MASS SPECTROMETRIC STUDY OF GAS-PHASE THERMAL STABILITY OF YTTRIUM(III) TRIS(DIPIVALOYLmethanate)

A. F. Bykov, P. P. Semyannikov and I. K. Igumenov

INSTITUTE OF INORGANIC CHEMISTRY, NOVOSIBIRSK-90, 630090 RUSSIA

The processes of thermal decomposition of yttrium(III) tris (dipivaloylmethanate) (Y(dpm)₃) vapour and its mixtures with oxygen were investigated by using the two-temperature variant of the double-chamber Knudsen cell, with mass spectrometric recording of the gas-phase composition within the temperature range 150°–650° C. The threshold temperatures of the stability of the complex vapour were determined. The temperature dependence of the rate constant was obtained for the thermolysis of Y(dpm)₃ vapour, and the effective activation energy of the process was determined. Qualitative data were obtained on the influence of Cu(dpm)₂ vapour on the thermolysis of Y(dpm)₃ vapour in oxygen atmosphere.

Keywords: kinetic parameters, mass spectrometry, superconducting films, thermal stability, yttrium(III) tris (dipivaloylmethanate)

Introduction

Numerous recent publications are indicative of the successful application of β-diketonates of such metals as yttrium, barium, copper, etc., as initial reagents for HTSC film preparation by the MO CVD method [1, 2]. This success is mainly limited by the use of precision equipment for the method of chemical deposition from the gas phase. However, the literature lacks data on the volatility, stability and chemical features of the compounds applied. In fact, only data on the volatility of copper complexes [3] and contradictory data on the volatility of yttrium(III) tris (dipivaloylmethanate) (Y(dpm)₃) are available [4, 5]. There is no information on the volatility of barium(II) β-diketonates or on the thermal stability of the vapour of metal complexes used for the preparation of superconducting films.

We recently reported [6] the thermolysis of Cu(dpm)₂ and Hdpm vapour under different conditions, using the same method. The system of injection of the vapour of the substances under study was described in detail. The results of that
work have been used for data analysis and in a number of the conclusions in the present publications.

Experimental

The work was done with an automated time-of-flight MSKh-6 (USSR) mass spectrometer with a mass recording range of 13000 M/Z and a resolution of 350 at 50% of the peak height. The system of injection of the vapour of the substance under study is a specialized, two-temperature variant of the double-chamber Knudsen cell, with molecular flow modulation at the effusion outlet. The volatile compound under study in a quartz container (or two substances in separate containers in the case of the co-vaporization of Y(dpm)$_3$ and Cu(dpm)$_2$ was placed in a separate vaporization chamber, which was evacuated, and heated to the temperature necessary for substance transport to the reaction zone. When necessary, the gas reagent was added to the substance vapour at the reaction zone inlet, and its influence on the thermolysis was studied. The gas-phase composition at the outlet from the reaction zone was determined mass spectrometrically. The whole system has been described in detail in [6].

The thermal stability of Y(dpm)$_3$ under various conditions was studied via the temperature dependence of the peak intensities of ions from the mass spectra of the vapour of the substance under study, the products of its thermolysis and reaction additives. Under real-time conditions, it was possible to trace the intensities of 20 peaks in the mass spectrum simultaneously. The temperature sweep in the reaction zone was 2.5 deg/min. We checked the coincidence of the direct (in the direction of temperature increase) and reverse behaviour of the dependence of ion peak intensities.

Y(dpm)$_3$ was investigated in vaporization chamber at temperatures of 110°-140°C which corresponds to a saturated vapour pressure of from 1·10$^{-3}$ to 2.6·10$^{-2}$ Torr, taking into account the data from [3], approximated over the low-temperature range. Investigations of the interaction with oxygen involved a 550-fold excess of oxygen relative to Y(dpm)$_3$. Calculations were carried out with theoretical values of ionization cross-sections and the additivity law [7]. The gas-phase decomposition was studied in the temperature range 150°–650°C.

Results and discussion

Mass spectrum of Y(dpm)$_3$

Figure 1 shows the mass spectrum of Y(dpm)$_3$, which is mainly comprised of peaks of metal-containing ions, the most intensive among them being [Y(dpm)$_2$]$^+$,