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## Micro-Structural Properties Of $\text{Te}^{+4}$ -Doped $\text{Mg}_{1-x}\text{Te}_x\text{B}_2$ Superconductor Regime

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### ABSTRACT

The pure and tellurium-doped samples having formula  $\text{Mg}_{1-x}\text{Te}_x\text{B}_2$  (where,  $x = 0.0, 0.05, 0.1$  and  $0.2$  mole) were prepared via high temperature solid state reaction route. The synthesis was depending upon diffusion mechanism of both Mg- and Te-vapours through boron-matrix. The solubility limits of tellurium were found to be too tide to substitute higher than  $0.2$  mole on Mg-sites. X-ray diffraction analysis for investigated samples proved that all samples were found mainly belong to single hexagonal phase with P6/mmm symmetry with very small traces from MgO and  $\text{TeO}_2$  as secondary phases in minor. From SE-microscopy and EDX analyses only MgO was detected in between grains and no existence for any aggregations of expected  $\text{TeO}_2$  secondary phase. Magnetic susceptibility measurements indicated that only the sample with maximum thrium doping ratio  $x = 0.2$  mole exhibited slight depression on its value of  $T_c$ -offset which found to be  $35.1$  K.

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### KEYWORDS

Te-doping;  
 X-ray;  
 Crystal structure;  
 SE-microscopy;  
 $\text{MgB}_2$ ;  
 Superconductor.

### INTRODUCTION

The discovery of superconductivity in magnesium diboride regime at elevated temperature ( $T_c = 40$  K)<sup>[1-2]</sup> was considered one of the most interesting scientific area for the researchers and solid state scientists. Since this discovery at 2001 reasonable progress has been achieved in material synthesis as well as in

understanding of its physical properties<sup>[3-11]</sup>. From these initial days of research on superconducting  $\text{MgB}_2$  many attempts were made to tailor the physical properties of the material to suite different needs as well as to explore the neighboring compounds in search of even higher  $T_c$  values. Many investigators and researchers undertook synthesis and characterization of  $(\text{Mg}_{1-z}\text{T}_z)\text{B}_2$  or  $\text{Mg}(\text{B}_{1-y}\text{M}_y)_2$  ( $T$ =transition

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metal, Li, Be, Ir, Al;  $M=C, F, Si$ ) materials. The agenda was multi-fold: to look for changes in  $T_c$ , to perform tests of the superconducting mechanisms in  $\text{MgB}_2$ , and to introduce additional pinning centers that could lead to higher critical current densities. Since many diborides crystallize in the same, hexagonal  $\text{AB}_2$  type of structure as  $\text{MgB}_2$ , and these compounds have been known and studied for decades<sup>[12]</sup> these substitutions initially were viewed as feasible. In spite of considerable efforts, substitutions in  $\text{MgB}_2$  appeared to be difficult and in many cases unsuccessful or, at best, ambiguous.

For magnesium site substitutions apparently only Al was shown to enter the structure unambiguously<sup>[13-17]</sup> although in a limited concentration range. For boron site substitutions a number of attempts with different elements were made.

Carbon substitution was reported in several publications<sup>[18-23]</sup>. Most of these attempts had elemental magnesium, boron and carbon as starting materials and the synthesis was performed at different pressures and temperatures.

According to Medvedeva et al.<sup>[24]</sup>, copper should behave as a hole dopant, producing a shift of  $E_F$  to higher binding energies and an increase of the density of states  $N(E_F)$ , at least for concentrations as high as 25%. Claims of an increase of  $T_c$  up to 49 K by Cu substitution have been reported<sup>[25]</sup>, but they were not confirmed and the original claim withdrawn. In fact, the synthesis of  $\text{Mg}_{1-x}\text{Cu}_x\text{B}_2$  has proved to be hard and, to our knowledge, no successful method for his preparation has so far been published and even stated as impossible<sup>[26]</sup>. Doping  $\text{MgB}_2$  with Cu is difficult because of the high affinity of Cu and Mg to form cubic inter-metallic compounds with Cu/Mg ratio ranging from 2/3 to 3. Cu-B binary systems are known, starting from the composition  $\text{CuB}_2$ <sup>[27]</sup>. Phases with higher Cu/B ratio are unstable and copper diboride does not exist. For these reasons, attempts to synthesis  $\text{Mg}_{1-x}\text{Cu}_x\text{B}_2$  solid solutions by a simple addition of Cu to  $\text{MgB}_2$ , followed by thermal treatments in argon atmosphere, were not successful. On the contrary, they<sup>[27]</sup> obtained the desired result by using  $\text{CuB}_{24}$ , instead of B, as starting material.

The essential goal of this work is classified into two categories; (a) Possibility for substitutions on

$\text{MgB}_2$  regime at vapour state to understand its chemistry. (b) Studying the effects of dopings on the micro-structural and superconducting properties of  $\text{MgB}_2$  regime.

## EXPREMENTAL

### Samples preparation

$\text{Mg}_{1-x}\text{Te}_x\text{B}_2$  (where,  $x = 0.0, 0.05, 0.1$  and  $0.2$  mole) was prepared through high temperature solid state reaction technique for stoichiometric amounts of the nominal compositions of starting materials (Mg, B and Te) all as metal powders. This narrow range of doping was selected experimentally after preparations of wide range of doped samples reach to 1 mole. The solubility limits of tellurium doping was found to be  $\sim 0.2$  mole. The average particle size of boron metal powder used was  $< 50 \mu\text{m}$ . All powders are with purity grade  $\gg 99.9\%$ . Te-metal was dispersed in very small amount of Mg-powder using mechanical grinder then mixed and ground together with the rest metals stoichiometrically and placed into evacuated Ta-ampule under argon pressure, the Ta-tube carefully sealed in goodly way and forwarded to tublar quartz furnace at  $1000^\circ\text{C}$  sintering temperature.

The thermal cycle of preparation pure  $\text{MgB}_2$  and Te-doped  $\text{MgB}_2$  included intermediate fixation step at  $660^\circ\text{C}$  for 3 hrs, then gradual increasing till  $1100^\circ\text{C}$  by rate  $100^\circ\text{C}/\text{hr}$  and finally samples were sintered at  $1000^\circ\text{C}$  for 12 hrs then the temperature cooled down till R.T. by rate  $50^\circ\text{C}/\text{h}$ . It is known that, Mg and Te melt/or boil and convert into vapour at temperature over  $648.6, 449.5^\circ\text{C}$  respectively<sup>[28]</sup> while, boron has very high melting point  $2180^\circ\text{C}$ , so pure and doped- $\text{MgB}_2$  are produced through diffusion reaction mechanism of Mg/Te ions vapour into boron matrix.

From this point of view one can conclude that Te over  $450^\circ\text{C}$  becomes vapour and can diffuse with Mg ions at sintering temperature by the same efficiency into boron matrix.

### Structural measurements

1. The X-ray diffraction (XRD) measurements were carried out at room temperature on the ground samples using Cu-K $\alpha$  radiation source and a com-

puterized Shimadzu (Japan) diffractometer with two theta scan technique.

2. Scanning Electron Microscopy (SEM): Scanning electron microscopy measurements were carried out along ab-plane using small pieces of the prepared samples by using a computerized SEM camera with elemental analyzer unit Shimadzu (Japan).

### Superconducting measurements

The cryogenic AC-susceptibility of the prepared materials was undertaken as a function of temperature recorded in the cryogenic temperature zone down to 30K using liquid helium refrigerator. Magnetization measurements were performed with a quantum design SQUID magnetometer with field amplitude  $H_{AC}=20\text{Oe}$  and frequency 27 Hz. Powdered samples were used for measurements in order to reveal how much the content of superconductivity inside the bulk of superconductor sample.

## RESULTS AND DISCUSSION

### Structural measurement

Figure 1 displays X-ray diffraction patterns for investigated samples

$\text{Mg}_{1-x}\text{Te}_x\text{B}_2$  (where,  $x=0.0, 0.05, 0.1$  and  $0.2$  mole) which were found mainly belong to single hexagonal phase with P6/mmm symmetry corresponding to  $\text{Mg}_{1-x}\text{Te}_x\text{B}_2$  superconductor in major beside MgO as secondary phase which was assigned by (\*) mark in the back ground in minor. The calculated lattice pa-

rameters were found to be  $a=3.0806 \text{ \AA}$  and  $c=3.5698 \text{ \AA}$  for undraped  $\text{MgB}_2$  sample, while  $a$  and  $c$  axes exhibit slight elongation with increasing mercuric dopant from  $x=0.05$  to  $x=0.2$  mole respectively (see TABLE 1).

It is clear that increasing in the  $c$  axis is much noticeable than increasing of  $a$  axis (see Figure 1a). This increasing in  $c/a$  ratio can be explained on the bases of first ionic size effect that, mercuric ionic radius is larger than magnesium ionic radius ( $\text{Mg}^{2+}=72\text{pm}$  while  $\text{Te}^{4+}=97\text{pm}$ <sup>[28]</sup>) and second increasing of repulsion in-and inter-plane depending upon difference in electro negativity between tellurium which is more electronegative than Mg-ion .

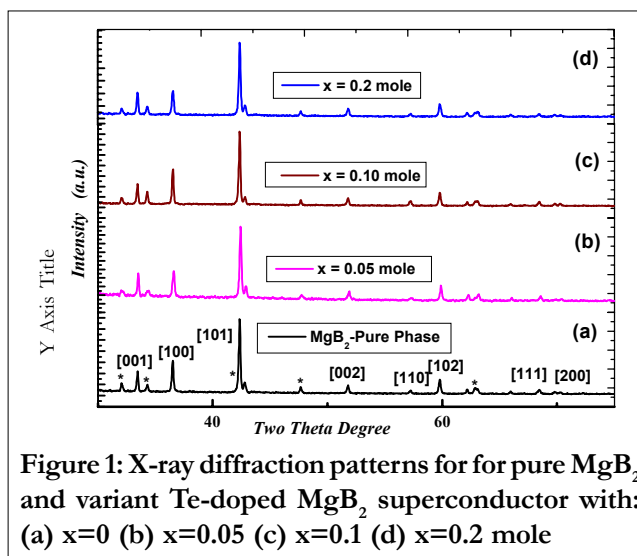
According to present results tellurium dopant in this narrow range of investigations has a slight effect on the X-ray diffraction patterns as clear on figure 1.

Similar results were reported by Cimberle et al.<sup>[29]</sup>, they reported that Li cation dopant can substitute magnesium on  $\text{MgB}_2$  regime up to 30% without noticeable change on x-ray diffraction patterns only few peaks changed its place.

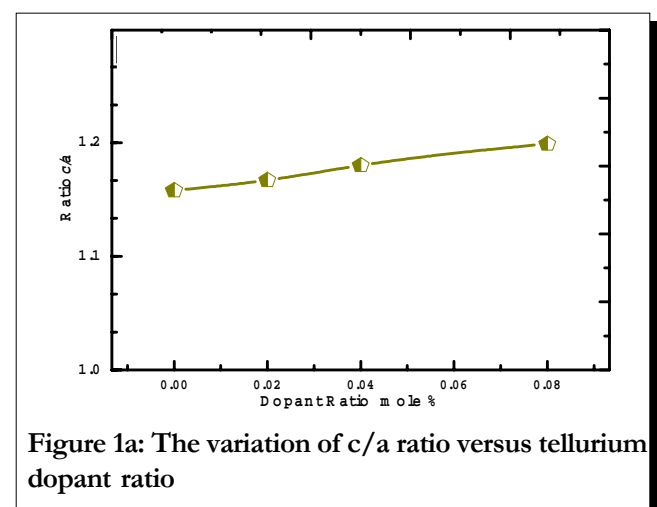
It is well known that,  $\text{MgB}_2$  has  $\text{AB}_2$  structure type which is commonly found for many metals diborides. This structure consisting of interleaved

**TABLE 1: The calculated lattice parameter for doped and undoped  $\text{MgB}_2$  samples**

Dopant Ratio mole %	a $\text{ \AA}$	c $\text{ \AA}$	c/a
0.00	3.0806(5)	3.5698	1.158
0.05	3.0834(2)	3.6012	1.167
0.10	3.0841(1)	3.6621	1.180
0.20	3.0959(3)	3.7316	1.299



**Figure 1: X-ray diffraction patterns for for pure  $\text{MgB}_2$  and variant Te-doped  $\text{MgB}_2$  superconductor with (a)  $x=0$  (b)  $x=0.05$  (c)  $x=0.1$  (d)  $x=0.2$  mole**



**Figure 1a: The variation of  $c/a$  ratio versus tellurium dopant ratio**

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graphite-like layers of boron and triangular layers of metal atoms. This kind of structures was found to be very restricted for dopings or substitutions. For these difficulties we already tried this trend of substitutions depending on dopings of vapour ions are more efficient than ordinary solid state solution.

Many researchers like<sup>[30,10]</sup> have been reported the minimal criteria for judging a successful chemical substitution in magnesium diboride system which are; 1<sup>st</sup> the second phases should not grow systematically with propagation of dopant ratio concentration in the solid state solution and special care must be apply to peak inexting of impurity phases, 2<sup>nd</sup> the shift of lattice parameter of by more than three standard deviations in least squares lattice parameter refinements in the series of doped samples should be seen. 3<sup>rd</sup> the properties of superconductor should change on doping and 4<sup>th</sup> the atomic size of the dopant element must be harmonize and thermodynamically compatible with the solid solution of system on doping whatever this system.

According to the later criteria for judging successful substitutions reported by<sup>[30,10]</sup> our results are considered partially consistent with them specially in the point of particle size fitting such that the ionic radius of tellurium is larger than magnesium ion.

### Superconducting measurements

Figure 2 shows the AC-susceptibility curves measured as a function of absolute temperature for pure  $\text{MgB}_2$  and Te-doped family having general formula  $\text{Mg}_{1-x}\text{Te}_x\text{B}_2$  ( $x = 0.05, 0.1$  and  $0.2$  mole).

It is obviously that nearly no change on the values of the  $T_c$ s-offsets for the first three samples  $\Delta T_c \sim 0.75$  K which is very small to discuss or analyze. The measured  $T_c$ s-offsets were found (38.7, 38.3 and 38K) for those with  $x=0.0, 0.05$  and  $0.1$  mole respectively.

The only noticeable depression on the value of  $T_c$ s-offset was exhibited by the sample which has maximum doping ratio  $x=0.2$  mole. The measured transition temperature for this sample was  $T_c$ -offset = 35.1 K (see Figure 2a).

In our view this depression on the value of  $T_c$ -offset is due to two factors 1<sup>st</sup> existence of MgO-impurity phase which is insulator oxide<sup>[31]</sup> inhibits

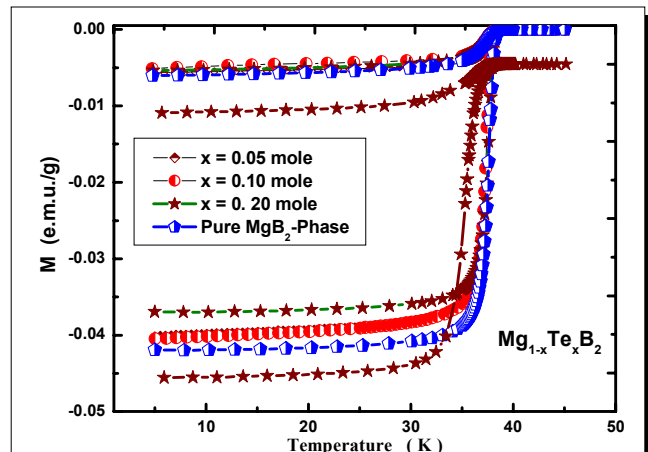


Figure 2: MT-magnetic susceptibility curves (Meissner & Shielded lines) for pure and Te-doped  $\text{MgB}_2$ : (a)  $x=0$  (b)  $x=0.05$  (c)  $x=0.1$  (d)  $x=0.2$  mole

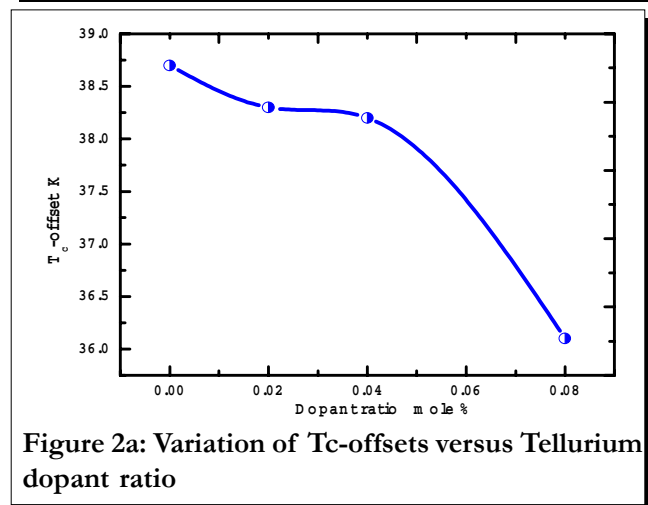


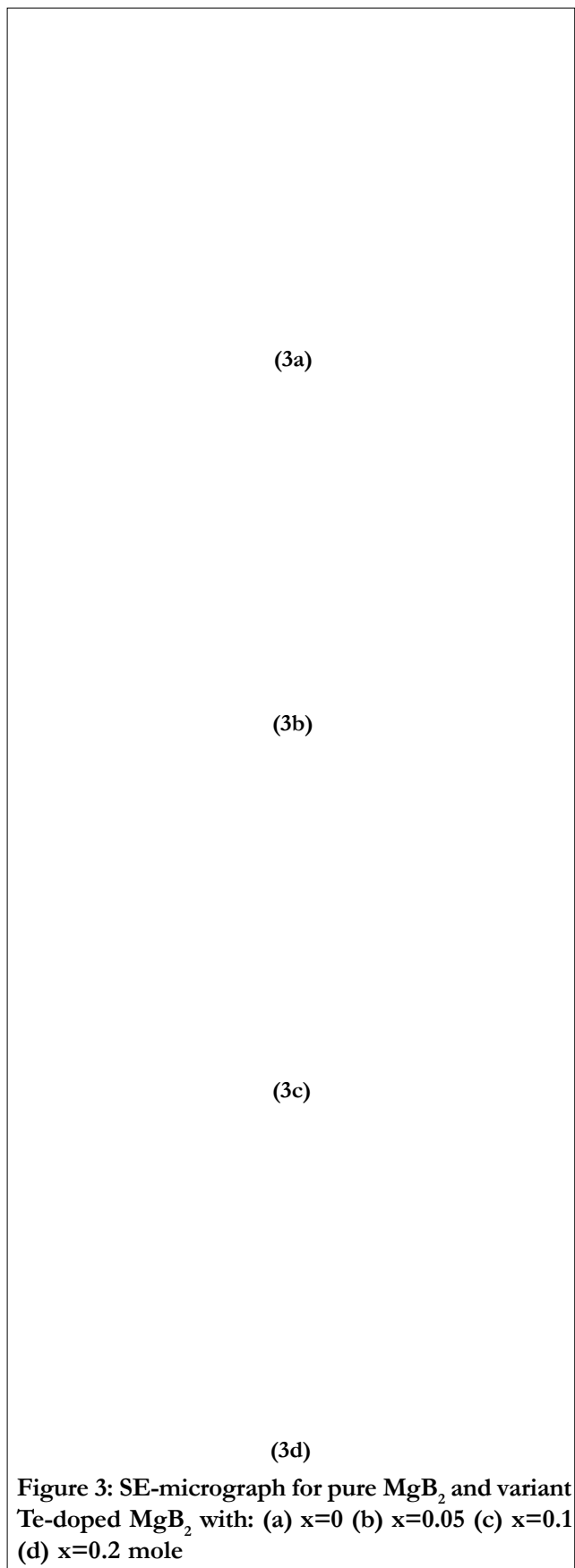
Figure 2a: Variation of  $T_c$ -offsets versus Tellurium dopant ratio

the super currents specially if it is present in between the grains of  $\text{MgB}_2$ . In our work MgO was detected as secondary phase in both XRD and SEM pictures, 2<sup>nd</sup> it might  $\text{TeO}_2$  is incorporated in the material bulk as secondary phase but does not observed because its ratio of existence is too small to detect by both XRD and SEM techniques.

### Micro-structure properties

Figure (3a,d) show SEM-images (with different magnification factors) for pure  $\text{MgB}_2$  and variant tellurium-doped magnesium diboride regime ( $x = 0.0, 0.05, 0.1$  and  $0.2$  mole respectively) with boron particle size  $\leq 50 \mu\text{m}$ .

From the analysis of SEM-images and EDX elemental analysis for different spots on each sample we concluded the following facts;



1<sup>st</sup> unreacted B impurity phase does not noticeable at the intergrain-layers confirming quality of preparations, 2<sup>nd</sup> only MgO impurity phase begins to appear in between grains in very small aggregation, 3<sup>rd</sup> the average grain size estimated was found to be in between 0.28 and 1.86  $\mu\text{m}$ , 4<sup>th</sup>  $\text{MgB}_2$  is the major phase with high degree of homogeneity which appears in degree of gray colouration and 5<sup>th</sup> no existence for any aggregations of  $\text{TeO}_2$  which expected as impurity phase.

These observations and facts emphasis and confirm our XRD measurements such that only MgO impurity phase appears clearly with considerable intensities in all samples see figure 1.

### CONCLUSIONS

The substitution limits of Te-ions was found to be  $\sim 0.2$  mole which emphasizes that substitutions on  $\text{MgB}_2$  regime is still too limited and needs many precautions to be chemically successful.

To dopings in the investigated range ( $0.0 < x < 0.2$  mole) has a moderate effect on crystal structure accompanies with slight elongation on c-axis. Tcs-offsets for the undoped and first two samples  $\Delta T_c \sim 0.75$  K (for  $x = 0.0, 0.05$  and  $0.1$  mole). The measured Tcs-offsets were found (38.7, 38.3 and 38 K) for those with  $x = 0.0, 0.05$  and  $0.1$  mole respectively.

The only noticeable depression on the value of Tcs-offset was exhibited by the sample which has maximum doping ratio  $x = 0.2$  mole. The measured transition temperature for this sample was Tc-offset = 35.1 K.

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