performance computers etc), electronics & 360 telecommunications (Superconducting Quantum Interference Device (SQUID), single-361 guantum flux devices (SFQ devices), and cellular filters etc.) and medical diagnostic systems 362 (magnetic resonance imaging (MRI))[32]. In this section some typical applications of high 363 temperature superconductors are discussed.

The fundamental technologies for applications of superconductivity are discussed here with the classifications of Superconducting bulks, Superconducting tapes and Superconducting devices.

# 367 6.1. Superconducting bulk and its applications

Materials for superconducting bulk are REBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> where RE is Sm, Nd, Gd or Y. The bulk is made using the oxygen controlled melt growth (OCMG) method under a low partial pressure of oxygen except for YBCO where the quenched melt growth (QMG) method is used, here the superconducting bulk YBCO is grown using half-melt materials at a high temperature of nearly 1000 <sup>0</sup>C, followed by a very slow cooling. The bulk almost has a single-crystal like structure, and a large critical current of more than 10<sup>5</sup>A/cm<sup>2</sup> is obtained at liquid-nitrogen temperature [14,33].

The special feature of the bulk is that the introduction of pinning centres is easily carried out by controlling the density of fine  $Y_2BaCuO_5$  particles as pinning centres in the bulk. The most distinguishing characteristic is that it is possible to trap a strong magnetic field of 2 to 3 T, even at liquid-nitrogen temperature. This value is much higher than the magnetic field of an ordinary permanent magnet. Recently, the mechanical strength of bulk has been increased by polymer impregnation, and this bulk has trapped a very high magnetic field of 17 T at 30K. The applications of the bulk are of two types:

382 (i). As the pining force of the magnetic flux is so strong, the outside magnetic field cannot 383 penetrate the bulk in the superconducting state. This results in strong levitation force of 384 about 15 Kg/cm<sup>2</sup> when the bulk is close to an ordinary permanent magnet at 77 K. This phenomenon is exploited to make Flywheel electric storage systems that can store about 10 385 386 KW/h, based on frictionless superconductor bearings. Using bulk HTS self-cantering bearings allows levitation and rotation in a vacuum, thereby reducing friction losses. 387 388 Conventional flywheels suffer energy losses of 3-5% per hour, whereas HTS based 389 flywheels operate at <0.1% loss per hour. Large and small demonstration units are in 390 operation and development [3,14,33].

(ii). When the bulk is in normal state, a magnetic field applied from outside is uniformly
distributed throughout the bulk. But after the bulk is cooled to below the critical temperature
the magnetic field is quantized and quantized flux is pinned by strong pinning centres. Then
when the external field is removed the quantized flux is left inside and behaves like a
permanent magnet. One fruit full application of this bulk is in water cleaning using the
magnetic separation effect. The impurity particles in water join magnetic particles, and they

are removed from the filter by the strong magnetic field of the bulk. The operation can be
continuous and results have been impressive which is 100 times efficient than the present
cleaning system available today. Other opportunities are in materials manufacturing such as
semiconductor production in high magnetic field and induction heating [3, 14, 33, 34].

# 401 6.2. Superconducting tapes

#### 402 6.2.1. First-generation superconducting tapes

The first generation of superconducting tape using high temperature superconductors is the so-called Silver-sheathed Bi-compound Tape. The Bi-compound usually used is  $Bi_2Sr_2Ca_2Cu_3O_{10}$  (Bi-2223). The tape is 4mm in width and 0.25mm in thickness, and inside the sheath there are 55 filaments of Bi-2223 superconductor. Recently, Sumitomo has succeeded in producing higher-quality tapes by introducing a heat-treatment process under a high pressure of 300 atmospheric pressures, and has obtained a critical current of 200A at 77 K [14,33,35].

# 410 6.2.2. Second-generation superconducting tapes

411 Although mechanical properties of the first generation wires are reasonably robust and the critical current values have reached more than 10<sup>4</sup> A/cm<sup>2</sup> at 77K and at commercial lengths, 412 413 there are several weak points in this system in that high critical current density decreases 414 rapidly with increasing magnetic field at liquid nitrogen temperature. Therefore, recent 415 developments in the second generation coated conductors to improve the magnetic field 416 dependence, where a thin film of (RE)Ba<sub>2</sub>Cu<sub>3</sub>O<sub>v</sub> superconductors is deposited on an 417 appropriate substrate with specifications required by the specific application, gain a lot of 418 interest [35]. YBCO tape consists of a thin metal plate, a buffer layer and a superconducting 419 layer has developed with critical current density of 3 x 10<sup>6</sup> A/cm<sup>2</sup> in a magnetic field of 20 T 420 at approximately 20 K that have law dependence in magnetic field [3, 14, 33].

# 421 6.2.3. Electric Power

# 422 6.2.3.1 Superconducting electric power cable

423 A possibility of electric energy transportation without loss is the most attractive property of 424 superconductors. A high transition temperature of the cuprate HTS has enabled their 425 practical applications by development of HTS power cables which are able to carry up to ten 426 times greater current and power capacity per cross section than conventional copper cables. 427 HTS coated conductor tapes are used in fabricating power cables. American 428 Superconductor Company (AMSC) produces a single phase power cable using GdBCO 429 tapes that are fabricated by using pulsed laser deposit technique and having greater current 430 density than YBCO tapes. To reduce HTS cable cost three phase power cables were 431 developed by AMSC, Where three 2G wires are concentrically placed around the common 432 central core surrounded by a copper shield. The Triax HTS cable was developed jointly by 433 Southwire and nkt cables companies. This compact construction has several advantages 434 over the single-phase cable: in the three-phase cable, only about one-half of the quantity of 435 HTS wire is needed and the cables cold surface area is reduced, which lower the cost 436 associated with cryogenic cooling equipment. A single HTS Triax cable operating at 13 kV 437 carries 3,000 A, which is equivalent of 18 conventional underground cables [3,34, 36].

#### 438 6.2.3.1 Fault Current Limiters

439 As new generators are added to the network, many local grids face a rising risk of 440 unacceptably high power surges that result from "faults" or short circuits. A fault current 441 occurs in the event of a short circuit caused by lightning, accidental contact between the 442 lines or the ground, etc. In this case, the power current flowing through a local network can 443 increase enormously damaging electrical equipment. To protect the transmission or 444 distribution of electric systems from outages caused by fault currents a special device - a 445 fault current limiter (FCL) is installed in the transmission grid. Conventional line reactors 446 widely used as FCLs have high AC losses and can produce voltage drop in the grid in the 447 case of a fault current. HTS technology enables a new solution: compact, "smart" fault 448 current limiters (FCLs) that operate, passively and automatically, as power "safety valves" to 449 ensure system reliability when individual circuits are disrupted. Taking advantage of the 450 inherent properties of superconductors, they sense such dangerous over currents and 451 reduce them to safe levels by changing state instantaneously, from "super" conductors to 452 resistors when the electric current exceeds the materials critical current.

453 The HTS FCL represents a coated conductor consisted of lavers of HTS material within 454 layers of resistive materials. Under normal operating conditions, the current in the cable 455 flows through the HTS layers in the FCL. In the case of a fault, the current exceeds the HTS 456 material's critical current and the HTS layers become normal. In that case, the current is 457 automatically shunted within a millisecond to flow through the higher resistance layers, 458 effectively quenching the fault current amplitude. The very rapidly operated HTS FCLs 459 greatly reduce damage to electrical equipment caused by system faults. They are fail-safe 460 since they require no external sensing of the current to initiate the transition [3, 34].

#### 461 6.2.4. Transportation

# 462 6.2.4.1 Superconducting Magnet for Maglev Trains

463 Expulsion of magnetic field by superconductors in superconducting state is useful in 464 magnetically levitated trains, called as Maglev trains, which are operational in a few 465 countries. Themagnet for maglev train has been made by using Bi-2223 superconducting 466 tape. This magnet has a racetrack shape and consists of twelve pancake coils, of 1m length 467 and 50 cm height. This magnet is operated at 20k and generates a magnetic field of 2.5 T at 468 the center of the magnet. The huge magnetic field that can be sustained by the 469 superconductors is used to levitate and propel the trains. Furthermore, the rate of decay of 470 the persistent current is only 0.5% a day. This magnet is very successful and recently a train 471 using this magnet reached a speed of 500 km/h [3,37].

# 472 <u>6.2.5. Marine</u>

#### 473 6.2.5.1 Superconducting Motor for Ships

The ship propulsion system is undergoing a revolution. In the new system, propellers and the electric motor are directly connected and they are outside the body of the ship and this propulsion system is called a "pod motor". By employing such a system, freedom of boat design is very much improved, and as a result, energy saving becomes possible.

The large size and heavy weight of conventional copper-based electrical propulsion motors and generators has been a barrier to broad adoption of electric propulsion. A HTS motor is most suitable for this pod motor system, because the superconducting motor generates a large torque even at a slow rotating propeller speed of about 100 rpm; furthermore, it is much smaller and much lighter than ordinary motors using Medical Imaging and Diagnostics copper wire. In the United States, various types of superconducting motors are being 484 developed; all of them use Bi-2223 superconducting tape. In Japan, a superconducting 485 motor using YBCO tape has been recently developed, and this is the first such motor in the 486 world [3,34].

#### 487 **<u>6.2.6. Medical application</u>**

#### 488 6.2.6.1 Magnetic Resonance Imaging (MRI)

One of the largest commercial power applications of superconductors at present is magnetic resonance imaging (MRI), with thousands of units in hospitals and global sales of several billion US dollars per year. The superconducting portion consists of a "basic" solenoid, which creates the background strong magnetic field that forces hydrogen atoms that exist in the body's water and fat molecules to accept energy from the magnetic field. These species then release this energy at a certain frequency which can be detected and displayed in the form of an image by a computer [3,4,37].

# 496 **6.3. Superconducting electronic devices**

One of the most prominent phenomena of superconductors is the Josephson tunnelling effect and most of the applications of superconductors in electronics and sensors are based on this phenomenon. Applications of superconductors have arisen in areas other than electromagnets, more specifically in electronics and sensors, wherein the materials required are often small thin films which are much easier to produce in highly perfect forms, especially from HTS. [4].

#### 503 6.3.1 Superconducting Quantum Interference Devices (SQUID)

504 SQUIDs are superconducting loops with integrated Josephson junctions which can be used 505 as the most sensitive measurement for magnetic fields, voltage, and related electromagnetic 506 quantities based on the Josephson tunnelling phenomena. The magnetic field resolution of 507 HTS SQUIDs operating at 77 K temperature is about 10 times lower than the commercial 508 LTS SQUIDs operating at 4K [3]. However, a large commercial impact is only expected for 509 HTS SQUID systems that are able to observe magnetic signals even in the presence of 510 disturbing background fields without the burden of magnetic shielding [38]. SQUID 511 magnetometers may be the most sensitive measurement device known. The threshold for 512 SQUID is of the order of 1 fT,( 100 billion times smaller than the Earth's field), making it 513 capable of measuring extremely feeble magnetic fields. Because of their extreme sensitivity, 514 SQUIDs have established themselves very accurate devices for both as 515 Magnetocardiography and Magnetoencephalography [4,39]. The application of high 516 temperature SQUIDs to a magnetocardiography has been made recently by Hitachi, Ltd. It 517 consists of 51 SQUIDs on one plate and is used for the diagnosis of human heart diseases 518 [3].

#### 519 6.3.2 Microwave filters

520 The simplest applications of high-quality high-temperature superconducting films with commercial availability are HTS passive RF and microwave filters for wide-band 521 522 communications and radar. These are based on conventional microstrip and cavity designs 523 with superconductors used for the microstrips or to line the metal cavity. They have the 524 advantages of very low noise and much higher selectivity and efficiency than conventional 525 filters [14]. In early stages of development it was hoped that many filtering systems would be 526 used in the base stations of portable telephone systems. However, at present, only several 527 thousand filters are employed in the world, because of the cost of the cooling system [12].

#### 528 6.3.3 Single-Quantum Flux (SFQ) Devices

529 Another important application of HTC is the single quantum flux device (SFQ). The principle 530 operation of SFQ device is that in a superconductor ring of a SQUID the magnetic field is 531 guantized, and by applying a current pulse to the ring, the Josephson junction reaches a 532 normal state for a short duration, and the quantized flux appears or disappears in the ring 533 depending on the original state. The state of the flux in the ring is 0 or 1, and responds to the 534 0 or 1 of an information signal and so logical circuits can be made by combining SFQ 535 devices [12,33]. The electricity consumption of the SFQ circuits is very small, 0.1 mW per 536 one logic gate, and this is about one hundredth that of semiconductor circuits. The operation 537 speed is about 100 GHz, and this is one hundred times faster than that of semiconductor 538 circuits [3].

539 In the past fifteen years, the circuit technology of SFQ circuits using Nb-based SFQs has made a good progress, the integration of more than  $10^4$  junctions has become possible. 540 541 high-speed shift registers and highspeed switching systems have been developed. Special 542 feature of SFQ circuits based on high-temperature superconductors are a high-speed operation of over 100 GHz and a high-temperature operation at approximately 40 K. On the 543 544 other hand, the integration is more difficult than that of Nb-based SFQ circuits owing to the 545 complexity of process technology. A high-speed sampler and a toggle flip-flop circuit are 546 examples of SFQ circuits with about twenty Josephson junctions and operating at about 40 547 K. The high-speed sampler is very useful for observing waveforms of a very short pulse 548 greater than 40 GHz, which will be popular in future, communication systems. And the toggle 549 flip-flop circuit generates two output pulses for one input, and can be used as demultiplexer and this circuit is operates faster than 370 GHz [12]. At present, the integration of a high-550 551 temperature SFQ circuit is limited to about 100 junctions, but it is hoped that this will reach to 552 more than 500 junctions.

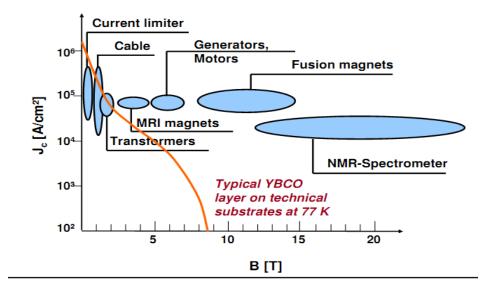
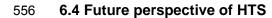






Fig.7. Required properties for different power applications of HTSC



The last ~30 years have seen the development of a number of prototypes of new high temperature superconducting power and electronic equipment's that are mentioned above and many others. But, so far only few of them are successfully commercialized. The problem has usually been the cost of the HTS version versus other LTS and non-superconducting solutions. Superconducting motors and generators are one strong example; a number of prototypes have been successfully built and tested to full function, but the economics have not allowed commercialization [4].

The future of HTS applications and commercialization is a persistent question and can only be answered once the scientific and technological challenges hindering the large-scale application of HTS are addressed. First, the geometrical shapes of HTS wire are limited. It is mostly available in tape format. Fabrication of HTS wire (tape) requires an expensive and special technology and process machinery.

The second challenge has to deal with the material properties that result in high values of TC and HC. These properties include high normal state resistance, proximity of superconductivity to competing Anti-Ferromagnetic (AF) state, large anisotropic ratios and sensitivity of superconducting properties to local nonstoichiometry. These lead to the lack of widespread applications of HTS. In addition, absence of any validated microscopic theory of superconductivity in HTS materials means we cannot predict new superconducting materials with higher TC values.

576 If these challenges of HTS are addressed, then the HTS will bring the features of save 577 energy, compact, lightweight, high performance and save resources, and could play a trump 578 on forthcoming low-carbon society in our life.

# 579 **7. CONCLUSION**

580 One of the most brilliant events in the 20th century was the discovery of ceramic-type HTS 581 materials that led to extensive research for new discoveries and theories. The physics of 582 HTS is complicated, that the theoretical basis is uncertain yet, and it may be in the far front 583 of solid state physics. Till this moment high temperature superconducting properties has been discovered with in many types of materials and research will continue to synthesize 584 585 new materials that may expose these new phases in an experimental sense or improve on 586 those already known. We have studied historic view of HTS, theories of superconductivity, 587 and characteristics and different properties of HTS materials. We also studied the application 588 of HTS in different sectors. As the properties of HTS continue to improve, more applications 589 are expected to become a commercial reality. Steady improvement of the HTS materials 590 basis will surely widen this spectrum of applications within near future.

# 591 8. REFERENCES

- Atikur Rahman Md, Zahidur Rahaman MD, Nurush Samsuddoha MD. A Review on Cuprate Based Superconducting Materials Including Characteristics and Applications.
   American Journal of Physics and Applications. 2015; 3(2): 39-56.
- Sign and Applications: 2013, 5(2), 59-50.
   Bray JW. Superconductors in Applications; Some Practical Aspects. IEEE/CSC & ESAS, European Superconductivity New Forum, October 2009; No 8.
- Marcos Rigol B, Sriram Shastr, Stephan Haas. Fidelity and superconductivity in twodimensional t-J models. Physical Review. B 2009; 80; 094529.
- 4. Dew-Hughes D. The critical current of superconductors: an historical review. Low
   Temperature Physics. 2001; 27;967–979.
- 5. Andrei Mourachkine.Room-temperature superconductivity. Cambridge CB1 6AZ, UK:

603 Cambridge International Science Publishing, 2004. 604 Martin Nisenoff. Microwave superconductivity."IEEE/CSC & ESAS European 605 superconductivity news forum (ESNF), July 2011; No.17. 606 7. Brent A. Howe. Crystal Structure and Superconductivity of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>. M.Sc 607 Thesis, Minnesota State University, Mankato Minosota, 2014. 608 8. Chapman SJ. Macroscopic Models of Superconductivity. Ph.d Thesis, St. Catherine's 609 College, Oxford, 1991. 9. Josephson BD. Phys. Rev. Lett. 1962; 1: 251. 610 10.Shoji Tanaka. High-Temperature Superconductivit. Japanese Journal of Applied 611 612 Physics, 2006; 45: No. 12. 613 11. Bray JW. Superconductors in Applications; Some Practical Aspects."IEEE/CSC&ESAS 614 European Superconductivity New Forum, October 2009: No 8. 615 12. Europhysics news 2001; http://dx.doi.org/10.1051/epn:2001302 616 13. Basov DN, Timusk T. Electrodynamics of high-Tc superconductors. Reviews of Modern 617 Physics, 2005;77, 721-770. 618 14. Shreelekha M. Synthesis and Characterization of Superconductor Composite 619 Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>1</sub>Cu<sub>2</sub>O<sub>8</sub>/La0.85Sr0.15MnO<sub>3</sub>. MSc Thesis, National Institute of Technology 620 Rourkela, Rourkela, 2012. 621 15. Tadashi A, Takayuki K and Yoji K. Novel Electronic State and Superconductivity in the 622 Electron-Doped High-Tc- T'Superconductors. Journal of Condensed Matter, 2017;, 2: 2. 623 16. Marten SJOSTROM. Hysteresis Modelling of High Temperature Superconductors.Phd 624 thesis Swiss federal Institute of technology, Laussane. 2001. 625 17. http://en.wikipedia.org/w/index.php?oldid=434797930. 626 18. Bardeen J. Superconductivity in Science and Technology. University of Chicago Press, 627 Chicago & London 1968, Mar-Apr 2004. 628 19. Meretl lev SH, Sadykov KB, Berkel lev. Doping of High-Temperature 629 Superconductors.Turk. J. Phy.2000;, 24: 39 - 48. 630 20. Bulaevskii LN, Ginzburg VL and Sobyanin AA.Macroscopic theory of superconductors 631 with small coherence length. Sov. Phys. JETP. 1988; 68:1499-1510. 632 21. Holtz RL, Soulen RJ, Osofsky M, Claassen JH, Spanos G, Gubser DU, Goswami R, and Patten M.High Temperature Superconductors for Naval Power Applications. 633 Materials Science and Technology.NPR REVIEW 2006. 634 635 22. Paul Attfield JJ. "Chemistry and High Temperature Superconductivity." Edinburgh EH9 636 3JZ. UK. 637 23. Catherine E. Hausecroft and Alan G.Sharpe.4th ed. Pearson Education.2012. 638 24. Foley CP. Superconducting Materials and Devices. Electrical Engineering – Vol. II 639 25. Antony RW. Basic solid state chemistry. 2nd ed. John Willey & Sons Ltd. 1988. 640 P 287- 292. 641 26. James E. Huhev, Ellen A. Keiter, Richard L. Keiter and OkhilK, Medhi, Principles of 642 Structure and Reactivity."4th ed. Dorling Kindersley Pvt. Ltd.P.112-114. 643 27. Georgeta A. Crystal Structures of Some High-Temperature Superconductors'. Advanced 644 Research Institute for Electrical Engineering, ICPECA.2014;56(3): 404 – 412. 645 28. Daniel CH, Marian EH and Terrell AH, Preparation, Iodometric Aanalysis, and Classroom 646 Demonstration of Superconductivity in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>8-x</sub>. Journal of Chemical 647 Education. 1987; 64(10). 648 29. Ytridium barium oxide wikipedia 30. Igbal, S.A Perspective on Medical Applications of High Temperature Superconductors. 649 650 J. Bioena, Biomed, Sci. 4: e119. doi:10.4172/2155-9538.1000e119 651 31. Shoji Tanaka JSAP international No. 4 July 2001. 32. Present and Future Applications 2008 CCAS / IEEE CSC Outreach. 652 33. Van Driessche I, Schoofs B, Penneman G, Bruneel E, Hoste S, J. Measurement 653 654 Science Review, 2005; 5: Section 3. 655 34. Ken-ichi SatoSeiTechnical Review • Number 66 • April 2008.

- 656 35. Meretllev SH, Sadykov KB, Berkel A. Doping of High-Temperature Superconductors.
   657 Turk J Phy 2000; 24:39 48.
- 658 36. Roland Hott.Application Fields of High-Temperature Superconductors, Karlsruhe,
   659 Germany.
- 660 37. Malik M. A, Malik B.A. High Temperature Superconductivity: Materials, Mechanism and 661 Applications.Bulg. J. Phys, 2014, 305–314.
- 38. Dr.Serdar Gozpinar. High-Temperature Superconductivity experiment Development. The
   State University of New York, Spring 2015.

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