

Effect of α -TeO₂ Substitution on Hg- System Properties

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Abstract

Specimens of $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ with $x = 0, 0.15, 0.3$ and 0.45 , were prepared by traditional method (SSR). The results showed enhancing structural and electrical (resistivity vs temperature) properties, where XRD analysis shows a tetragonal structure for all specimens and high ratio of Hg-1223 phase with an increase of the lattice parameter and T_c , except $x=0.45$, it shown semiconductor. The $\text{HgBa}_{1.70}\text{Te}_{0.30}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ specimen with $x=0.3$ shows the highest ($T_c=143\text{K}$) than with T_c of the basic compound $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ equal (135K), at increment of Te content. While mechanical properties have been weakened as consequence to increasing brittleness of $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compounds at increment Te content

Keywords: $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compound; brittleness; Ba-Te substitution.

الخلاصة

تم تحضير العينات $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ بالطريقة التقليدية (تفاعل الحالة الصلبة SSR). اظهرت النتائج تحسن الخواص التركيبية و الكهربائية (تغير المقاومة مع درجة الحرارة)، حيث اظهرت نتائج حيود الاشعة السينية ان التركيب السائد هو الرباعي لكل النسب ماعدا نسبة 0.45 فإنه يظهر تركيب شبه موصل. تبين العينة $\text{HgBa}_{1.70}\text{Te}_{0.30}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ لها اعلى انتقال ($T_c=143\text{K}$) مقارنة مع المركب الاساس $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ (135K) عند زيادة محتوى Te. بينما ضعفت الخصائص الميكانيكية لمركب $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ نتيجة ازدياد الهشاشة مع زيادة محتوى Te.

Introduction

In 1993, the family of the Hg-based (HTC) superconductor was discovered by Putilin et al [1-3]. It consists crystalline structures of the Hg-system layers are insulating block [BaO - HgO - BaO] with a thickness of 0.55 nm, and [(CuO₂) + Ca (n - 1)] conducting blocks [0.4 + 0.32 (n - 1)] nm [4-6], as shown in Figure (1)[7].

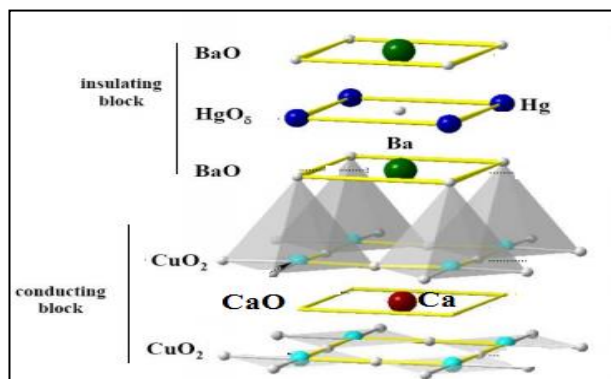


Figure 1: crystal structure of the Hg-[1212][7]

The HBCCO system, contain multi phases of the homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ where n (CuO₂ layers) = 1, 2, 3, 4, 5, which yields 94, 104 and 130 K superconducting phases, respectively. Figure 2 [8] shows, in depending on layers of CuO₂, the unit cell has single [Hg-2201], double [Hg-1212] and triple [Hg-1223] phases respectively [9, 10].

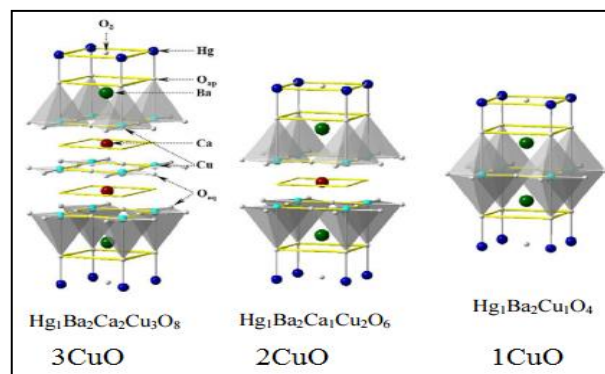
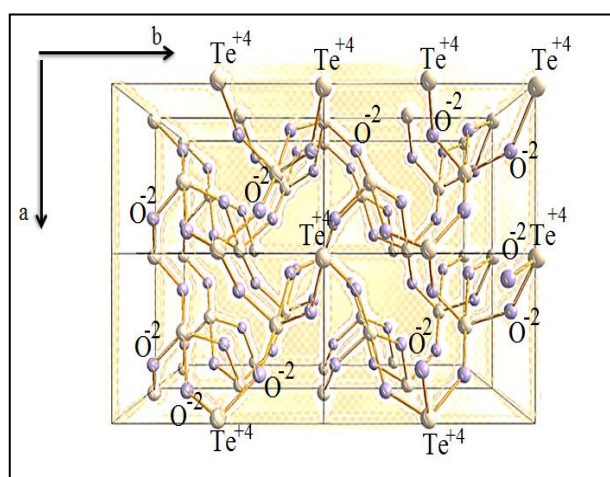


Figure 2: Crystal structure of the Hg [12(n-1)n]-system, at (n = 1, 2, 3)[8].

It has recently observed that pressure has an effect on the (T_c) of mercury system, where a transmission rate of (133.5 to 135.5) K in normal atmospheric pressure, rising to 153(K) at 23(GPa), and up to 164.5 (K) at high pressure [11]. To enhancement or destruction of the superconducting characteristics depends on the properties of the dopant or substitution of ions and radius of replaced in the structure [12]. In this paper, the effect of the partial substitution of Te with barium in the mercury system was studied on the structure and the electrical as well as its mechanical properties. Tellurium dioxide (α -TeO₂) was used. Table 1 shows the properties and Figure 3 shows its composition [13].

Table 1: Properties of α -TeO₂[12]

Tellurium dioxide	α -TeO ₂
Density	6.04 g/cm ³
System	(tetragonal)
Molar mass	159.60 g/mol
Melting point	732 °C
Appearance	White solid

Figure 3: Composition of α -TeO₂ [13]

Materials and Methodologies

Experimental

After preparing appropriate amounts of HgO, Te₂O₃, BaO, CaO and CuO powder. The weights were calculated depending on the atomic weights, and then weighed by a sensitive balance (4-deg). These materials are mixed by using the traditional solid state reaction method to produce the HgBa_{2-x}Te_xCa₂Cu₃O_{8+ δ} specimens when ($x=0.0, 0.15, 0.3$ and 0.45). The specimens were formed in the

pellet (15) mm in diameter and (5 mm) thick, under pressure of 7ton per cm², by using hydraulic press,. The pellets were sintered in air at 860 °C for 60 h.

The research includes three tests are:

- 1- X - Ray diffraction technique to determine crystalline structure. A program (Mach)[14] was adopted to calculate the lattice parameter and determine the crystalline structure.
- 2- Four-probe technique to determine the resistivity of the HgBa_{2-x}Te_xCa₂Cu₃O_{8+ δ} compound as a function of the temperature to determine T_c (transition temperature).
- 3- Vickers Hardness (Hv) test was adopted to calculate the mechanical properties and by applying equations, the (Young modulus: $E = 81.96$ Hv), (yield strength: $Y = Hv / 3$), (fracture toughness $K_{c-\alpha} = (E / Hv)^{1/2} \cdot (F / \sqrt{r^3})$), where F: load and r: length of the crack, (surface energy: $\gamma = (K_C)^2 / 2E$) and (brittleness: $B = Hv / K_C$)[17-20] were calculated.

Results and Discussion

The nature and characteristics of the structure were determined by x-ray diffraction, for the HgBa_{2-x}Te_xCa₂Cu₃O_{8+ δ} specimens when $x=(0.0, 0.15, \text{ and } 0.3)$. It was noted the disappearance of some peaks and the emergence of peaks higher, especially at (0.15 and 0.3) This shows the effect of temperature on the good development in building crystal structure, which in turn has reduced the stress generated at the grain boundary and that it also resulted in reducing the crystal defects and the granting of atoms sufficient energy to rearrange itself and growth new phases. Illustrated from diffraction pattern of the structure dominates is the tetragonal. Figures 4, 5 and 6 show the X-ray diffraction of HgBa_{2-x}Te_xCa₂Cu₃O_{8+ δ} specimens. Table 2 shows that parameter of all systems refer to structure is tetragonal, where a and the c parameter value equal to 15.0180 Å for (HgBa₂Cu₃O_{4+ δ}), it can be calculated by (Mach) program [14], 15.6486 Å for (HgBa_{1.85}Te_{0.15}Ca₂Cu₃O_{8+ δ}) and 15.7644 Å for (HgBa_{1.70}Te_{0.30}Ca₂Cu₃O_{8+ δ}) increases with the increasing x, this is give an indication of an increase in the interlayer distance. The

influence that is usually acquired from the Ba–Te substitution is the increasing of this distance, as a result of c-axis increasing, associated to the so-called chemical pressure. According to the instantaneous replacement of Ba by Te. According to the partial replacement of Ba by Te increases the distance between the blocking planes (Cu: Hg: Cu distance), creating an increase of the c-axis, but the distance between the neighboring Cu layers increases. One reason is a simultaneous substitution of Ba by Te, due to the variance in ionic radius both Ba (149pm) and Te (207pm), and notices that c/a ratio change with increasing Te concentration as compared with $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ specimen. From Table 2 and 3, the density changes with increase the value of x due to existence of porous in structures. The $\text{HgBa}_{1.70}\text{Te}_{0.30}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ specimen shows the highest ($T_c=143\text{K}$). While $\text{HgBa}_{1.55}\text{Te}_{0.45}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compound at $x=0.45$ become non superconductor, due to changes of the microstructure and carrier concentration by the partial replacement, Figure 7: show the resistivity as function of the temperatures.

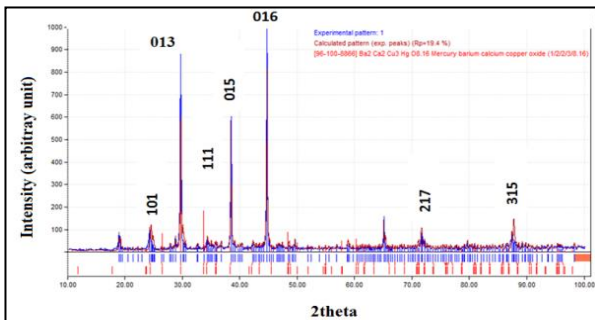


Figure 4: XRD of $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$

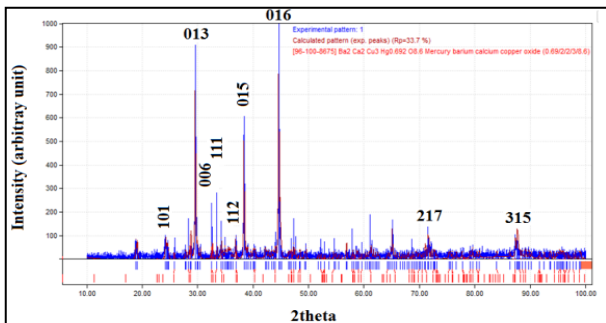


Figure 5: XRD of $\text{HgBa}_{1.85}\text{Te}_{0.15}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$

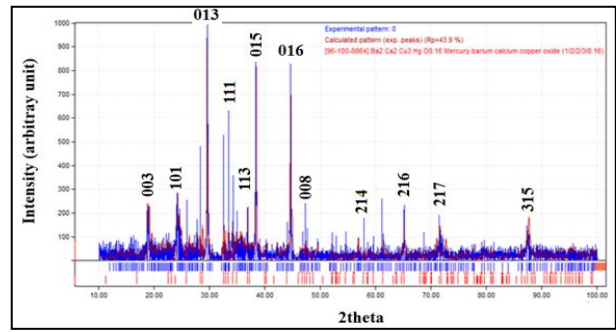


Figure 6: XRD of $\text{HgBa}_{1.70}\text{Te}_{0.30}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$

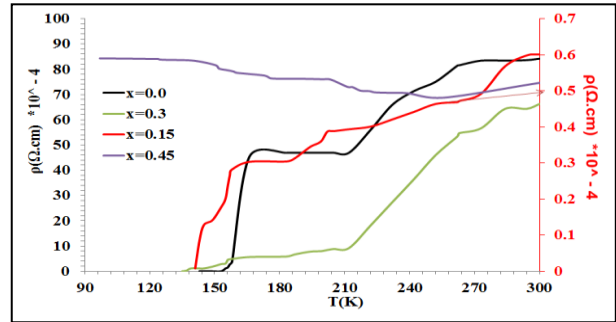


Fig. 7: The resistivity as function of the temperatures.

Table 2, Parameters of unit cell, ratio of c/a.

Specimens	a(Å)	c(Å)	c/a
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	3.608	15.0180	4.162417
$\text{HgBa}_{1.85}\text{Te}_{0.15}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	3.8652	15.6486	4.048587
$\text{HgBa}_{1.70}\text{Te}_{0.30}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	3.8516	15.7644	4.092948
$\text{HgBa}_{1.55}\text{Te}_{0.45}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	-	-	-

Table 3, volume and density of unit cell and $T_c(\text{k})$

Specimens	$V(\text{Å})^3$	d (gm/cm^3)	$T_c(\text{k})$
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	195.4993	6.85200	135
$\text{HgBa}_{1.85}\text{Te}_{0.15}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	233.7865	5.83600	141
$\text{HgBa}_{1.70}\text{Te}_{0.30}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	233.8621	6.22400	143
$\text{HgBa}_{1.55}\text{Te}_{0.45}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$	-	-	-

Hardness test results are used for several purposes: control the level of production and control during manufacturing and the study of heat treatment operations and sure them and know some of the mechanical properties such

as brittleness from without using destructive tests for the sample. The hardness measurements of $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ specimens such that $x=0.0, 0.15, 0.3$ and 0.45 . It was applied load on the samples during a time load of 15 seconds. Table 3 shows the variations of all the H_v (GPa) and volume of the unit cell (V) with Te constriction of the $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ specimens. As the radius ion of the Te (207pm) is larger than the radius of the barium ion Ba (149pm), the size of the unit cell of the $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compound will increase when increasing the concentration of tellurium ion (Te), causing increasing along bond linking ions inside the volume of the unit cell of the compound and weaken. Therefore, decreasing hardness (H_v) with increasing the size of the unit cell (V) is achieved when increasing the concentration of tellurium ions (Te) in the compound [19]. On the other hand, the increasing size of the (Permeable and Impermeable) open pores when increasing the concentration of tellurium ion (Te) in the $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compound will allow the pyramid to the Diamond to test the hardness by Vickers method penetration and an impact diameter greater length. Therefore, decreasing hardness (H_v) with increasing porosity is made when increasing the concentration of tellurium ion (Te) in the compound [19]. Table 4 illustrates the volume of unit cell, and H_v (Vickers Hardness).

Table 4: volume of unit cell, and H_v (Vickers Hardness).

x	$V(\text{\AA})^3$	H_v (GPa)
0	195.4993	0.143
0.15	233.7865	0.128
0.3	233.8621	0.0637
0.45	-	0.0630

Table 5 shows the effect of the partial replacement of tellurium ion (Te) barium ion Ba on the mechanical properties of the $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ specimens, where leading to the increasing in length of the bond which linking ions inside the volume of the unit cell of the compound, lead to increase the size of the unit cell where it causes weaken links in the compound and therefore a decrease the flexible

behavior and yield strength of the compound and decreasing (E). The purpose of the study of the mechanical properties for any compound is to identify the fracture toughness and surface energy, these characteristics determine whether the compound is brittle or not.

Vickers hardness was measured for the compound $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ and onset of crack length, measured from the top the corner of Vickers indentation, where it was applied load equal to 1.98 N at a loading time of (15 Sec).

The (K_{ic}), Young's modulus (E) (γ) and (B) was calculated depending on the results of hardness measurement and the onset of the notch as shown in the table (3), the results were shown the hardness decreases at increasing the concentration of tellurium ion (Te) this mean decrease (Y), because the increase length of the crack when exposed to effect of external stress.

Increase the length of the crack (r) led to a decrease in decreasing the (K_{ic}), while increased brittleness of the $\text{HgBa}_{1.55}\text{Te}_{0.45}\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compound

In general, the hardness (H_v) decreases and the length of the crack increases, resulting in increased brittleness for all specimens than with the $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compound has larger (H_v) and a small crack length (r).

The decrease (E) means decrease elastic behavior and (Y) of the compound at $x=0.45$. Therefore decreasing the (K_{ic}) and increases (B) when the decrease (E) of the compound.

Conclusion

From the above results you can summarize our conclusion at that increasing the partial replacement of Te leads to increasing the size of the unit cell of the $\text{HgBa}_{2-x}\text{Te}_x\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ compound when ($x=0.0, 0.15, 0.3$ and 0.45), which improved the structure and the critical transition rate but at the same time caused a weakness in the mechanical properties, where we observed a decrease in fracture toughness and surface energy and increased brittleness due to decreased of Vickers hardness and increased the crack length (r) with the increased concentration of Te ions.

Table 5, crack length (r), (Hv), E(Young modulus), Y(yield strength), K_{Ic} (fracture toughness), γ (surface energy) and B(brittleness).

X	r (μm)	H_v (GPa)	E (GPa)	Y (GPa)	K_{Ic} ($\text{MPa}\cdot\text{m}^{1/2}$)	γ (mJ/m^2)	B (m^{-1})
0	32	0.143	11.73	0.0477	1.584	107.01	90.32
0.15	46	0.128	10.55	0.0429	0.919	40.05	140.00
0.3	61	0.0637	5.23	0.021263	0.602	34.65	105.96
0.3	78	0.0630	5.17	0.021027	0.416	16.76	151.51

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