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# High-Pressure High-Temperature (HPHT) Synthesis of Functional Materials

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## Abstract

High-pressure techniques have been used extensively in effecting phase changes in materials science for decades. The use of high-pressure high temperature enables changes in material atomic arrangement or structure which in turn brings about changes in functional properties such as magnetism, optical, electrical and thermal conductivity. High-pressure technology is highly specialised and requires understanding to fully utilise its potential as a tool for the development of new and novel functional materials with improved properties. This chapter explores the various high-pressure technologies available and how they have been utilised to obtain a wide range of functional ceramic materials for a wide range of applications.

**Keywords:** high-pressure high-temperature sintering, functional materials, high-pressure synthesis, phase transition

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## 1. Introduction

The discovery of novel properties and quantum states at high pressure has led to a number of new functional material categories. Pressure has long been recognised as a fundamental thermodynamic variable which can be used to manipulate electronic, magnetic, structural and vibrational properties of materials for a wide range of applications. High pressure effectively decreases the atomic volume and increases the electronic density of reactants which results in unusual and interesting properties. There are two basic approaches evident to high-pressure synthesis which involves structural transformation on the one hand and formation of new chemical bonds on the other. Particularly noticeable discoveries in high-pressure physics include metallisation of hydrogen, quantum criticality, high  $T_c$  superconductors, polymorphism and exotic metals [1].

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The impact of the pressure dimension has not been very conspicuous because a number of substances that exist at high pressure cannot be retained at ambient pressure [2]. Strictly speaking pressure-induced transitions result in *metastable phases* whose properties may or may not change reversibly over a period of an experiment or observation [2]. Such a metastable condition is enabled by the existence of an energy barrier which when surpassed results in a transition to a thermodynamically equilibrium ground state [2]. This explains the crystallisation of amorphous materials upon heating and the conversion of diamond (high-pressure phase) to graphite (ambient pressure phase) at temperatures above 1500 K under normal pressure [2]. Brazhkin in his analysis explains the stability of high-pressure phases on the basis of a simple thermodynamic argument. Simply put, a metastable high-pressure phase possesses Gibb's free energy,  $G$  higher than that of a stable phase [2]. He went on to argue that the equilibrium melting temperature of a metastable crystal ( $T_m^*$ ) is always lower than that of the equilibrium melting temperature of the stable phase ( $T_m$ ). This basically explains why all metastable high-pressure phases transform to more stable phases upon heating at far lower temperatures than the melting temperature of the stable phase ( $T_m$ ) [2].

The advancement of high-pressure technology has not been as widespread as other synthesis techniques such as high temperature and catalysis [2]. This emanates from the fact that most high-pressure apparatus are quite complex and costly and the volumes of material obtainable at high pressure are very small [2]. Despite these negative factors, the apparatus that have been developed up to date have given rise to some of the most intriguing material properties ever known to mankind. Lower static pressures in the range 0.1–1 GPa are achievable in fairly large volumes  $\sim 0.01$ – $1\text{ m}^3$  using gas containers, piston-cylinder type and autoclave presses [2]. Pressures in excess of 1 GPa can only be achieved in apparatus which are mechanically operated [2].

## 2. High-pressure technology and apparatus

High-pressure synthesis can be broadly divided into static and dynamic technologies. Traditionally there are two most widely used static-type apparatus, namely, the piston-cylinder and Bridgeman anvil type. The piston-cylinder pressure zone can accommodate volumes in the range  $1$ – $1000\text{ cm}^3$  for pressures of up to 1 GPa [2]. They can reach maximum pressures of 3 GPa where smaller pressure zone volumes and very large presses are needed [2]. The Bridgeman anvil type can achieve very high pressures depending on the type of anvils: for hard alloy anvils, pressures in the range 15–20 GPa, for SiC anvils 20–70 GPa and for diamond anvils 100–300 GPa are achievable [2]. Commercial presses which incorporate concepts from the Bridgeman anvil and piston-cylinder designs have been developed to synthesise superhard materials obtaining pressures over 5 GPa with volumes of  $\sim 1\text{ cm}^3$  [2]. The most widely used presses in this class are known as the *belt*, multi-anvil apparatus and toroid [2]. Another important laboratory-scale high-pressure tool is the diamond anvil cell (DAC). The DAC is used extensively for exploratory high-pressure synthesis and for characterisation of materials under high pressure. It basically consists of two gem-quality diamonds ( $\sim 1/3$  carat) with flat surfaces (culets) capable of compressing small samples on a metal gasket containing

a small hole to accommodate the sample. The DAC can reach very high pressures in excess of 150 GPa and can be heated easily using infrared lasers reaching temperatures in excess of 5000 K [3].

Alternative methods which make use of dynamic pressures generated through the shock wave technique allow for pressures of ~100–1000 GPa over short times of dynamic pressure action (nanoseconds) [3]. The shock wave technique has been used to produce materials in large volumes typically 1–10 cm<sup>3</sup> at pressures of 10–100 GPa [2].

## 2.1. Theory of sintering

Sintering involves powder compaction at elevated temperatures with or without pressure application to obtain densified solid compacts. Thus the driving force of sintering is a function of surface-free energy, temperature and pressure of the system. At low temperatures and pressures (typically <0.5  $T_m$ ), the energy available is insufficient to allow for diffusional mass transport in solid-state sintering of most materials with micron-sized particles [4]. The diffusion coefficient,  $D$ , is temperature dependent and follows an Arrhenius relationship with the absolute temperature,  $T$  as follows:

$$D = D_0 \exp\left(-\frac{\Delta H}{RT}\right) \quad (1)$$

$D_0$  is a constant dependent on the atomic planar distance, and the mean frequency of vibration,  $\Delta H$ , represents the enthalpy change associated with overcoming the diffusion energy barrier, and  $R$  is the gas constant.

The application of pressure during sintering is an effective way of improving the rate of densification as it lower diffusion distances between adjacent particles. This is well articulated by the various creep equations which relate creep rate (linear strain rate) to the densification rate (volumetric strain rate). During hot pressing, the density  $D$  of the sample increases with a decrease in thickness  $L$ . The variables  $D$  and  $L$  are related as follows:

$$\frac{M}{A} = LD = L_0 D_0 = L_f D_f \quad (2)$$

$M$  represents the sample mass,  $A$  the cross-sectional area and the subscripts  $0$  and  $f$  refer to initial and final states. Differentiating Eq. (2) yields

$$L \frac{dD}{dt} + D \frac{dL}{dt} = 0 \quad (3)$$

This can be simplified to

$$-\frac{1}{L} \frac{dL}{dt} = \frac{1}{D} \frac{dD}{dt} \quad (4)$$

This equation relates the linear strain rate of the body ( $dL/dt$ ) to its densification rate ( $dD/dt$ ). This is the basis of the Nabarro-Herring creep equation which in essence argues that self-diffusion within the crystal will cause the solid to deform in an attempt to relieve stress [5].

The creep being a result of atoms diffusing from interfaces subjected to a compressive stress (where they have a higher chemical potential) towards those subjected to a tensile stress (lower chemical potential). Herring derived an important relationship between the atomic fluxes  $\varepsilon$  to the grain size,  $G$ :

$$\varepsilon'_c = \frac{40}{3} \left( \frac{D_e \Omega P_a}{G^2 kT} \right) \quad (5)$$

where  $D_e$  is the lattice diffusion,  $\Omega$  atomic volume,  $P_a$  applied pressure,  $G$  grain size,  $k$  Boltzmann constant,  $T$  absolute temperature and  $\varepsilon'_c$  creep rate.

The value of  $\varepsilon'_c$  is the creep rate equivalent to the linear strain rate  $(1/L)dL/dt$  in (5) above. It can be deduced that the densification rate can be enhanced by an application of pressure,  $P_a$ , and a reduction in grain size  $G$ ; the grain size reduction is more enhanced due to the higher power factor. The use of ultrafine nanometric powders has been proven to lower sintering temperatures owing to shorter diffusion distances between particles [6]. Existing experimental evidence has proven that faster densification rate allows full density to be attained at smaller grain size before serious grain growth occurs [6]. In principle, the mechanisms that promote densification (increased temperature) are also responsible for grain growth, and both these mechanisms are proportional to the reciprocal of grain size [6]. Thus the control of the two competing mechanisms presents a challenge in the production of fine-/nano-grained microstructures under conventional sintering.

## 2.2. Synthesis of functional materials under high pressure

As discussed earlier, the high-pressure techniques are capable of tuning the structure and properties of materials resulting in the synthesis of novel materials. The most widely used high-pressure techniques consist in the synthesis of equilibrium high-pressure phases that can be maintained after the release of pressure [2]. The low- and high-pressure phases are associated with thermodynamic stability regions in the pressure and temperature ( $P$ ,  $T$ ) diagram of the material [2]. It is noteworthy to mention that in a number of cases under moderate temperatures, pressure transformations result in energy intermediate *kinetic* phases which are associated with lower activation barrier for transformation [2]. Furthermore, high pressure can also modify micro- and macrostructure of a material at nano- and meso-level, i.e. grain size, texture, morphology, defect structure and concentration [2]. That means the morphology and structure of a material can easily be manipulated by varying the  $P$ ,  $T$  conditions. A number of high-pressure materials have shown intriguing characteristics, among them superconducting, semiconducting, optical, electron-transport, thermal and dielectric. Moreover, pressure tuning has proven to be an invaluable tool for obtaining material properties more rapidly and cleanly in comparison to chemical techniques [3]. This is because the entropy changes associated with volumetric transitions are comparatively small which makes pressure much easier to treat than temperature [3]. Pressure studies also provide valuable information on the properties of materials under compression. This information has been used to produce the same materials at ambient pressure by chemical tuning, e.g. doping of host lattice with smaller atoms to induce chemical pressure that produces a high-pressure equivalent with a metastable phase [2, 3].

## 2.3. Superconducting materials

In July 1908 a Dutch physicist Heike Kamerlingh Onnes discovered the superconductivity of mercury. He observed that the electrical resistance of mercury dropped down to zero under cryogen conditions (helium cooling at 4.2 K). The temperature at which the resistance becomes zero is known as the critical temperature,  $T_c$ . Most conventional metallic superconductors were found to possess such behaviour under liquid helium making the technology complex and costly because helium has limited supply and is costly compared to nitrogen, for example. Over the years, the  $T_c$  value of superconducting state has been increasing in steps with the discovery of more and more superconducting materials. In 1986, Bedworz and Muller discovered high temperature  $T_c$  at around 35 K in the La-Ba-Cu-O system. This initiated a rapid development in the research of ceramic oxide superconductors [7]. The term 'high temperature  $T_c$ ' is generally used in literature to denote superconductors with a  $T_c > 30$  K. In 1987, Wu et al. discovered the  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (123 phase) which was superconducting at 93 K which was followed by discovery in 1988 of compounds based on Bismuth ( $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ) and thallium ( $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ) with transition temperatures near 110 and 125 K, respectively [8–10]. The most exciting feature of the oxide ceramic superconductors is that superconductivity can be achieved in liquid nitrogen (77 K) which has lower cooling costs than helium [7]. Moreover, the superconductivity of ceramic superconductors can be maintained at considerably high magnetic fields than the conventional metallic superconductors [7].

Another interesting group of superconducting materials is the cubic perovskite and its derivatives. Which have been in existence for over three decades now. They possess a cubic structure and low  $T_c$ . Values such as  $\text{SrTiO}_3$  ( $T_c = 0.4$  K),  $\text{Ba(Pb,Bi)O}_3$  ( $T_c = 12$  K) and  $\text{BaPbO}_3$  ( $T_c = 0.4$  K). In the late 1990s, Cava et al. discovered a high  $T_c$  perovskite ( $\text{Ba,K)BiO}_3$  ( $T_c = 40$  K) [11].

As mentioned earlier, the discovery of La-Ba-Cu-O superconductors triggered the experimentation of a number of copper oxide ceramics with high  $T_c$ . The copper oxide ceramics possess layered perovskite structure with alternate stacks of  $\text{CuO}_2$  sheets and blocks along the c-axis.

The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO) possesses an oxygen-deficit orthorhombic perovskite structure [7].

The metal atom ratio in the structure is well defined as 1:2:3 the oxygen stoichiometry varies widely depending on the synthesis condition [7]. The oxygen content is key in regulating the structures and electrical properties (1.5 in Fei). In the stoichiometry Y-123,  $\delta$  is always positive and can vary from 0.0 to as high as 1.0 [7]. An optimum superconducting property can be obtained by maintaining  $\delta$  at lower value. The YBCO structure undergoes phase transition during heat treatment from a tetragonal-insulating state ( $\delta < 0.4$ ) to orthorhombic superconducting state ( $0.5 < \delta < 1.0$ ) by adjusting oxygen content.

There are two routes to obtaining oxide superconductors, i.e. doping of parent material through cationic substitution or oxygen nonstoichiometry. The more popular method is doping based on oxygen nonstoichiometry compared to cationic (or anion) substitutions. However oxygen doping mechanisms are not completely understood.

The critical magnetic field ( $H_c$ ) and the critical current density ( $J_c$ ) are the other two important factors that are critical for superconductivity to occur [7, 12]. The  $T_c$  and  $H_c$  are intrinsic properties of the material, while  $J_c$  can be varied by the microstructure of the material [7, 12]. It has been observed that the critical value of each parameter ( $T$ ,  $H$  and  $J$ ) for superconductivity varies with the other two, i.e. the critical current density  $J_c$  will decrease with increasing  $H$  and  $T$  [7, 12].

Superconductors are divided into two categories, type I and type II. Type II superconductors show a more complicated magnetic behaviour but are practically more important [7, 12]. The science behind the operation of these superconductors is found elsewhere [7, 12].

The use of superconducting devices is limited due to the fact that most superconductors must be cooled to low temperatures to be superconducting. A great technological revolution may be triggered by the discovery of a room temperature (RT) superconducting material. It is widely accepted based on scientific literature that the highest  $T_c$  at 1 atm is 135 K in the Hg-Ba-Ca-Cu-O system which can be increased to about 160 K through the use of high-pressure synthesis.

## 2.4. High-pressure synthesis of superconductors

Since the application of high pressure, a number of new superconductors have been discovered which include 22 elemental solids bringing the total number of elemental solid superconductors to 51 [13]. High-pressure studies have provided ideas to enhance  $T_c$  values through chemical means under ambient pressure. For instance, the substitution of the smaller ion  $Y^{3+}$  for  $La^{3+}$  to generate lattice pressure in La-Ba-Cu-O has led to a large  $T_c$  enhancement [13]. Strictly speaking, the majority of the high-pressure superconductors entered this state as a result of pressure-induced insulator to metal transition [13]. In his theoretical analysis in 2002, Schilling showed that the  $T_c$  decreases under pressure for most known superconductors, sometimes rapidly depending on the  $(dT_c/dP)$  value. In most simple metal superconductors,  $dT_c/dP$  is negative; this arises predominantly from lattice stiffening with increasing pressure [12–14]. On the other hand, transition metals were found not to follow a universal behaviour, thus reflecting complexity and potency of electronic properties in the d-system [13].

High pressure is key in stabilising high-order oxide superconductors and can enhance the  $T_c$  to values  $>100$  K [15]. The HP synthesis of oxide superconductors is usually conducted at pressures of up to 8 GPa and temperatures up to 1400°C [15]. The energy developed by pressure in solid synthesis processes is small compared to temperature; moreover, the observed kinetic effects are more profound for high-pressure synthesis [15]. For instance, it takes 70 h to obtain a  $LaFeO_3$  perovskite structure at normal pressure and temperature of 1000°C and only 5 min using pressures close to 5 GPa at a constant temperature of 1000°C using  $Fe_2O_3$  and  $La_2O_3$  as precursors [15].

Since the discovery of high- $T_c$  superconducting in the cuprate oxide La-Ba-Cu-O at  $T_c = 35$  K three decades ago, there is still controversy on the mechanism responsible for the superconducting pairing [13]. In 1993, the Hg-bearing cuprates have been reported to possess one

of the highest  $T_c$  values reaching 130 K for  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$  (Hg-1223) at ambient pressure [12, 13, 16–18]. These compounds have been synthesised under high pressure (2–4 GPa) to produce suites of Hg-1234 and Hg-1223 in the general formula  $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+x}$  [19]. In a separate study, the  $T_c$  value of Hg-1223 was found to increase to 164 K when measured in situ under high pressure (30 GPa) [20]. Despite the complexity of these compounds, researchers have reached consensus on the factors that enhance the value of  $T_c$  in the superconducting oxides [13]:

- i. Cationic substitution can be varied until an optimal value is reached beyond which the hole carrier concentration in the  $\text{CuO}_2$  planes reduces.
- ii.  $T_c$  is enhanced by increasing the number of  $\text{CuO}_2$  planes which lie close together in the oxide structure while maintaining optimal doping.
- iii. Defects should be positioned as far from  $\text{CuO}_2$  planes as possible.
- iv. Develop structures with  $\text{CuO}_2$  planes that are as flat as possible.

It is interesting to note that the most studied superconducting property under pressure is the transition temperature  $T_c$  which depends on a number of factors such as the system studied, doping level  $n$ , type and mobility of defects and sometimes the pressure medium used [13, 21].

High-pressure synthesis has also been used to induce superconductivity in compounds containing rare-earth (RE) elements particularly those containing  $\text{Pr}^{3+}$  [17]. The parent compound  $\text{PrBa}_2\text{Cu}_3\text{O}_2$  (Pr123) is not superconducting under ambient pressure; however, these materials were found to be superconducting with  $T_c = 52$  K under highly oxidising conditions using high-pressure synthesis [17]. The  $T_c$  value improved to 97 K under reducing conditions [17]. The high-pressure route offers additional control over experimental parameters which can be used to search for new high  $T_c$  materials.

In 2001, magnesium boride ( $\text{MgB}_2$ ), a quasi-2D material with strong covalent bonding within the boron layers, was discovered [13]. The superconductive  $\text{MgB}_2$  is produced under high-pressure conditions and possesses a  $T_c$  of 39 K. Latbalestier et al. in their work observed the absence of the problematic weak-link behaviour of the high  $T_c$  oxides and the ease of synthesis of  $\text{MgB}_2$ . This basically raised interest for the discovery of high-temperature analogues of  $\text{MgB}_2$ . Studies carried out soon after the discovery of  $\text{MgB}_2$  reveal that  $T_c$  decreased under high pressure. A variation in the pressure dependences ( $dT_c/dP$ ) of the various samples reported were attributed to differences in the samples or shear stress effects in the frozen or solid pressure media [13].

Magnesium diboride can be synthesised under ambient or elevated pressures [22]. However the superconducting characteristics such as critical current density and irreversible magnetic field are very sensitive to material density, impurity content and structural defects. Serquis et al. reported that the reason for the limited current density  $j_c$  at high field in  $\text{MgB}_2$  could be a result of weak connectivity between domains and the presence of impurities in the grain boundaries of  $\text{MgB}_2$  (Table 1) [22].

Sample composition	Synthesis conditions	$T_c$ value	References
HgBa <sub>2</sub> Ca <sub>3</sub> Cu <sub>4</sub> O <sub>10+x</sub> (Hg-1223)	Static high-pressure synthesis: 30 GPa	164 K	[20]
PrBa <sub>2</sub> Cu <sub>3</sub> O <sub>2</sub> (Pr123)	Static high-pressure synthesis	52 and 97 K (under reducing conditions)	[17]
MgB <sub>2</sub>	Static high-pressure synthesis.	39 K	—
LaFeO <sub>3</sub>	5 GPa, 5 min static high pressure	—	[15]

**Table 1.** A representation of some superconducting materials that have been produced under high-pressure conditions.

2.5. Thermoelectric materials

Thomas Seebeck’s accidental discovery in the 1820s proved that a junction between a bimetallic couple (any two metals) generates a potential as a function of the temperature gradient at that junction. This effect was explained later in the form of an equation below:

$$V = S(T_h - T_c) \tag{6}$$

where  $V$  is the applied potential,  $S$  is a proportionality constant relating the temperature gradient to the potential for the specific bimetallic couple and  $T_c$  and  $T_h$  are the cold and hot temperatures forming the thermal gradient.

In 1838, Lenz demonstrated that a bimetallic couple was capable of serving a heat sink or source when an appropriate current was passed through it [23]. This concept was coined into an expression referred to as the *Figure of Merit* in 1910 by Altenkitch and was later developed into its modern form by Ioffe in 1949:

$$Z = \frac{S^2 \delta}{\lambda} \tag{7}$$

$S$  represents the Seebeck coefficient,  $\delta$  is the electrical conductivity, and  $\lambda$  is the thermal conductivity.

The units of  $Z$  are inverse of temperature, and it is a common practice to express the figure of merit as a dimensionless value  $ZT$  as follows:

$$ZT = \frac{S^2 \delta T}{\lambda} \tag{8}$$

The dimensionless figure of merit  $ZT$  is the primary tool for comparison of thermoelectric materials. It ranges from zero for poor thermoelectrics to 1.5 for high-performance thermoelectrics [24].

The magnitude of the Seebeck coefficient gives a measure of the ability of a material to develop an electrical potential in response to an applied thermal gradient. Simply put, the

charge carriers in a given material possess kinetic energy which is directly proportional to the temperature. The charge carriers on the hot side possess higher kinetic energy than those on the cold side and will drift towards the cooler side establishing a potential gradient in response to the thermal gradient. Thus to improve the efficiency of thermoelectric generators, it is a common practice to pair an electron conductor (n-type component) with a hole conductor (p-type component) in the thermoelectric circuit. Generally speaking, the Seebeck coefficient is expected to be high to ensure a large steady current, and the thermal conductivity and resistivity must both be low. This essentially explains why thermoelectric research is focused on semiconductors rather than metals or insulators.

Today, the *Figure of Merit* concept is used to develop thermoelectric devices which convert thermal gradients into useful electric current or convert electric current into a heat source/sink. They can be used in systems where power is in demand and waste heat is in ample supply or conversely where power is readily available and temperature control is critical. However, the wide application of thermoelectric devices has been limited due to their inefficiency (~ 3%) compared to other power sources [25]. The main attraction to the use of thermoelectric devices is that they do not require any refuelling, high reliability, quiet operation, moving parts and low environmental impact [26]. Thus they are often used under extreme environments where access is difficult and reliability is mandatory. The thermocouple remains the most common application of the thermoelectric effect providing an important service to temperature control systems. However, recent improvements in thermoelectric materials will likely push power applications such as thermoelectric generators and heaters into the mainstream. Thermoelectrics (TE) are expected to drive environmentally friendly power systems which produce no pollutants, are compact and are available in a wide temperature range [26].

The most advanced thermoelectric materials are  $\text{Bi}_2\text{Te}_3$ - and  $\text{PbTe}$ -based tellurides [27].  $\text{Bi}_2\text{Te}_3$  is used as a refrigerator and possesses a maximum  $ZT$  value at 300–400 K, whereas  $\text{PbTe}$  alloys are mainly used in power generation with a maximum  $ZT$  at 600–900 K [27]. It must be noted that there are a few thermoelectric materials reported to possess high performance between 400 and 600 K [27]. However, the widespread application of  $\text{Bi}_2\text{Te}_3$  and  $\text{PbTe}$  has been hindered by the toxicity and rarity of these elements [28]. Another group of TE materials is the skutterudite compounds which possess a general formula  $\text{MX}_3$  or  $\text{VM}_4\text{X}_{12}$  where  $M = \text{Co}, \text{Rh and Ir}$  and  $X = \text{P, As and Sb}$ , and the  $V$  represents a vacancy inside the relatively large cages formed by  $M$  and  $X$  ions [29]. The binary compounds  $\text{CoSb}_3$  are of interest for applications owing to the large Seebeck coefficient (high power factor  $S^2\sigma$ ) and high hole mobility [30]. However, the lattice thermal conductivity  $\lambda$  is very high which limits the TE applications of binary skutterudites. The large vacancies in skutterudite structure form cages into which guest atoms can be introduced without structural distortion of the parent lattice. These vacancies can be partially occupied by rare-earth (RE) ions such as La, Ce and Yb or alkali metal ions such as Ca and Ba [30]. A number of studies have hypothesised that the ions inserted into these cages often rattle around disrupting the phonon modes in the system and reducing the thermal conductivity [25, 30–38]. Furthermore, theoretical calculations in referenced literature reveal that the filling fraction limit (FFL) of RE atoms in  $\text{CoSb}_3$  depends on the charge state of the atom [29]. RE atoms with a charge state of +2, for instance, exhibit relatively high FFLs in comparison to those of a higher charge state of say +3 [29].

A practical challenge associated with the fabrication of TE materials with a high  $ZT$  is the interdependence of  $S$ ,  $\delta$  and  $\lambda$  values. The improvement in one parameter usually adversely influences the others [32]. In 1995, Slack proposed a concept based on ‘glass-like’ thermal conductivity values referred to as the phonon-glass electron crystal (PGEC) [31]. A number of approaches have been adopted to improve the TE performance of skutterudites such a void filling and lattice atom substitution [32–35]. It is noteworthy to mention that in comparison to n-type  $\text{CoSb}_3$ -based skutterudites which are well researched, the development of p-type skutterudites still lags behind [32, 35]. Elemental filling is effective in suppressing the thermal conductivity  $\lambda$  due to the rattling filler atoms (near unit filling fraction), and a low resistivity is ensured by the high hole concentration ( $>10^{21} \text{ cm}^{-3}$ ) while maintaining a moderate Seebeck coefficient,  $S$  [39]. The enhancement of  $ZT$  by elemental filing is possible through enhancing power factor  $PF (= S^2/\rho)$  and supressing thermal conductivity (Table 2).

2.6. Development of thermoelectric materials using high-pressure techniques

The high-pressure technique is one of the modern synthesis methods used to improve the efficiency of TE materials. As mentioned earlier, high pressure enables the synthesis of compounds with a crystal structure or composition which is not achieved at ambient pressure [39].  $\text{Bi}_2\text{Te}_3$  and its alloys have been fabricated using a variety of methods which include powder metallurgy techniques such as hot pressing, spark plasma sintering (SPS) methods [40], Bridgman and zone melting techniques [40] and ultra-high-pressure sintering (HPS) methods [40]. High-pressure sintering (HPS) is advantageous in that it provides a low-cost route, is suitable for large-scale production and results in more homogeneous nanocrystalline grain and is effective in restraining grain coarsening during sintering [40].

Recent studies have shown that grain refinement of  $\text{Bi}_2\text{Te}_3$ -based alloys can enhance the thermoelectric performances [40]. In one experiment, a p-type  $\text{Bi}_2\text{Te}_3$ -based nanomaterial was fabricated using HPS, and a  $ZT$  of 1.16 was obtained at room temperature (RT) [27]. The nano-grain structure was attributed to effective reduction in the thermal conductivity. Zou et al. obtained an n-type  $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$  compound doped with Gd through HPS at 6.6 GPa followed by annealing. A maximum  $ZT$  of 0.74 was obtained at 423 K which was attributed to the nano-grain

Composition	Synthesis conditions	ZT value	References
p-Type $\text{Bi}_2\text{Te}_3$ (nano)	Static high-pressure synthesis	1.16 at room temperature	[27]
n-Type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ doped with Gd (nano)	Static high pressure at 6.6 GPa followed by annealing	0.74 maximum at 423 K	[40]
Te doped with 0.1% Bi	Static high-pressure synthesis	0.72 at 517 K	[37]
Yb-doped $\text{Yb}_{0.29}\text{Co}_4\text{Sb}_{12}$ (highest Yb doping reported)	Static high pressure at 2 GPa	—	[25]
Ba-filled $\text{Ba}_{0.51}\text{Co}_4\text{Sb}_{14}$ (improved filling for Ba from 0.28 to a maximum 0.51)	Static high-pressure synthesis	0.95 at 883 K	[41]

Table 2. A representation of high-pressure-synthesised thermoelectric materials from selected literature.

structure [40]. HPS also allows high dopant solubility and affects formation energy of defects both of which can strongly influence electrical transport properties [37, 41]. Yang et al. proved this concept by doping Te with 0.1 mol% Bi under HPS to produce a ZT of 0.72 at 517 K which is comparable to that of more complex composition alloys such as  $\text{Bi}_2\text{Te}_3$  and  $\text{PbTe}$  [37].

The concept of elemental filling of  $\text{CoSb}_3$ -based skutterudites is most promising in the production of thermoelectric materials working in the mid-temperature range (600–900 K) [41]. The concept involves filling the  $\text{Sb}_{12}$ -icosahedron voids of  $\text{CoSb}_3$  crystal which in turn donate electrons to improve the power factor and promote rattling inside crystal voids to scatter phonons and reduce lattice thermal conductivity, leading to enhanced thermoelectric performance [41]. Recently  $\text{CoSb}_3$ -based skutterudites with ZT values as high as 2 have been produced through multiple elemental filling [41].  $\text{CoSb}_3$ -based skutterudites are traditionally prepared through a process melting, quenching, annealing and final consolidation at ambient pressure [41]. This process usually takes several hours; moreover, theoretical investigations suggested the fillable elements, and their filling fraction limits (FFLs) are restricted using such processing methods [41]. This points to the necessity of utilising alternative preparation methods which can broaden the fillable elements and increase FFL [41]. The high-pressure (HP) synthesis method is effective in lowering the reaction temperature and can promote increased filling fraction into  $\text{CoSb}_3$  voids [41]. Kang et al. used HP synthesis method to fabricate a Ba-filled skutterudite compound ( $\text{Ba}_{0.51}\text{Co}_4\text{Sb}_{12}$ ) with a maximal ZT of 0.99 reached at 883 K. The high-pressure synthesis was effective in increasing the filling fraction of Ba into the  $\text{CoSb}_3$  structure from 0.28 to a maximal of 0.51. In a separate study, the highest doping ratio of Yb was reported in the compound  $\text{Yb}_{0.29}\text{Co}_4\text{Sb}_{12}$  synthesised under a pressure of 2 GPa [25]. The FFL value is the highest reported so far and shows a substantial decrease in conductivity with increasing Yb filling ratio  $x$ .

Magnesium sulphide ( $\text{Mg}_2\text{S}$ ) has been identified as an environmentally friendly TE material likely to replace the TE compounds containing rare elements such as Bi, Te, Pb, Co and Sb in the mid-temperature range (600–900 K) application. Thermodynamic studies have shown that it is difficult to synthesise  $\text{MgS}_2$  with a stoichiometric ratio at high temperatures without unreacted Mg [29]. This is attributed to the Mg boiling point (1363 K) which is very close to the melting point of  $\text{Mg}_2\text{S}$  (1358 K) [29]. The use of high-pressure synthesis can control the melting and boiling point temperatures to obtain a stoichiometric  $\text{Mg}_2\text{S}$  ratio without residual Mg. The high pressure was also attributed to a decrease in synthetic temperature which is favourable for the relaxation of the n-type defects resulting in improved TE properties [29].

## 2.7. Magnetic materials

A wide range of major families of permanent magnets have been in use over the years which include the low-cost and low energy ferrites and the more expensive and higher-performance rare-earth magnetic materials. Alnico an alloy of aluminium, nickel, and cobalt is one of the first magnetic materials developed in the 1930s for military electronic applications. Alnico magnets are known for their high induction levels with good resistance to demagnetisation and stability; they also possess a high working temperature limit (550°C) at a reasonable cost. It is well suited for automotive and aircraft sensor applications. However in comparison to

newer materials, Alnico possesses lower coercivity which limits its applications. Ferrite magnets referred to as ceramic magnets were commercialised in the mid-1950s and are the least expensive permanent magnets available. The ferrites are produced through sintering of fine iron oxide mixed with either strontium (Sr) or barium (Ba) and a ceramic binder (MM 2018). Ferrites find use in motors in the form of arc-shaped magnets, in magnetic chucks and magnetic tools. Because of their brittle nature, ferrites are not suitable for structural applications, and moreover their thermal stability is limited to 300°C.

Samarium cobalt (Sm-Co) is the first commercially viable rare-earth permanent magnetic material formulated in the 1970s. Their excellent thermal stability, high corrosion resistance and resistance to demagnetisation make them suitable for high-performance application such as most demanding motor applications and medical applications. It is the most expensive magnetic material on a 'per kg' basis; however, this is offset by the low volume required to fulfil a certain task because of its high energy 16MGOe up to 33MGOe. The most powerful commercial permanent magnets are sintered neodymium-iron-boron (Nd-Fe-B) rare-earth magnets with maximum energy product ranging from 26MGOe to 52MGOe. Nd-Fe-B magnets were developed in the 1950s and have found use in applications where higher efficiency and more compact devices are demanded. They are however prone to oxidation and can only be used at temperatures  $\leq 200^\circ\text{C}$ .

The function of permanent magnetic materials in electric machines is to provide magnetic flux [42]. The most important factors required to achieve this function are the saturation magnetisation ( $J_s = \mu_0 M_s$ ) which is required to be as high as possible and affordable; the other factor is high coercivity,  $H$  [42]. There exists two coercivity parameters used to grade magnetic hardness, i.e. intrinsic coercivity,  $H_c$  (or  $H_{ci}$ ), and technical (or normal) coercivity,  $H_c$  [42]. Coercivity is basically the ability to resist demagnetisation either from electric or magnetic circuit and thermal demagnetisation from the operating temperature [42]. Soft magnetic materials possess a typical  $H_c < 1 \text{ kAm}^{-1}$ , and hard magnetic materials have  $H_c$  up to approx.  $2800 \text{ kAm}^{-1}$  (about 35 kOe) [42]. Permanent magnets suitable for high-temperature applications under strong electric and magnetic circuits must possess high coercivity, ideally  $H_{ci} > H_c$ . There are only three permanent magnets which show such a characteristic, i.e. hard ferrites and Nd-Fe-B and Sm-Co magnets [42]. The research focus is the development of Dy-free Nd-Fe-B magnets with high  $H_c$  for high-temperature applications [42]. Dy is a very rare metal, and 97% of the world supply is of Chinese origin [42].

In recent years, there is much interest in high-performance permanent magnets based on rare-earth and 3d transition metals (3-TMs) intermetallic compounds [42]. This has been triggered by the need for maximised energy densities at various operating temperatures and to replace the more expensive Dy (dysprosium) in high-performance magnets. Manganese-based magnetic compounds such as Mn-Bi, Mn-Al-C and Mn-Li-N have attracted considerable attention as alternative permanent magnetic materials without critical elements [43]. However, the reaction between alkali earth metals and 3d transition metals to form intermetallic compounds at ambient pressure is not feasible owing to the large difference in atomic radii and electronegativity [2, 43]. Another approach which has been adopted is to incorporate nanoscale soft magnetic phases into a hard magnetic phase matrix to enhance energy density of the composite due to interphase exchange coupling at a reduced cost [42].

## 2.8. Development of magnetic materials using high-pressure techniques

The use of high-pressure synthesis in magnetic materials has not been fully explored, and there are very limited reports on permanent magnetic alloys consisting of alkali metals (AMs) and 3d metals [43]. With the current research focus towards finding alternatives to traditional high-performance rare-earth magnetic materials, high pressure presents a rare opportunity to be exploited in this area. A majority of materials have been exploited in these groups, the so-called 'multiferroic' (MF) materials which possess ferroelectricity, ferromagnetism and ferroelasticity in a single material [44]. The most desirable property in these materials is the magneto-electric (ME) coupling which is extremely rare in most compounds [44]. Magneto-electric coupling refers to either induction of magnetisation by an electric field or polarisation by a magnetic field [44]. The scarcity of these materials can be explained from the symmetry and electronic properties point of view details of which is discussed elsewhere [44]. Recent studies have proven that ferromagnetism and ferroelectricity can occur simultaneously in a single phase through an additional electronic or structural driving force which supports ME coupling [44]. High-pressure high-temperature synthesis allows stabilisation of metastable or highly distorted structures which might achieve ME coupling [44]. The majority of MF materials exhibit a perovskite structure ( $ABO_3$ ), typically consisting of corner sharing  $BO_6$  octahedra with B ions (usually magnetic ions such as Mn or Fe) in the centre of the octahedral site and A ions at the centre of a cube formed by eight  $BO_6$  octahedra [44]. The application of HP has been used to induce MF in perovskite compounds by introducing magnetic ions (ferromagnetism) in a non-centromagnetic structure (distorted). Typical examples include  $BiFeO_3$  which require high-pressure synthesis to obtain a high-temperature solid-state reaction when using oxides as precursors ( $Bi_2O_3$  melts at  $824^\circ\text{C}$  at ambient pressure) [44]. One of the challenges in the synthesis of  $BiFeO_3$  (BFO) is the evaporation of  $Bi_2O_3$  at high temperatures during solid-state synthesis also under applied fields of about  $200\text{ kVcm}^{-1}$ ; BFO can decompose leading to hematite  $Fe_2O_3$  [45]. Furthermore,  $BiFeO_3$  is metastable in air and above  $675^\circ\text{C}$ ; it decomposes into various products, and below  $675^\circ\text{C}$  the density of the sintered product produced by conventional sintering methods is very low which makes evaluation of electrical and magnetic properties impossible [45].

$BiMnO_3$  possesses a simple perovskite structure and has been obtained under HP/HT synthesis ( $P = 4\text{ GPa}$ ,  $T = 1273\text{ K}$ ) [44]. In 2016, Drygas et al. reported an increase in Mn contents (3–5 at%) in (Ge, Mn)N magnetic materials produced by HP/HT synthesis (7 GPa,  $1000^\circ\text{C}$ , 10 min). The Mn solubility in hexagonal GaN is limited to 2.4 at% predicted from a calculated Ga-Mn-N phase diagram [46]. The use of nanomaterials has shown an increase in Mn doping at 7 at% for nano-powders and 10 at% for nanowires [46]. This further proves the advantageous impact of HP/HT synthesis on incorporation of a doping element into a foreign matrix.

The binary Mn-Ge system contains intermetallic phases which exhibit antiferromagnetism with relatively low magnetic ordering temperatures [47]. The phases,  $Mn_5Ge_3$  ( $T_c = 304\text{ K}$ ) and  $MnGe_4$  ( $T_c = 340\text{ K}$ ), are the most interesting as they are known to exhibit ferromagnetism with  $T_c$  above room temperature [47]. It is clear that high-pressure synthesis has been the method of choice in the development of intermetallic compounds which would otherwise not react under ambient pressure conditions owing to differences in atomic radii and electronegativities. Under high-pressure conditions, for instance, alkali earth metals are able acquire properties of

Composition	Synthesis conditions	Target structure	References
BiMnO <sub>3</sub>	4 GPa, 1273 K under static high-pressure conditions	Perovskite structure with improved magnetic properties	[44]
Higher Mn doping of (Ge, Mn)N	7 GPa, 1000°C, 10 min under static high pressure	Improved doping (3–5 at%) to above the limit of (2.4 at%) resulting in superior magnetic properties	[46]
Mn <sub>5</sub> Ge <sub>3</sub> , MnGe <sub>4</sub>	—	Improved reaction kinetics to form intermetallics exhibiting ferromagnetism	[47]

**Table 3.** Magnetic properties and corresponding high-pressure synthesis conditions of some representative magnetic materials.

transition metals which enables them to easily interact and react with d-metals to form inter-metallic compounds (**Table 3**) [2].

### 3. Outlook

The above examples are evident of the importance the pressure parameter that plays in the tuning of structural, electronic and magnetic properties of functional materials. The commercial production of functional materials under high-pressure conditions is however still severely restricted owing to the small volume of product obtained at high pressures. The major drawback of high-pressure synthesis is the destabilisation after pressure release. However, high-pressure synthesis still remains a powerful research tool in the discovery of novel materials with unique properties which can be recreated through alternative chemical paths. I agree with the sentiments of most high-pressure specialists that high-pressure research is not yet fully appreciated to its true value.

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