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Micro-Structural Properties Of Te^{+4}-Doped $Mg_{1-X}Te_xB_2$ Superconductor Regime

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ABSTRACT

The pure and tellurium-doped samples having formula $Mg_{1-x}Te_xB_2$ (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 0.2mole 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 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 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 Tc-offset which found to be 35.1 K.

KEYWORDS

Te-doping;
X-ray;
Crystal structure;
SE-microscopy;
MgB_2;
Superconductor.

INTRODUCTION

The discovery of superconductivity in magnesium diboride regime at elevated temperature (T_c=40 K)[1-2] 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[3-11]. From these initial days of research on superconducting 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 $(Mg_{1-z}T_z)B_2$ or $Mg(B_{1-y}M_y)_2$ (T=transition 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 MgB_2, and to introduce additional pinning centers that could lead to higher critical current densities. Since many diborides crystallize in the same, hexagonal AB_2 type of structure as MgB_2, and these compounds have been known and studied for decades[12] these substitutions initially were viewed as feasible. In spite of considerable efforts, substitutions in 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[13-17] 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[18-23]. 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.[24], 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[25], but they were not confirmed and the original claim withdrawn. In fact, the synthesis of $Mg_{1-x}Cu_xB_2$ 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[26]. Doping 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 CuB_2[27]. Phases with higher Cu/B ratio are unstable and copper diboride does not exist. For these reasons, attempts to synthesis $Mg_{1-x}Cu_xB_2$ solid solutions by a simple addition of Cu to MgB_2, followed by thermal treatments in argon atmosphere, were not successful. On the contrary, they[27] obtained the desired result by using CuB_{24}, instead of B, as starting material.

The essential goal of this work is classified into two categories; (a) Possibility for substitutions on MgB_2 regime at vapour state to understand its chemistry. (b) Studying the effects of dopings on the micro-structural and superconducting properties of MgB_2 regime .

EXPREMENTAL

Samples preparation

$Mg_{1-x}Te_xB_2$ (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 ~0.2 mole. The average particle size of boron metal powder used was <50 μm. All powders are with purity grade >>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°C sintering temperature.

The thermal cycle of preparation pure MgB_2 and Te-doped MgB_2 included intermediate fixation step at 660°C for 3 hrs, then gradual increasing till 1100°C by rate 100°C/hr and finally samples were sintered at 1000°C for 12 hrs then the temperature cooled down till R.T. by rate-50°C/h. It is known that, Mg and Te melt/or boil and convert into vapour at temperature over 648.6, 449.5°C respectively[28] while, boron has very high melting point 2180°C, so pure and doped-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°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-Kα 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}=2Oe 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

Figure1 displays X-ray diffraction patterns for investigated samples

$Mg_{1-x}Te_xB_2$ (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 $Mg_{1-x}Te_xB_2$ superconductor in major beside MgO as secondary phase which was assigned by (*) mark in the back ground in minor. The calculated lattice parameters were found to be a=3.0806 A° and c =3.5698 A° for undraped 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).

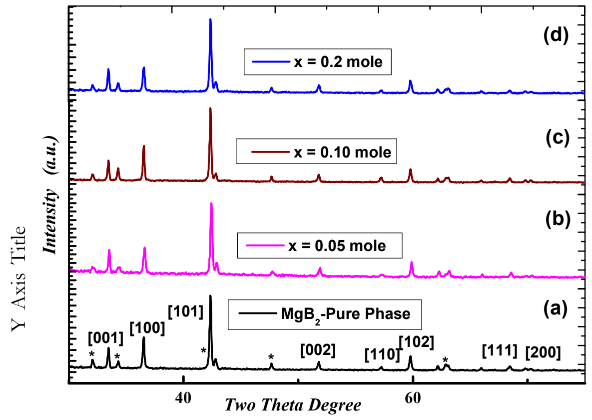

Figure 1: X-ray diffraction patterns for for pure MgB_2 and variant Te-doped MgB_2 superconductor with: (a) x=0 (b) x=0.05 (c) x=0.1 (d) x=0.2 mole

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 (Mg^{2+} =72pm while Te^{4+} =97pm[28]) 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.[29], they reported that Li cation dopant can substitute magnesium on 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, MgB_2 has 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 MgB_2 samples

Dopant Ratio mole %	a A°	c A°	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

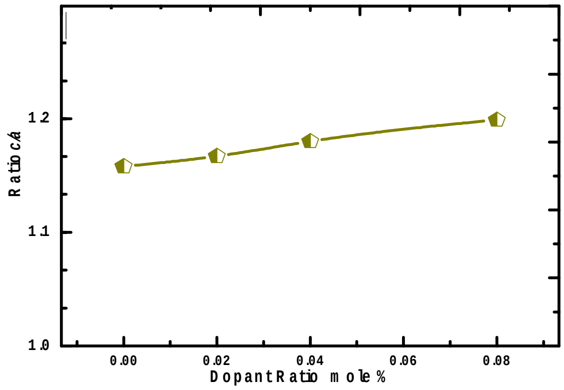

Figure 1a: The variation of c/a ratio versus tellurium dopant ratio

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[30,10] have been reported the minimal criteria for judging a successful chemical substitution in magnesium diboride system which are; 1st 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 inexing of impurity phases, 2nd 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. 3rd the properties of superconductor should change on doping and 4th 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[30,10] 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 MgB_2 and Te-doped family having general formula $Mg_{1-x}Te_xB_2$ (x =0.05, 0.1 and 0.2 mole).

It is obviously that nearly no change on the values of the Tcs-offsets for the first three samples ΔTc ~0.75 K which is very small to discuss or analyze. The measured Tcs-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 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 (see Figure 2a).

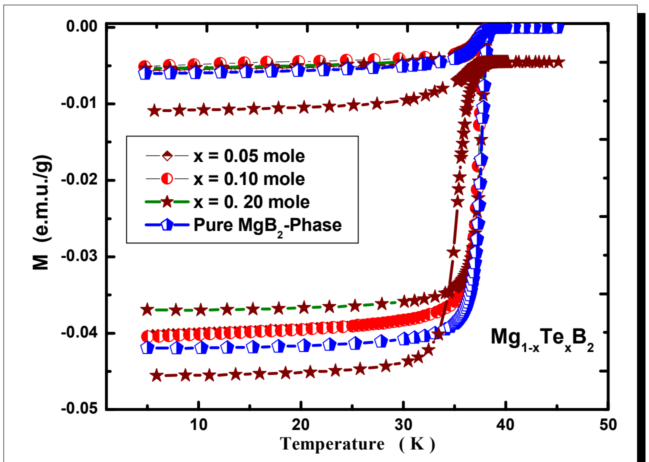

Figure 2: MT-magnetic susceptibility curves (Meissner & Shielded lines) for pure and Te-doped MgB_2: (a) x=0 (b) x=0.05 (c) x=0.1 (d) x=0.2 mole

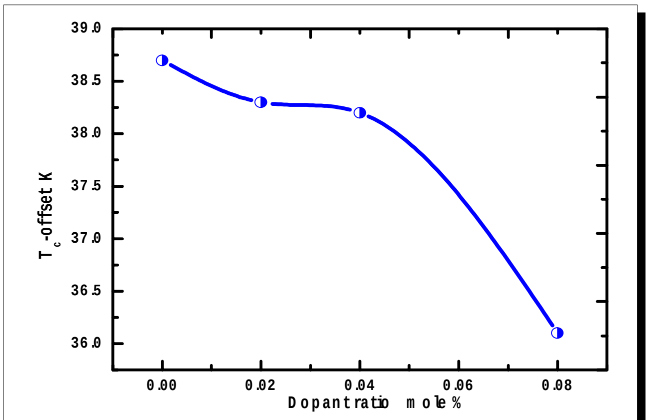

Figure 2a: Variation of Tc-offsets versus Tellurium dopant ratio

In our view this depression on the value of Tc-offset is due to two factors 1st existence of MgO-impurity phase which is insulator oxide[31] inhibits the super currents specially if it is present in between the grains of MgB_2. In our work MgO was detected as secondary phase in both XRD and SEM pictures, 2nd it might 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 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 ≤ 50 μm.

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

(3a)

(3b)

(3c)

(3d)

Figure 3: SE-micrograph for pure MgB_2 and variant Te-doped MgB_2 with: (a) x=0 (b) x=0.05 (c) x=0.1 (d) x=0.2 mole

1st unreacted B impurity phase does not noticeable at the intergrain-layers confirming quality of preparations, 2nd only MgO impurity phase begins to appear in between grains in very small aggregation, 3rd the average grain size estimated was found to be in between 0.28 and 1.86 µm, 4th MgB_2 is the major phase with high degree of homogeneity which appears in degree of gray colouration and 5th no existence for any aggregations of 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 ~0.2 mole which emphasizes that substitutions on 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 ΔTc ~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.

REFERENCES

[1] J.Akimitsu; Symposium on Transition Metal Oxides, Sendai, January 10, **(2001)**.

[2] J.Nagamatsu, N.Nakagawa, T.Murakana, Y.Zenitani, J.Akimitsu; Nature, **410**, 3 **(2001)**.

[3] S.L.Bud'ko, G.Lapertot, C.Petrovic, C.E.Cunningham, N.Anderson, P.C.Canfield; Phys.Rev.Lett., **86**, 1877 **(2001)**.

[4] D.K.Finnemore, J.E.Ostenson, S.L.Bud'ko, G.Lapertot, P.C.Canfield; Phys.Rev.Lett., **86, 2420 (2001)**.

[5] P.C.Canfield, D.K.Finnemore, S.L.Bud'ko, J.E.Ostenson, G.Lapertot, C.E.Cunningham, C.Petrovic; Phys.Rev.Lett., **86**, 2423 **(2001)**.

[6] S.L.Bud'ko, C.Petrovic, G.Lapertot, C.E.Cunningham, P.C.Canfield, M.H.Jung, A.H.Lacerda; Phys.Rev., **B63**, 220503 **(2001)**.

[7] S.L.Bud'ko, V.G.Kogan, P.C.Canfield; Phys.Rev., **B64**, 180506 **(2001)**.

[8] S.L.Bud'ko, P.C.Canfield; Phys.Rev., **B65**, 212501 **(2002)**.

[9] M.M.A.Sekkina, K.M.Elsabawy; Solid State Communi., **123**, 1 **(2002)**.

[10] M.M.A.Sekkina, K.M.Elsabawy; Physica, **C391**, 217 **(2003)**.

[11] M.M.A.Sekkina, K.M.Elsabawy; Physica, **C377**, 411 **(2002)**.

[12] J.Castaing, P.Costa In: V.I.Matkovich; 'Boron and Refractory Borides', Springer-Verlag, Berlin, Heidelberg, New York, and references therein, 390 **(1977)**.

[13] J.S.Slusky, N.Rogado, K.A.Regan, M.A.Hayward, P.Khalifah, T.He, K.Inumaru, S.M.Loureiro, M.K.Haas, H.W.Zandbergen, R.J.Cava; Nature, **410**, 343 **(2001)**.

[14] B.Lorenz, R.L.Meng, Y.Y.Xue, C.W.Chu; Phys.Rev., **B64**, 052513 **(2001)**.

[15] J.Q.Li, L.Li, F.M.Liu, C.Dong, J.Y.Xiang, Z.X.Zhao; Phys.Rev., **B65**, 132505 **(2002)**.

[16] H.W.Zandbergen, M.Y.Wu, H.Jiang, M.A.Hayward, M.K.Haas, R.J.Cava; Physica, **C366**, 221 **(2002)**.

[17] H.Luo, C.M.Li, H.M.Luo, S.Y.Ding; J.Appl.Phys., **91**, 7122 **(2002)**.

[18] M.Paranthaman, J.R.Thompson, D.K.Christen; Physica, **C355**, 1 **(2001)**.

[19] J.S.Ahn, E.J.Choi; cond-mat/0103169.

[20] T.Takenobu, T.Ito, D.H.Chi, K.Prassides, Y.Iwasa; Phys.Rev., **B64**, 134513 **(2001)**.

[21] W.Mickelson, J.Cumings, W.Q.Han, A.Zettl; Phys.Rev., **B65**, 052505 **(2002)**.

[22] Z.H.Cheng, B.G.Shen, J.Zhang, S.Y.Zhang, T.Y.Zhao, H.W.Zhao; J.Appl.Phys., **91**, 7125 **(2002)**.

[23] A.Bharathi, S.Jemina Balaselvi, S.Kalavathi, G.L.N.Reddy, V.Sankara Sastry, Y.Hariharan, T.S.Radhakrishnan; Physica, **C370**, 211 **(2002)**.

[24] N.J.Medvedeva, A.L.Ivanovskii, J.E.Medvedeva, A.J.Freeman; Phys.Rev., **B64**, 205020 **(2001)**.

[25] Y.P.Sun, W.H.Song, J.M.Dai, B.Zhao, J.J.Du, H.H.Wen, Z.X.Zhao; Superconductivity at 49 K in copper doping magnesium diboride, Preprint cond-mat/0103101 at http://xxx.lanl.gov (withdrawn by Authors), **(2001)**.

[26] S.M.Kazakov, M.Angst, J.Karpinski, I.M.Fita, R.Puzniak; Solid State Commun., **119**, 1 **(2001)**.

[27] I.Higashi, Y.Takahashi, T.Atoda; J.Less-Common Met., **37**, 199 **(1974)**.

[28] Periodic Table of the Elements, WILEY-VCH GmbH, 2nd edition **(1999)**.

[29] M.Cimberle, M.Novak, A.Palenzona; Supercond.Sci. Technol., **15**, 43 **(2002)**.

[30] R.J.Cava, H.W.Zandbergen, K.Inumaru; Physica, **C385**, 8 **(2003)**.

[31] R.F.Klie, J.C.Idrobo, N.D.Browning, K.A.Regan, N.S.Rogado, R.J.Cava; Nature, **410**, 343 **(2001)**.