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Thermal analysis of sol-gel aluminosilicate systems

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Aluminosilicate systems containing radioactivable elements (Y or Dy) and/or Fe are investigated for possible applications in internal radiotherapy and hyperthermia, or in combined therapies. The samples were prepared by sol-gel method, using two different sources for SiO_2: $C_8H_{20}O_4Si$ (TEOS) and $SiO_2 \cdot xH_2O$ (silicic acid), and nitrates as sources of Al_2O_3, Y_2O_3, Dy_2O_3 and Fe_2O_3, added in different ratios. The dried gels were heat treated at 500 ºC for 1 hour and at 1200 ºC for 24 hours, in order to engineer their structure. The samples were studied by differential thermal analysis/thermogravimetry and differential scanning calorimetry and the results were correlated with the data obtained by X-ray diffraction analysis.

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1. Introduction

The investigated aluminosilicate systems are of great interest in medicine for the treatment of different types of tumours by internal radiotherapy and hyperthermia [1]. Glasses containing yttrium or certain rare earth elements which can be activated by neutron irradiation take the advantage that they become radioactive in the last stage of preparation and are suitable for in situ irradiation of tumours [2]. The addition of iron oxide can confer properties suitable for hyperthermia [3 - 6]. An important target in processing biomaterials is to obtain a controlable and reproducible nanostructure. In the last decades one of the commonest methods applied to achieve nanostructured materials is sol-gel method [7].

Radioactivable xerogels with magnetic properties can be used for internal radiotherapy of the tumours and, at the same time, for hyperthermia. The combined effect of the two methods of therapy may enhance the efficiency of the treatment [8].

The purpose of this work is to study the influence of composition and preparation conditions on the structure of aluminosilicate systems containing radioactivable elements (Y or Dy) and/or iron oxide.

2. Experimental procedure

The samples were prepared by sol-gel method. Two types of precursors were used as SiO_2 source: $C_8H_{20}O_4Si$ (tetra-ethyl-ortho-silicate TEOS) and $SiO_2 \cdot xH_2O$ (silicic acid), while as source for Al_2O_3 was used $Al(NO_3)_3 \cdot 9H_2O$. An amount of TEOS/silicic acid was dissolved in distilled water and mixed at the ambient temperature for ~30 minutes. Then a solution of water with $Al(NO_3)_3 \cdot 9H_2O$ was added and the stirring continued for other ~30 minutes on a magnetic agitator heated at 90 ºC. In this solution were introduced $Y(NO_3)_3 \cdot 6H_2O$, $Dy(NO_3)_3 \cdot 5H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, also dissolved in distilled water, in different ratios. When the solution appeared like a gel, it was filtered and then dried in an electric oven at ~110 ºC, about 20 hours. The as prepared samples studied in this work have pH 8.5. In order to obtain this pH value we added to the final solution a few drops of aqueous ammonia (NH_4OH). The dried samples were subjected to heat treatments carried out at 500 ºC for 1 h and at 1200 ºC for 24 hours.

DTA/TG measurements were performed on Shimadzu analyzer DTG-60H (simultaneous TG/DTA) in air, using alumina crucibles, with heating rate of 10 ºC/min, from room temperature to 1400 ºC. The DSC curves were recorded on Shimadzu DSC-60 differential scanning calorimeter, in air, using aluminium crucibles, with a heating rate of 5ºC/min, from room temperature to 500 ºC. The structure of the treated and non-treated samples was investigated by X-ray diffraction with a Shimatzu XRD-6000 diffractometer, using CuK_α radiation (λ = 1.5418 Å), with Ni–filter. The measurements were performed at a scan speed of 1˚/min.

3. Results and discussion

The DSC curves of the samples having TEOS and silicic acid as SiO_2 precursor are shown in Fig. 1 and 2, respectively. Five endothermic events occur in iron containing samples prepared from TEOS, while for the sample without iron only two major endothermic events are present. This behaviour was earlier observed also for $Al_2O_3 \cdot 2SiO_2$ and $Al_2O_3 \cdot 3SiO_2$ matrices [9]. It is worth

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noting that these samples have pH 8.5, obtained by ammonia addition. Taking into account the chemical reaction which ammonia can produce, the first four peaks, very sharp and narrow, can be associated with the following processes:

- peaks 1 and 2, at $T \sim 55$ ºC and 92 ºC, the removal of the water from the reaction

$$NH_4OH + HNO_3 \rightarrow NH_4NO_3 + H_2O$$

- peak 3, at $T \sim 129$ ºC, a structural transformation of NH_4NO_3, shifted to higher temperature as compared to data reported in literature [10], at $T \approx 125.2$ ºC;
- peak 4, at $T \sim 160$ ºC, the melting of NH_4NO_3, shifted to lower temperature as compared to data reported in literature [10], at $T \approx 169$ ºC.

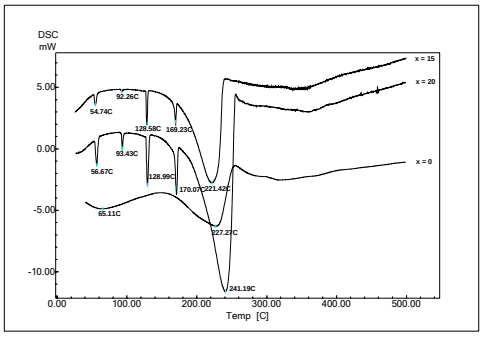

Fig. 1. DSC curve of of $xFe_2O_3 \cdot (80\text{-}x)SiO_2 \cdot 20Al_2O_3$ samples prepared from TEOS.

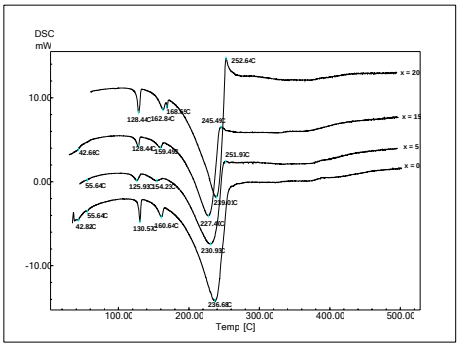

Fig. 2. DSC curve of $xFe_2O_3 \cdot (80\text{-}x)SiO_2 \cdot 20Al_2O_3$ samples prepared from silicic acid.

The peak 5, at $T \sim 235$ ºC, very large and broad, could be related to an overlapping effect [11] of the thermal decomposition of NH_4NO_3, which begins at $T \sim 220$ ºC, according to the reaction

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \rightarrow N_2 + 1/2\ O_2 + 2H_2O$$

and of the decomposition of the organic phase.

Concerning the samples prepared from silicic acid, the same peaks were evidenced, even for the sample without iron. Moreover, in the iron containing samples, after the large and broad peak from $T \sim 236$ ºC, one can see a small exothermic peak that increases with the Fe_2O_3 concentration of the sample.

The DTA/TG profiles are shown in Fig. 3. One can observe that the large and broad peak occurring at ~ 240-260 ºC is accompanied by a considerably weight loss, indicating a decomposition process in the sample. Afterwards, the mass of the sample remains constant over the whole investigated temperature range. This behaviour together with the observed exothermic peak in the DTA and DSC curves respectively, point out the crystallisation phenomena which occur in these samples at temperatures $T > 236$ °C.

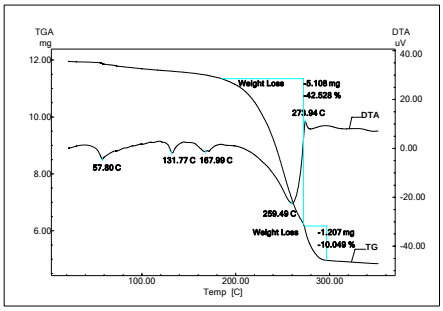

Fig. 3. DTA/TG curves of 20Fe2O3·60SiO2·20Al2O3 sample from silicic acid.

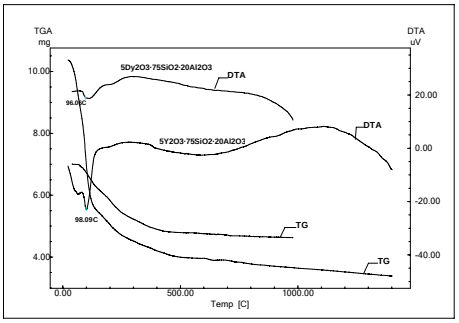

Fig. 4. DTA/TG curves of $5Y_2O_3 \cdot 75SiO_2 \cdot 20Al_2O_3$ and $5Dy_2O_3 \cdot 75SiO_2 \cdot 20Al_2O_3$ samples.

The samples containing yttrium and dysprosium oxides (Fig. 4) showed an endothermic event at $T \sim 100$ ºC, which can be identified with the removal of physically adsorbed water and alcohol, remained in the sample after the hydrolysis and polycondensation of the inorganic components in the sol-gel process. Afterwards we can observe a broad and large exothermic event in the temperature range 200-600 ºC for Dy containing sample, respectively two exothermic events, between 200-600 ºC and 800-1200 ºC, also large and broad for yttrium containing sample.

The thermaly treated samples at $T = 500$ ºC for 1 h, and at $T = 1200$ ºC for 24 hours were than analysed by X-ray diffraction, in order to determine their structure.

In Fig. 5 are presented the X-ray diffraction patterns of as prepared aluminosilicates samples with identical composition, but prepared from two different precursors of

SiO_2. In both cases the identified crystalline phases are crystoballite and mullite. For the sample prepared from TEOS (Fig. 5b) the amorphous phase and mullite are prevalent.

The average crystallite size was determined by using the Scherrer equation [12]. For crystoballite crystals the determined average size is 12.8 nm in the sample prepared with silicic acid (Fig. 5a) and 8.4 nm in the sample prepared with TEOS (Fig. 5b).

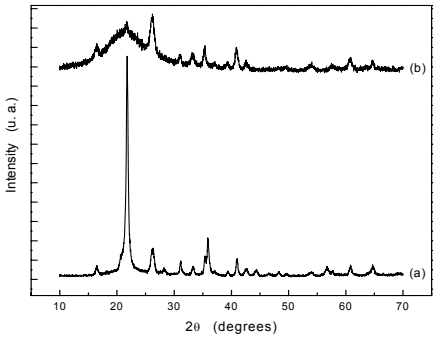

Fig. 5. XRD patterns for $80SiO_2 \cdot 20Al_2O_3$ samples prepared with silicic acid (a) and with TEOS (b).

Fig. 6 illustrates the X-ray diffraction patterns recorded from iron containing samples of similar composition, prepared under identical conditions, but thermally treated at 500º and 1200 ºC, respectively. The identified phases are hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), mullite ($Al_6Si_2O_{13}$) and crystoballite (SiO_2).

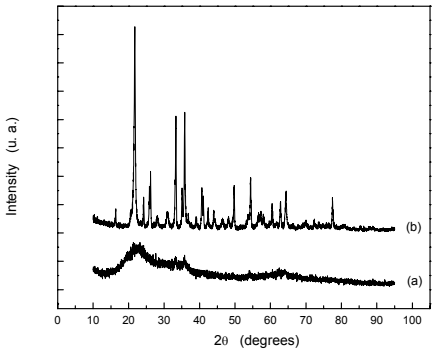

Fig. 6. XRD patterns for $60SiO_2 \cdot 20Al_2O_3 \cdot 20Fe_2O_3$ samples thermally treated for 1 hour at 500 (a), respectively for 24 hours at 1200 ºC (b).

Using the Scherrer formula, we determined for the crystoballite crystals 23.2 nm. The size of hematite crystals is 10.3 nm, for the sample treated at T = 500 ºC, and 30.2 nm for the sample treated at T = 1200 ºC. One can remark that for the samples treated at 500 ºC we obtained maghemite nanocrystals of ~10 nm, that implies superparamagnetic behaviour and recommend them to be considered for magnetic hyperthermia [13]. The current thinking is that superparamagnetic particles are the most promising agents of hyperthermia [14].

4. Conclusions

The thermal analysis measurements on aluminosilicate samples prepared by the sol-gel route from both silicic acid and TEOS as Si_2O source reveal endothermic events related to dehydration, dehydroxylation and decomposition of the organic phase, as well as events related to crystallisation process. They depend on the nature and content of transitional metal oxide added to the aluminosilicate matrix. For the samples prepared from silicic acid as precursor the dehydration appears at lower temperature than for those prepared from TEOS. The X-ray diffraction results reveal that after drying at 110 ºC the samples from silicic acid as precursor are vitreous, while those prepared with TEOS present some crystalline phases. After heat treatment applied at 500 ºC and 1200 ºC, crystalline phases of hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), mullite ($Al_6Si_2O_{13}$) and crystoballite (SiO_2) type are developed, with crystals of nanometric size.

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