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THERMAL PROPERTIES OF BARIUM COMPLEXES USED FOR DEPOSITING THIN FILMS OF $YBa_2Cu_3O_7$ SUPERCONDUCTORS

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Abstract

The thermal properties of several barium containing complexes are compared by using thermogravimetric analysis and solids probe mass spectrometry. The properties of complexes containing flourinated and non-fluorinated β-diketonates with and without the presence of a polyether to occupy additional barium coordination sites are compared. Barium complex thermal properties are heavily dependent on the structure of the β-diketones and polyether comprising the complex. Barium complexes containing fluorinated ligands are better suited for chemical vapour deposition of barium than complexes containing non-fluorinated ligands because they efficiently evolve vapours containing barium at lower temperatures.

Keywords: mass spectrometry, superconductors, thermogravimetric analysis, volatile barium complexes

Introduction

The recent discovery of high temperature superconductors [1] has opened up new possibilities for the electronics industry. One method that can be used to prepare $YBa_2Cu_3O_7$ superconducting thin films for use in making integrated circuits is "Metal–Organic Chemical Vapour Deposition" (MOCVD). Volatile β-diketonate complexes containing Y, Ba, and Cu are commonly used to make $YBa_2Cu_3O_7$ films by MOCVD [2]. However, barium containing β-diketonate complexes are not as volatile as the Y and Cu complexes and suffer from decomposition and oligomerization when heated [3]. To improve the volatility of barium β-diketonate complexes, polyethers have been used to occupy coordination sites not filled by the β-diketonate ligands [4]. In this study, thermogravimetric analysis (TG) was used to evaluate the thermal properties of barium

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β-diketonate complexes containing fluorinated and non-fluorinated ligands and cyclic and linear polyethers. Solids probe mass spectrometry was also employed in this study to help elucidate multiple thermal processes detected by TG. All analyses were performed under identical conditions so that a valid comparison of the thermal properties of the barium complexes could be made.

Experimental

Thermogravimetric analyses were performed with DuPont (Wilmington, DE) model 951 TGA analyzer. Helium was used as a purge gas at a flow rate of 100 ml/min. Five mg samples were employed for all substances and a heating rate of 10 deg·min^{-1} from 50 to 450°C was employed for all analyses.

Solids probe mass spectra were obtained with a Hewlett Packard (Palo Alto, Ca) 5985 quadrupole mass spectrometer. Mass spectra were obtained with an ion source temperature of 200°C by using 70 eV electron impact ionization. Samples were heated in the vicinity of the ion source (~10^{-6} Torr) at a rate of 30 deg·min^{-1} from 30 to 300°C.

All of the barium complexes were synthesized by appropriate modifications of methods described previously [5]. Typically, barium hydride, the β-diketone, and the polyether were mixed in a 1:2:1 molar ratio with or without THF solvent. After stirring under N_2 for several hours, the solvent was evaporated and the product was purified by sublimation under reduced pressure. The non-fluorinated β-diketones used in this study were: 2,4-pentanedione {H(acac)} and 2,2,6,6-tetramethyl-3,5-heptanedione {H(tmhd)}. The fluorinated β-diketones used in this study were: 1,1,1,5,5,5-hexafluoro-2,4-pentanedione {H(hfac)}; 1,1,1-trifluoro-2,4-pentanedione{H(tfac)};1,1,1-tri-fluoro-5,5-dimethyl-2,4-hexanedione {H(tfpv)}; and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione {H(fod)}. The polyethers employed in this study were: 1,4,7,10,13,16-hexaoxacyclooctadecane {18-crown-6}; 1,4,10,13-tetraoxa-7,16-diaza-cyclooctadecane {diaza 18-crown-6}; and 2,5,8,11,14-pentaoxapentadecane (tetraglyme). Barium hydride, H(tmhd) and H(fod) were purchased from Strem Chemicals (Newburyport, MA). The polyethers, THF, H(acac), H(tfac), H(hfac) were obtained from Aldrich Chemical Co. (Milwaukee, WI). H(tfpv) was obtained from Lancaster Research Chemicals (Windham, NH).

Results

Thermogravimetric analysis

TG curves for the non-fluorinated and fluorinated barium complexes evaluated in this study are shown in Figs 1 and 2 respectively. All TG measurements were made while keeping the operating conditions of the instrument constant so that the thermal properties of the complexes could be compared. The $Ba(tmhd)_2$ TG curves shown in Fig. 1 exhibits a single weight loss step which ends with about 10% of the initial sample weight left at 400°C. The $Ba(tmhd)_2$ weight loss occurred at a higher temperature than any of the other complexes tested in this study. The variability in the $Ba(tmhd)_2$polyether TG curves shown in Fig. 1 suggests that the thermal desorption processes for these substances were highly dependent on the nature of the polyether. In contrast to the $Ba(tmhd)_2$ single weight loss step, the TG curves measured for the $Ba(tmhd)_2$polyethers exhibited multiple steps. In spite of the variability in the shapes of the TG curves for the $Ba(tmhd)_2$polyethers, all of these substances yielded less residue than $Ba(tmhd)_2$ at 400°C. Whereas $Ba(tmhd)_2$diaza18-crown-6 and $Ba(tmhd)_2$18-crown-6 TG curves exhibited multiple, overlapping weight loss steps, the $Ba(tmhd)_2$tetraglyme TG curve exhibited two clearly defined weight loss steps, the first of which was complete by 250°C. In contrast to the $Ba(tmhd)_2$polyether TG curves, the major weight loss in the $Ba(acac)_2$tetraglyme TG curve occurred below 175°C and about 45% of the initial sample weight was still present in the TG sample pan at 400°C.

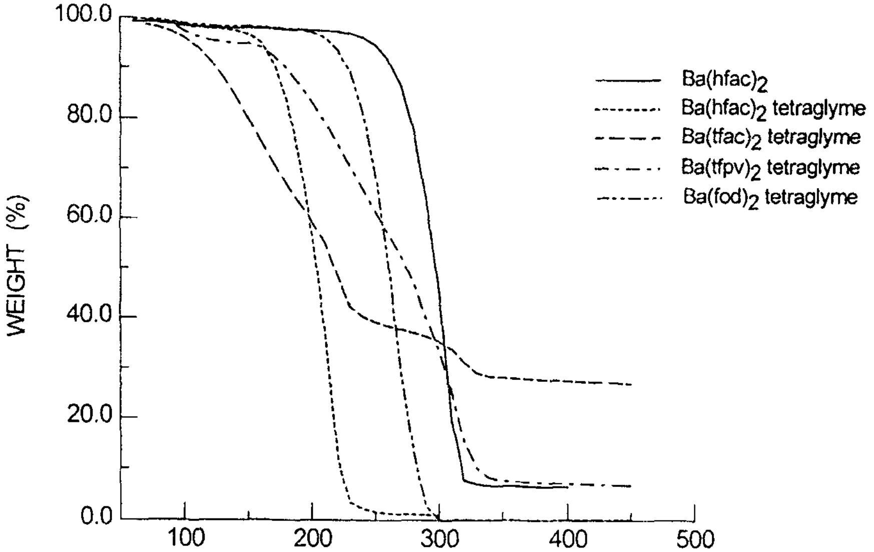

Fig. 1 TG curves for barium complexes containing non-fluorinated β-diketone ligands

Figure 2 shows that the single weight loss step in the TG curve for $Ba(hfac)_2$ was complete at a temperature about 40°C lower than that for $Ba(tmhd)_2$. Like $Ba(tmhd)_2$, a significant residue was left at 400°C when the $Ba(hfac)_2$ sample was heated. Like $Ba(hfac)_2$, the TG curves for $Ba(hfac)_2$tetraglyme and $Ba(fod)_2$tetraglyme exhibit single weight loss steps. Unlike $Ba(hfac)_2$, very little residue was left at 400°C when $Ba(hfac)_2$tetraglyme and $Ba(fod)_2$tetraglyme were heated. The weight loss curves for $Ba(hfac)_2$tetraglyme and $Ba(fod)_2$tetraglyme were shifted to the lower temperature by 90 and 30 deg, respectively, when compared to the $Ba(hfac)_2$ weight loss curve. The $Ba(tfac)_2$tetraglyme and $Ba(tfpv)_2$tetraglyme TG curves exhibited multiple weight loss steps and more residue was detected at 400°C for these materials than for the other fluorinated substances.

Mass spectrometric analysis

Because the barium complexes studied here had similar structures, the mass spectra of these substances contained similar features. None of the complexes yielded molecular ions under the ionization conditions used in this study. The $Ba(acac)_2$tetraglyme sample was unique in that no barium-containing ions were detected for this substance. At low thermal desorption temperatures, mass spectra measured for the $Ba(L)_2$polyether complexes did not include barium-containing ions but were instead characteristic of the β-diketone and polyether. The total amount and relative abundance of β-diketone and polyether produced by each substance was highly variable and depended on β-diketone structure. After the initial evolution of β-diketone and polyether, $[M-L]^+$ ions indicating evolution of monomer were detected for all but $Ba(acac)_2$tetraglyme sample. At higher temperatures, the $[M-L]^+$ ion signal disappeared in $Ba(L)_2$polyether mass spectra and $Ba_2L_3^+$ ions were detected for all but the $Ba(acac)_2$tetraglyme, $Ba(hfac)_2$tetraglyme, $Ba(fod)_2$tetraglyme samples. In contrast to $Ba(L)_2$polyether mass spectral results, the $Ba_2L_3^+$ ion was present in all $Ba(tmhd)_2$ and

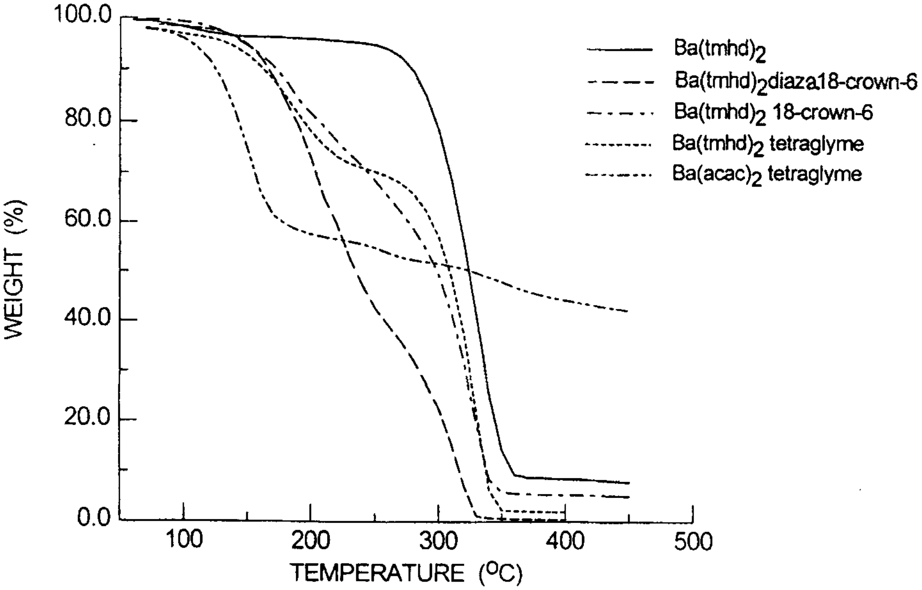

Fig. 2 TG curves for barium complexes containing fluorinated β-diketone ligands

$Ba(hfac)_2$ mass spectra that contained barium-containing ions. The appearance of $Ba_2L_3^+$ in $Ba(L)_2$polyether mass spectra measured at high temperatures suggested that material volatilized at these temperatures did not contain the polyether. Unfortunately, if $Ba_2L_3^+$ ions were produced by heating $Ba(fod)_2$tetraglyme they, were not detected because the mass of this ion exceeded the upper limit of the mass scan employed for these studies. However, because the TG curve for this material exhibited a single weight loss step and no residue remained above 300°C, it was unlikely that $Ba(fod)_2$ was formed and that $Ba_2L_3^+$ was produced.

Discussion

Unfortunately, quality mass spectra were not obtained for $Ba(tmhd)_2$tetraglyme because of limited monomer production and no barium-containing ions were detected for $Ba(acac)_2$tetraglyme. After comparing mass spectra obtained for the other $Ba(L)_2$polyether complexes, interesting trends were observed in the relative intensities of the $[M\text{-}2L]^{2+}$ and $[M\text{-}L\text{-polyether}]^+$ ions. The intensities of the $[M\text{-}2L]^{2+}$ and $[M\text{-}L\text{-polyether}]^+$ ions were about the same in mass spectra for $Ba(tmhd)_2$diaza18-crown-6 and $Ba(tmhd)_2$18-crown-6. In contrast, the $[M\text{-}2L]^{2+}$ and $[M\text{-}L\text{-polyether}]^+$ ion abundance ratios in mass spectra for the barium complexes containing fluorinated ligands were 2:1 for $Ba(tfac)_2$tetraglyme, 3.5:1 for $Ba(tfpv)_2$tetraglyme, 5:1 for $Ba(hfac)_2$tetraglyme and 14:1 for $Ba(fod)_2$tetraglyme. Clearly, as the numbers of fluorines in the β-diketone increased, the electron bombardment production of the $[M\text{-}2L]^{2+}$ ion increased relative to the $[M\text{-}L\text{-polyether}]^+$ ion, suggesting that the polyether in these complexes was held more tightly than the β-diketone.

The residue at 400°C for the $Ba(tmhd)_2$ and $Ba(hfac)_2$ samples was likely due to decomposition and oligomerization during sublimation of these species, which is consistent with previously reported studies of these materials [5, 6]. For all complexes except $Ba(acac)_2$tetraglyme, barium-containing vapour was produced at lower temperatures when a polyether was included in the complex. With the exception of $Ba(acac)_2$tetraglyme, all $Ba(L)_2$polyethers yielded monomer at some point during the applied temperature ramp. However, the fraction of sample evolved as monomer varied greatly among the $Ba(L)_2$polyether complexes and depended on the choice of β-diketone and polyether, with the most efficient monomer evolution observed for tetraglyme complexes containing hfac and fod ligands.

Mass spectra obtained for $Ba(acac)_2$tetraglyme exhibited no barium-containing ions. The TG curve for this sample exhibited a single weight loss step corresponding to about 40% of the sample weight which is roughly equal to the weight percentage of tetraglyme in the material. Thus, $Ba(acac)_2$tetraglyme apparently undergoes thermal decomposition between 100 and 175°C resulting in the formation of $Ba(acac)_2$, which does not appreciably sublime. As stated previously, mass spectrometric results indicated that the amount of $Ba(tmhd)_2$tetraglyme monomer evolved was very small. Apparently, the first step in the TG curve for this substance corresponded to loss of tetraglyme. The 30% first weight loss step is consistent with the approximately 30% by weight content of tetraglyme in this substance. Therefore, above 250°C $Ba(tmhd)_2$tetraglyme was converted into $Ba(tmhd)_2$. However, the solid obtained by removing tetraglyme from $Ba(tmhd)_2$tetraglyme was not equivalent to the neat $Ba(tmhd)_2$ employed in this study because the decomposition of the $Ba(tmhd)_2$tetraglyme derived $Ba(tmhd)_2$ occurred at lower temperature than that for neat $Ba(tmhd)_2$.

Fluorinated $Ba(L)_2$tetraglyme complexes, particularly those incorporating hfac and fod β-diketonates, yielded barium-containing vapours more efficiently and at lower temperatures than non-fluorinated barium complexes, suggesting that they would be more suitable for use in MOCVD. Apparently, the negative charge of the fluorinated β-diketones is delocalized by the electron withdrawing effect of the fluorine atoms which tends to reduce the overlap between Ba^{2+} orbitals and β-diketone negative charge centers. This hypothesis is supported by the fact that the $[M\text{-}2L]^{2+}$ ion signal intensity was much larger than the $[M\text{-}L\text{-}polyether]^{+}$ ion signal intensity in mass spectra for the hfac and fod containing complexes, indicating that the Ba-β-diketone interaction was weaker in these complexes than in the non-fluorinated barium complexes.

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Zusammenfassung — Unter Einsatz der gravimetrischen Methode und der Massenspektroskopie wurde ein Vergleich der thermischen Eigenschaften einiger bariumhaltigen Komplexe angestellt. Dabei handelt es sich um Komplexe mit Gehalt an fluorierten und nicht fluorierten β-Diketonen im Molekül in und ohne Anwesenheit von Polyether. Die thermischen Eigenschaften der Bariumkomplexe hängen in entscheidendem Maße von der Struktur des im Komplex enthaltenen β-Diketons und Polyethers ab.Bariumkomplexe mit fluorierten Liganden sind besser für die chemische Dampfabscheidung geeignet als Bariumkomplexe mit nichtfluorierten Liganden.