

Figure 3. SEM photographs of electrodeposited Ru surfaces on (a) TiO and (b) Ebonex (Ti₄O₇).

tematic study on electrochemical behavior of noble metals and their oxides thin films on the conductive ceramics TiO and Ti₄O₇ is currently under investigation on their characteristics as electrode substrates.

In conclusion, conductive ceramics, TiO and Ti₄O₇ are chemically and mechanically stable and the overpotentials for oxygen evolution on the TiO and Ti₄O₇ electrodes are very large. Both Ru and RuO₂, well known electrochemical catalysts for oxygen evolution, can be deposited electrochemically and thermally, respectively, well onto TiO or Ti₄O₇. Thin layers of Ru and RuO₂ on either TiO or Ti₄O₇ show electrochemical properties of Ru and RuO₂, and the overpotentials for O₂ evolution have decreased dramatically.

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Precursor Approach to Synthesis of New Ca-deficient Bi-2212 Superconductor

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Since the discovery of superconductivity in the Bi-based cuprate oxides,^{1,2} numerous efforts have been made to synthesize single-phasic materials. Isolation of the materials from nominal compositions was often hampered owing to the multiphasic nature of the homologous series Bi₂Sr₂Ca_{n-1}Cu_nO_{2n+4} (*n* = 1, 2, 3; hereafter denoted as Bi-22(*n* - 1)*n*). The Bi-2212 compound was generally obtained from a Ca-rich composition Bi₂Sr_{1.5}Ca_{1.5}Cu₂O₈ since the synthesis of the compound from the stoichiometric composition easily yielded ternary oxides rather than the final Bi-2212 product.^{3,4} An excess amount of Ca in the starting composition is known to facilitate the formation of the Bi-2212 phase. The isolation of the Bi-2223 phase is even more complicated. The only successful way to synthesize the Bi-2223 phase is to add

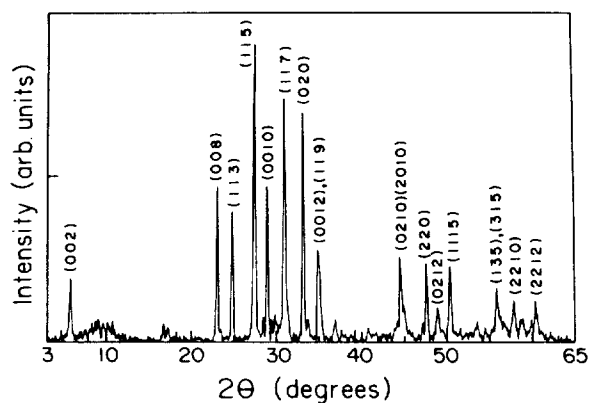


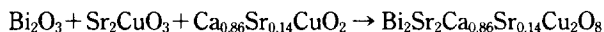
Figure 1. X-ray powder diffraction patterns of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_2\text{O}_8$.

excess Pb in the starting composition and react under a low oxygen pressure.⁵⁻⁷ In this communication, we report the isolation of new Ca-deficient Bi-2212 phase using a precursor method. For the successful synthesis of Bi-2212, we utilized an infinite-layer like $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$ as a starting material. The infinite layer compound is considered as a parent structure of high- T_c cuprate superconductors⁸ and has also been proved to be a powerful reagent to synthesizing other metastable superconductors.^{9,10}

Polycrystalline samples of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_2\text{O}_8$ were obtained by solid state reaction of Bi_2O_3 (Kojundo Chemical Co., 99.99%), Sr_2CuO_3 , and $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$. Stoichiometric mixtures of the starting materials were compacted into pellets which were then sintered at $840\text{ }^\circ\text{C} \sim 860\text{ }^\circ\text{C}$ for 20 h in low oxygen pressure (10% of O_2 in an argon base). The two precursor compounds, Sr_2CuO_3 and $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$, were prepared by reacting appropriate mixtures of individual metal oxides and carbonates as illustrated in the references.^{8,11} The purity of the precursor materials was checked by XRD prior to use.

In order to make a pseudo stoichiometric Bi-2212 compound, we used $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$ and Sr_2CuO_3 as precursor materials and Bi_2O_3 . The precursor Sr_2CuO_3 is selected to satisfy the required composition of the Bi-2212 product and also has an orthorhombic structure which is structurally related with the final Bi-2212 phase. Therefore, the use of an infinite-layer like $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$ and an orthorhombic Sr_2CuO_3 , as starting materials is expected to ease the formation of the product.

As we anticipated from the structural matching between reactants and the final product, the reaction of $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$, Sr_2CuO_3 , and Bi_2O_3 easily produced pure $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_2\text{O}_8$ even at $840\text{ }^\circ\text{C}$ for 20 h. For the preparation of the Ca-rich Bi-2212, however, reaction normally takes place for about 2 days at $865\text{ }^\circ\text{C} \sim 875\text{ }^\circ\text{C}$.^{3,12} A typical reaction can be represented as below:



In comparison with the method using the Ca-rich composition, the reaction temperature and time required for the formation of Bi-2212 phase by this precursor method is lowered and shortened, respectively.

Figure 1 displays the X-ray powder diffraction patterns

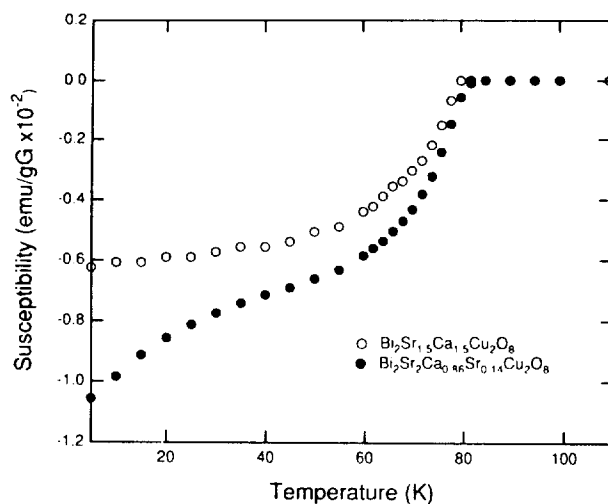


Figure 2. Zero-field-cooled magnetic susceptibilities of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_2\text{O}_8$ (closed circle) and $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Cu}_2\text{O}_8$ (open circle).

of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_2\text{O}_8$. All the diffraction lines can be well indexed on an orthorhombic cell ($Fm\bar{m}m$). The calculated unit cell parameters of a , b , and c are $5.3949(5)\text{ \AA}$, $5.3970(5)\text{ \AA}$, and $30.8816(1)\text{ \AA}$, respectively. The values of the lattice parameters are essentially identical with those of the Ca-rich Bi-2212 compound.⁴ The above results clearly demonstrate that monophasic Bi-2212 can be synthesized from pseudo-stoichiometric compositions using the precursor method. The major factor facilitating growth of the 2212 phase in this method could be the structural matching between the starting precursors and the product. The use of ternary oxides $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{CuO}_2$ and Sr_2CuO_3 for the synthesis would be also beneficial because it will prevent the formation of undesirable by-products such as Bi_2CuO_4 and Ca_2CuO_3 . Figure 2 shows zero-field-cooled magnetic susceptibility versus temperature plots for $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Cu}_2\text{O}_8$, which were measured at 20 G using a SQUID magnetometer. The onset superconducting transition temperatures (T_c) of both samples are close to 80 K, indicating that the T_c is virtually independent of the Ca : Sr ratio. This is consistent with the previous results obtained for the high T_c oxides in which the substitution of the isovalent elements in the noncopper sites does not significantly affect the superconducting properties.¹³ However, the superconducting volume fraction of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_2\text{O}_8$ is slightly increased compared with that of Ca-rich Bi-2212 compound.

In summary, using the precursor method we have successfully prepared a new Ca deficient Bi-2212 compound, $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_2\text{O}_8$, which is almost of the stoichiometric composition. The T_c values are found to be insensitive to the Ca content in Bi-2212. The ternary oxide precursors turned out to be powerful reagents for the synthesis of the Bi-based cuprate oxides.

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DMSO-based Reagents for the Oxidation of Alkenes and Alkynes to 1,2-Diketones

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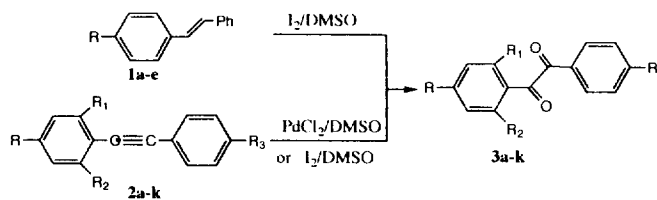
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There has been a deficit of convenient and selective reagents for the oxidation of carbon-carbon double and/or triple bonds to 1,2-dicarbonyl compounds.¹ We have recently reported that a triple bond of 1,2-diarylethyne can be successfully oxidized to 1,2-diketone with iodine or palladium(II) chloride in DMSO.²⁻⁴

In this paper, we would like to report not only the relative

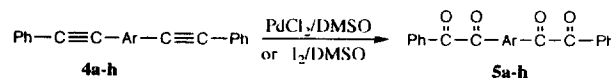
reactivity and selectivity of these DMSO-based reagents in the process of oxidation of 1,2-diarylethenes and/or 1,2-diarylethyne but also a new method using Pd/C with copper(II) halide in DMSO for the oxidation of 1,2-diarylethyne.



| 1-3 | R | R ₁ | R ₂ | R ₃ | 1-3 | R | R ₁ | R ₂ | R ₃ |
|-----|------------------|----------------|----------------|----------------|-----|------------------|-----------------|-----------------|------------------|
| a | H | H | H | H | g | NO ₂ | H | H | H |
| b | CH ₃ | H | H | H | h | CH ₃ | CH ₃ | CH ₃ | H |
| c | OH | H | H | H | i | CH ₃ | H | H | CH ₃ |
| d | OCH ₃ | H | H | H | j | OCH ₃ | H | H | OCH ₃ |
| e | Cl | H | H | H | k | Cl | H | H | Cl |
| f | CHO | H | H | H | | | | | |

Various 1,2-diaryl-1,2-ethanediones **3a-k** have been synthesized in good yields by heating corresponding diarylethenes **1a-e** or diarylethyne **2a-k** in DMSO with equimolar quantities of iodine (reagent A). (Table 1) With reagent A, the oxidation of tolans **2** turns out to proceed in two times, at least, faster than that of the corresponding stilbenes **1** and the oxidation rate has a tendency to decrease in the presence of electron-withdrawing substituent in the reactants **1** and **2**. It is also interesting to note that methoxy-substituted stilbene **1d** and tolans **2d, j** can be effectively oxidized with reagent A without iodination. However, heating hydroxy-stilbene **1c** or tolan **2c** with reagent A led to the formation of several unidentified iodine containing compounds.

In contrast with iodine, palladium(II) chloride in DMSO (reagent B) does not oxidize stilbenes **1** but shows high reactivity for the oxidation of tolans **2**. (Table 1) Besides its chemoselectivity, reagent B can oxidize **2c** to **3c** without producing any by-product. On the other hand, reagent B has been found to be more sensitive to the steric factor of substrates. For example, application of reagent B for the sterically hindered tolan **2h** produced benzil **3h** in 5% yield with a low conversion of **2h**. However, **2h** could be oxidized to **3h** in 33% yield with reagent A. It is noteworthy that smooth oxidation of triple bond in the labile tolan **2f** is effected by both reagents.



| 4, 5 | Ar | 4, 5 | Ar |
|------|----|------|----|
| a | | c | |
| b | | f | |
| c | | g | |
| d | | h | |