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Zeolites from fly ash embedded in a thin niobium oxide matrix for optical and sensing applications

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Abstract. Thin films consisting of a sol-gel Nb2O5 matrix doped with fly ash zeolites in different volume fractions were deposited by the method of spin-coating. Zeolites of Na-X phase were prepared by long-term alkaline atmospheric conversion of coal ash collected from the electrostatic precipitators in TPP “AES Galabovo” supplied by lignite coal from the “Maritza East” basin using two different molarities of alkaline activator (NaOH). The surface morphology and structure of zeolite powders and films were studied by scanning electron microscopy and X-ray diffraction, respectively. Optical constants (refractive index and extinction coefficient) along with thickness of the films were calculated using a previously developed procedure comprising two steps of nonlinear minimization of the discrepancies between the measured and calculated reflectance spectra of films deposited on silicon substrates. The liquid adsorption and vapor sensing ability of fly ash zeolites were tested by measuring the reflectance spectra of the films prior to and after exposure to probe acetone molecules. The application of zeolites from fly ash for optical sensing is demonstrated and discussed.

1. Introduction
Fly ash (FA) is an industrial waste material produced by the combustion of coal in coal fired power stations when used as a fuel source. It can cause many environmental problems if discharged to the air. It is also harmful for people’s health because it contains a variety of heavy metals and radionuclides carried by small particles, typical with diameters of less than 2.5 microns, that can easily be inhaled or digested through drinking water. Thus, efficient utilization of fly ash that diminishes its disposal is one important issue for environmental protection. FA has been studied for many potential applications such as the synthesis of geopolymers, the manufacture of glass and ceramics, soil amelioration agent, for use as low-cost catalysts, and for adsorbents for air and water pollutants [1,2]. In addition, due to the high silica and alumina content, fly ash can be converted into zeolite [3-6]. The synthesized fly ash zeolites (FAZ) are preferable when adsorption issues are concerned because they are more crystalline, possess mixed micro-mesoporous structures that facilitate mass transport phenomena, and have more voids and channels on their surfaces [7]. Zeolites synthesized from fly ashes have already been implemented for adsorption of NOx, SO2, CO and other harmful air pollutants [8], removal of fluoride from drinking
water [7] and heavy metal cations such as Cu(II), Pb(II) and Zn(II) from wastewater [9,10], and as an anticancer agent for alternate or complementary therapy [11].

In most cases, the synthesized zeolites are used in powder form that sometimes is inconvenient from the viewpoint of reutilizing. Therefore, in the present paper we study fly ash zeolites deposited in thin film form which according to our knowledge is done for the first time. In order to deposit thin films with good optical quality that is essential for optical sensing application, we incorporate FAZ particles in a niobium oxide matrix thus overcoming to a great extend the scattering. We have already demonstrated that the sensing properties of oxide/zeolite composites substantially improve as compared to an undoped matrix benefitting additionally from tunable optical properties [12].

The goal of this paper is to prepare composite thin films consisting of Nb$_2$O$_5$ matrix doped with synthesized FAZ in different volume fractions and to study their optical and sensing properties.

2. Experimental part

Fly ash (FA) used as a starting material for the synthesis of zeolites was collected from the electrostatic precipitators in one of the biggest Thermal Power Plants in Bulgaria TPP “AES Galabovo”, which is supplied by domestic lignite coal from the “Maritza East” basin. Chemical and phase composition of the raw FA studied by a combination of classical and instrumental analytical methods was summarized in [6].

Zeolite samples FAZ1 and FAZ2 were prepared by long-term alkaline atmospheric conversion of fly ash at molarities of 1.25 M and 1.50 M of the alkaline activator NaOH, respectively. The ratios of the alkaline activator to coal fly ash were 0.5 and 0.6 for FAZ1 and FAZ2, correspondingly. The obtained fly ash zeolites were characterized with respect to their phase composition by X-ray diffraction using Bruker D8 Advance diffractometer with CuKα-radiation and a Ni filter, while their morphology was investigated by scanning electron microscopy using a MIRA 3 TESCAN microscope.

Thin composite films comprising a Nb$_2$O$_5$ matrix with embedded FAZ particles were deposited on silicon substrates by the method of spin-coating and annealed at 320 °C. Niobia matrix, prepared by the sol-gel method [13] was mixed with 5 wt% dispersion of FAZ particles in ethanol in a volume concentration of 1, 2.5 and 5 %. The refractive index, extinction coefficient and thickness of FAZ-Nb$_2$O$_5$ composites were calculated from reflectance measurements (Cary 5E, Varian) using previously developed two-stage curve fitting [13]. A liquid sensing experiments were performed by measuring reflectance spectra prior to and after exposure to liquid acetone at one and the same spot using an optical profiler (Zeta-20, Zeta Instruments) with a built-in spectrometer. For the vapor sensing experiments the samples were put in a measuring cell and their reflectance spectra are collected in air, argon and acetone vapors atmospheres [14].

3. Results and discussion

It was found [6] that the raw FA contains about 47 wt. % SiO$_2$ and 23 wt % Al$_2$O$_3$, which means that the aluminosilicate part predominates in its composition and makes it suitable for the synthesis of zeolites. The molar ratio of SiO$_2$/Al$_2$O$_3$ is approximately 3.4 making this FA a suitable starting material for the synthesis of high-silica zeolites of the faujasite type [4]. Experimental X-ray diffractograms of the studied FAZ are plotted in figure 1 in comparison with a pattern of a faujasite type (FAU) zeolite regarded as a referent one. Obviously, both studied samples refer to the faujasite phase as their main diffraction lines coincide with those of the referent zeolite. It may be expected that the supplementary crystalline phases that are resistant to alkaline treatment be transferred from the raw FA into the reaction products. Therefore, the reflexes of quartz (Q), magnetite (M) (Fe$_3$O$_4$), hematite (H) (α-Fe$_2$O$_3$) and anorthite (A) (CaAl$_2$Si$_2$O$_8$) are also observed in figure 1.

Figure 2 presents SEM pictures of FAZ1 and FAZ2 in powder form. Both zeolites are composed of agglomerates with a size of 1-2 μm and have an octahedral shape typical of the FAU crystalline phase. Although the two zeolites are very similar, they have different behaviour when added in Nb sol. From the SEM pictures of the surface of thin Nb$_2$O$_5$ films doped with FAZ1 and FAZ2 presented in figure 3 it is seen that FAZ1 is buried in the oxide matrix and is mostly covered with it, while the FAZ2 particles...
are mainly found on the surface and are not veiled by the oxide. Different optical and sensing properties could be expected due to the different morphology observed.

**Figure 1.** X-ray diffractograms of FAZ1, FAZ2 and a referent zeolite of faujasite type (FAU): Q-quartz; A-anorthite; H-hematite; M-magnetite.

**Figure 2.** SEM pictures of fly ash zeolites powders FAZ1 (a) and FAZ2 (b)

The next step of our investigation concerns determination of the optical properties of deposited composites comprising niobium matrix and fly ash zeolites. Refractive index of Nb$_2$O$_5$ films with FAZ1 and FAZ2 particles with different doping levels are calculated from their reflectance spectra and are presented in figure 4(a). It is seen that the refractive index ($n$) of the films decreases with the addition of the FAZ particles mostly pronounced in the case of FAZ2 incorporation. Generally there is a substantial drop in refractive index of the doped thin film samples as compared to the undoped ones: the values of $n$ decrease from 2.14 to 1.65 / 1.61, 1.52 / 1.51 and 1.45 / 1.43 for FAZ1 / FAZ2 with concentrations of 1.0, 2.5 and 5.0 %, respectively. Simultaneously there is a slight increase in extinction coefficient from 0.018 for the undoped sample to 0.020 for the heaviest doped one that could be associated with slightly increased scattering due to the rougher surface.

The thickness of the studied thin films as a function of FAZ concentration is presented in figure 4(b). It is seen that the addition of FAZ particles results in an increase in films thickness mostly pronounced for FAZ2 zeolites.
Figure 3. SEM pictures of thin films comprising sol-gel Nb$_2$O$_5$ matrix with embedded fly ash zeolites FAZ1 (a,b) and FAZ2 (c,d) at different magnifications.

Figure 4. Dispersion curves of refractive index (a) and dependence of thickness on zeolite concentration (b) of thin Nb$_2$O$_5$ films embedded with fly ash zeolites FAZ1 and FAZ2.

Considering both that the weight amount of FAZ1 and FAZ2 is the same and their shapes and sizes are very similar we could assume that the incorporation of FAZ particles is accompanied with the introduction of additional free volume (air) in the samples which volume fraction is different for the two FAZ-doped samples thus leading to different levels of swelling of Nb$_2$O$_5$ matrix. Further, the stronger swelling in the case of FAZ2 indicates more free volume in these films. This assumption is confirmed by the smaller refractive index values of films doped with FAZ2. It is seen from figure 4(a) that for all the studied concentrations the incorporation of FAZ2 particles leads to lower values of the refractive index as compared to FAZ1 particles. Therefore the FAZ2 composites are less dense as compared to the FAZ1 ones and have more free volume. Thus considering the presence of porosity we assumed that the immersion of samples in liquid analyte will lead to analyte penetration in the empty pores and a subsequent increase in the effective refractive index and drop in the measured reflectance of the sample. To verify this we measure reflectance spectra for Nb$_2$O$_5$ thin films doped with FAZ2 particles before and after immersion in liquid acetone for 5 min and calculate the acetone induced change in reflectance (figure 5).
Figure 5. Measured reflectance before and after immersion in liquid acetone (a) and liquid acetone induced change of reflectance at wavelength of 650 nm (b) for thin Nb$_2$O$_5$ films doped with FAZ2 particles in denoted concentrations.

A decrease in reflectance after immersion is seen in all samples that confirms the expected increase in effective refractive index due to replacement of air in the pores with acetone with a higher refractive index. Interestingly, with an increasing in the zeolite concentration above 2.5% a decrease of the reflectance change is observed (figure 5b) although the free volume is the highest for the heaviest doped sample. A possible reason could be the different ratio of open to closed porosity with a predominantly closed type for 5% doped sample.

The final step of our investigation concerns vapor adsorption of the oxide-zeolite composites. Accordingly, the reflectance spectra of films is measured prior to and after acetone vapor exposure and vapor-induced relative changes in reflectance ($\Delta R/R$) are presented in figure 6. It should be noted that all adsorption measurements are performed at room temperature. The vapor-induced changes are similar for both types of FAZ particles and are slightly influenced by the concentration. As in the case of liquid acetone, a small decrease in the response for the 5% FAZ2 doped films is observed.

Figure 6. Zeolite concentration dependence of relative change in reflectance induced by exposure to acetone vapors of FAZ1 and FAZ2 zeolites embedded in thin Nb$_2$O$_5$ films annealed. Measurements are conducted at room temperature.
In our previous investigation [14] we demonstrated an enhancement of the sensitivity of acetone sensing by Bragg stacks comprising Nb$_2$O$_5$ and zeolite thin films after annealing at 450 °C. However, in the present case, for Nb$_2$O$_5$ / FAZ composite, annealing at 450 °C does not lead to an improvement. Indeed there is a slight drop in relative reflectance change (not shown here). This could be due to the contraction of the oxide matrix and a decrease in the total pore volume.

4. Conclusions
The successful deposition of composite thin films comprising a Nb$_2$O$_5$ matrix and fly ash Na-X zeolite in concentrations of up to 5% is demonstrated. Long-term alkaline atmospheric conversion of fly ash at two different molarities (1.25M and 1.5M) of the alkaline activator (NaOH) is applied for Na-X zeolite synthesis. A decrease of refractive index and increase of thickness of the composite films relative to the undoped matrix are obtained in both cases associated with porosity generation in the films and mostly pronounced for the zeolite sample synthesized at higher molarity. The presence of porosity is verified and confirmed by reflectance measurements of the films before and after exposure to acetone in liquid and vapour physical states. Changes in reflectance are detected in both cases but they are stronger for liquid acetone. The vapor-induced changes are similar for both types of fly ash zeolites and are slightly influenced by concentration, while for liquid acetone a reduction of response is observed for heavily doped sample (5%).

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