Optical Properties of Natural Armenian and Syrian Zeolites

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Received 22 April 2020

Abstract. We study the luminescence properties of natural Syrian and Armenian zeolites. The luminescence properties are studied in the UV-visible (390 - 450 nm) and red-near infrared IR (620 - 800 nm) regions of the spectrum. The excitation is performed using a light of 370 nm of wavelength at temperature equal to 290 K. We conclude from the measurement of optical characteristics that the studied zeolitic samples are of a complex structure and present a complex intergrowth. We also observe the twin cross-form structure of the chabazite crystals.

Keywords: Natural zeolites; Optical, Luminescence, UV and IR spectrum.

1. Introduction

The natural Armenian zeolite contains up to 85% of clinoptilolite including Si / Al at 9.8% and amorphous SiO_2 at less than 3%. The Syrian zeolitic tuff contains mainly about 50% of three types of zeolite (analcime, phillipsite and chabazite). Other contaminations in raw materials for Armenian natural zeolite are: feldspar -5%, quartz -5%, mica -2%, clays -3%. These values differ widely in the case of natural Syrian zeolite where the availability of calcite, quartz, clays and amorphous phase is proven in most samples. The quantity of each of the mentioned minerals depends on the location where the sample was taken along the borehole.

Environment's contamination by heavy metals has long been recognized as a cause of serious health problems, and increasing pressure is being put on industries to reduce their heavy metal's wastes. Current abatement and remediation procedures for wastes containing heavy metals include pH adjustment with hydroxides, other precipitation methods, reverse osmosis, coagulation-sedimentation and the use of organic ion-exchangers. Such processes, however, have drawbacks that limit their use [1]. Natural zeolites have an excellent cation exchange capacity among other naturally occurring products, which enables them to be used as cation exchangers.

They frequently display good selectivity for heavy metal cations, which makes them valuable for the purification of industrial wastewater [2]. Very interesting results were obtained about lead removal from water [3-10]. Colella and Pansini [4,5] demonstrated the favorable behavior of *Na*-loaded chabazite towards *Pb*. Selectivity and efficiency were as high as 91 and 76% respectively, provided that the concentration of competing ions is less than that of tap water. As far as *Na*-phillipsite is concerned, Pansini [11] reported that all data gave high values of working cation exchange capacity, selectivity and efficiency even in the presence of competing cations.

Clinoptilolite with the simplified formula $(Na, K)_6 Si_{30}Al_6O_{72}.nH_2O$ is the most common natural zeolite found mainly in sedimentary rocks of volcanic origin. Such deposits aroused strong commercial interest because clinoptilolite tuffs are often rather pure and can be treated with simple techniques. Tarasevich et al. [12] performed K^+ and Pb^{2+} exchange experiments on *Na*-exchanged forms of two different natural clinoptilolite samples and noted different selectivity for these samples although the difference in the SiO_2 / Al_2O_3 ratio was insignificant and the cation exchange capacities were virtually the same. Additional exchange isotherms of Pb^{2+} (solution) $\rightarrow 2Na^+$ (clinoptilolite) were recorded [13,14] under comparable conditions as in [12]. However, a maximum exchange level of *Ca*.80% [13,14] is in contrast to *Ca*.95% for two different samples [12]. Such discrepancies in the exchange behavior were discussed by Langella et al. [14] concluding that the cation exchange selectivity of clinoptilolite is markedly dependent on its original cationic composition, as not all the cationic sites in the structure can be made available for exchange (for more details concerning the applications of clinoptilolite, look at the review of Armbruster [15]).

On the other hand, the first data on luminescence properties of zeolites were published during the second half of the 20th century [16-18]. Therein, it was shown that the zeolite is able to irradiate under exposure of UV light at 365nm band. Although fully hydrated zeolite has not luminescence abilities, a considerable cathode-luminescence with hydration increase was obtained in clinoptilolite-heulendite systems [19-21]. Moreover, few luminescence spectral bands at visible region were obtained for silver form zeolite, and they are attributed to color centers with different charge state [22].

This work is intended to shed some light on the luminescence properties of natural Syrian and Armenian zeolites.

2. Materials and techniques

The luminescence spectra were measured in red (660-710nm) and ultra-violet (UVvisible, 390-450nm) regions under excitation of 370nm band. The luminescence measurements were carried out on standard equipment using 1kW Xenon lamp and SFspectrophotometer. A bandwidth at 280-400nm range was applied for excitation; the monochromatization of luminescence light was adjusted by DMR-4 monochromator. Optical devices like slits, filters etc. were also used. Spectral registration was carried out by photomultipliers in the 380-800nm bandwidth range. Measurements were carried out at room temperature (295*K*). First, all optical measurements were performed for the 'raw' samples containing 85% clinoptilolite. This was followed by chemical treatment in thermo- static vessel and mixer, with temperature at $85-87^{\circ}C$ during treatment time of 4 hours, with solid-liquid ratio equal to 1:5. After treatment, the samples were washed in Bunsen funnel under vacuum 10^{-1} Torr by distillated water with pH = 5.8-6.2 for HCl and pH = 7-7.5 for NaOH. After having been washed, the samples were dried for 3 hours at $120^{\circ}C$ with slowing rate of $5^{\circ}C/\text{min}$.

3. Samples' characterization

In this work, the investigated samples have been prepared from grounded Syrian (S and M) and Armenian (A) natural zeolites. The Armenian zeolite, denoted by A11, contains up to 85% of clinoptilolite with a ratio of Si/Al equal to 9.8 and amorphous SiO_2 less than 3%. The Syrian zeolitic tuff contains mainly about 50% of three types of zeolite (analcime, phillipsite and chabazite). Other contaminations in raw materials for Armenian natural zeolite are: feldspar -5%, quartz -5%, mica -2%, clays -3%. These values differ widely in the case of natural Syrian zeolite where the availability of calcite, quartz, clays and amorphous phase is proven in most samples. The quantity of each of the mentioned minerals depends on the location from which the sample was taken along the borehole. The results were obtained using chemical and thermo-gravimetric analysis. According to the latter, the endothermic effect of dehydration is observed at temperatures in the range of $70-300^{\circ}C$ with simultaneous mass loss of up to 8.2%. The chemical composition of the studied samples is given in the Table 1.

It is important to mention that natural zeolites of different deposits are different either by their chemical contents or by adsorbing properties. To date, the known zeolitic minerals are distributed on the earth surface in an inhomogeneous way. It is supposed that there is a clear relationship between the chemical contents of zeolitic minerals and their enclosing rocks. Concerning natural Syrian zeolites, which are characterized by a wide variation in contents (phillipsite, chabazite and analcime), they could be enclosed in different rocks and usually the contents of each zeolitic sample reflects the content of the enclosing rocks. For example, phillipsite, enclosed in the cavities of the basalt rocks, is characterized by a low content of silicon and a relatively high content of calcium, whereas phillipsite in other enclosing rocks may contain high percentage of silicon and alkaline.

One of the interesting morphologic characteristics of phillpsite is its tendency to form mimetic twins. The X-ray diffractometric investigation of the Syrian samples shows that all samples transfer to meta-phillipsit. The thermal stability of meta-phillipsite strongly depends on the initial content of the samples. It was found, in agreement with available experimental results, that phillipsite of calcium-rich and silicon-low content is destroyed at temperature equal to $300^{\circ}C$, while phillipsite with sodium, potassium and silicon-rich content conserves its structure

up to temperatures in the range of 450 to $500^{\circ}C$. In general, phillipsites could be divided into three groups depending on the ratio Si/Al. In our case, corresponding to phillipsite phase in the studied Syrian samples, the ratio Si/Al is in the range of 1.3-2.4. This indicates that they are rich in calcium and that they are hydrothermal in nature.

Chabazites are also different according to the Si/Al ratio. In the chabazite vein, Si/Al ratio varies from 1.4 to 2.3 while in the sedimentary rocks this value varies from 2.8 to 4.0. Contrary to the case of phillipsite and clinoptilolite, a clear relationship between the ratio Si/Al and the dominant exchange cation was established in chabazite. In fact, the simple isomorphic replacements 2Na > Ca are characteristic of chabazite. Moreover, chabazite is one of the most porous natural zeolites. Its structure could be destroyed at temperature in the range of $700-800^{\circ}C$.

On the other side, analcime is one of the narrow porous molecular sieves. Our investigations show that analcim Ca-form has the largest adsorption ability and in non-active analcime, the main cation is Na.

4. Results and discussions

In the UV-visible region (Figure 1.a), we observed luminescence maxima at wavelengths 395nm, 405nm, 410nm, 425nm, while in the red region the corresponding values are -630nm, 660nm, 680-710nm, 730-745nm (Fig. 1.b). When we compare the Syrian and Armenian natural zeolites in these figures, we observe an increase and a decrease of the relative luminescence intensity in the neighborhood of new maxima. The observed bandwidth luminescence in the UV-Visible regions may be due to excitonic radiation where, as a result of *Si* or *Al* emigration to the carcass structure, a new state (free vacancy + hole) is formed. Moreover, the probability of formation of such a state is always non negligible, and consequently the bandwidth luminescence in these regions of spectrum would have a relatively high intensity.

The maxima in the UV-Visible region (395, 405, 410, 427*nm*) probably have an excitonic character, with large excitons located near the intrinsic structural or impurity defects [17-22].

The maximum excitation luminescence spectra was observed at 285*nm* bandwidth, which allows to determine the most intensive luminescence range and the mechanism of its excitation. It was also shown that thermal treatment results in a decrease of excitation level and an increase of luminescence intensity.

In the red region of the spectrum, the relative intensity of bandwidth luminescence changes strongly depending on the zeolite state. One can assume that the observed maxima in the red region are due to the centers, formed by cations, ions and hydroxide group OH^- , type [*Me*, *OH*], and that they are localized where the electric field is strong.



Fig. 1. Luminescence spectum of Syrian (M5 and S) and Armenian natural zeolites. a- UV-visible region; b- Red region.

The water loss always takes place in the samples and this is accompanied with dissociation leading to H^+ and OH^- group formation which affects luminescence. Moreover, the hydroxide groups OH^- could form nano-clusters with tetrahedra of type $[(SiO_2)_n OH^-]$ which play a role in the process of luminescence formation. Thus, one can conclude that luminescence properties depend on the state characterized by a definitive carcass – cation – water relation.



Fig. 2. Luminescence spectrum of Syrian (16,18 and 20 S14) natural zeolites. a- UV-visible region; b- Red region.

The investigation of optical absorption for the natural Syrian and Armenian zeolites in the near IR region of spectrum was carried out under the same conditions for all samples. Here we used the Russian spectrophotometer $C\Phi$ -8 which allowed to scan the wavelength from 1 micron to 2.2 microns at room temperature. For this study, we prepared samples in the form of disc shaped tablets of 20mm in diameter and 0.3mm in thickness. Each tablet contains 50g of zeolite and 100mg of KBr. In order to eliminate the influence of bonding KBr on the zeolite spectrum, a double ray measuring technique is used. This method allows to measure the spectrum in relation to that of KBr. Figure 2 represents the characteristics of the spectrum for non-treated natural zeolite which are related to the presence of absorption bandwidth at wavelengths $\lambda_1 = 1.42 \,\mu m$ and $\lambda_2 = 1.91 \,\mu m$. The last bandwidth is interpreted as a combination of valence and molecular vibrations of hydroxide groups (O - H), with the frequency of the fundamental vibrations in the far IR region (~ 3570 and 1630 cm⁻¹).



Fig. 3. The spectral dependence of optical transmission of natural Syrian and Armenian zeolites. (a) represents data for some samples: Am for Armenian and 2, 10, 16,18/S14 for Syrian samples; (b) represents data for other Syrian samples M5,4,6,8, 12, 20/S14.

Here it should be mentioned that the optical investigation of the luminescence properties of different natural Syrian zeolites showed that natural zeolites are different from each other. This conclusion was based on comparison between the results of Syrian and Armenian zeolites; the latter are relatively pure and contain up to 85% of clinoptilolite.

The integral absorption bandwidth of $\lambda = 1.91 \mu m$ could be used in order to evaluate the molecular concentration of water and hydroxide groups (O - H). In the spectrum of some studied Syrian zeolites (M5; 4, 6, 18/S14) we observed a new absorption bandwidth at wavelength $\lambda = 2.21 - 2.22 \mu m$ which is absent in the Armenian samples. This could be due to the neighbor state like water hydration or clusters adsorbed on the zeolite structure. The obtained results for Syrian and Armenian natural zeolitic samples are shown in Fig 3.

In order to justify somehow our proposition, the zeolite hydration isotherm is investigated experimentally. For this purpose zeolite grains of 20-60m in dimensions have been extracted under microscope from the volcanic tuff of the above mentioned Syrian samples. The different values of relative humidity was obtained using silica gel and $CaCl_2$ solutions of different concentrations for values of relative humidity varied from 32% to 98% and *LiCl* solutions for values of relative humidity varied from 15% to 32%. Each of the samples was put at these conditions for 24 hours. The zeroth value of relative humidity of each sample was obtained by thermal treatment at $150^{\circ}C$ for several hours until the moment that its mass does not change with time. The measurements were provided with decreasing the relative humidity from 98% to 0%. The obtained results are given on Figure 4 from which it is seen that there are different slopes and three different stages. The existence of such slopes shows that there are at least three nonequivalent positions of water molecules in the zeolite elementary cell.



Fig. 4. Water content (mass of H₂O/mass of zeolite) as a function of relative humidity

Moreover, the kinetics of ion exchange may shed a light on the observed phenomenon. Therefore, this question was treated regarding Syrian samples. The analysis of experimental data shows that the water sorption ability of the studied samples is highly dependent on cation exchange form. Moreover, when studying Syrian samples regarding the ion exchange of different cations we observed three steps (see Figures 5- 8 related to sample M5) which confirms the obtained steps shown on Figure 4. In addition to the above mentioned, the dependence of ion exchange capacity on time reveals a new phenomenon (see Fig. 9). The ion exchange capacity is practically constant within a time interval of one hour started after 2 hours. This behavior is stable and has a repetitive character. In our opinion, this could be related to the different observed stages (see Fig. 4) and could have a relation with the ionic radius of the cations, their valence and polarization ability. A further investigation in this field should be done in order to give a complete explanation.



Fig. 5. The ion exchange of Na as a function of time.



Fig.6 The ion exchange of Ca as a function of time.



Figure 7: The ion exchange of Na as a function of time.



Figure 8: The ion exchange of Mg as a function of time.



Fig.9. The ion exchange capacity (mg/l) as a function of time.

Sample	TiO ₂	Mn ₂ O ₃	Cr ₂ O ₃	P_2O_5	L. I.
A11	0.20	-	-	-	14.19
2S14	1.60	0.2	0.03	0.44	12.3
4S14	1.48	0.17	0.03	0.46	14.10
6S14	1.60	0.17	0.03	0.52	15.16
8S14	1.37	0.15	0.03	0.52	16.52
10S14	1.64	0.22	0.04	0.41	10.98
12S14	1.84	0.20	0.03	0.49	10.46
M5	1.75	0.18	0.03	0.47	10.71
16S14	2.10	0.20	0.03	0.52	9.28
18S14	1.92	0.19	0.03	0.49	9.31
20s14	1.87	0.19	0.03	0.47	9.24

Table 1: The chemical composition of the studied samples.

Sample	SiO ₂	Al_2O_3	Na ₂ O	K ₂ O	CaO	Fe ₂ O ₃	MgO
A11	67.11	11.69	0.79	2.22	4.9	2.23	1.28
2S14	39.51	10.48	1.22	1.01	8.77	11.68	12.21
4S14	38.69	9.98	0.93	0.89	11.01	10.41	11.09
6S14	37.64	10.15	0.99	1.08	11.92	10.65	9.74
8S14	37.14	9.80	0.75	0.84	14.95	8.97	8.55
10S14	39.95	10.42	1.13	1.02	6.73	13.20	14.17
12S14	40.76	11.65	1.50	1.13	8.24	12.02	9.99
M5	40.17	10.97	1.66	1.13	8.95	11.75	10.65
16S14	41.36	13.04	1.45	1.24	8.26	12.60	9.01
18S14	41.08	12.00	1.43	1.19	8.18	11.99	10.45
20s14	41.23	11.63	1.65	1.18	7.96	12.30	10.62

5. Conclusions

Finally one can conclude that:

- In the UV-visible and red regions, luminescence maxima at wavelengths 395*nm*, 405*nm*, 410*nm*, 425*nm*, 630*nm*, 660*nm*, 680–710*nm*, 730–745*nm* are observed.
- The observed maxima in the red region are, probably, due to the centers, formed by cations, ions and hydroxide group OH^- , type [*Me OH*].
- The luminescence properties depend on the state characterized by a definitive carcass cation water relation.
- The absorption bandwidth at wavelengths $\lambda_1 = 1.42 \,\mu m$ and $\lambda_2 = 1.91 \,\mu m$ is interpreted as a combination of valence and molecular vibrations of hydroxide groups (O H), with the frequency of the fundamental vibrations in the far IR region (~ 3570 and 1630 cm^{-1}).
- A new absorption bandwidth at wavelength $\lambda = 2.21 2.22 \,\mu m$ which is absent in the Armenian samples is observed in the spectrum of some studied Syrian zeolites.

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