*Proceedings*

# Effect of Milling Time on the Sensing Properties of Fly Ash Zeolite Composite Thin Films †

**Katerina Lazarova [1,*], Silviya Boycheva [2], Marina Vasileva [1], Denitza Zgureva [3] and Tsvetanka Babeva [1,*]**

[1] Institute of Optical Materials and Technologies ''Acad. J. Malinowski'', Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 109, 1113 Sofia, Bulgaria

[2] Technical University of Sofia, Department of Thermal and Nuclear Power Engineering, 8 Kl. Ohridsky Blvd. 1000 Sofia, Bulgaria

[3] Technical University of Sofia, College of Energy and Electronics, 8 Kl. Ohridsky Blvd. 1000 Sofia, Bulgaria

* Correspondence: klazarova@iomt.bas.bg (K.L.); babeva@iomt.bas.bg (T.B.); Tel.: +359 02-979-3521 (K.L.)

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**Abstract:** : Thin films consisting of a sol-gel $Nb_2O_5$ matrix doped with zeolite Na-X synthesized from fly ash through ultrasonic-assisted double stage fusion-hydrothermal alkaline activation were deposited by the spin-coating method. In order to improve the optical quality and sensing properties of the thin films zeolites were wet-milled for 60, 120 and 540 seconds prior to incorporation in the film. The liquid adsorption ability of thin films were tested by measuring the reflectance spectra prior to and after exposure to liquid acetone and the change in the reflection coefficient ΔR of the films was calculated. The influence of milling time of zeolites on the sensing and optical properties of the films was studied.

**Keywords:** optical sensor; sol-gel; $Nb_2O_5$; thin films; zeolites; fly ash

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## 1. Introduction

Adding zeolites to a metal oxide matrix is one possible way to increase overall porosity when deposited in form of thin film [1]. In addition to the intrinsic microporosity of the zeolites, it is also possible additional free volume (air) to be introduced into the samples with different volume fractions depending on the concentration and size of the zeolite particles [2]. Example of rare natural zeolites is Faujasite (FAU) and its synthetic sodium form - Na-X is widely used because of its structural supercage, large pore size and high specific surface area [3]. Zeolite Na-X can be obtained by utilizing waste aluminosilicates, including fly ash (FA) from coal combustion. FA generated as a by-product in the energy production from coal-fired Thermal Power Plants (TPP) typically contains above 70 wt. % of amorphous and crystalline aluminosilicates [4]. Different synthesis approaches have been studied for the conversion of FA to zeolites, among which the atmospheric crystallization, alkaline hydrothermal activation and double-stage fusion-hydrothermal synthesis have been considered as the most technologically viable. Zeolite Na-X, which crystallizes as a metastable phase upon alkaline activation of FA, can be obtained by all three synthesis techniques. However, the highest degree of conversion of raw FA to a single Na-X phase is achieved by applying two-stage synthesis. The high-temperature alkaline fusion stage preceding the hydrothermal synthesis facilitates the conversion of the resistant crystalline phases from the FA composition, such as quartz, mullite and anorthite in soluble alkaline silicates and aluminates and their assimilation in the final product. When ultrasonic treatment is applied for homogenization of the reaction mixture between the fusion and hydrothermal stages, a nanocrystalline structure of the obtained zeolite Na-X is achieved with fine distribution in the zeolite matrix of the iron oxides transferred from the raw FA [5]. Moreover, the ultrasonic fragmentation of the crystallization seeds increases the external surface of the zeolite particles, which is essential for their application as sensor materials.

In this paper, the effect of zeolites milling time on optical and sensing properties of $Nb_2O_5$ thin films doped with Na-X zeolites synthesized from coal fly ash was studied. Zeolites were wet-milled for 60, 120 and 540 seconds prior to the incorporation in the sol-gel matrix in order to achieve different levels of porosity. Optical and sensing properties were studied through reflectance measurements before and after exposure to testing analyte (liquid acetone in this case).

## 2. Materials and Methods

FA was sampled from the electrostatic precipitators of the lignite coal supplied TPP "AES Galabovo" in Bulgaria in order to be utilized for the synthesis of zeolite Na-X. Powder samples were synthesized by ultrasonic-assisted double stage fusion-hydrothermal alkaline conversion and were studied with respect to their phase composition, morphology and surface properties [6]. Zeolite powders were subjected to wet ball milling with a PULVERISETTE 23 Mini-Ball Mill (FRITSCH) for 60, 120 and 540 s and 50 osc/min, as 0.08 g of Na-X powder were added to 3 ml distilled water.

For the deposition of metal oxide thin films 0.010 ml zeolites from the milled water solution was mixed with 0.030 ml ethanol and then added to 0.190 ml Nb sol [7].

Thin $Nb_2O_5$-Na-X films were deposited by spin-coating at a rate of 4000 rpm for 60 s by dropping of 0.3 mL of the sol/zeolite solution on pre-cleaned Si substrates. After deposition, the films were annealed in air at 320 °C for 30 min. The thickness and optical constants (refractive index *n* and extinction coefficient *k*) were determined from the measured reflectance spectra of the films at a normal light incidence using a non-linear curve-fitting method [8]. In order to study sensing properties of the films reflectance spectra were measured prior to and after exposure to liquid acetone using 3D Optical profiler, Zeta-20, Zeta Instruments.

## 3. Results and Discussion

Measured reflectance spectra R of all thin films are similar but the calculations of the thickness *d* showed that increasing of milling time leads to decrease of *d* from 38.0 nm (60 s) to 35 nm (540 s), while refractive index *n* of the films increases from 1.72 to 1.83, respectively. Extinction coefficient *k* showed no change with milling time of zeolites–0.019.

The liquid adsorption ability of thin Na-X films were tested by measuring the reflectance spectra prior to and after exposure to liquid acetone and the change in the reflection coefficient ΔR of the films was calculated. Figure 1 shows reflectance spectra R measured in air (blue curve) and after exposure to liquid acetone (green curve) for the thin film doped with zeolites milled for 60 s.

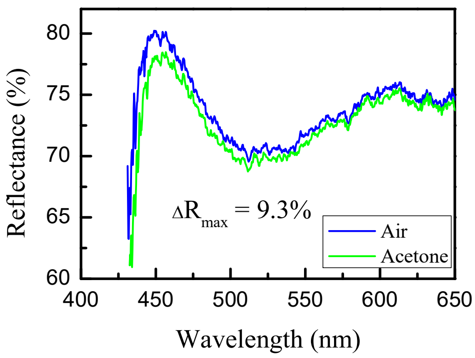


**Figure 1.** Reflectance spectra R in air (blue line) and after exposure to liquid acetone (green line) for $Nb_2O_5$ thin film doped with fly ash zeolites milled for 60 s.

Maximum change in R is observed for milling time of 60 s - ΔR = 9.3 % for wavelength 435 nm. The increase of milling time to 540 s leads to decrease of reflectance change ΔR almost twice. Possible reason for this is the decrease in the proportion of micro and mesopores with increasing grinding time.

## 4. Conclusion

The successful deposition of composite thin films comprising $Nb_2O_5$ matrix and fly ash Na-X zeolites milled for 60 s, 120 s and 540 s is demonstrated. An increase of refractive index with increasing the milling time of zeolites is observed probably due to decrease of thickness of the composite films or decrease of porosity. Different levels of porosity are obtained and confirmed by reflectance measurements of the films before and after exposure to acetone in liquid state. Measured reflectance change is decreasing with increasing the milling time of the zeolites. The greatest liquid-induced change in R is observed for thin film sample doped with zeolites milled for 60 s—9.3%.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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