

Colored Sodalite and A Zeolites

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In this work, ultramarine-like pigments were obtained in one step synthesis from NaA zeolite, sodium carbonate, and sulfur as precursors. To reduce the typical synthesis temperature (higher than 600 °C), sealed tubes were used. Ultramarine-like pigments were successfully synthesized at temperatures lower than 400 °C. The ratio S/Na₂CO₃ was varied, and the percentage of sulfur/gram of zeolite remained constant.

1. Introduction

Lapislazuli, from Latin “lapis” = stone and from Arabic “lazuli” = blue, is a rock composed by several minerals. Its intense blue color comes from the rare mineral lazurite. Two main lapislazuli resources have been reported in our planet: in Badakhschan, Afghanistan, or east of Ovalle, a small town north of Santiago, Chile.

The attractive deep blue color was first recorded 5500 years ago in the Sumerian city Ur, in Chaldea, where the blue stone was used for the magnificent ornaments of the Queen Schubad.^{1,2} In Egypt, the death mask of the pharaoh Tutankhamon is made with lapislazuli.¹ In Russia, the columns of St Isaac’s Cathedral in Saint Petersburg are lined with lapislazuli, and the Pushkin Palace, also in Saint Petersburg, has lapislazuli paneling.

Ground lapislazuli was the secret of the ultramarine blue that painters used until the 19th century when it was synthesized, in France, using inexpensive materials as kaolin, sulfur, and soda.^{1,3,4} The procedure is fairly simple. Sulfur species, mainly anionic polysulfides, are the chromophores responsible for the color; yellow, blue, and red have been associated to S₂⁻, S₃⁻, and S₄⁻, respectively.^{5–7} These chromophores may be inserted into the sodalite cage of zeolites.⁸ Nevertheless, this procedure ends up with a high volume of volatile sulfur compounds in waste gases. Hence, new methods, under friendly conditions, have to be established. In this sense, some works have been reported.^{9,10}

The polysulfides are usually obtained from the reaction of sulfur and sodium carbonate. The polysulfide formed, and hence the obtained color, is determined by the ratio S/Na₂CO₃.¹¹ Previous studies¹² have shown that the reaction occurs at 300 °C. If S/Na₂CO₃ < 3.3 (sodium carbonate excess), the only polysulfide formed is S₃⁻ (blue color), but if S/Na₂CO₃ > 3.3 (sulfur excess), S₂⁻ (yellow color) is obtained too, giving rise to a green color due to the mixture of these two chromophores. Still, it is not clear if such limits are independent of the synthesis temperature of the preparation method. Nowadays, it is accepted that either the inclusion of the chromophore happens during the sodalite cage formation or, the other way round, the sodalite cage is first built and the polysulfides diffuse because of the high temperature involved.¹³ The attempt to crystallize, hydrothermally, zeolite A in the presence of polysulfides resulted in

sodalite zeolite structure, as well as through the thermal treatment of faujasite in the presence of polysulfides.¹³

Sodalite and zeolite A are built by sodalite cages (diameter 6.6 Å) linked, in the first case, through square faces and, in the second, through square prisms. The number of cationic exchange sites, but not the configuration of the sulfur hosting sodalite cage, varies from one zeolite to the other. In the two zeolites, the access to the sodalite cage is through six-membered windows (6R) whose diameter is 2.8 Å. In sodalite and zeolite A, Si/Al = 1.

Several preparation methods have been reported in the bibliography.^{13–15} The procedure most frequently used includes two steps: (1) The polysulfides are first prepared from different sources (S, Na₂CO₃, Na, NaS, etc.). (2) The material is thermally treated at temperatures higher than 400 °C to produce structural changes and to propitiate the migration of S₂⁻, S₃⁻, or S₄⁻ into the structure. The product, then, turns out to be colored. The material may be washed to eliminate sulfur excess. Hence, it is not clear if the structure of the zeolite is destroyed due to temperature and recrystallizes as sodalite or if the crystalline transformation is induced by sulfur diffusion.

In this work, to reduce preparation temperature, sealed tubes were used. Under these conditions, ultramarine-like pigments were synthesized, in only one step. The ratio S/Na₂CO₃ was varied systematically, and the (percentage of sulfur)/(gram of zeolite) remained constant. The starting zeolite was dehydrated NaA.

To determine which crystallization mechanism (sulfur induced or not) was followed, the reaction of zeolite A with sodium carbonate is also discussed. The samples were prepared as previously proposed, but in the absence of sulfur.

2. Experimental Methods

2.1. Materials. Anhydrous sodium carbonate (Aldrich), sulfur (Aldrich), and zeolite NaA (Type 4A, provided by Union Carbide) were used.

2.2. Synthesis. 2.2.a. Reference Samples. Zeolite A (1.00 g) was ground and mixed with sulfur (0.20 g). A second sample was prepared mixing zeolite A (1.00 g) with 1.85 g of Na₂CO₃. For comparative purposes, sodium zeolite was separately studied. The samples were sealed under vacuum, heated gradually up to 380 °C, and maintained at this temperature for 12 h. The products were washed with deionized water, dried, and characterized by X-ray diffraction (XRD) and nuclear magnetic resonance (NMR). The samples were labeled as follows: R–NaA–S, R–NaA–C, and R–NaA, respectively.

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2.2.b. Ultramarine-like Pigments. Zeolite (1.00 g) was mixed with a mixture of S and Na_2CO_3 ; the amount of S was always 20 wt %, and the used molar ratios S/ Na_2CO_3 were 0.30, 0.35 (the expected color was blue), and 4.30 (the expected color was green). The mixture was, then, treated as previously. The samples were labeled as follows: S–NaA-0.30, S–NaA-0.35, and S–NaA-4.3, respectively. The expected color in the various samples was based on keeping in mind that the total of S and Na_2CO_3 react to form S_3^{2-} or S_2^{2-} and that all of this chromophores are stabilized into the materials.

It should be remarked that, in the synthesis of reference samples as well as of ultramarine-like pigments, prior to the encapsulation of the reagents (A zeolite, Na_2CO_3 , and S), they were dehydrated. Zeolite A was outgassed (10^{-4} Torr) at 400 °C for 10 h; other reagents were heated at 200 °C for 10 h.

2.3. Characterization. 2.3.a. X-Ray Diffraction. A Siemens D500 powder diffractometer coupled to a copper anode tube was used. The filtered $\text{K}\alpha$ radiation was used. The cell parameters were obtained using a graphite standard to correct the shift of the (320) peak of the zeolite A or the (211) of the sodalite.

2.3.b. Nuclear Magnetic Resonance (NMR). ^{29}Si NMR spectra were obtained at 79.46 MHz on a Bruker Avance 400 spectrometer by using the combined techniques of magic angle spinning (MAS) and proton dipolar decoupling (HPDEC). Direct pulsed NMR excitation was used throughout, employing 90° observing pulses (3 μs) with a pulse repetition time of 8 s. Powdered samples were packed in zirconia rotors. The spinning rate was 5 kHz. Chemical shifts were referenced to TMS.

^{27}Al NMR spectra were obtained by operating the spectrometer at 104.22 MHz. Samples were spun at 10 kHz, and ^{27}Al chemical shifts were referenced using $\text{Al}(\text{H}_2\text{O})_6^{3+}$ in aqueous solution of $\text{Al}(\text{NO}_3)_3$ as the external standard. In all samples, the effective relaxation delay was determined in a saturation recovery experiment, with appropriate relaxation delays for all experiments.

2.3.c. Raman Spectroscopy. Raman spectra were obtained at room temperature in air with a double monochromator (SPEX 1403). The signal was recorded with a photomultiplier and a standard photon-counting system. The power level was of the order of 50 mW; and the laser spot at the sample surface was ~ 100 microns; care was taken in order to avoid photodegradation of the sample. The 514.5 nm excitation permitted one to observe simultaneously the Raman bands of the yellow and blue chromophores at 590 and 550 cm^{-1} .

3. Results

3.1. Reference Samples. The X-ray diffraction patterns of the treated R–NaA (white), R–NaA–C (white), and R–NaA–S (slightly blue) materials are compared in Figure 1. The diffraction peaks, in all diffractograms, correspond to sodalite. Still, in sample R–NaA, some zeolite A remains. The background line in these X-ray diffraction patterns is not flat; thus, a fraction of the sample is constituted by a noncrystalline compound. The percentage of each compound is estimated from peak areas, assuming that the X-ray absorption coefficient is the same in these aluminosilicate compounds; see Table 1. Note that, if the percentage of crystalline compounds is measured by this way, the percentage of noncrystalline material is determined (amount required to complete 100%). The three samples have a similar amount of sodalite. In the sample R–NaA–S, the amount of noncrystalline compound is 35%, whereas in the other two materials, it is 21 and 19%.

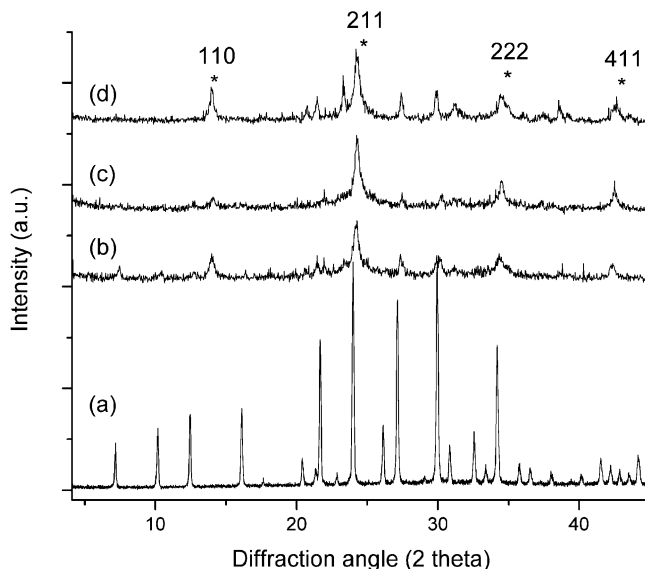


Figure 1. X-ray diffraction patterns of (a) parent zeolite NaA, (b) R–NaA, (c) R–NaA–S, and (d) R–NaA–C. Peaks labeled * correspond to sodalite (samples b–d). All other peaks correspond to zeolite A. The peaks were indexed with JCPDS cards: 11-0401 to sodalite zeolite and 14-0298 to zeolite A.

In the R–NaA–C sample, before washing, X-ray diffraction peaks, corresponding to crystalline Na_2CO_3 , were present; with washing, they disappeared. In the other reference samples, R–NaA–S and R–NaA, differences between washed and nonwashed samples were not observed.

When the initial A zeolite (dehydrated) was sealed and thermally treated, it turned out to be sodalite (47%) and zeolite A (32%). The cell parameter of the sodalite present in this mixture was found to be 9.08 Å. When zeolite A was heated in the presence of either Na_2CO_3 or S, sodalite (46 and 41%, respectively) was also obtained and the corresponding cell parameters were 9.03 and 9.05 Å, respectively. The differences, ca. 5%, are relevant and beyond experimental error.

In Figure 2, the ^{29}Si NMR spectrum for zeolite A exhibited a single intense peak close to -90 ppm, which has been controversially assigned to Q^3 units. However, it is now usually agreed that this peak must be assigned to Q^4 units, i.e., in zeolite A each silicon tetrahedron is linked through oxygen bridges to four aluminum atoms. On the contrary, the spectra for R–NaA and R–NaA–S samples are composed of an intense peak close to -92 ppm and by other weak signals at stronger and at weaker fields, revealing that these samples contain tetrahedron oxygen–silicon surrounded by 4, 3, 2, 1, and 0 aluminums.¹⁶

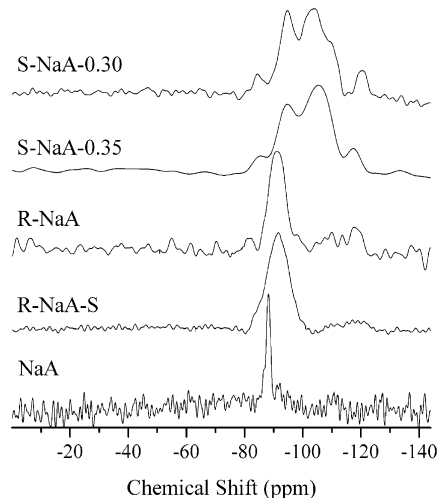
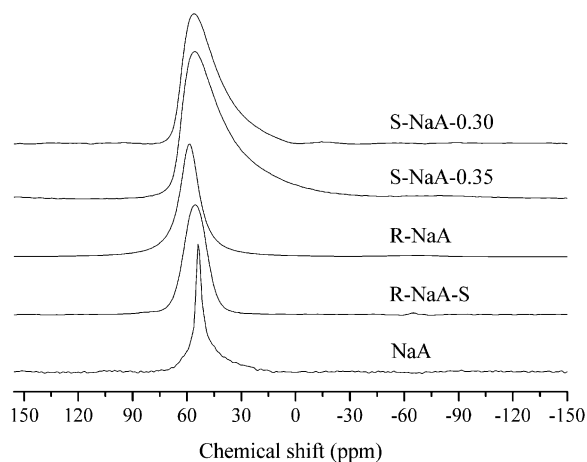
The ^{27}Al NMR spectra corresponding to these three samples (Figure 3) presented only one peak ca. 50 ppm, which is due to tetrahedral aluminum.^{17,18} The peak in the R–NaA–S spectrum was broader than the peaks in the other two samples.

3.2. Colored Samples. When sulfur was incorporated into the reacting mixture, the obtained samples were colored; S–NaA-0.35 was weak blue, S–NaA-4.30 was deep blue, and S–NaA-0.30 was green. X-ray diffraction patterns showed that no zeolite A was present in the blue samples (S–NaA-0.35 and S–NaA-4.30); only sodalite (72–76%) and a noncrystalline compound (28–24%) were found. Instead, in the green sample, no sodalite was identified; the compound was constituted by 70% of zeolite A (whose cell parameter was found to be 12.35 Å) and 30% of a noncrystalline solid; see Figure 4.

It is worth mentioning that XRD patterns included in Figures 1 and 4, correspond to samples at end of preparation, including a washing with deionized water. However, in the green sample,

Table 1. Summary of XRD Results, Identification, and Cell Parameters

mixture components	code sample	color	identification			cell parameter (Å)	
			sodalite %	NaA %	noncrystalline %	sodalite	zeolite A
S + Na ₂ CO ₃ + NaA	S-NaA-0.35	blue	72.00		28.00	8.99	
S + Na ₂ CO ₃ + NaA	S-NaA-4.30	deep blue	75.95		24.05	9.05	
S + Na ₂ CO ₃ + NaA	S-NaA-0.30	green		69.62	30.38		
NaA	R-NaA	white	46.88	31.70	21.42	9.08	24.56
S + NaA	R-NaA-S	slightly blue	40.93	23.99	35.08	9.05	24.54
Na ₂ CO ₃ + NaA	R-NaA-C	white	45.54	35.03	19.43	9.03	

**Figure 2.** ²⁹Si MAS HPDEC NMR spectra for the white and colored zeolites.**Figure 3.** ²⁷Al MAS NMR spectra for the white and colored zeolites.

before washing, carbonate sodium was detected. This result reveals that, for a high amount of carbonate in the sealed tube of reaction, this reactant does not react completely; in consequence, the nonreacted Na₂CO₃ contributes to the stabilization of the zeolite A structure. Furthermore, S₃⁻ chromophores are produced as shown by Raman spectroscopy, and they are stabilized in the sodalite and the noncrystalline phases. This stabilization inhibits the formation of S₂⁻, the yellow chromophore. Nevertheless, the mixture of S₃⁻ and nonreacted elemental sulfur gives a green sample.

Strictly, an ultramarine pigment is composed close to 100% by sodalite; samples synthesized in this work were named ultramarine-like pigments or simply colored zeolites.

Figure 5 shows the XRD peaks used to calculate the cell parameters of the samples S-NaA-0.35, R-NaA-C, and S-NaA-4.30; these samples turned out to be sodalite. In Table 1, the sodalite cell parameters values are compared to the

reference samples. Note that the R-NaA-S and the S-NaA-4.30 samples, both blue, present the same cell parameter (9.05 Å).

The observed ²⁹Si chemical shifts in the NMR spectra (Figure 2) of both the S-NaA-0.35 and S-NaA-0.30 samples are comprised in the interval -85 to -115 ppm shielded with respect to tetramethylsilane. Within this range, a regular paramagnetic shift is correlated to the number of aluminum neighbors surrounding silicon.

In Figure 2, NMR peaks of S-NaA-0.35, at -85.4, -92.4, -99.8, -106.2, and -117.4 ppm, are assigned to Si(4Al), Si(3Al), Si(2Al), Si(1Al), and Si(0Al) units, respectively.¹⁸ Deconvolution of spectra provides the ratio of peak intensities reported in Table 2. A similar distribution of Si(*n*Al) units is obtained for green and blue samples, S-NaA-0.35 and S-NaA-0.30.

The ²⁷Al MAS NMR spectra, Figure 3, consist of a single signal typical of tetrahedrally coordinated aluminum. The line width of the signal is not the same in both samples. It is broader in the blue sample than in the green; see Table 3. For comparison purposes, the line widths of the signals corresponding to reference samples are also included.

To identify the chromophores present in the colored zeolites (sodalite or A zeolites), Raman spectra were recorded in the range 510–660 cm⁻¹. The 514.5 nm excitation line allowed one to observe simultaneously the Raman band of the yellow (S₂⁻, 590 cm⁻¹) and the blue chromophores (S₃⁻, 550 cm⁻¹), respectively. In all samples, a well-defined band at 550 cm⁻¹ shows that S₃⁻, responsible for the blue color, is present, as shown in Figure 6. The yellow chromophore, S₂⁻, produces a stretching band at 590 cm⁻¹, and it is observed, although with a very low intensity, in the two blue samples. The S₃⁻/S₂⁻ ratio is, of course, high enough to give blue color to human eye. The green sample constituted by zeolite A does not present the peak at 590 cm⁻¹; hence, the yellow chromophore originating the green color is not in the form S₂⁻; thus, it has to be either as elemental sulfur or sulfate, because some sulfates present a yellowish color.

4. Discussion

If zeolite A (R-NaA) is treated in the same way as zeolite A with sulfur (R-NaA-S) or zeolite with sodium carbonate (R-NaA-C), the amount of remaining zeolite A, sodalite, and amorphous compound is the same. All experiment sets were repeated at least three times, and the results were consistent. It seems then that the formation of sodalite from zeolite A in such proportions is only due to the hydrothermal treatment. Sulfur or carbonate do not propitiate such phase transformation. Indeed, the transformation from zeolite A to sodalite was not observed as a consequence of a thermal treatment temperature as low as 380 °C. However, our work conditions should be emphasized: zeolite A was dehydrated prior to encapsulation, and the thermal treatment was performed in the absence of any gas flux (sealed tubes). In these conditions, there is no water that promotes a

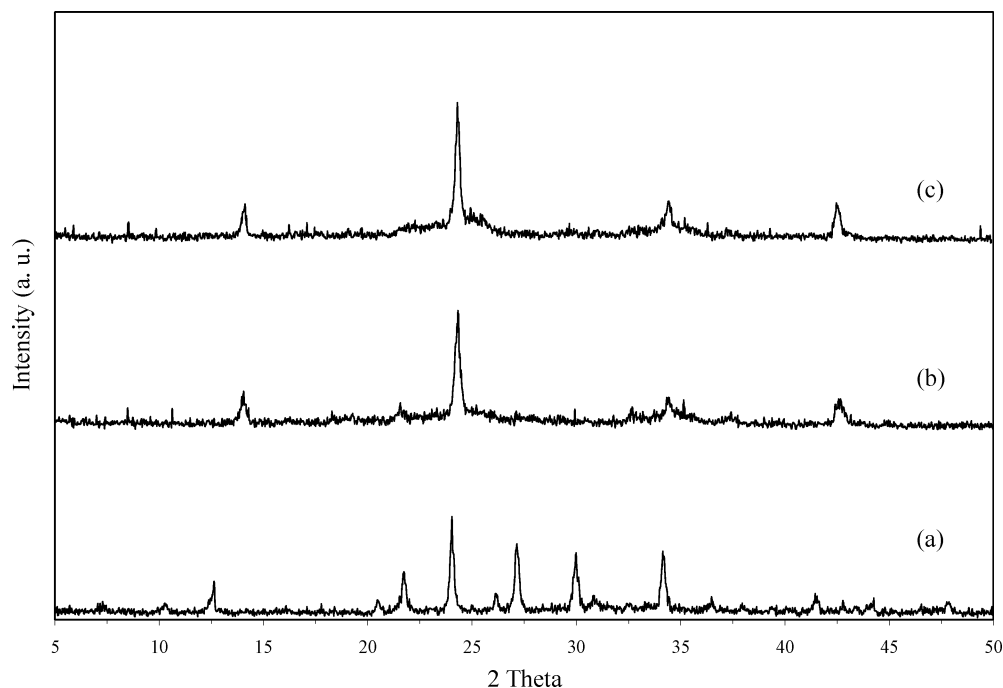


Figure 4. X-ray diffraction patterns of (a) S-NaA-0.30, (b) S-NaA-0.35, and (c) S-NaA-4.30. The crystalline peaks in (b) and (c) correspond to sodalite structure and the peaks in (a) correspond to zeolite A.

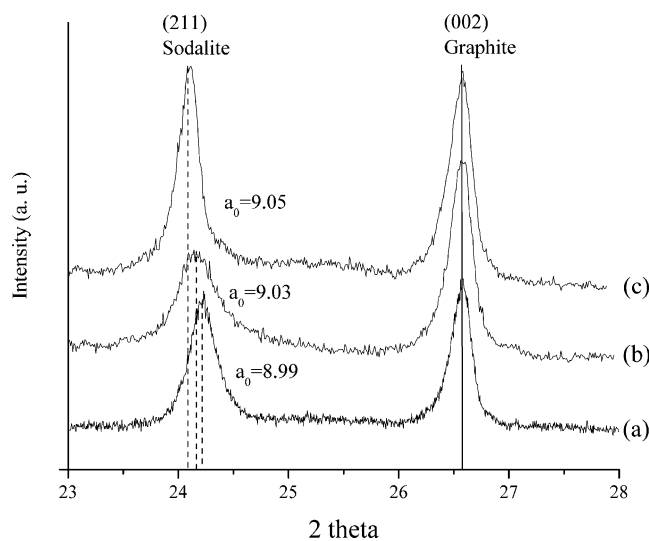


Figure 5. (211) Peak of sodalite used to calculate the cell parameters of (a) S-NaA-0.35, (b) R-NaA-C, and (c) S-NaA-4.30. As standard, the (002) peak of graphite was used.

stabilizing effect due to the action of repulsive van der Waals forces between the zeolite framework and water molecules. Moreover, Kosanovic and co-workers^{19–21} have shown that zeolite A can be mechanically amorphized, even at room temperature. They proposed that the amorphous material is formed by the breaking of the external T–O–T bonds. The preparation of the R-NaA sample was repeated, but the encapsulated zeolite was hydrated; then the transformation from zeolite A to sodalite was not observed. A conclusion emerges: zeolite A treated thermally in sealed tubes is amorphized and transformed to sodalite because water is not present to act as a stabilizing agent.

The sample R-NaA-S exhibited a slightly blue color, revealing that some sulfur is incorporated into the mixture, forming sulfur ions (S_3^-), either in zeolite A or sodalite or both. It is clear that S_3^- concentration is small as the blue color is very weak. Therefore, in the absence of Na_2CO_3 , the content

Table 2. ^{29}Si NMR Intensities, Measured and Calculated from the Binomial Formula (See Text)

sample	signal	relative spectral intensities (%)	
		from experimental ^{29}Si NMR spectra ^a	from the binomial formula ^b
S-NaA-0.30	Si(4Al)	7.0	6.2
	Si(3Al)	29.3	25
	Si(2Al)	29.9	37.5
	Si(1Al)	19.6	25
S-NaA-0.35 (blue)	Si(0Al)	14.2	6.3
	Si(4Al)	7.2	6.2
	Si(3Al)	28.6	25
	Si(2Al)	30.4	37.5
	Si(1Al)	20.5	25
	Si(0Al)	13.3	6.3

^a Deconvolution of the ^{29}Si MAS HPDEC NMR spectra shown in Figure 2. ^b Binomial formula where the distribution of Si and Al is fully random.

Table 3. Line Width (Hz) of ^{27}Al NMR Peaks in the Various Zeolites

sample	chemical shift (ppm)	line width (Hz)
NaA	54.0	404
R-NaA	55.8	901
R-NaA-S	58.5	1 812
S-NaA-0.30	55.4	2 349
S-NaA-0.35	55.7	2 682

of Na^+ in the sample is the required one to balance the charge due to the framework aluminum tetrahedra, but it is not enough to balance the S_3^- produced, which are most probably compensated by hydronium ions.

The cell parameters of treated zeolite A (R-NaA) are 9.08 Å for sodalite and 24.56 Å for zeolite A, and, in sample R-NaA-S, 9.05 Å for sodalite and 24.54 Å for zeolite A. Because S_3^- anions are larger than sodium ions and are encapsulated into the cavity, the tension should be high; thus, the cell parameter of the zeolites should noticeably increase. Such is not the case; hence, S_3^- anions must be located in the noncrystalline material or on the external surface of the zeolites. This second possibility has to be discarded because the zeolite

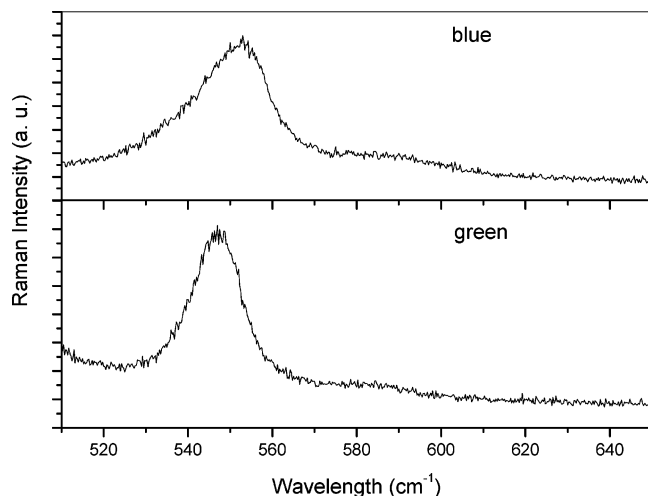


Figure 6. Raman spectra of blue (S-Na-4.3) and green samples.

surface is attractive to cations and not to anions. This observation is most important as it reveals that the local environment of S_3^- ions is not crucial for color; the encapsulation into the sodalite cages is required for the stability of the anion radicals and for the amount of retained ions and, thus, the color intensity.

Results obtained with the carbonated zeolite (R-NaA-C) sample confirm our previous discussion; indeed, the sample has almost the same crystalline composition, and it is not colored. Chromophores have been already retained in porous silicas.²² ^{27}Al NMR results show that the tetrahedral coordination of aluminum does not change with the thermal treatment. However, the line width becomes broader in the sulfur containing sample if compared with the corresponding sodalite. This is due to the paramagnetism induced by the polysulfides. Furthermore, because no octahedral aluminum was detected, it has to be assumed that the noncrystalline material is an aluminosilicate with a Si/Al ratio similar to the starting zeolite A. Therefore, the noncrystalline or microcrystalline material is composed by Al^{3+} , Si^{4+} , O^{2-} , Na^+ , H^+ , and S_3^- . ^{29}Si NMR results reveal that zeolite A and sodalite are Q^4 and Q^3 ordered, respectively, in agreement with literature.^{16,23} However, the amorphous aluminosilicate formed in R-NaA and R-NaA-S samples should be composed by Q^4 , Q^3 , Q^2 , Q^1 , and Q^0 units, i.e., the material appears to be more disordered when noncrystalline material is present.

It remains unclear how the S_3^- species are formed only in the presence of zeolite and the thermal treatment. In our opinion, sulfur which has a structure of S_8 rings, with temperature, becomes unstable and, then, by homolytic fission, free radicals and open chains are formed, such as S_3 , S_5 , and S_6 .²⁴ In the presence of the zeolite that has polarized sites, S_3^- anions are stabilized.

When both reactants (sulfur and carbonate) were incorporated to the reacting mixture, two blue samples were obtained; only sodalite and a noncrystalline compound were formed. For higher sulfur content, a deeper color is obtained. In our conditions, blue color was obtained even for a ratio $\text{S}/\text{Na}_2\text{CO}_3 > 3.3$ (sample S-NaA-4.30). Furthermore, it seems that, the higher the ratio, the bluer is the sample. As the sodalite cell parameter increases with the amount of sulfur, some of the chromophores must be encapsulated into the zeolite lattice. However, a part of the produced S_3^- chromophores should be also stabilized in the noncrystalline material, which is able to retain these species as shown above with the R-NaA-S sample. Because the chromophore responsible to blue color is stabilized in both phases, sodalite and noncrystalline, the resulting solid is blue, pointing

out that phases present in the solid are crucial to the color of the pigment. This result is below confirmed by the NMR results.

Still, the sample with no carbonate (R-NaA-S), i.e., with the highest amount of sulfur, was not the bluest. Then, an optimal ratio $\text{S}/\text{Na}_2\text{CO}_3$ should fulfill, on the one hand, the transformation of zeolite A toward noncrystalline and sodalite phases and, on the other, provide as much sulfur as possible. If the ratio $\text{S}/\text{Na}_2\text{CO}_3$ was very low (sample S-NaA-0.30), no sodalite was obtained and the color was green. In this case, zeolite A structure was partially destroyed and disorder was generated by the formation of amorphous material, as supported by the XRD and NMR results. This sample was prepared with the highest amount of sodium carbonate per gram of zeolite. With thermal treatment, CO_2 and H_2O are produced in the gas phase; however, sodium from zeolite and Na_2CO_3 may remain in the solid phase, either as a cation or by forming oxides. These species can sorb OH^- and H_2O , propitiating a dynamic adsorption-desorption of H_2O and resulting in a better thermal stability of the zeolite.

In the green sample, the Raman spectrum did not reveal the presence of S_2^- chromophores; then the green color must be due to a mixture of blue (S_3^-) and yellow sulfates or elemental sulfur. To compare between these two possibilities, the attenuated total reflectance Fourier infrared (ATR/FTIR) spectrum of the green sample was obtained. The absorption bands at 570, 543, and 463 cm^{-1} were observed, which can be ascribed to elemental S_8 sulfur. Indeed, the band at the lowest wavenumber was assigned to stretching, ν_s , vibration. Other two absorptions (570 and 543 cm^{-1}) are due to combinations of two stretching bands, which individually are not observed in the midinfrared spectral window.

Again, from the cell parameters, no sulfur anions seem to be encapsulated into the zeolite cavities; they must be adsorbed on the non-crystalline compound and on the crystal external faces of the zeolite.

^{29}Si NMR results show that colored samples are not short-range ordered as noncolored sodalite or A zeolites. Table 2 reveals that relative intensities of measured ^{29}Si NMR signals are compatible with a model where the distributions of Si and Al are fully random. In agreement with the results of Klinowski et al.,²⁵ the intensities are given by the polynomial formula as $[1/((\text{Si}/\text{Al})^{+1})]^4$ for Si(4Al), $4[1 - (1/((\text{Si}/\text{Al})^{+1}))][1/((\text{Si}/\text{Al})^{+1})]^3$ for Si(3Al), $6[1 - (1/((\text{Si}/\text{Al})^{+1}))]^2[1/((\text{Si}/\text{Al})^{+1})]^2$ for Si(2Al), $4[1 - (1/((\text{Si}/\text{Al})^{+1}))]^3[1/((\text{Si}/\text{Al})^{+1})]$ for Si(1Al), and $[1 - (1/((\text{Si}/\text{Al})^{+1}))]^4$ for Si(0Al). This model suggests that the distribution of Al and Si is random and Al-O-Al linkages are allowed.

Aluminum in colored samples, as well as in the white samples, remains tetrahedrally coordinated, but the ^{27}Al NMR peaks become broader in samples containing sulfur because paramagnetic effects take place.

5. Conclusion

The preparation method discussed in this work provides colored samples in one step. In colored samples, almost all sulfur reacts and, hence, pollution is reduced.

In this study, comparing reference and conventionally colored zeolite A, the following points have been established. The synthesis of the ultramarine-like pigments, in the presence of sulfur and sodium carbonate, should occur with a ratio $\text{S}/\text{Na}_2\text{CO}_3$ as high as possible if the structure of the sample is sodalite to obtain a deep blue material. Chromophores are formed by the reaction between sodium carbonate and sulfur, S_3^- is formed up to a ratio $\text{S}/\text{Na}_2\text{CO}_3$ of 4.3 in the presence of sodalite or noncrystalline compound. When zeolite A is not destroyed, it

exerts a catalytic effect, which results in a simultaneous formation of S_3^- chromophores (blue) and remaining elemental sulfur (yellow). The physical mixing of these species gives green samples.

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