

Sulfur radicals embedded in various cages of ultramarine analogs prepared from zeolites

Stanisław Kowalak^{a,*}, Aldona Jankowska^a, Sebastian Zeidler^a, Andrzej B. Więckowski^b

^a*A. Mickiewicz University in Poznań, Faculty of Chemistry, Poznań, Poland*

^b*University of Zielona Góra, Faculty of Physics & Astronomy, Institute of Physics, Zielona Góra, Poland*

Received 20 November 2006; received in revised form 29 December 2006; accepted 4 January 2007

Available online 14 January 2007

Abstract

The colored (greenish) products analogous to ultramarine obtained from zeolite A, cancrinite and erionite by means of high-temperature (500–800 °C) treatment of zeolites mixed with elemental sulfur and alkalis can maintain the original structure of the parent zeolite under certain preparation conditions. The ESR spectra of samples recorded at room temperature always indicate the presence of radicals $\cdot S_3^-$ (the blue chromophore). The spectra of samples prepared from zeolites recorded at 77 K exhibit additional signals that could be assigned to the yellow chromophore (the radical $\cdot S_2^-$) encapsulated inside the β or ϵ -cages. It is remarkable that in the case of products with preserved cancrinite structure, where the $\cdot S_2^-$ radicals are encapsulated inside the ϵ -cages, the above signals are visible already at room temperature. It may result from retarded mobility of these species in small cancrinite cages.

© 2007 Elsevier Inc. All rights reserved.

Keywords: Ultramarine; Zeolites; Cancrinite; Erionite; ESR; Sulfur radicals

1. Introduction

Natural and synthetic ultramarines are aluminosilicate sodalites that contain anion radicals (mostly $\cdot S_3^-$) encapsulated inside the β -cages. The sulfur anion radicals combined with sodium cations behave as chromophores. Ultramarine can be also obtained from zeolites [1–8]. The structure types such as LTA, FAU and SOD containing sodalite cages appeared most suitable for syntheses of ultramarine [4–6]. The procedure always comprises mixing of zeolites with sulfur radical precursors (such as oligo-sulfides or elemental sulfur and alkalis) and heating the mixture at high temperatures (500–800 °C). Zeolites starting materials form products with a broad range of colors and shades due to controlled modulation of different contribution of $\cdot S_3^-$ or $\cdot S_2^-$ radicals. The structure of parent zeolites often undergoes transformation towards sodalite upon thermal treatment, although the original structure

can be also maintained under certain conditions of syntheses [9].

It appears likely that besides the most common sodalite cages, other intra-crystalline voids may appear suitable for accommodation and stabilization of the introduced sulfur radicals. ϵ -cages are present in the structure of cancrinite and erionite (Fig. 1) and several other zeolites. They are smaller than the β -cages, but sufficiently large to host some sulfur species. Our recent experiments [8] as well as works of Hund [10] and Lindner [7] showed, indeed, that the colored products could be obtained from cancrinite or erionite. Lindner claimed that the sulfur radicals obtained by X-ray irradiation or heating of cancrinite-containing sodium thiosulfate were located in the channels. We believe that their stability can be attained only inside the ϵ -cages.

It seems possible that the size and the geometry of the host cage can favor the generation of certain kinds of sulfur species (e.g. $\cdot S_3^-$ or $\cdot S_2^-$). It can also affect the interaction between the encapsulated sulfur radicals and the atoms forming the inner walls of the cages. The differences in such interactions should be reflected in the ESR spectra. The main aim of the following study was to record and

*Corresponding author. Fax: +48 61 8658 008.

E-mail address: skowalak@amu.edu.pl (S. Kowalak).

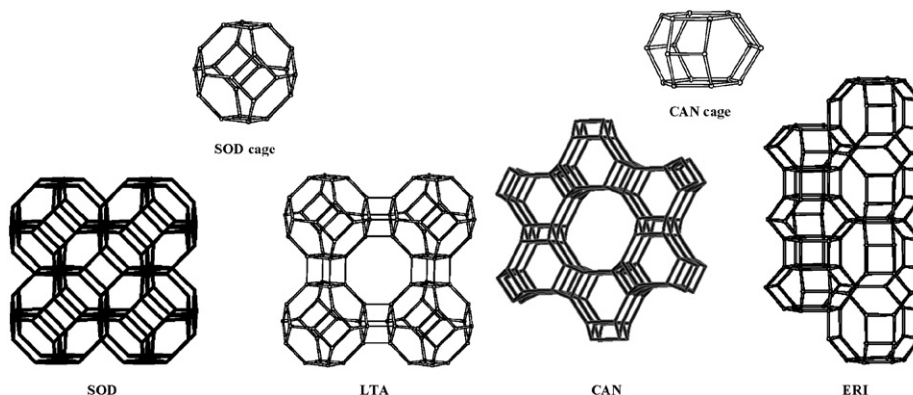


Fig. 1. Structures of SOD, LTA, cancrinite and erionite.

Table 1
Properties of the samples under study

Sample	Parent zeolite	Synthesis, Na ₂ /S, temp.	Product color	Product structure	ESR <i>g</i> (293 K)	ESR <i>g</i> (77 K)
1	Comm. Ultr.		Int. blue	SOD	2.0296	2.0302
2	NaA	0.2 (800 °C)	L. green	LTA	2.0289	2.0343; 2.0005
3	NaA	0.8 (800 °C)	Turquoise	SOD	2.0288	2.0346
4	Erionite	0.8 (500 °C)	Blue with turq. shade	ERI ^a	2.0273; 1.9966	2.0311; 1.9987
5	Erionite	0.8 (800 °C)	L. green	SOD	2.0257; 1.9971	2.0323; 1.9998
6	Cancrinite	0.4 (500 °C)	L. green	CAN	2.0341; 2.0095	2.0338; 2.0006
7	Cancrinite	0.6 (500 °C)	L. green	CAN	2.0338; 2.0091	2.0342; 2.0004
8	Cancrinite	0.2 (800 °C)	Turquoise	CAN	2.0301; 2.0096	2.0351; 2.0006
9	Cancrinite	0.6 (800 °C)	Turquoise	SOD + CAN	2.0339	2.0345; 2.0005

^aPoor crystallinity.

compare the ESR spectra of the sulfur radicals embedded in zeolites such as LTA, SOD, CAN and ERI. Special attention has been paid to comparison of the spectra recorded at room temperature and at 77 K.

2. Experimental

Ultramarine analog samples were prepared from commercial zeolite A (Atofina, Poland), erionite (Leuna) or with cancrinite prepared in our laboratory [8] by means of re-crystallization of zeolite A in the presence of NaOH and NaNO₃. The ultramarine analogs were prepared by thermal treatment of the initial mixtures obtained by grinding zeolites with elemental sulfur (40% of zeolite weight) and Na₂CO₃. Alkalinity of the mixtures was rather moderate (Na₂/S = 0.2–0.8), which always resulted in greenish coloration of the products. The presence of both yellow and blue chromophores (i.e. radicals $\cdot\text{S}_2^-$ and $\cdot\text{S}_3^-$) in the samples was desired in our study. The mixtures were heated in covered ceramic crucibles in muffle furnace at 500 or 800 °C for 2 h. Then the samples were cooled, washed with water and dried. The characterization of the products comprised XRD (Tur M-62) with CuK α radiation in the range 2θ of 4–60°. The UV–vis spectra were recorded with Cary 100, Varian spectrometer using diffuse reflectance

mode in the range 200–900 nm. The FTIR spectra were taken with Bruker, Vector 22 spectrometer using KBr wafers in the range 400–2000 cm⁻¹, resolution was 1 cm⁻¹. The ESR spectra were measured either at room temperature or in liquid nitrogen temperature by means of X-band (Radiopan, Poland SE/X 2547 spectrometer) with microwave frequency 8.9 GHz and magnetic modulation 100 kHz. The spectra of the samples were compared with those of commercial ultramarine (Prayon-Rupel).

3. Results and discussion

As indicated in Table 1, the samples obtained from cancrinite (samples 6–7) and erionite (sample 4) at low temperature preserve their original structure (Fig. 2) so does the zeolite A (sample 2) in the low-alkaline mixture heated at 800 °C.

The higher-temperature treatment (800 °C) and higher alkalinity of the mixtures always result in zeolite structure transformation towards sodalite. The samples selected for this study showed greenish color (Figs. 3 and 4), which resulted from the presence of both yellow ($\cdot\text{S}_2^-$ radicals) and blue ($\cdot\text{S}_3^-$ radicals) chromophores. The samples prepared at higher temperature usually show more intense coloration which is reflected in higher intensity of UV–vis

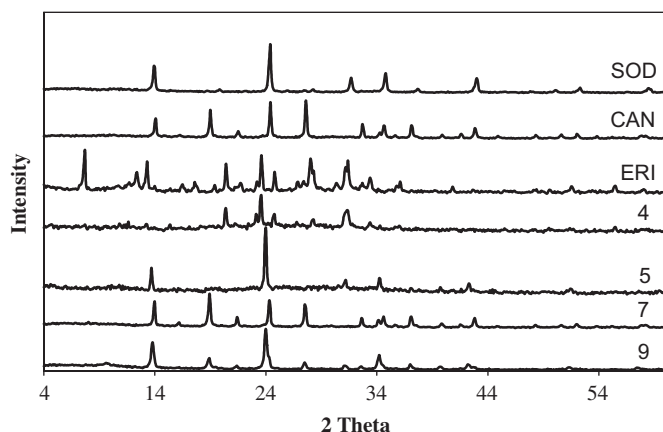


Fig. 2. XRD patterns of the indicated samples.

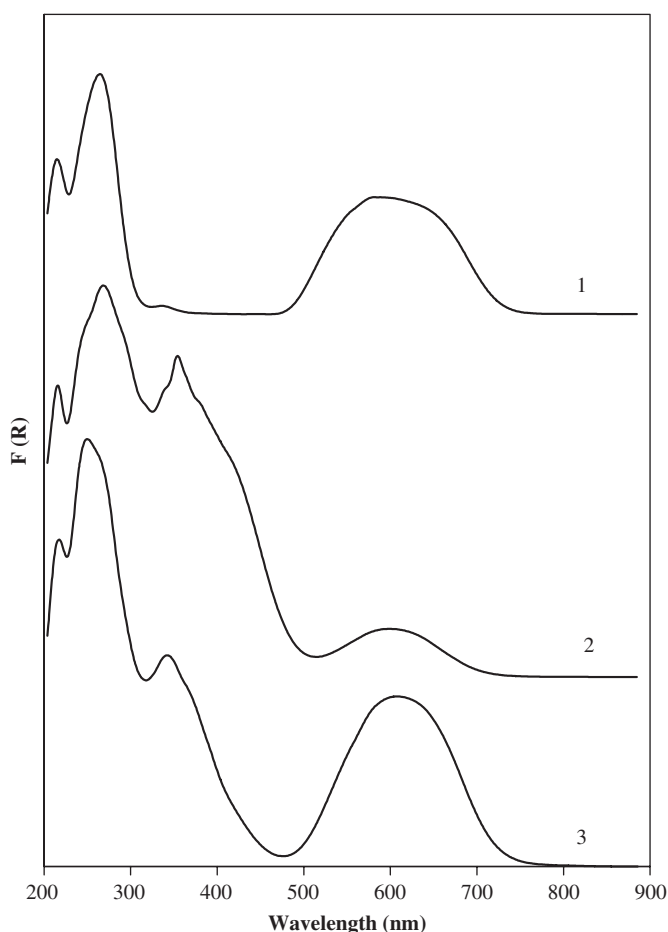


Fig. 3. UV-vis spectra of selected samples.

absorption bands at ~ 600 and ~ 380 nm (Fig. 4). The yellow color is prevailing for all the samples prepared from cancrinite at 500°C [8]. Table 1 contains also the properties of commercial ultramarine (Prayon-Rupel) for comparison. The IR spectra of washed products do not show any presence of SO_4^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ anions.

ESR spectroscopy is a very important tool for characterization of ultramarine and it provided the decisive

argument proving the radical nature of the sulfur-bearing chromophores [11–13]. The isotropic signal with g value 2.028 is always assigned to S_3^- radicals [11–14]. ESR spectra of S_3^- radicals at low temperature show a superposition of a symmetric line caused by rotating (exchange-narrowed) species and an asymmetric line caused by non-rotating species (with anisotropic g -factor) entrapped inside the cages. There are controversies concerning an identification of other radicals by means of ESR spectroscopy. Some authors (particularly in earlier works) claimed that the radicals S_2^- could be detected at low temperature as broad signal with g near 2.4 [12,15]. For S_2^- radicals formed in alkali halides, the values of g -factor were found to be within the range 1.7286–2.1318 [11,14]. On the other hand, some later works put in doubt a possibility to detect these radicals in ultramarine by means of the ESR spectra [3,15–16]. One of two signals noticed in green ultramarine is attributed to radical S_3^- , whereas the other one reflects rather impurities (e.g. Fe) [16], but not S_2^- , because the intensity of the later signal does not correlate with intensity of the Raman peak (590 cm^{-1}) assigned to this radical.

ESR spectra of the colored samples with SOD or LTA structures, recorded at room temperature (Fig. 5A) indicate the typical signals with g value ~ 2.029 (sample 1, $g_{\text{iso}} = 2.0296$; sample 2, $g_{\text{iso}} = 2.0289$; sample 3, $g_{\text{iso}} = 2.0288$) which are certainly attributed to S_3^- radicals. It is no significant difference in spectra of the samples prepared from zeolites A, regardless of their final structure type (LTA or SOD). The signals in the spectra of the samples prepared from zeolite A are slightly broader than that recorded for commercial ultramarine. The spectra of the above samples recorded at 77 K (Fig. 5B) are much different. In the case of samples 2 and 3 prepared from zeolite A (green or turquoise), the new signals with g value ~ 2.0005 are seen and perhaps, they may be assigned to the S_2^- radicals as suggested in earlier works [11,13]. The signals in spectrum of sample 2 with preserved LTA structures are more distinctive than that in sample 3, where the original structure was transformed to SOD. Such signals are not seen in the spectrum of commercial ultramarine blue that does not show the presence of yellow chromophore in the electronic spectrum (Fig. 3). The appearance of new signals at low temperature could result from retarded rotation of S_2^- inside β -cages [4668]. The mobility of the bigger radicals, S_3^- , is sufficiently reduced in limited space of the sodalite units (~ 0.6 nm in diameter), and therefore their ESR signals are noticeable at room temperature, whereas the mobility of smaller, S_2^- , species is not hindered substantially at this temperature in the voids of β -cages.

Geometry of the cancrinite cages [4665] differs significantly from that of β -cages and their size is almost twice as small as the latter ones. The space inside ϵ -cages can still accommodate the S_3^- radicals, whereas rotation of the encapsulated smaller sulfur radicals (S_2^-) can be reduced markedly because of spatial constraint (similarly as in the

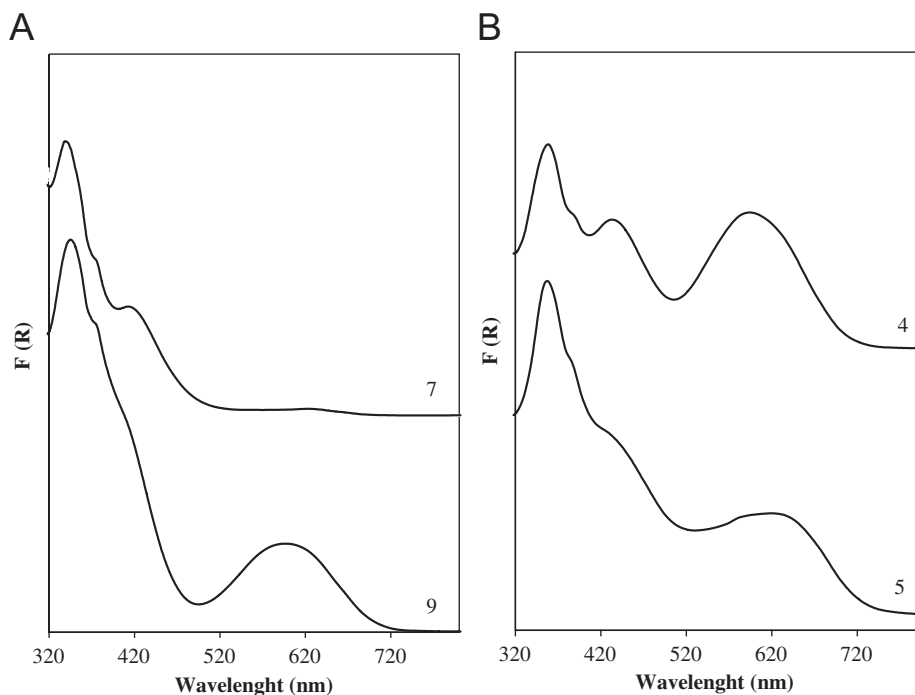


Fig. 4. UV-vis spectra of the samples obtained from cancrinite (A) and erionite (B).

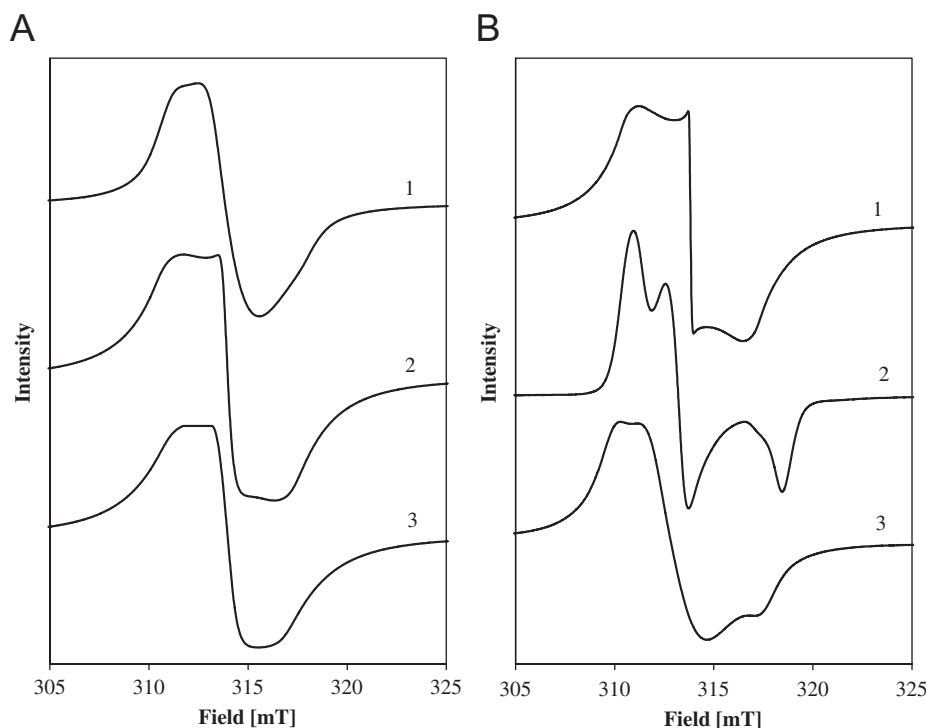


Fig. 5. ESR spectra of commercial ultramarine (1) and of the samples obtained from zeolite A with preserved structure LTA (2) and with structure transformed into SOD (3). The spectra recorded at room temperature (A) or at 77 K (B).

case of $\cdot\text{S}_3^-$ radicals embedded inside β -cages). ESR spectra recorded at room temperature (Fig. 6A) indicate two distinctive signals for samples 6–8 obtained from cancrinite at 500 °C. The samples show light green coloration and they maintain the original CAN structure of parent zeolite.

It means that the ϵ -cages are the only places suitable for hosting the sulfur radicals. The broad signal with distinct shoulder ($g = 2.03$) reflects the presence of $\cdot\text{S}_3^-$ radicals. It is tempting to assign the other signal ($g = 2.0095, 2.0091, 2.0096$) to the radicals $\cdot\text{S}_2^-$. It could support our

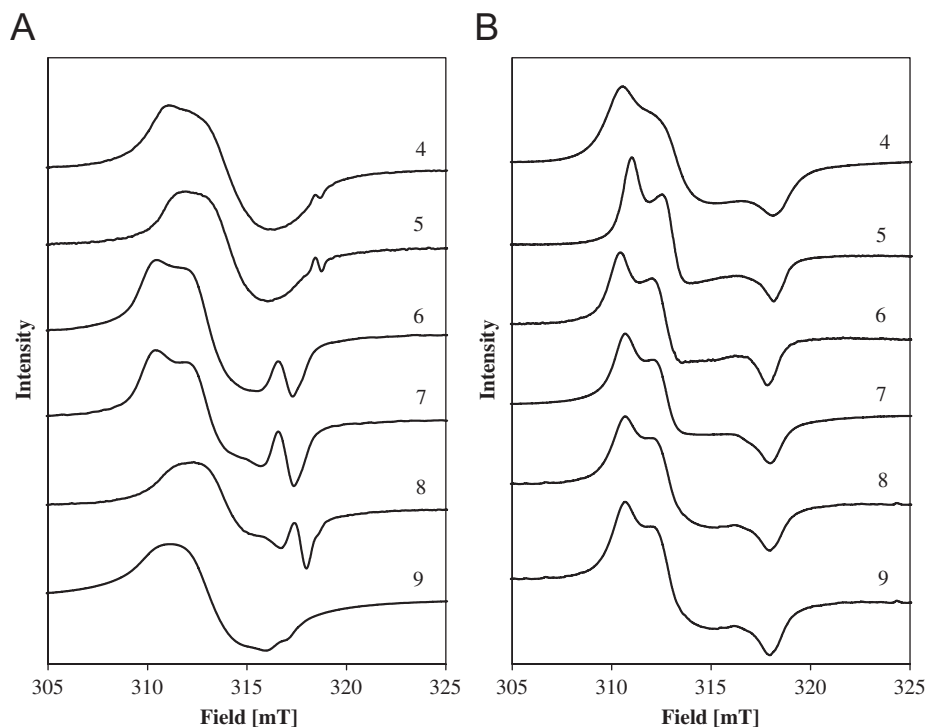


Fig. 6. ESR spectra of indicated samples recorded at room temperature (A) or at 77 K (B).

supposition that the smaller cages retard the mobility of the radicals $\cdot\text{S}_2^-$ and make them visible in the room-temperature ESR spectra. The new signals cannot be assigned to the impurities (e.g. Fe) as suggested by Gobeltz [15,16], because such impurity should be seen also in the samples with SOD structure, prepared from the same reagents, which is not the case. A predomination of yellow chromophore in the samples prepared from cancrinite at 500 °C could result from easier penetration of smaller sulfur species into small cancrinite cages and subsequently forming the $\cdot\text{S}_2^-$ radicals. The product obtained from the mixture of cancrinite, sulfur and Na_2CO_3 with Na_2/S ratio 0.6, but treated at 800 °C (sample 9) undergoes the structure transformation and XRD patterns (Fig. 2) indicate the presence of both CAN and SOD types of structure. The room-temperature ESR spectrum of this sample differs markedly from that of analogous samples obtained from cancrinite at 500 °C. It resembles the spectra of samples 2 or 3 containing sodalite units in their structure. The main signal ($g = 2.0339$) reflecting the presence of $\cdot\text{S}_3^-$ is much broader than in the case of former samples, and the other signal (from $\cdot\text{S}_2^-$) is almost negligible. It is interesting question, why the influence of sodalite type of structure in the sample is more conspicuous than that of CAN and no evident signal attributed to $\cdot\text{S}_2^-$ is detected in the spectrum. Perhaps, the sulfur radicals prefer to occupy the larger β -cages than the cancrinite ones.

The low-temperature ESR spectra (Fig. 6B) of all the samples obtained from cancrinite (6–9) look alike and in all cases the signals from $\cdot\text{S}_3^-$ ($g = 2.0338, 2.0342, 2.0351, 2.0345$) and $\cdot\text{S}_2^-$ ($g = 2.0006, 2.002.0004, 2.0006, 2.0005$)

are visible. The signals of $\cdot\text{S}_3^-$ show a distinctive shoulder resulting from anisotropic component, similarly as in spectra recorded for other ultramarine analogs obtained from zeolites (Fig. 5B).

In the case of samples obtained from erionite (Fig. 1) that also contains ϵ -cages in its structure, but separated from each other by means of hexagonal prisms, the room-temperature ESR spectrum of sample 4 (with preserved ERI structure) exhibits (Fig. 6A) one broad signal from $\cdot\text{S}_3^-$ ($g = 2.0273$) and very small peak, which most likely results from impurities in parent erionite. We expected that the presence of cancrinite cages should result in a similar spectrum as those recorded for the samples prepared from cancrinite at 500 °C, and the signal presumably attributed to $\cdot\text{S}_2^-$ could be seen too. Perhaps, a lack of the $\cdot\text{S}_2^-$ signal results from lower contribution of the yellow (Fig. 4B) chromophore (blue coloration of the sample). Poor crystallinity of the sample, compared to the parent erionite (Fig. 2), could also affect a localization of the embedded radicals. It is worth to mention that the ESR spectrum of similar sample prepared at 500 °C from the same mixture of erionite and sulfur, but with K_2CO_3 (instead of Na_2CO_3), which presents a good crystallinity indicates two distinct signals resembling the spectra of cancrinite samples (6 and 7) [17]. The sample obtained from erionite at 800 °C shows the spectrum with intense signal due to $\cdot\text{S}_3^-$ ($g = 2.0257$) and small one from erionite impurities. Such a result is not surprising, since the sample has attained the SOD structure after the thermal transformation, and therefore the spectrum resembles that of other ultramarine analogs with SOD structure (Fig. 5). The low-temperature spectra of the

samples prepared from erionite are like the other samples prepared from zeolites, but in the case of the sample prepared at 500 °C, the splitting of the signal at lower field value is less pronounced.

Regardless of controversies in literature concerning the identification of $\cdot\text{S}_2^-$ radicals by means of ESR spectroscopy, the role of these radicals as the yellow chromophore is not questionable. The Raman spectroscopy provides a clear evidence of both types of radicals and they could be distinguished as bands at $\sim 550\text{ cm}^{-1}$ ($\cdot\text{S}_3^-$) and at $\sim 590\text{ cm}^{-1}$ ($\cdot\text{S}_2^-$). The samples under study exhibit the presence of both bands in their Raman spectra [18].

Even if our assumption that the ESR signals (with $g \sim 2.009$) could be attributed to $\cdot\text{S}_2^-$ radicals was not correct, the presented spectra still illustrate the remarkable influence of the host zeolite cages on the behavior of encapsulated sulfur radicals. If the recorded signals were attributed only to the $\cdot\text{S}_3^-$ radicals, the presence of several signals (particularly those recorded at room temperature for the CAN sample) could reflect the difference in radical environment resulting from different types of hosting cages.

4. Conclusions

The ultramarine analogs of greenish coloration obtained from zeolites (LTA, CAN, ERI) by thermal treatment with sulfur and sodium carbonate show always two main absorption bands in the visible range of the electronic spectra which suggest the presence of two radicals $\cdot\text{S}_3^-$ and $\cdot\text{S}_2^-$ responsible for blue and yellow coloration, respectively. The ESR spectra recorded at 77 K indicate two main signals. One of the signals ($g \sim 2.03$) reflects ambiguously the presence of the $\cdot\text{S}_3^-$ radicals. The origination of another signal ($g \sim 2.0005$) is not quite certain, but we assumed that it could be assigned to the $\cdot\text{S}_2^-$ radicals (the yellow chromophore) as suggested in some early works [11]. The spectra recorded at low temperature are quite similar for all the samples prepared from zeolites, regardless of their different crystalline structure.

It is very interesting that the spectrum of the sample that maintains the CAN structure shows two signals already at room temperature. If the second signal ($g \sim 2.009$) results

indeed from the presence of the $\cdot\text{S}_2^-$ radicals, its appearance at room temperature could be caused by retarding the mobility of these radicals in the limited space of small ε -cages. The effect of the ε -cages is much less evident in the case of erionite, which probably results from poor crystallinity of the sample and lower contribution of yellow chromophore.

Acknowledgment

Financial support was provided by the Polish Ministry of Scientific Research and Informational Technology (Grant N20415931/3576).

References

- [1] C.A. Kumins, A.E. Gessler, *Ind. Eng. Chem.* 43 (1953) 3.
- [2] W.D. Galastianin, A.K. Nadiarin, S.S. Karakhanian, E.B. Oganiesjan, F.S. Shakhazarian, C. Grigoroan, *Soviet Patent* 16381447, 1991.
- [3] D. Arieli, D.E.W. Vaughan, D. Goldfarb, *J. Am. Chem. Soc.* 126 (2004) 5776.
- [4] S. Kowalak, M. Stróżyk, *J. Chem. Soc. Faraday Trans.* 92 (1996) 1639.
- [5] S. Kowalak, A. Jankowska, *Micropor. Mesopor. Mater.* 61 (2003) 213.
- [6] S. Kowalak, A. Jankowska, S. Łączkowska, *Catal. Today* 90 (2004) 167.
- [7] G.-G. Lindner, W. Massa, D. Reinen, *J. Solid State Chem.* 117 (1995) 386.
- [8] S. Kowalak, A. Jankowska, S. Zeidler, *Micropor. Mesopor. Mater.* 93 (2006) 111.
- [9] S. Kowalak, A. Jankowska, *Eur. J. Miner.* 17 (2005) 861.
- [10] F. Hund, *Z. Anorg. Allg. Chem.* 509 (1984) 153.
- [11] J.R. Morton, in: E.P. Averbuch (Ed.), *Proceedings of the 15th Colloquium on Ampere*, North-Holland Publ. Co., Amsterdam, 1969, p. 299.
- [12] F. Seel, H.J. Guttler, A.B. Więckowski, B. Wolf, *Z. Naturforsch.* 34B (1979) 1671.
- [13] P. Kobler, G. Winter, F. Seel, K.P. Klos, *Z. Naturforsch.* 42B (1987) 663.
- [14] J. Schneider, B. Dischler, A. Rauber, *Phys. Stat. Sol.* 13 (1966) 141.
- [15] N. Gobeltz, A. Demortier, J.P. Lelieur, A. Lorriaux, *New J. Chem.* 20 (1996) 19.
- [16] N. Gobeltz, A. Demortier, J.P. Lelieur, C. Duhayon, *J. Chem. Soc. Faraday Trans.* 94 (1998) 677.
- [17] S. Kowalak, A. Jankowska, in: 13th I.Z.A. Conference, Beijing, 2007, accepted for publication.
- [18] S. Kowalak, A. Jankowska, to be published.