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Volatile barium β-diketonates for use as MOCVD precursors

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CONTENTS

ABSTRACT

Metal-organic chemical vapor deposition (MOCVD) techniques have been used to deposit thin superconducting films of $YBa_2Cu_3O_{7-x}$. A limitation of the technique lies in the volatility of the barium(II) precursors. A review of attempts to enhance volatility through substitution of fluorinated chelating agents and studies to limit oligomerization of the barium chelates are reviewed. Within the past five years, substantial progress has been made in synthesizing more volatile barium complexes, and the most volatile barium compound yet reported is a monomeric chelate in which five hexafluoroacetylacetonato ligands are bonded to barium(II).

1. INTRODUCTION

In 1986, Bednorz and Muller first discovered a new type of superconducting cuprate oxide that had a critical temperature, T_c, of 30 K [1]. Soon after, Wu et al. discovered that a material with stoichiometry $YBa_2Cu_3O_{7-x}$ ($x = 0.1–1.0$) was superconducting at 93 K when x is small, but non-superconducting when x is large [2]. This discovery was particularly significant because the onset of superconductivity for this material occurs above liquid-N_2 temperatures. Since this discovery, there has been a great amount of research in this area and several related compounds

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* Dedicated to the memory of Professor John C. Bailar, Jr.

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have been found to exhibit superconductivity at relatively high temperatures. The most well-known of these materials is the superconductor $YBa_2Cu_3O_{7-x}$, but other materials based on copper oxides containing elements such as bismuth [3] and thallium [4] are also superconducting at relatively high temperatures. In the near future, the most promising applications of these materials will most likely be in the electronics industry, where thin films of the high-temperature superconductors can be used in magnetic and microwave sensors and in circuitry junctions [5]. It has also been found that, while the bulk cuprate materials are limited in the amount of current they can carry in the presence of a magnetic field, this has not been as much of a problem with the highly oriented thin films of the high-temperature superconductors.

Because of the practical electronic applications, developing methods to produce high-quality thin films of these materials has been an important priority. The quality of the thin-film superconductors depends on achieving the correct stoichiometry, producing highly oriented films, and avoiding substrate/film interactions. With most methods described, a thin film of the metals or metal oxides in the correct stoichiometry is deposited, followed by an annealing process which inserts additional oxygen and converts the material into a superconductor.

One important method for producing thin films of high-temperature superconductors is metal-organic chemical vapor deposition (MOCVD), and the best precursors are metal coordination compounds. MOCVD techniques have long been used in the semiconductor industry to produce epitaxial thin films [6]. With MOCVD, each volatile metal precursor is thermostatted individually, in accordance with its vapor pressure, to produce the correct ratio of metal species in the gas phase. The precursors can then be transported to a heated substrate where they decompose to form thin films of the metal or metal oxides in the correct stoichiometry. One major advantage of MOCVD is that films can be deposited at high rates while still controlling growth to give highly oriented epitaxial layers, which is important in achieving high J_c values. Also, substrates of any varied sizes and dimensions may be used with this method. In addition, the equipment needed for MOCVD is relatively inexpensive as compared with other techniques, and a wide variety of deposition environments, such as oxidizing or hydrolyzing conditions, can be utilized.

Certain β-diketonate metal complexes are suitable precursors for MOCVD because of their high volatility and thermal stability. The use of some of these compounds for thin-film metal deposition was reported 28 years ago by Sievers and co-workers [7] and subsequent advances have been documented [8,9]. Earlier work done in order to perform gas chromatographic analysis on metal derivatives has demonstrated that, not only are there volatile β-diketonato complexes of transition metals [10,11], but also of the alkaline earths [12], and of the rare earth metals [13–15].

In an early report on MOCVD to form superconducting metal oxides, Berry et al. described preparation of thin films of superconductors using MOCVD of β-

diketonate complexes onto a MgO substrate in an oxygen-rich atmosphere, although these films were not of extremely high quality, having a T_c of 20 K [16]. Others have produced higher-quality superconducting films with the 2,2,6,6-tetramethyl-3,5-heptanedionato (thd) compounds of Y, Ba and Cu [17–23]. For example, Watanabe et al. [18] have prepared thin-film superconductors with a critical current density of 190 000 A cm^{-2} at 10 Tesla and an onset of superconductivity at 89 K using this technique. A recent report from workers at Mitsubishi indicated that critical current densities in the absence of a magnetic field of films prepared by MOCVD from β-diketonates were approximately 1 400 000 A cm^{-2} [23]. Other workers have used different β-diketonato complexes, including the more volatile fluorine-containing complexes to make thin films of $YBa_2Cu_3O_{7-x}$ [24,25].

One difficulty in making superconducting films by MOCVD with β-diketonate precursors is that the barium(II) chelates are less volatile and thermally stable than the copper(II) and lanthanide(III) precursors. This has led to renewed interest in studying the stabilities, compositions, and thermal properties of alkaline earth β-diketonates [26,27]. Purdy et al. [27] have recently published a study on the synthesis, characterization, and thin-film deposition of a series of fluorinated alkaline earth chelates. Although many alkaline earth β-diketonate chelates were synthesized a decade or two ago [10,12,28,29], these compounds need further characterization with respect to their structures, volatilities and thermal stabilities, particularly in the light of their great importance in MOCVD of ordered superconducting films.

2. CHARACTERIZATION OF MOCVD PRECURSORS

While the thermal properties of many of the β-ketoenolate chelates have been studied individually [11–15,28,30], it is useful to compare the thermograms of the precursors being used to make thin films of the $YBa_2Cu_3O_7$ superconducting material because comparisons of relative volatilities and thermal stabilities are facilitated when the same apparatus and operating conditions are used. From the thermograms shown in Fig. 1, it is clear that the barium complexes of each ligand are much less volatile than the corresponding yttrium or copper compounds. It is also evident that the complexes made from 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (H(fod)) are more volatile than those made from H(thd).

Early mass spectral analysis indicated that the less volatile alkaline earth chelates may exist as oligomers. Specifically, ions corresponding to $M_2L_3^+$, $M_3L_5^+$, $M_4L_7^+$, etc. were observed in the electron ionization spectra of the alkaline earth complexes of thd by Schwarberg et al. in 1970 [12]. Similar ions are observed in the spectra for the Ca, Sr and Ba chelates of fluorinated β-diketonates [27,28]. We recently described negative chemical ionization mass spectra of these chelates, which show the molecular ions characteristic of oligomers [31]. In the case of the oligomeric thd complex of Ba(II), the major peaks in the negative chemical ionization spectrum are ions at m/z 1513 and 1008, which correspond to what may be either molecular

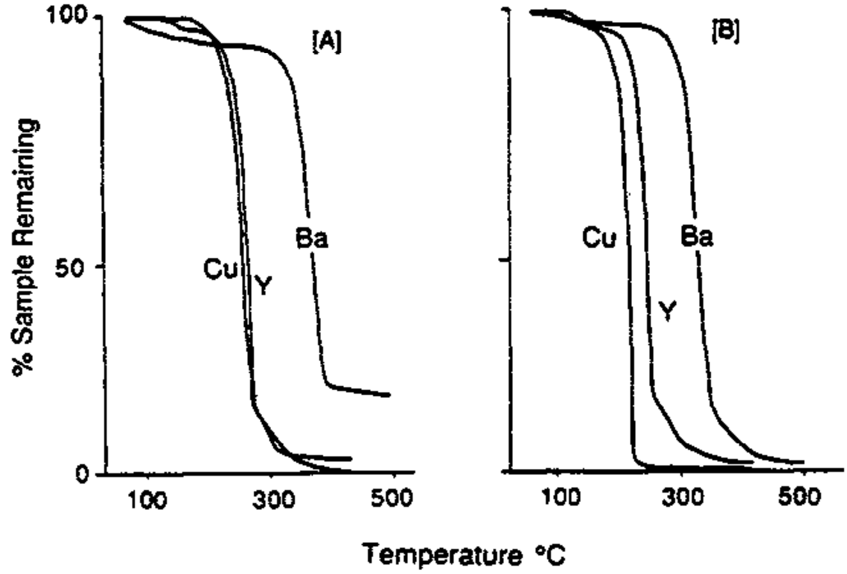

Fig. 1. Thermogravimetric analysis curves for copper(II), yttrium(III), and barium(II) complexes of thd (A) and fod (B).

ions of the dimer and trimer, respectively, or fragment ions of a higher oligomer. The experimentally observed isotope pattern for what may be trimeric $[Ba(thd)_2]_n$ has been compared with the calculated pattern using the natural abundances of barium, carbon, and oxygen, and good agreement was found. The spectra of the fod complexes of Ba(II) and Ca(II) are similar, but more complicated due to fluorine transfer that occurs upon the loss of CF_3 fragments.

X-ray studies also show that the alkaline earth chelates of β-diketonates exist as oligomers. The X-ray structure analysis of strontium and calcium complexes of the anion of 1,3-diphenyl-1,3-propanedione, solvated with ethanol or acetone, were shown to be tetrameric [32,33]. The Ba(II) chelate of the anion of thd recrystallized from pentane was determined to be a β-diketonate-deficient pentanuclear complex, with five barium ions clustered in a square-pyramidal geometry, of the formula $Ba_5(thd)_9(H_2O)_3(OH)$. Both β-diketonate and water ligands act as bridges between barium ions in this structure, resulting in a thermally unstable compound [31,34].

3. INCREASING VOLATILITY OF BARIUM β-DIKETONATES BY LIMITING OLIGOMERIZATION

One approach to limit the oligomerization in these complexes, and thereby to increase their volatility, is to coordinate the metal ions with neutral ligands. For example, it has been found that the addition of uncomplexed (protonated) β-ketoenolate ligand to the carrier gas stream greatly improves the gas chromatographic behavior of these alkaline earth chelates, probably owing to adduct formation accompanying the dissociation of the oligomers. In fact, the addition of excess protonated ligand to the barium source in MOCVD produces higher-quality superconducting thin films than are obtained without the additional β-diketone [22]. Barron has reported an even more dramatic improvement of Ba chelate volatility and thermal stability by using nitrogen-containing Lewis bases as the neutral species in the carrier gas of a chemical vapor deposition apparatus [35]. In this case, apparently no stable complex with the nitrogen donor is observed; a transient species in the gas phase acts to enhance the thermal properties of the barium chelates.

The crystal structures of monomeric barium β-diketonate complexes containing neutral ligands have been reported. The monomeric tetraglyme adducts of $Ba(hfa)_2$, $Ba(tfa)_2$ and $Ba(thd)_2$ have been synthesized, in which the coordination of the barium ion is nine, with a monocapped, twisted square prism structure [36,37]. A report of the structure of a Ba(II) complex of thd recrystallized from methanol shows that solvent molecules can act as neutral ligands, eliminating β-diketonate ligands bridging between metal ions, to give what appears to be a mononuclear complex with the formula $Ba(thd)_2 \cdot [CH_3OH]_3$ in which the barium ion is coordinated by seven oxygens [38]. In another example of this approach, Rees et al. have reported a new dimeric complex prepared by reacting ammonia with the thd chelate of Ba(II) to give a compound with the structure $[Ba(thd)_2 \cdot 2NH_3]_2$ [39]. In this case, each barium ion is coordinated by one bidentate ligand, and two thd ligands bridge the two metal ions. Two neutral ammonia moieties are also bonded to each metal ion to give a coordination number of eight for each barium ion.

Formation of ion pairs of an anionic chelate is another approach to making

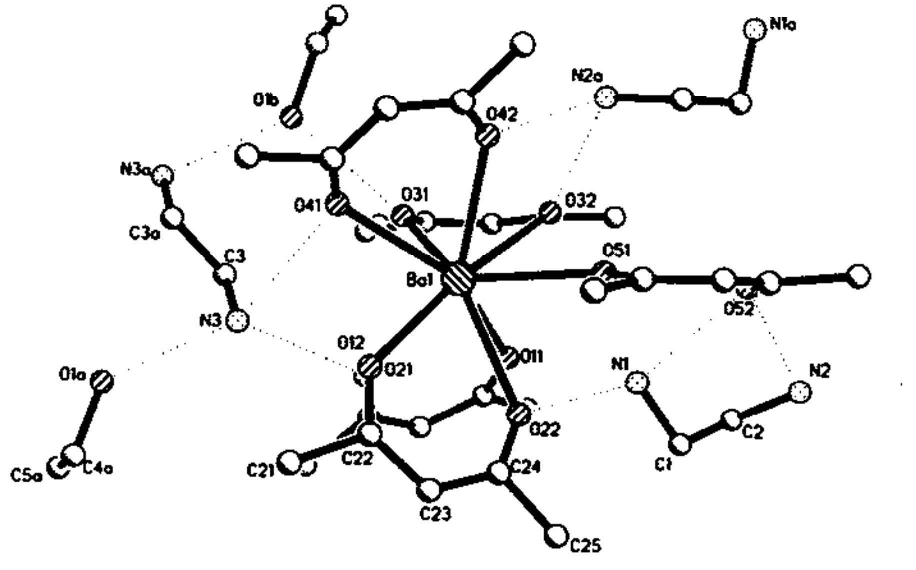

Fig. 2. Structure of $(enH_2)_{1.5}[Ba(hfa)_5] \cdot C_2H_5OH$ [34].

metal ions more highly coordinated so that formation of oligomers is prevented. Using this approach, we have synthesized and characterized a new highly volatile, monomeric, barium chelate, $(enH_2)_{1.5}[Ba(hfa)_5]$, in which enH_2 is protonated ethylenediamine (Fig. 2) [34]. The barium ion is coordinated by nine oxygen atoms of the β-diketonates, while the protonated en molecules in the lattice are weakly hydrogen bonded to the chelate anions. This is one of the first monomeric β-diketonate barium chelates known which is produced by forming an anionic chelate. The vaporization of $[Ba(hfa)_2]_n$ occurs at about 340°C with 15–19% sample remaining, while the vaporization of $(enH_2)_{1.5}[Ba(hfa)_5]\cdot C_2H_5OH$ occurs at a lower temperature (centering at about 280°C) and yields less residue (1–4%). It is evident that, for the same ligand, the monomeric chelate $(enH_2)_{1.5}[Ba(hfa)_5]\cdot C_2H_5OH$ is more volatile than the oligomeric $[Ba(hfa)_2]_n$. This appears, for the present at least, to be the most volatile compound of barium known.

In spite of the remarkable progress that has been made in developing and using volatile metal chelates in the last half of the 20th century, the search for increasingly more suitable volatile chelate precursors of superconductors will doubtless continue into the next century. My group's work on volatile chelates and on a wide range of other subjects was inspired and encouraged by my Ph.D. mentor in the 1950s, Professor John Christian Bailar, Jr. Countless scientists owe him a great debt of gratitude, and he has left a legacy of which we can all be proud.

NOTE ADDED IN PROOF

Two papers on barium β-diketonates have been published since this paper was originally submitted [41,42].

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