Optical and sensing properties of thin films from Na-X zeolites synthesized from fly ash.

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1. Coal ash - pollutants and possibilities for their utilization

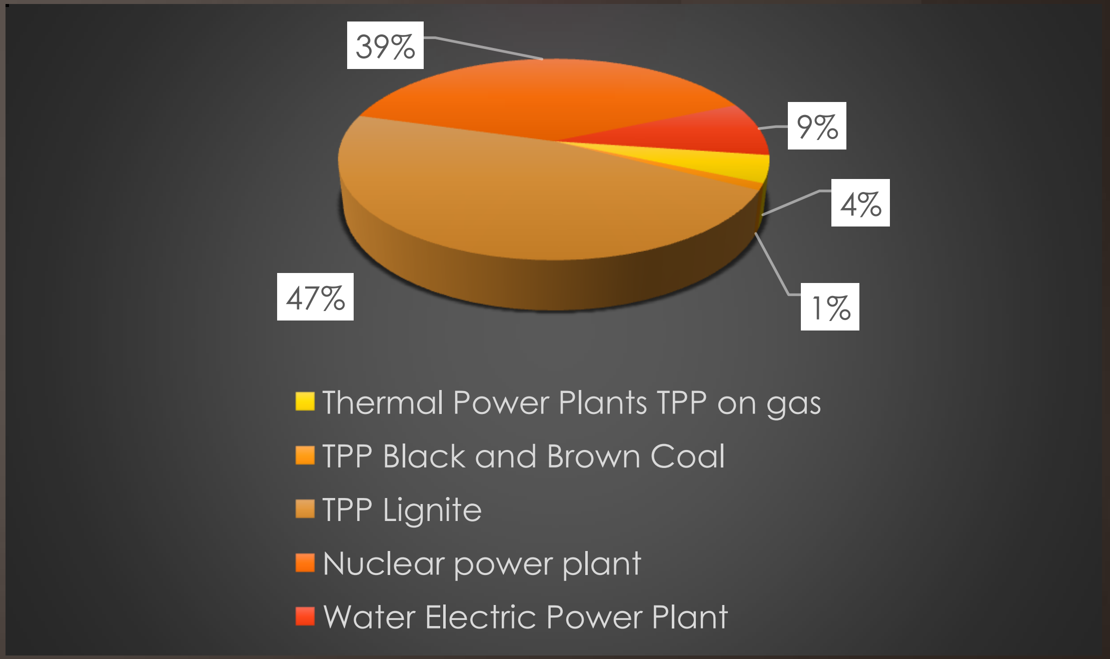
Coal is the largest source of energy from fossil fuels used for generating electricity in the world

releases of gaseous emissions - sulfur, nitrogen and carbon oxides

generation of solid waste - ash

- Its macro-component composition is considered as an alumosilicate material.
- Different opportunities for utilization have been explored, including for the synthesis of zeolites.

The electricity produced in Bulgaria in 2017, allocated according to the primary energy resource and the used production technology.



1. Coal ash - pollutants and possibilities for their utilization

Carbon dioxide CO_2

Volatile Organic Compounds (VOCs)

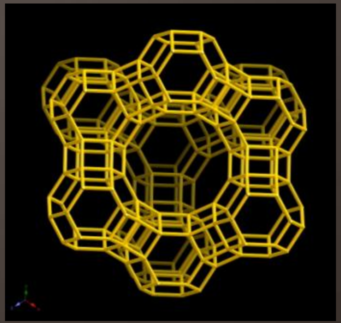
Greenhouse effect

! For the purposes of developing CO_2 capture technologies in the search for new solid phase sorbents, **zeolites** have also been studied.

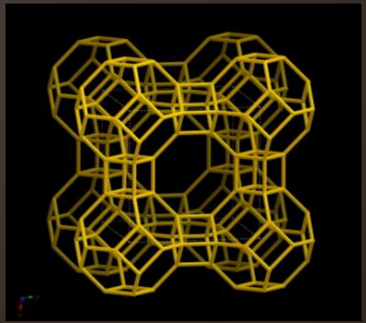
They have valuable features such as :

- adsorbents
- catalysts
- ion exchangers
- separators

Zeolites are materials with a unique porous structure with active centers and mobile cations of alkaline and alkaline-earth metals. !



FAU



LTA

2. Na-X(FAU) zeolites

High silica zeolite?

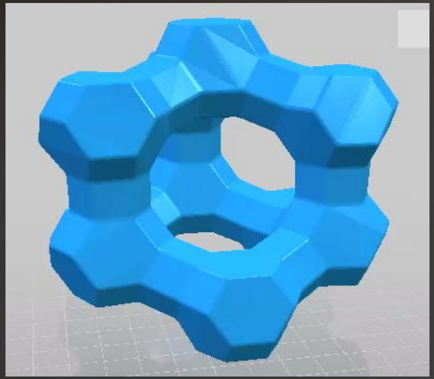
HIGH SILICA ZEOLITE

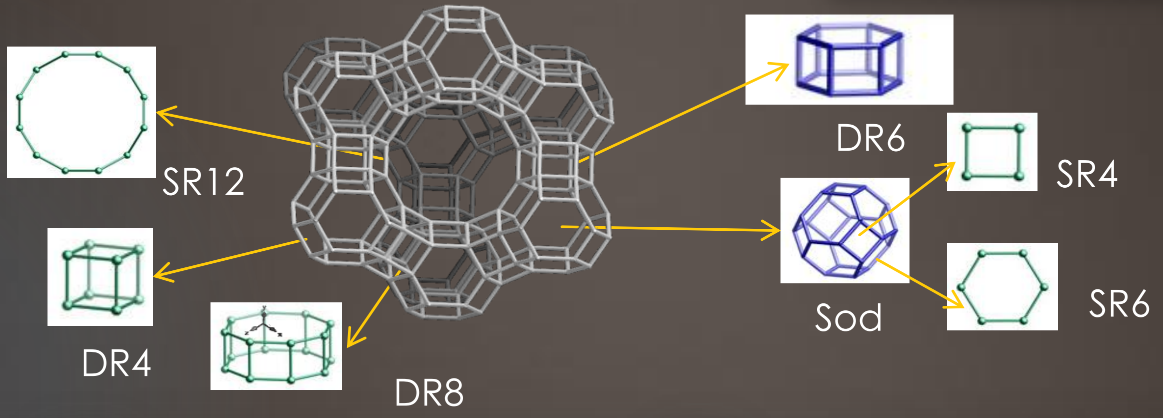
$|(Ca^{2+},Mg^{2+}Na^{+}_{2})_{29}\ (H_2O)_{240}|\ [Al_{58}Si_{134}\ O_{384}]$

Maximal diameter of sphere:
- ✓ To be included in the structure - 11.24 Å
- ✓ To diffuse around the structure - 7.35 Å

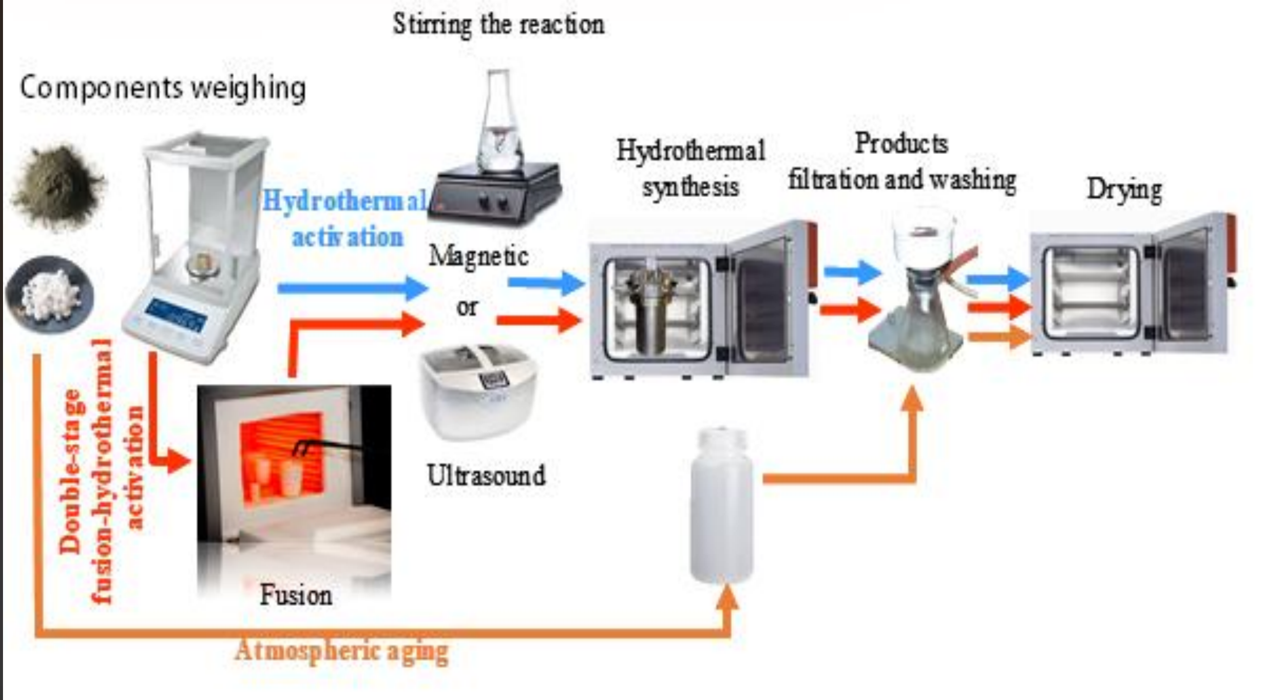
Free volume: 27 %

FAU



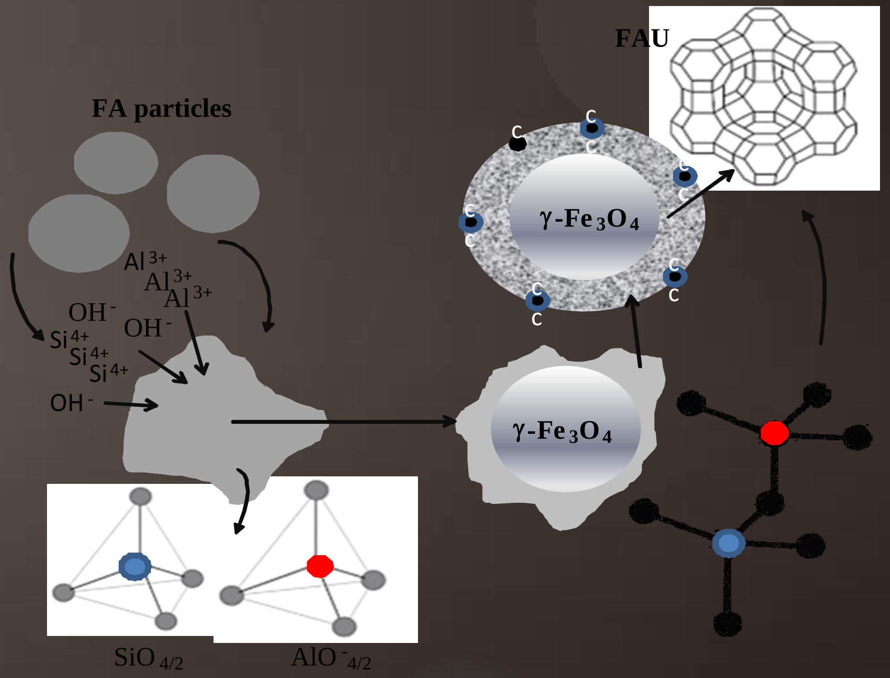


2. Na-X(FAU) zeolites



Coal ash alkaline conversion to zeolites

Integrated scheme of the synthesis approaches



Three synthesis approaches:

- Hydrothermal activation
- Double stage fusion-hydrothermal activation
- Atmospheric crystallization – Quasi-natural crystallization process

2. Na-X(FAU) zeolites

LTA and FAU zeolites have the highest carbon capture potential

highly developed specific surface

FAU	LTA
Pore size 7.35Å	Pore size 4.21Å
Free volume 27.42 %	Free volume 21.43 %

Allowing the physical adsorption of molecules of CO_2 from size 3.2 Å

!

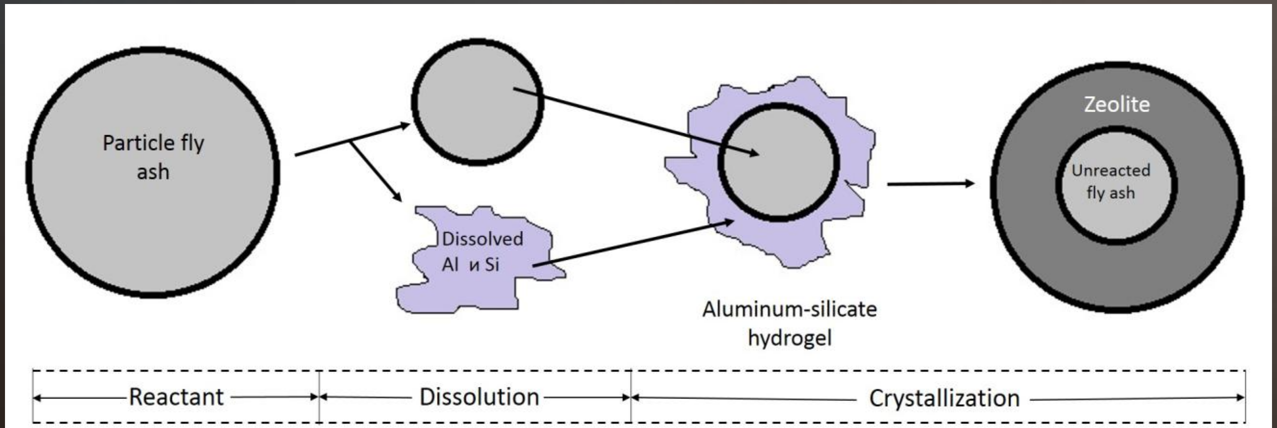
Zeolite from coal ash ≠ They are distinguished from zeolites synthesized from pure starting materials

High content of iron oxides (γ-Fe2O3, a-Fe2O3, γ-Fe3O4)

+

In combination with microcomponents such as Cu, Co, Mn, V, W

= Determine their good catalytic activity

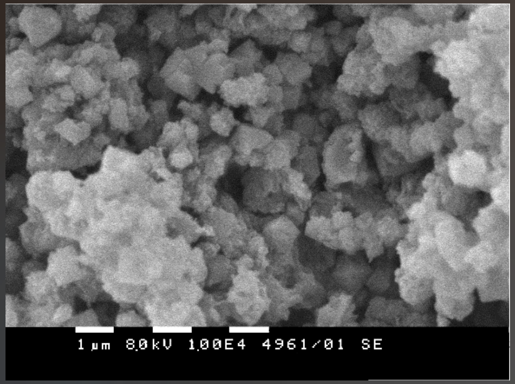


<u>The process is carried out in three stages:</u>

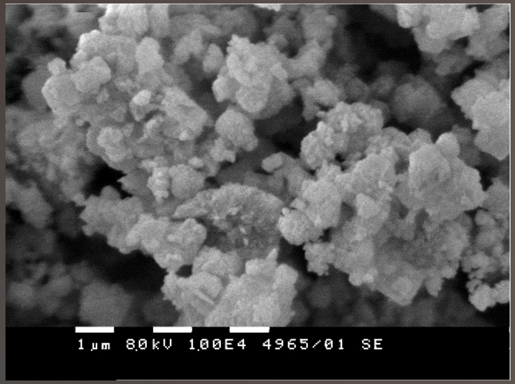
1) Dissolving aluminosilicates of the ash in the alkaline solution;
2) Precipitation of an alumosilicate hydrogel;
3) Crystallization of zeolite from the alumosilicate gel on germinator.

2. Na-X(FAU) zeolites

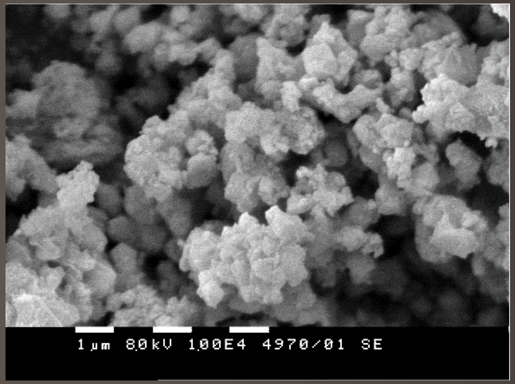
Na-X type zeolites obtained → Zeolites are subjected to subsequent wet milling in a ball mill to reduce their size to sub-micron values.



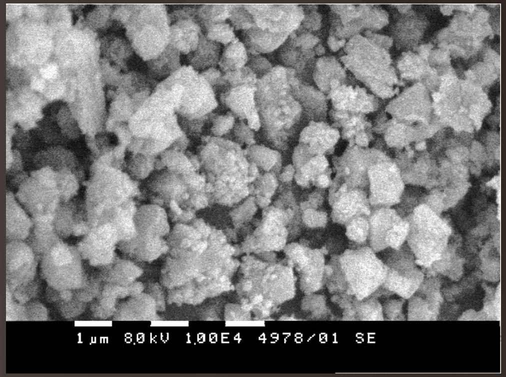
Not milled zeolites Na-X



Milled 60 seconds



Milled 120 seconds



Milled 540 seconds

2. Na-X(FAU) zeolites

- ✓ Crystalline character
- ✓ Micro-porosity
- ✓ Their ion-exchange properties

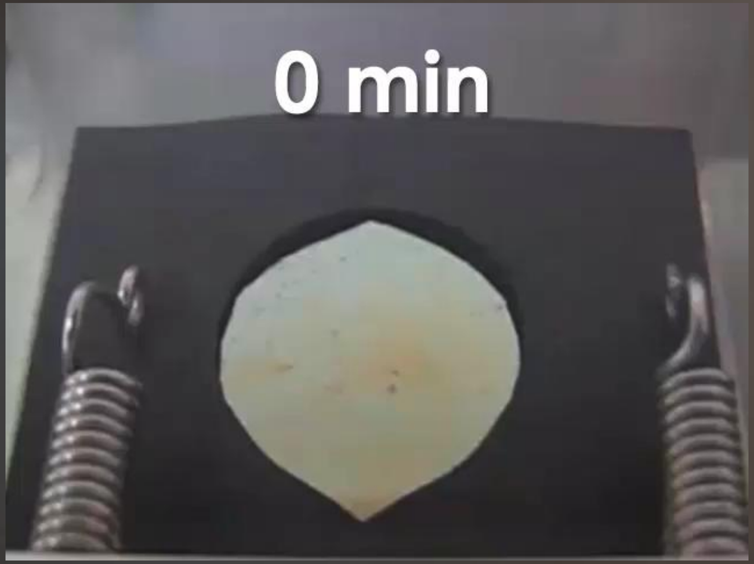
→ Intelligent photonic crystals with extended functionality focused on their adsorption capabilities.

↓

Thin layers of nano-crystalline zeolites that alter their effective refractive index when adsorbing gas or liquid.

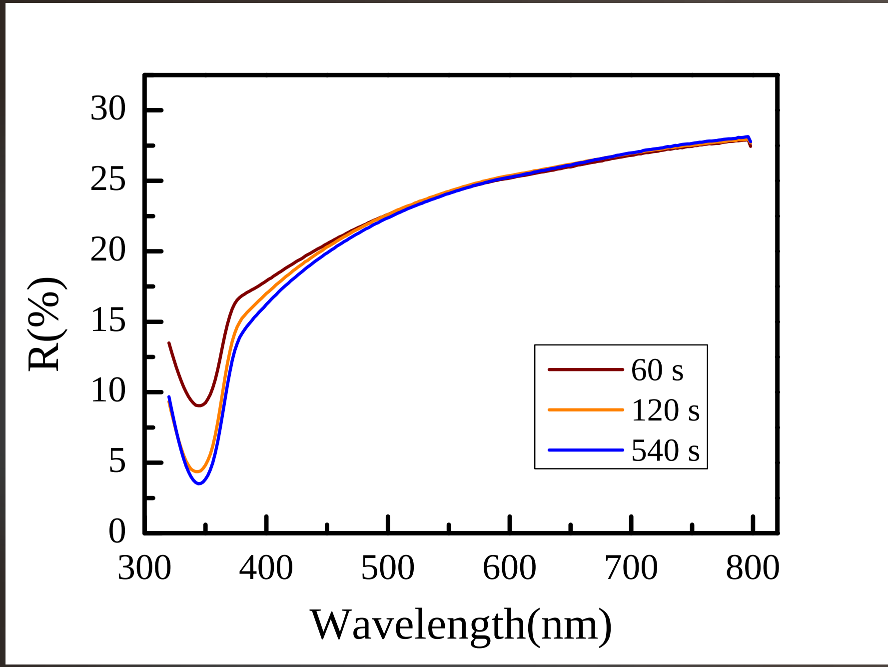
↓

They perform the function of a sensitive and transducer element in the sensor for analyzing fluids and vapors of volatile organic compounds.



3. Thin films from Nb_2O_5 doped with milled zeolites

Sol-gel method → Spin-coating → Thin layers from Nb_2O_5 doped with zeolites → Deposited on a silicon substrate, Speed - 4000 rpm, Heated for 30 min at 320°C

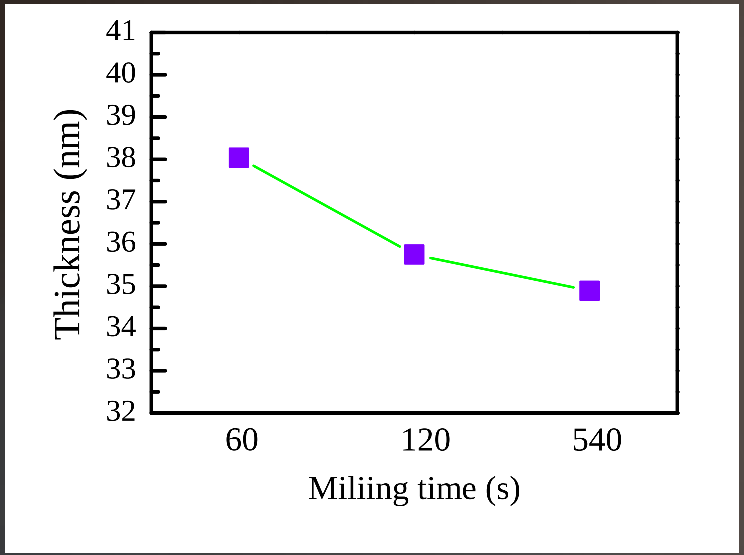


→ n, k и d - calculated by nonlinear algorithm for minimizing the difference between measured and calculated values of the reflectance R

d≈70nm

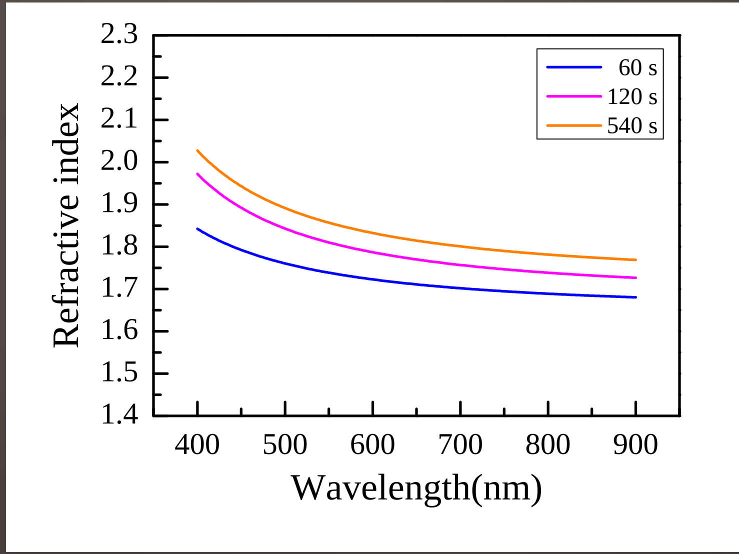
	Nb_2O_5	Nb+ FAU Milled 60 s	Nb+ FAU Milled 120 s	Nb+ FAU Milled 540 s
n	1.97	1.72	1.76	1.83
k	0.019	0.017	0.018	0.019

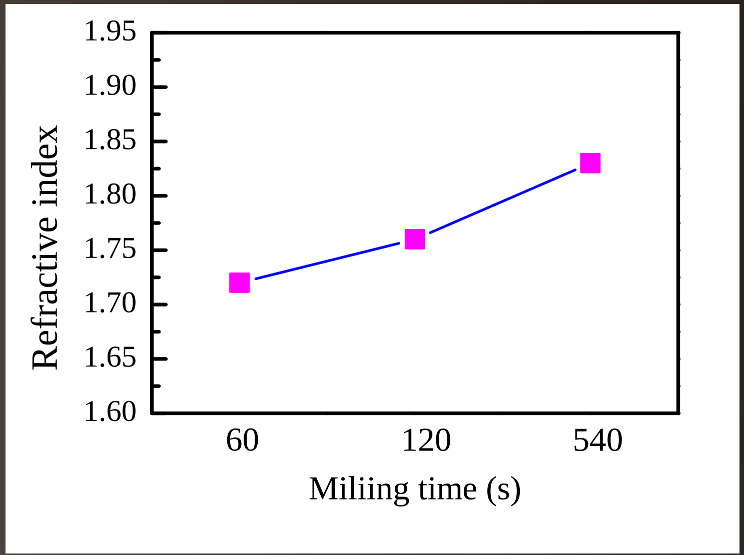
4. Characterization of thin composite films - optical and sensing properties



Increasing of milling time leads to decrease of *d* from 38.0 nm (60 s) to 35 nm (540 s)

dispersion of refractive index

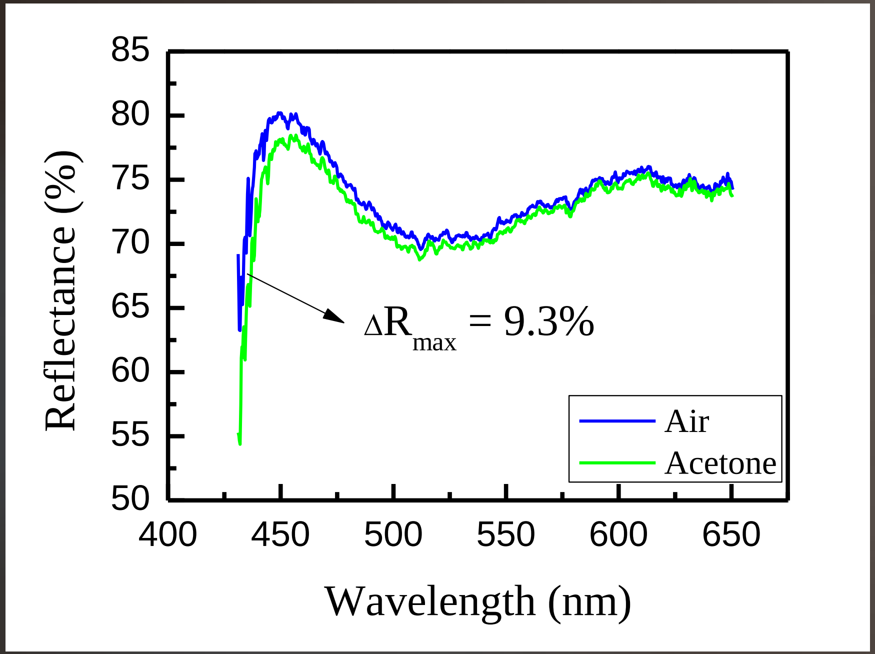




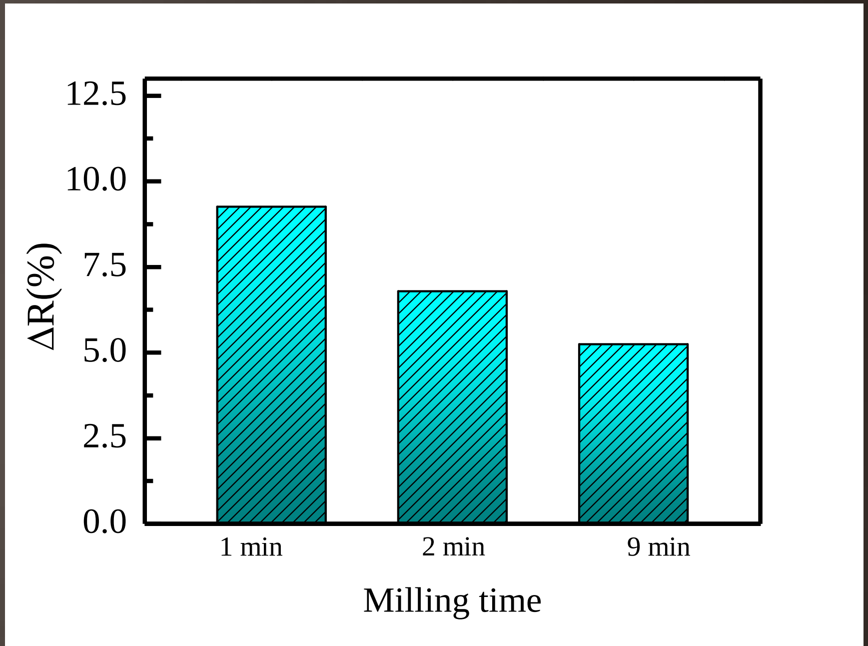
Refractive index *n* of the films increases from 1.72 to 1.83 when milling time increases.

4. Characterization of thin composite films - optical and sensing properties

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:



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.

5. Summary

- ✓ 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.
- ✓ Depending on the milling time, 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 %.

Thank you for attention!

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