Hydrogen uptake by barium manganite at atmospheric pressure

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Abstract

Investigation of the interaction of hydrogen with alkaline earth manganites (IV) $AMnO_3$ (A = Ca, Sr, Ba), dispersed with 1 atom % Pt, has revealed an unprecedented uptake of hydrogen by $BaMnO_3$/Pt to the extent of ~ 1.25 mass % at moderate temperatures (190 − 260 °C) and ambient pressure. Gravimetric sorption isotherms and mass spectrometric analysis of the desorption products indicate that approximately three hydrogen atoms per mole of $BaMnO_3$/Pt is inserted reversibly. The nature of hydrogen in the insertion product, $BaMnO_3H_3$, is discussed. The work suggests the possibility of developing new hydrogen storage materials based on electropositive metal - transition metal - oxide systems.

Keywords: A. Oxides; A. Hydrides; C. Thermogravimetric analysis (TGA)

1. Introduction

Availability of safe and efficient hydrogen storage materials is essential for the development of hydrogen-fueled automobiles. A solid material that can store hydrogen reversibly near room temperature and ambient pressure with a capacity of 6.5 mass % and 62 kg H_2 m^{-3} is the ideal target recommended by the U. S. Department of Energy (DOE) for mobile applications [1,2]. A wide variety of solids that include metals and intermetallics forming hydrides [3] (e. g. Mg_2NiH_4), various forms of carbon [2,4], nanotubes of BN [5] and metal salts such as nanoporous nickel (II) phosphates [6] have been investigated for hydrogen storage, but none of them meet the DOE target. Recently, Rosi *et al*. [7] have reported a new class of metal-organic porous framework materials consisting of zinc (II) dicarboxylates bridged by organic linkers like benzene/naphthalene that adsorb hydrogen up to 4.5 % by weight at 78 K and 20 bar pressure.

During the course of our investigation of the interaction of hydrogen with transition metal oxides, we found that certain alkaline earth manganites (IV) dispersed with platinum adsorbed significant quantities of hydrogen at relatively low temperatures and ambient pressure. Detailed gravimetric studies of sorption/desorption behavior of hydrogen which are reported herein show that, among the alkaline earth manganites, $BaMnO_3$/Pt is the most promising material that reversibly adsorbs ~ 1.25 mass % of hydrogen in the temperature range 190 − 260 °C at atmospheric pressure. We believe the results reported herein are significant for two reasons: first, they suggest the possibility of developing new hydrogen storage materials based on transition metal oxides; second, more important, the results indicate the existence of a whole new class of *metal oxide-hydrides*, which seem to be stable for certain combinations of electropositive/alkaline

earth metal - transition metal - oxides. To our knowledge, $LaSrCoO_3H_{0.7}$, is the only other transition metal oxide hydride that has recently been reported in the literature [8,9].

2. Experimental

$AMnO_3$ (A = Ca, Sr, Ba) oxides were prepared by conventional solid-state reaction of ACO_3 carbonates with $MnC_2O_4.2H_2O$ at elevated temperatures (900 − 1050 °C) in air. Powder XRD patterns showed that while $CaMnO_3$ forms in the orthorhombic perovskite structure, $SrMnO_3$ and $BaMnO_3$ forms in the 4H and 2H-perovskite polytypic structures respectively, as expected. 1 atom % Pt dispersed $AMnO_3$ were prepared by soaking the samples in an ethanolic solution of $H_2PtCl_6.6H_2O$ (containing 3.767 mg of Pt per ml) and drying the solids at 200 °C in air for 12 h. Thermogravimetric (TG) experiments were performed on a Cahn TG-131 system at a heating rate of 2 °C/min. H_2 gas (purity ≥ 99.9 %) dried over anhydrous $CaCl_2$ and P_2O_5 was passed over the sample at an approximate flow rate of 8 cc/min. Gravimetric isotherms of hydrogen sorption and desorption were recorded with the same TG system equipped with a vacuum attachment. For this purpose, the TG system was degassed at 250 °C/3 h prior to the experiments. Details are given in Table 1. Both gravimetric and volumetric hydrogen sorption/desorption experiments on $BaMnO_3$/Pt were also carried out and the desorption products characterized by mass spectrometry at DuPont C R & D. The details are as follows. Gravimetric analysis was performed with a Hiden "Intelligent Gravimetric Analyzer" (IGA) microbalance, measuring hydrogen adsorption under constant temperature and pressure. Samples were loaded into wire mesh basket that was located inside a stainless steel (or quartz) reactor. Initially samples were outgassed to remove any moisture or oxygen contaminants. The

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adsorption isotherm was measured in both static and flowing (dynamic) hydrogen. A volumetric adsorption apparatus made by Advanced Scientific Designs Inc., Michigan, U. S. A., was used to study the adsorption and desorption of hydrogen. The instrument is equipped with a mass spectrometer that is computer controlled so that desorption of several masses can be monitored simultaneously. Powder X-ray diffraction (XRD) patterns of the solid products were recorded with a Siemens D5005 powder X-ray diffractometer using CuKα radiation.

We developed a new method for the determination of hydride. First, we standardized the method with CaH_2. For this, a mixture of 5 mmols of CaH_2 (Merck) and 20 mmols of $AgNO_3$ taken in a Pt crucible was reacted at 220 °C for 12 h. The solid mass was extracted with water, metallic Ag formed according to the reaction, $Ag^+ + H^- \rightarrow Ag^0 + 1/2\ H_2$, was separated, dissolved in hot 4N HNO_3 and the $AgNO_3$ obtained was determined by titration [10] with KSCN. The procedure was repeated with the hydrogen sorption product of $BaMnO_3$/Pt.

3. Results and discussion

We investigated the interaction of hydrogen with alkaline earth manganites (IV), $AMnO_3$ (A = Ca, Sr, Ba) by thermogravimetry. While pristine materials showed conventional reactivity involving loss of oxygen due to formation of $AMnO_{3-x}$ phases, materials dispersed with 1 atom % Pt showed an unusual behavior for $BaMnO_3$ and $SrMnO_3$ (Fig. 1a). With $BaMnO_3$/Pt, there was a sharp increase in weight by about 2.8 % around 200 °C followed by a weight loss of 2 % around 300 °C, clearly indicating sorption-desorption of hydrogen at ambient pressure in the 200 − 300 °C range. With
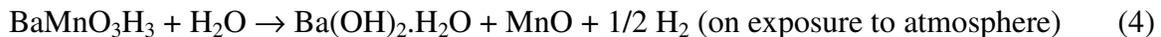
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SrMnO$_3$/Pt, there was an initial weight loss in the 200 − 250 °C range corresponding to the formation of SrMnO$_{3-x}$ (x ~ 0.25), followed by an increase in the weight (~ 1.5 %) and a plateau region between 300 − 450 °C, again signaling uptake of hydrogen. CaMnO$_3$/Pt, on the other hand, showed the usual hydrogen reduction behavior above 300 °C, forming a mixture of CaO and MnO as the final product.

We recorded the gravimetric hydrogen sorption and desorption isotherms for BaMnO$_3$/Pt by choosing the appropriate temperatures from the TG curves (Fig. 1a): 180 − 200 °C for sorption and 250 − 260 °C for desorption. The representative data obtained at 190 °C (sorption) and 260 °C (desorption) on the same sample are given in Fig. 1b and Table 1. We see that there is a mass increase/decrease of ~ 1.25 % during sorption/desorption at 190/260 °C. Gravimetric and volumetric sorption studies on BaMnO$_3$/Pt carried out at 1000 millibar pressure of hydrogen under static and dynamic conditions also show similar results (Fig. 2). We see that there is an increase of 1.40 and 1.20 mass % under static and dynamic conditions respectively. On the average, we find that there is a consistent uptake of 1.30 ± 0.10 mass % hydrogen around 190 − 200 °C, followed by desorption of nearly the same mass around 250 − 260 °C. This mass increase corresponds approximately to an uptake of 3 hydrogen atoms per mole of BaMnO$_3$/Pt (calculated mass % is 1.26). More importantly, mass spectrometric analysis (Fig. 3) clearly shows that H$_2$ is the dominant gas desorbed for the temperature range shown, indicating that BaMnO$_3$/Pt is a reversible hydrogen adsorber. Furthermore, the desorption profiles for H$_2$ and H$_2$O are significantly dissimilar such that they must arise from different desorption events.

We attempted to characterize the hydrogen sorption product of $BaMnO_3/Pt$ by powder XRD and chemical analysis. The sorption product obtained at the end of isotherm I is extremely sensitive to atmosphere, decomposing to a mixture of $Ba(OH)_2.H_2O$ and MnO (see later). However, the XRD pattern recorded immediately after the sorption experiment (Fig. 4b) shows a decrease of crystallinity and is distinctly different from that of $BaMnO_3/Pt$ (Fig. 4a), indicating the formation of a new phase on hydrogen sorption. Chemical analysis using $AgNO_3$ titration (see Experimental) showed formation ~ 3 gram atoms of silver per mole of the sorption product ($BaMnO_3H_3/Pt$), suggesting that the adsorbed hydrogens are likely to be hydridic in nature.

The sorption product ($BaMnO_3H_3/Pt$) is highly sensitive to atmosphere, decomposing rapidly to a mixture of $Ba(OH)_2.H_2O$ and MnO (Fig. 4c). The decomposed material does not show the presence of hydride in $AgNO_3$ experiments. Also the decomposed material loses its activity toward hydrogen sorption. A physical mixture of $Ba(OH)_2.H_2O$ and MnO dispersed with 1 atom % Pt does not show H_2 sorption activity either, under the same conditions.

The chemical reactions that occur during sorption-desorption could be formulated as follows:

$$H_2 \xrightarrow{\text{Pt}} 2\,H \tag{1}$$

$$BaMnO_3 + 3\,H \rightarrow BaMnO_3H_3 \text{ (isotherm I)} \tag{2}$$

$$BaMnO_3H_3 \rightarrow BaMnO_3 + 3/2\,H_2 \text{ (isotherm II)} \tag{3}$$

$$BaMnO_3H_3 + H_2O \rightarrow Ba(OH)_2.H_2O + MnO + 1/2\,H_2 \text{ (on exposure to atmosphere)} \tag{4}$$

The mass gain/loss observed during sorption-desorption experiments (Table 1) and

powder XRD characterization of the sorption product are consistent with the above scheme.

A plausible explanation for the chemical events that occur during sorption/desorption of H_2 on $BaMnO_3$/Pt could be as follows: First, H_2 is dissociatively adsorbed on Pt and the dissociated H atoms are inserted into $BaMnO_3$ in a manner similar to the Pt-catalyzed insertion of H atoms in transition metal oxides through the 'spillover' mechanism [11]. Hydrogen normally acts as a donor reducing the transition metal and forming hydroxyls in metal oxides [11] such as WO_3 and MoO_3. If this were to happen with $BaMnO_3$/Pt, we should have obtained $BaMnO(OH)_2$ as the insertion product, where Mn^{IV} would be reduced to Mn^{II}. But we find consistently in all our experiments *at least* three hydrogen atoms per $BaMnO_3$/Pt are adsorbed. Also, we do not observe H_2O or OH as major desorption products in TPD analysis; instead molecular hydrogen is the major desorption product (Fig. 3). Accordingly, we believe that the hydrogen is inserted as neutral H^0 that forms covalent bonding with the half-filled d orbitals of the Mn^{4+} ions. The half-filled t^3 manifold of an octahedral-site Mn^{4+} ion is split by the trigonal field into the half-filled configuration $e^2a_1{}^1$. These d orbitals are directed through faces of the $MnO_{6/2}$ octahedra; the a_1 is directed along the c-axis and the e orbitals are directed in the basal plane. The H^0 atoms would occupy octahedral-site faces to form spin-paired $Mn:e^1 - H:1s^1$ covalent bonds and, along the c-axis, $-Mn-H-Mn-H-$ bonds forming a half-filled, spin-paired band. This bonding is favoured over reduction of Mn^{4+} to Mn^{3+} because of a large cubic-field splitting of the Mn^{4+}/Mn^{3+} and Mn^{5+}/Mn^{4+} couples. A large $Mn^{4+} - Mn^{4+}$ electrostatic repulsion along the c-axis is relieved by the formation of $-Mn-H-Mn-H-$ bonding; and the 2H structure not only has a larger cubic-field splitting of the Mn d

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states, but also allows the H^0 atoms to enter an octahedral-site face without encountering a large alkaline-earth cation, as also does the 4H structure. However, the perovskite structure favours formation of OH^- ions with a reduction of Mn^{4+} to Mn^{3+} over the formation of $Mn-H$ bonds. With this model, $BaMnO_3$ can accept three H atoms per molecule to give $BaMnO_3H_3$ with a net spin of $S = 0$ in contrast to an $S = 3/2$ per formula unit for $BaMnO_3$. Desorption of hydrogen from $BaMnO_3H_3$ occurring in two steps approximately in 1:2 ratio (Fig. 3) lends support to this model. Magnetic susceptibility measurements would provide further support.

4. Conclusions

BaMnO$_3$ dispersed with 1 atom % Pt exhibits an unprecedented hydrogen sorption-desorption behaviour at moderate temperatures ($190 - 260$ °C) and atmospheric pressure that could be of significance for the development of hydrogen storage materials. The results suggest the formation of a novel oxide-hydride, $BaMnO_3H_3$, sorption product.

References

[1]   (a) L. Schlapbach, A. Züttel, Nature 414 (2001) 353. (b) L. Schlapbach, (Guest Editor), MRS Bulletin, September 2002.

[2]   R. Dagani, C & E News 80 (2002) 25 (14 January 2002).

[3]   (a) R. C. Bowman Jr., B. Fultz, MRS Bulletin, September 2002, p.688. (b) E. Akiba, M. Okada, ibid p.699. (c) B. Bogdanovic, G. Sandrock, ibid p.712.

[4]   (a) A. C. Dillon and M. Heben, Appl. Phys. A 72 (2001) 133. (b) G. Gundiah, A. Govindaraj, N. Rajalakshmi, K. S. Dhathathreyan, C. N. R. Rao, J. Mater. Chem. 13 (2003) 209.

[5]   R. Ma, Y. Bando, H. Zhu, T. Sato, C. Xu, D. Wu, J. Am. Chem. Soc. 124 (2002) 7672.

[6]   P. M. Forster, J. Eckert, J-S. Chang, S-E. Park, G. Ferey, A. K. Cheetham, J. Am. Chem. Soc. 125 (2003) 1309.

[7]   N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, Science 300 (2003) 1127.

[8]   M. A. Hayward, E. J. Cussen, J. B. Claridge, M. Bieringer, M. J. Rosseinsky, C. J. Kiely, S. J. Blundell, I. M. Marshall, F. L. Pratt, Science 295 (2002) 1882.

[9] $12CaO.7Al_2O_3$ possessing subnanometer-sized cages of oxide ions incorporates H^- ions in the cages. K. Hayashi, S. Matsuishi, T. Kamiya, M. Hirano, H. Hosono, Nature 419 (2002) 462. Other known metal oxide-hydrides include $Ba_3(AlO_4)H$ and $Ba_{21}Ge_2O_5H_{24}$. K. R. Poeppelmeier, Science 295 (2002) 1849.

[10]   J. Basset, R. C. Denney, G. H. Jeffrey, J. Mendham, Vogel's Textbook of Quantitative Inorganic Analysis, Longman, London, 1978; pp. 340–341.

[11]   (a) P. G. Dickens, S. C. Baker, M. T. Weller, Solid State Ionics 18 & 19 (1986) 89. (b) S. C. Baker, P. G. Dickens, Mater. Res. Bull. 19 (1984) 1457.

Table 1

Sorption-desorption of hydrogen (H_2) by 1 atom % Pt-dispersed $BaMnO_3$ at ambient pressure

Isotherm	Temperature (^{o}C)/gas	Weight gain/loss (%)	Ideal formula and weight gain/loss (%) expected
Isotherm I	190/hydrogen	+ 1.24	$BaMnO_3H_3$: + 1.26
Isotherm II	260/argon	− 1.28	$BaMnO_3$: − 1.24

About 300 mg of $BaMnO_3$/Pt sample taken in a fused silica bucket was suspended in the TG balance, degassed at 250 °C to 1×10^{-5} mbar pressure, cooled to room temperature and purged with argon to bring the system to atmospheric pressure. Then the system was flushed with hydrogen for 1 h, temperature raised rapidly (10 ^{o}C/min) to 190 ^{o}C and isotherm I (sorption) was recorded under H_2 flow. After completion of isotherm I, the system was cooled to room temperature, then H_2 flow stopped and the system was flushed with argon for 1 h. The temperature was raised rapidly (10 ^{o}C/min) to 260 ^{o}C and isotherm II (desorption) was recorded.

Figure Captions

Fig. 1 (a) TG curves for the interaction of hydrogen with 1 atom % Pt dispersed $BaMnO_3$, $SrMnO_3$ and $CaMnO_3$. (b) H_2 sorption-desorption isotherms for $BaMnO_3$-1 atom % Pt. I, sorption at 190 °C; II, desorption at 260 °C.

Fig. 2 Gravimetric hydrogen sorption isotherm of $BaMnO_3$/Pt at 200 °C and 1000 millibar pressure of hydrogen under static conditions.

Fig. 3 Temperature programmed desorption and mass spectrometric analysis of the desorbed species from the hydrogen sorbed $BaMnO_3$/Pt. Mass numbers of the desorbed species (H_2 and H_2O) are indicated.

Fig. 4 Powder XRD patterns of (a) $BaMnO_3$ - 1 atom % Pt, (b) H_2 sorption product of $BaMnO_3$ - 1 atom % Pt at the end of isotherm I, $BaMnO_3H_3$ and (c) sorption product exposed to atmosphere showing a mixture of $Ba(OH)_2.H_2O$ and MnO.
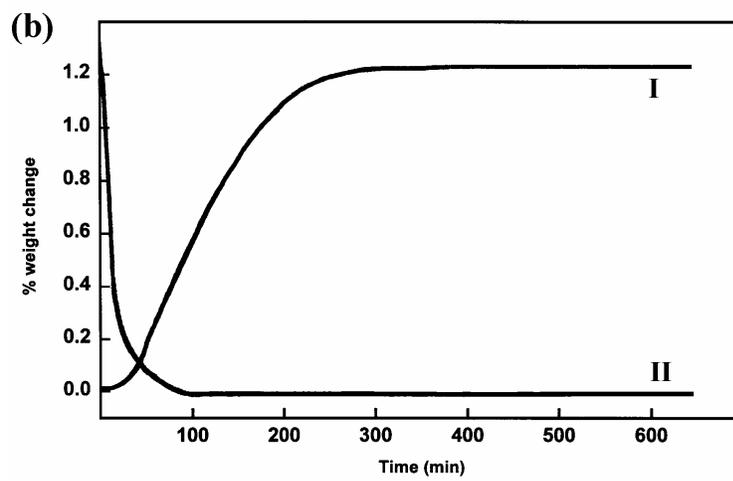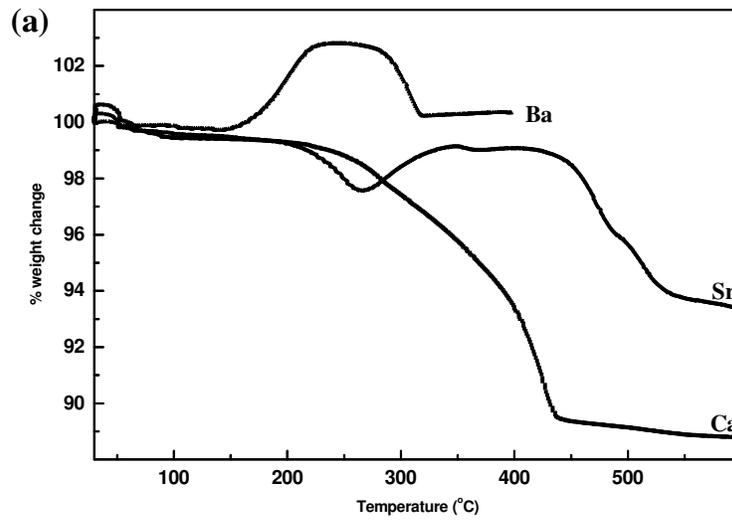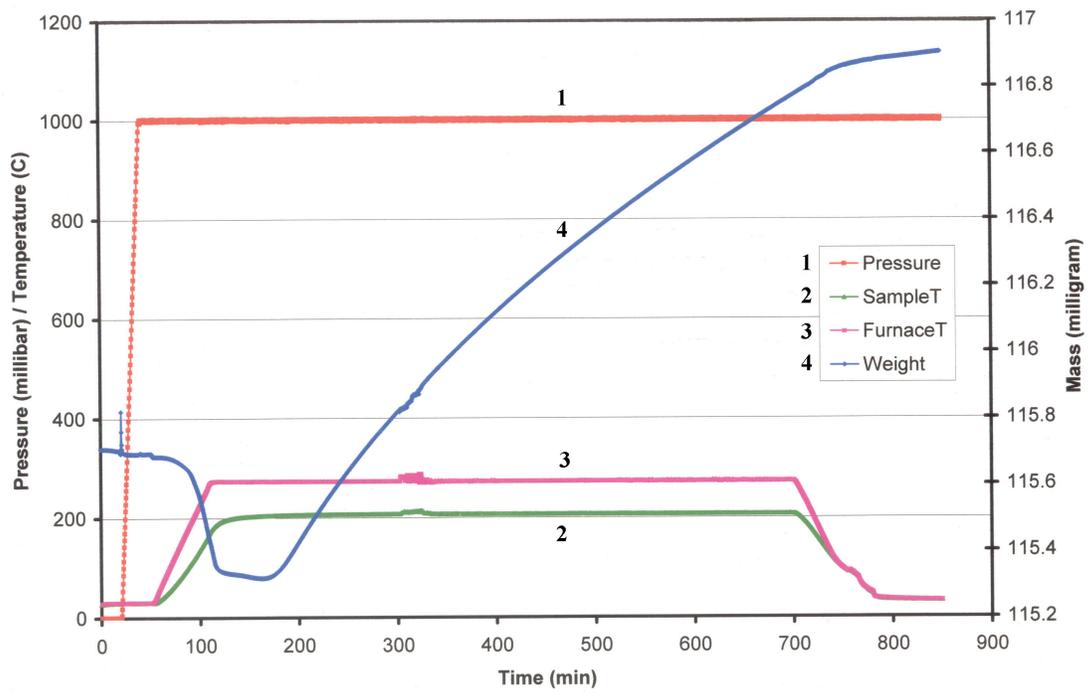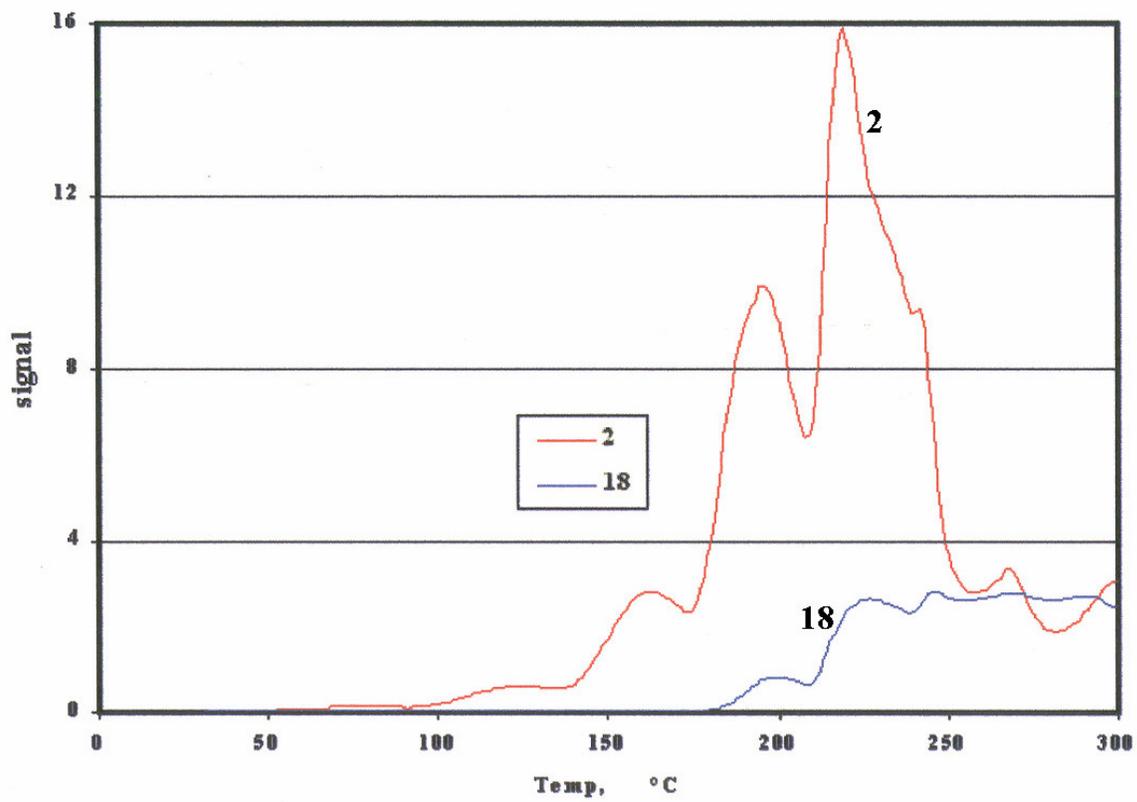
Fig. 1

Fig. 2

Fig. 3

Fig. 4