- Sci. J. Fac. Sci. Menoufia Univ, VoL.VI (1992). 27 - 43

THE CATALYSED DECOMPOSITION OF H_2O_2 BY $Bi_{1.6}\ Pb_{0.4}\ Sr_2\ Ca_2\ Cu_3\ O_x$ SUPERCONDUCTORS

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ASBTRACT

Bi-based High T_c ceramics srperconducting samples of nominal composition $Bi_{1.6}\ pb_{0.4}\ Sr_2\ Cu_3\ O_x$ were prepared and checked by electrical behaviour, x-ray diffraction, and meissner effect. We studied the catalytic activity of the ceramics superconductor (Bi-based) by its reaction withe the $H_2\ O_2$ solution. Evidence of the catlysed decomposiiton of $H_2\ O_2$ by the Bi-based superconductor is presented. The initial rates of the superconductor - $H_2\ O_2$ solution first order reaction at different temperature was used to determine both the activation enthaply and the activation entropy. The results indicate that the Bi-based superconductors are more stable than Y-based one.

INTORDUCTION

The field of superconductivity has been revived by the discovery of superconducting peroviskites [1] with the K_2 NIF_3 structure, which lead, soon after, to the discovery of oxygen deficient triperoviskite structure 90K oxide superconductor Y_1 Ba_2 Cu_3 O_y [2].

The intensive studies of Bi-Sr Ca- Cu-O sytstem have shown the presence of three sperconducting phases (2201 2212, and 2223) [3-9]. The first one (2201) phase has a critical temperature at about 22K, while the second one (2212) phase show zero resistance at about 85K. The third phase (2223) cannot be obtanied in single phase, it alwayse intergrows with the 2212 phase, where a drastic resistance drop is evident at about 110K [10]. Many authors pointed out that by adding pb element to the Bi-Sr-Ca-Cu-O Oxide system, it is found that zero resistance superconductivity can be obtained at 10 7 K [10&11].

The successful applications of high-T_c superconducting materials is stipulated also by their stability in the environment. For Y-Ba-Cu-O oxide superconductors, it well known that it react with water producing non-superconduting phase [12]. Also this behaviour and results was obtained for Tl-based superconducting system [13]. This process leads to complete suppression of the superconductivity in the sample [14&15].

The Bi-based superconductors are expected to be much more

stable, although there are some results indicating that their reaction with water has been detected [16].

A suitable reaction for studying the catalytic activity of powders is the decompositon of $H_2 O_2$ [17], where some thermodynamic parameters which is useful for the applications are got.

SAMPLE PREPARATION

The samples have been prepared by standard technique. The powerders of $Bi_2 O_3$, pb_3O_4, Sr Co_3, and Cu O were mixed together by electrical agate mortar in the molar ratio of Bi: pb: Sr: Ca: Cu = 1,6: 0.4: 2: 2: 3; calcined for 24 hours at 800°C in air, reground for 5 hours by agate moratr, pressed into pellets, annealed for 100 hours at 865°C in air, and cooled to room temperature in closed oven by cooling rate equal 50° c/h. It is worth to mention here that all the results in this publication have been obtained on samples cut from the same pellet.

RESULTS AND DISCUSSION

1- Superconductor quality

The superconducting transition (T_c) was detected electrically by using the four point method with contact attached by silver paste. A direct current of 10 mA was applied for the electric measurements; see figure 1.

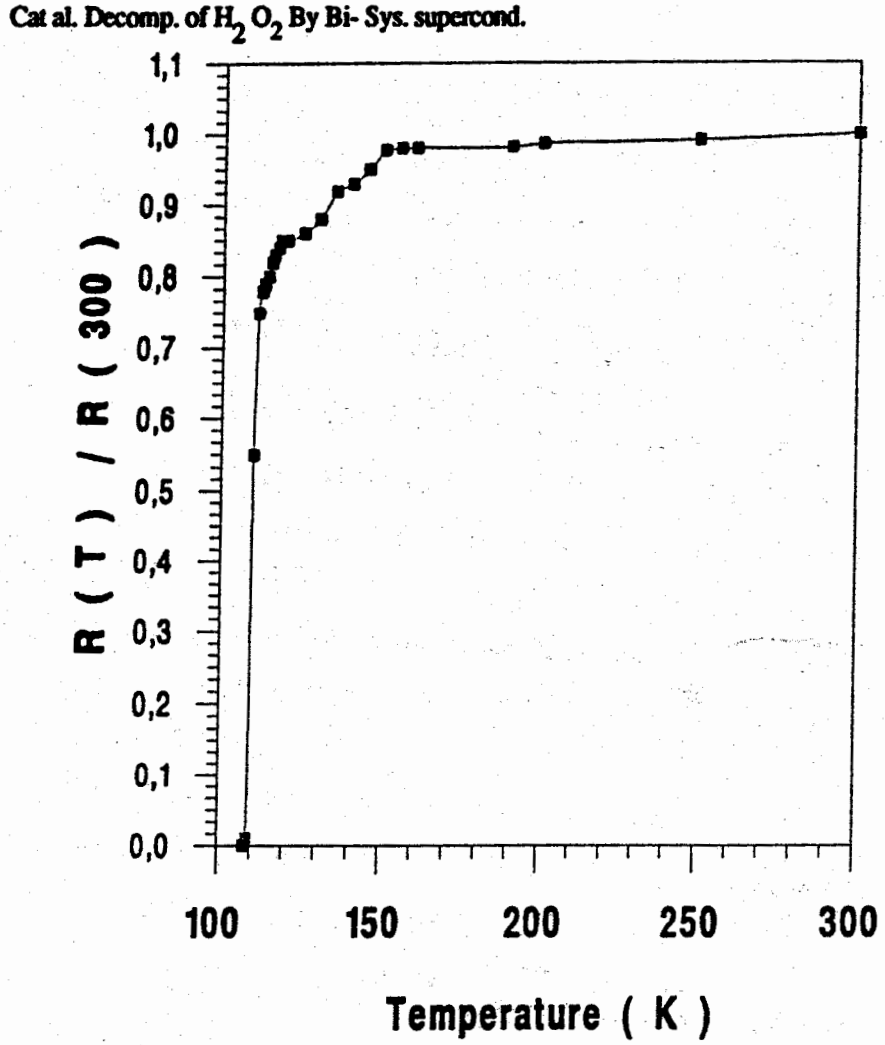

Fig. (1) : The temperature dependence of normalized resistivity of $Bi_{1.6}$ $Pb_{0.4}$ Sr_2 Ca_2 Cu_3 O_x superconductor.

The X-ray diffraction investigation has been carried out by powder diffractometer with filtered Cu K_a radiation; see figure 2.

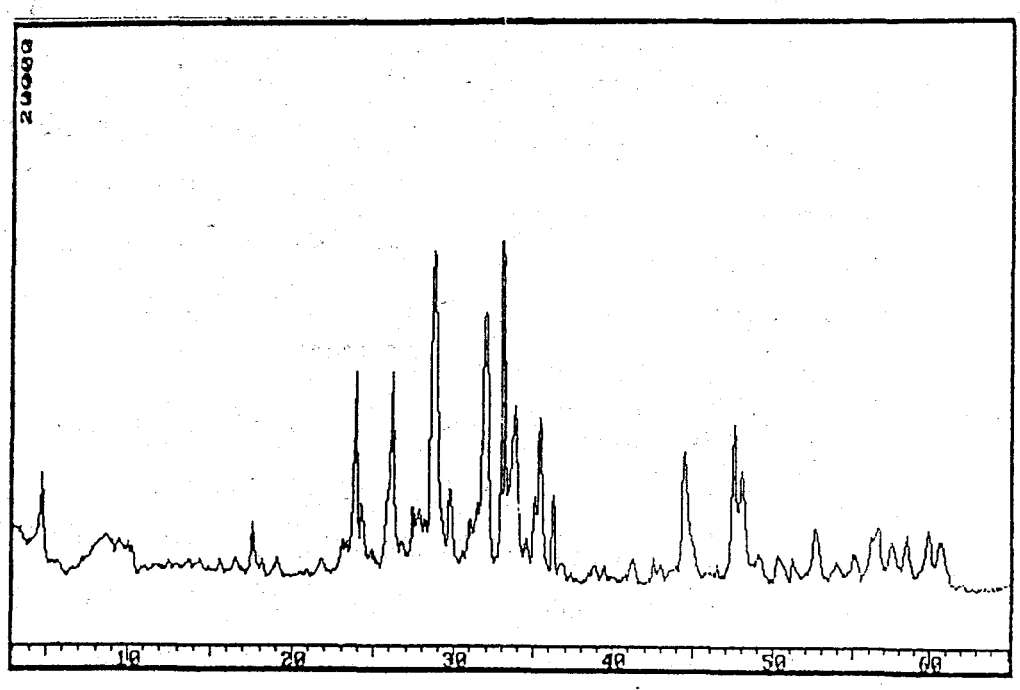

Fig. (2) : X-ray powder diffraction pattern of $Bi_{1.6}$ $Pb_{0.4}$ Sr_2 Ca_2 Cu_3 O_x superconductor with Cu K α.

The results of D.C conductivity, Meissner effect using samarium magnet, and X-ray diffraction indicate that the samples are single phase superconductor (223) and no impurities can be detected within the experinental errors [18 & 20].

2- Kinetics of the catalysed decomposition of H_2 O_2 by superconductor

Parts of powdered superconductors (150 mg) were equilibrat-

ed with 10 cm^3 of water in a flask and its temperature can be controlled by a heat mental. After adding 10 cm^3 of H_2O_2 solution of a given concentration, the oxygen volume in cm^3 was measured at different time intervals, keeping both the pressure equal to that of atmophere, and solid/solution ratio costant. The samples were also tested by different concentration of H_2O_2 solution over a range from 0.01 to 0.15 in a contstant temperature.

Figure no 3 rpresents the change of the volume of O_2 in cm^3 coming out from the reaction against time in minute. From this figure we can determined the variation of the initial rates of each reaction with its H_2O_2 concentration; see figure no.4. The order of the kinetics is determined from the slope of the line in figure no.4, which is about 1.269 indicating that the reaction is almost fist order reaction.

For a constant concentration of H_2O_2 equal 0.075 mol., the volume of O_2 in cm^3 is plotted against time in min. for six runs with different temperatures, see figure no 5. The initial rate constant of the decomposition (Kr) was determined from the figure no.5 and used to obtained figure no 6, where log (Kr h / kT) is plotted against 1 /T, where h,k, and T are being planck's constant, Boltzmann's constant, and absolute temperature, respectively.

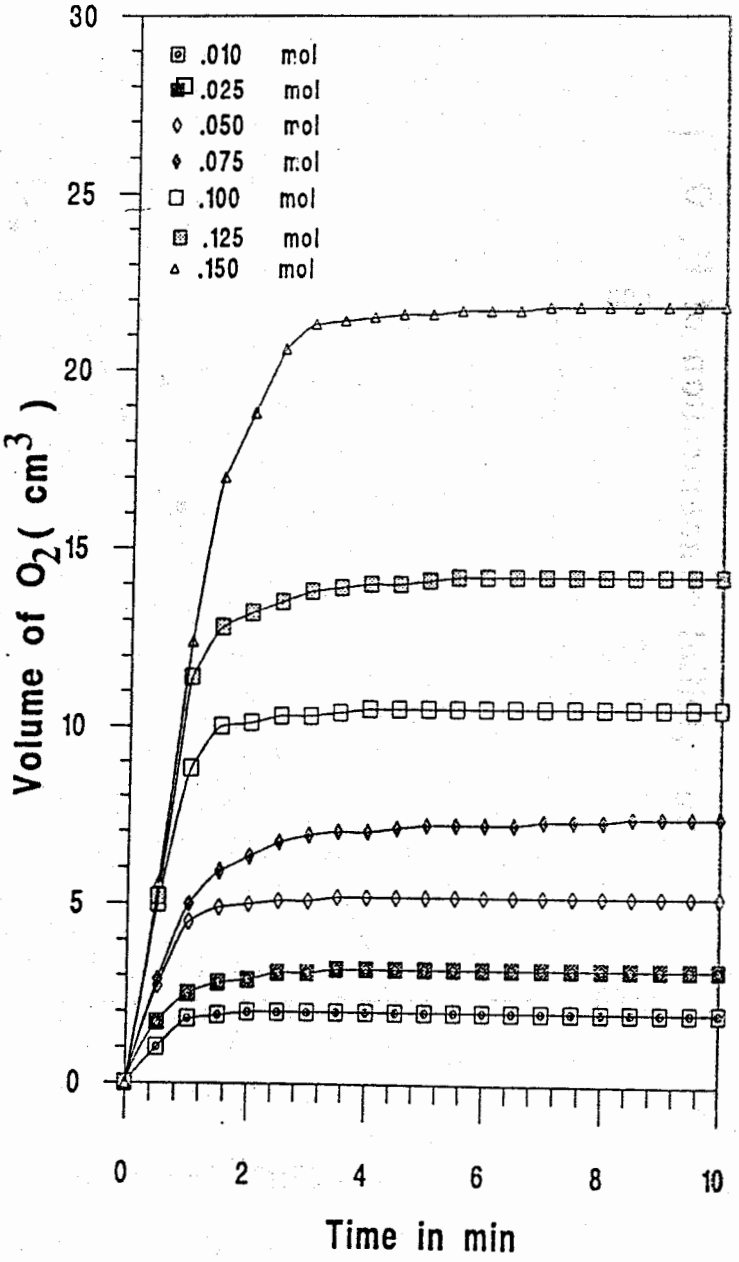

Fig. (3) The variation with time of the volume of O_2 collected at 25°C, at different initial H_2O_2 concentration for the Bi-based superconductor.

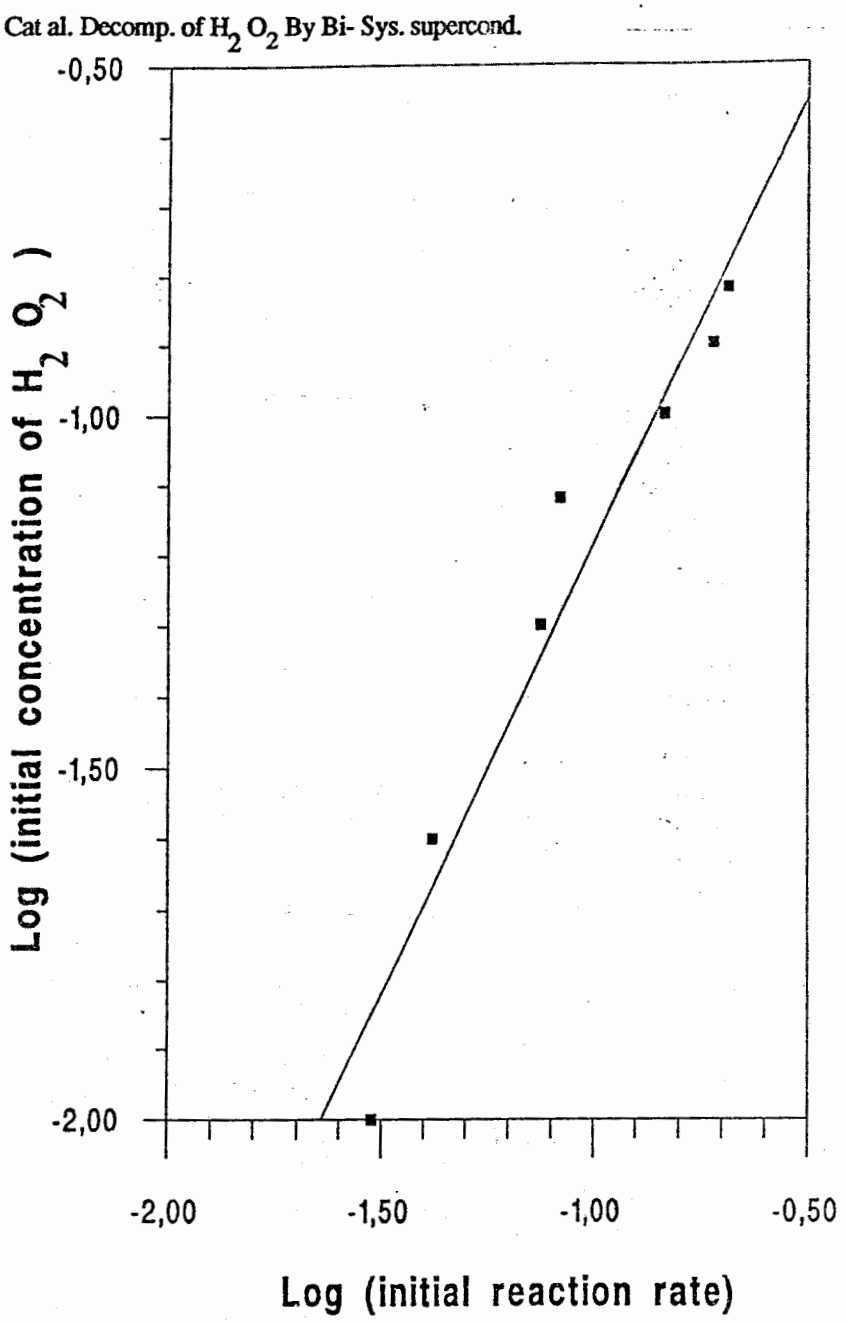

Fig. (4): Log (initial slope from the curves in figure no. 3) plotted against Log (initial H_2O_2 concentration) for Bi-bsded. supperconductor catalysed decompolition of H_2O_2.

Figure no.6 was used to determine the thermodynamic parameters (acivation enthalpy ΔH and activation entropy ΔS) by using Eyring equation [17] in the form:

$$\log\left(\frac{Krh}{kT}\right) = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT}$$

wher R is the gas constant.

From the slop and intercept of the line in figure no. 6, the activation enthalpy and activation ectropy were determined and found to be 24.27 K J mol^{-1} and 183.09 J K-1 mol^{-1} respectively. These values can be compared with that values calculated for Y_1 Ba_2 Cu_3 O_y system [17], indicating that the Bi-based ceramics superconductors react with H_2O_2 substantially slower than those of the Y_1 Ba_2 Cu_3 O_y system, i.e.more stable than Y-based ceramics superconducting system. This idea is supported by other work [21].

For testing the dependence of the activity on the particle size, three runs were carried with samples (unscreened, - 50 μm, and + 50 μm fractions) by keeping H_2O_2 concentration and temperature constant. Figure no.7 represent the results obtained, these results indicate that the total decompose materials are higher for the finer fraction, while the initial reaction rate are being constant. This results give us the conclusion that the sample can be suffer from the external environment rather than suface area [22].

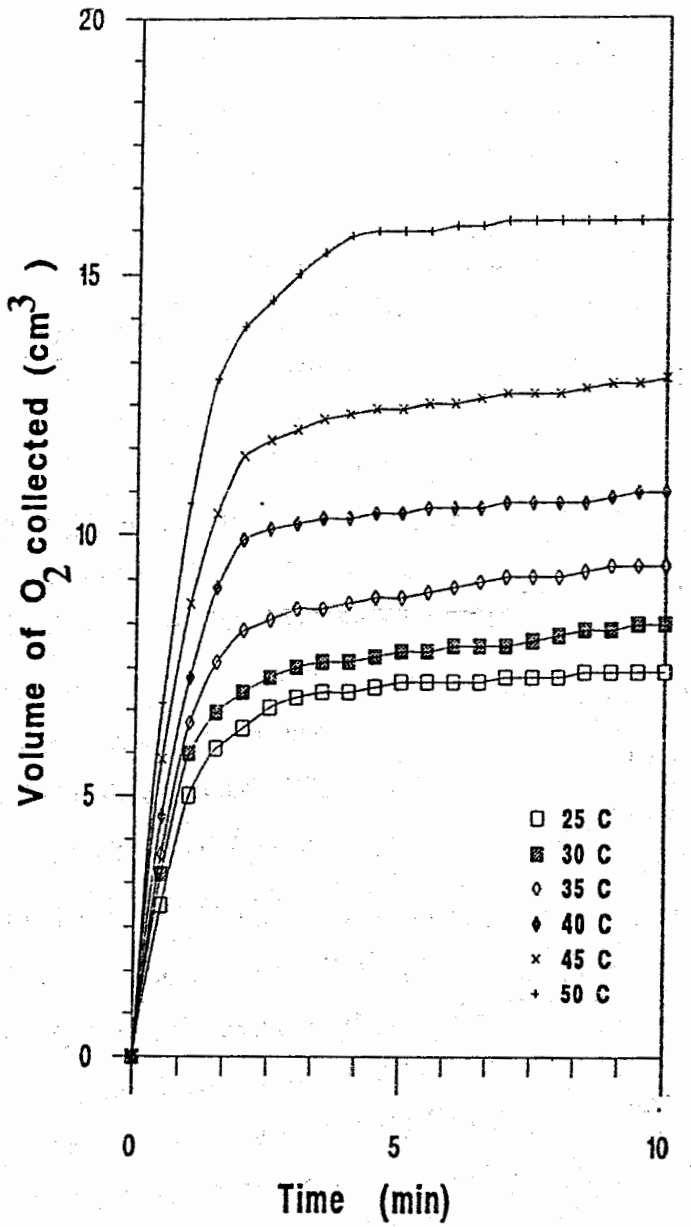

Fig. (5): The variation with time of the volume of O_2 collected using Bi-based superconductor as catalyst for different temperature. The initial H_2O_2. concentration = 0.075.

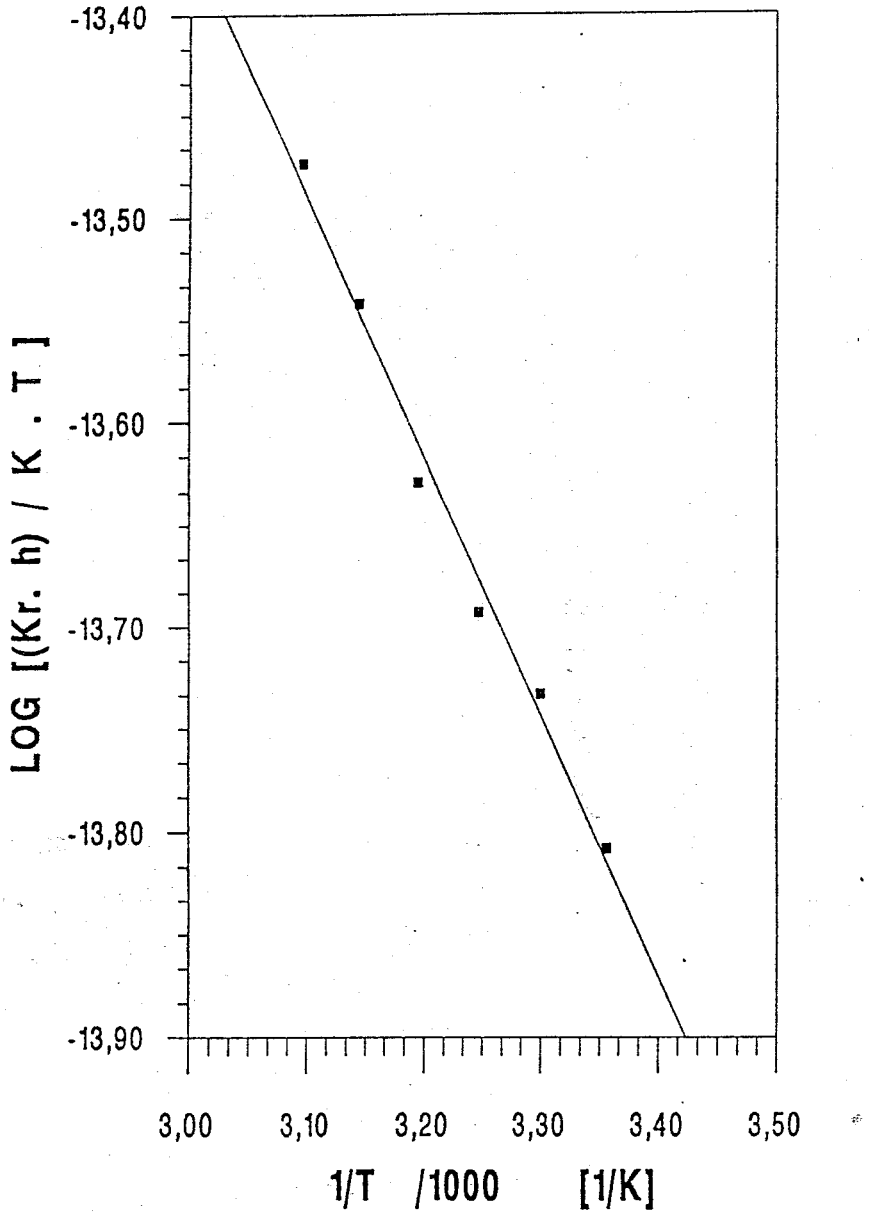

Fig. (6): The variation of Log $\frac{Krh}{kT}$ with $\frac{1}{T}$ for Bi-based superconductor. (Symbols are explained in the text.).

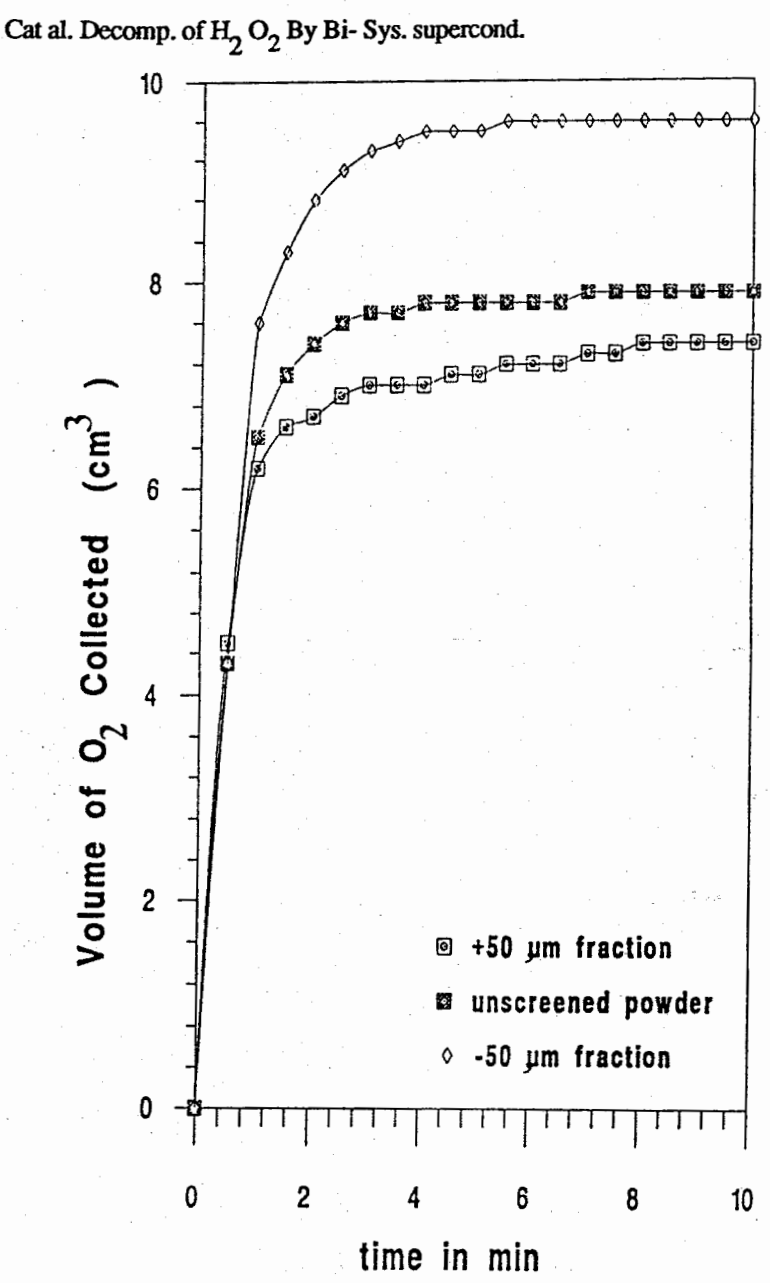

Fig. (7): The variation with time in minute of the volume of O_2 collected at 25°C using unscreened, -50µm fraction, and + 50 µm fractions powders; with 0.125 g of the powder in 10 cm^3 of H_2O_2 solution with initial concentrtion equal to 0.09.

From figure no.8: which represent the relation between the Tsm (the time in minute at which the value of oxygen was saturated) and the H_2O_2 concentraion; we can conclude that the Tsm can be limited to a certain time which means that by keeping the solid/ solution constant there is a maximum time at which almost a complete decomposition of the sample are achieved even at higher concentration of H_2O_2.

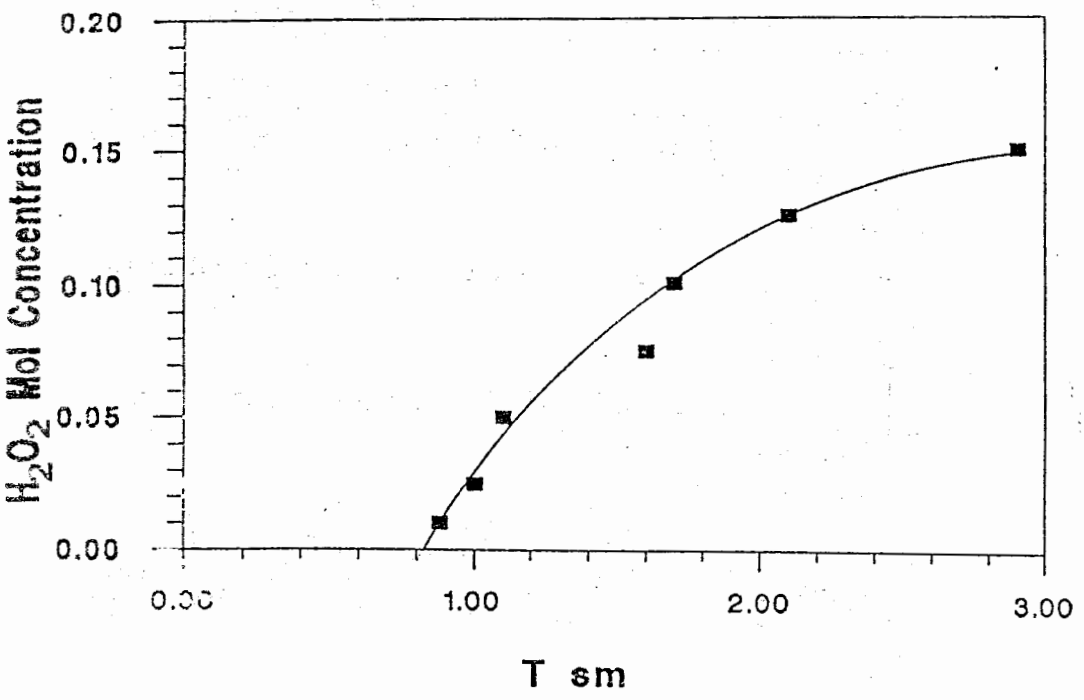

Fig. (8): The varivation of initial H_2O_2 concentraion with Tsm (symbole is explained in the text).

AKNOWLEDGEMENT

The author wish to thank Dr. I. Halasz; central research institute for chemistry, hungarian academy of science, Hugary, for his helpful discussions. Also I whish to thank Prof. Dr. F. El-Halafawy; dean of the faculty of electronic engineering, menofia university; for his encouragement.

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الانحلال الحفزي ل يدم أم بواسطة موصل فائق

بز ١.٦ د ٤.. ستم كام نحم أس

أحمد الحملاوى

معمل المواد الفائقة التوصيل

كلية الهندسة الالكترونية – جامعة المنوفية

تم تحضير موصل فائق خزفى من عائلة البيزمث نو تركيب كيميائى بز١.٦ د٤.. ستم كام نحم أس وتم اختباره كهربياً وكذلك أختبر بواسطة ظاهرة ميسنر والحيود السينى.

تم دراسة النشاط الحفزى لهذا المركب بواسطة تفاعله مع ماء الأوكسجين (يدم أم) وتم التأكد من الانحلال الحفزى لماء الاكسجين بواسطة موصل فائق من عائلة البيزمث. من النتائج تم التوصل الى ان مثل هذا التفاعل هو تفاعل من المرتبة الأولى – وكذلك تم تعيين بعض البارامترات الخاصة بالديناميكا الحرارية وعليه فقد تم التوصل الى ان الموصلات الفائقة التوصيل المنتمية الى عائلة البيزمث أكثر ثباتا من تلك المنتمية الى عائلة الإيتريوم.