

# Spectroscopic Properties of $\text{Se}_2^{2-}$ and $\text{Se}_2^-$ in Cancrinite

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Selenium has been introduced into the cancrinite matrix by hydrothermal methods. Hereby uniform red-brown hexagonal crystals of very good quality up to  $4 \times 1 \times 1$  mm in size have been obtained. Selenium was found to be homogeneously distributed in cancrinite—in contrast to post-synthesis loading. UV/VIS and Raman investigations identify  $\text{Se}_2^{2-}$  as the predominating coloring species besides  $\text{Se}_2^-$ . Because of the high optical anisotropy of cancrinite ( $\perp c$ ,  $\parallel c$ ) strong polarization effects were detected. © 1996 Academic Press, Inc.

## INTRODUCTION

Cancrinite, a zeolitic sodium aluminosilicate  $\text{Na}_6\text{Ca}[\text{Al}_6\text{Si}_6\text{O}_{24}]\text{CO}_3 \cdot \text{H}_2\text{O}$  (1), has a 12-ring channel structure (Fig. 1). Within these parallel channels a wide variety of anions can be found, e.g., sulfate, thiosulfate, carbonate, and hydroxide. By means of hydrothermal synthesis here diselenium anions were incorporated and single crystals as large as 4 mm in length and one millimeter in diameter of a sodium cancrinite were obtained. These were of good quality and homogeneous in color (red-brown) across the whole crystal. Polarized Raman and optical spectra were taken of preoriented single crystals. The structural single-crystal investigation (in cooperation with Prof. Dr. W. Massa, Philipps University, Marburg) revealed identical atomic positions to those found by Bogomolov *et al.* (2)—plus one water molecule placed in each  $\epsilon$ -cage (3). We give evidence that  $\text{Se}_2^{2-}$  dianions as well as—in minor concentration— $\text{Se}_2^-$  radical anions are present in the channels of the cancrinite, with both molecular species being nicely aligned by the channels having their main axis along with the crystal  $c$ -axis.

Poborchii *et al.* (4) prepared Se-containing cancrinite by surface reaction with elemental Se at a temperature of 500°C after dehydration of synthetic hydrocancrinite. This cancrinite was of minor optical quality because of inhomogeneously distributed selenium. The authors carried out UV/VIS and Raman measurements and assigned the observed bands to Se-chains placed in the channels.

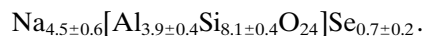
By comparison with spectroscopic data of Se-doped KI (5)/sodalite (6, 7, 8) and anionic Se-species in alkalimetal selenides (9) we conclude that  $\text{Se}_2^{2-}$  dianions are the main coloring Se-species in the investigated Se-containing cancrinite and are responsible for the observed Raman and UV/VIS spectra.

## EXPERIMENTAL SECTION

### Sample Preparation

First, 0.60 g quartz wool (crushed, high purity), 0.059 g  $\gamma\text{-Al}_2\text{O}_3$  (pro analysi), 0.0224 g NaCl (p.a.), 0.135 g NaOH (p.a.), and 0.1 g Se (high purity) were homogenized and placed in an Au-ampule ( $\varnothing$  3.7 mm). After addition of water (37% volume  $\equiv$  autogenous pressure of 1 kbar at 600°C) the ampule was sealed and placed in a stainless steel Morey-type autoclave which was filled likewise with water (37% volume) to achieve 1 kbar at the temperature of reaction. The autoclave was kept for 14 days at 600°C and then slowly cooled down ( $\sim$ 6 h) to room temperature in air. The product was washed thoroughly with water and dried at 80°C. Besides the red-brown colored Se-containing cancrinite (hexagonal needles) small amounts of slight reddish rhombododecahedral Se-doped sodalite crystals are found. Se-doped sodalite is the main fraction if the autoclave is cooled down rapidly by use of compressed air (6, 7). Whereas under UV-excitation Se-doped sodalite shows a bright red luminescence (8), the Se-containing cancrinite exhibits almost none. Hence under an UV-lamp (365 nm) both products can be sorted out quite easily.

The powder diffraction pattern of the hexagonal crystals was in accord with the cancrinite structure [cell parameters:  $a = 12.639(1)\text{Å}$ ,  $c = 5.157(1)\text{Å}$ ]. The quantitative analysis of the red-brown Se-containing cancrinite with the electron microscope (8 runs, without oxygen detection; Prof. Dr. Kniep, Mrs. Klink, Eduard-Zintl-Institut Darmstadt) yielded



Though chloride was used in the reaction mixture it was not present in the cancrinite. Au was incorporated into the cancrinite in an amount of  $0.1 \pm 0.05$  formula units due to the gold-dissolving properties of strong alkaline Se-solutions (distinct etched inner surfaces of the gold ampules!). For this reason experiments could not be carried out with prolonged reaction times (>14 d). Presumably gold is present in the oxidation state +1 on the Na<sup>+</sup> position. A remarkable aspect is the high Si/Al ratio, which is normally near to one (1). The sodium content in cancrinites is frequently underestimated when using electron microscopy (7), and this possibly may have occurred in this case also (the high energy of the electron beam induces diffusion of the mobile sodium ions away from the electron beam). Having this in mind and assuming that the composition deduced from electron microscopy is correct, the negative charge per Se atom is  $\leq 1$ , in accord with Se<sub>2</sub><sup>2-</sup> anions being the predominating color centers.

By Raman spectroscopy carbonate ions in low concentrations are detected. Because of homogenization of the educt mixture in air, CO<sub>2</sub> is absorbed by NaOH, which is present in high concentration.

#### Polarized Optical Spectra

The polarized UV/VIS spectra of selected crystals were measured with a Zeiss Microscope Spectrophotometer USMP 80. The optical half-width of the grating monochromator was 10 nm. Because of the intense absorption of Se-cancrinite, small crystals (about  $100 \mu\text{m} \times 20 \mu\text{m}$ ) had to be used. For the transmission measurements the irradiated crystal areas were chosen  $\geq 20 \mu\text{m}^2$ , depending on the crystal size. Using a Glan-prism, the polarization-dependent spectra were recorded by analyzing the transmitted light parallel and perpendicular to the crystal *c*-axis.

#### Polarized Raman Spectra

Raman spectra were recorded with a DILOR-XY-Spectrometer equipped with a nitrogen cooled ccd-camera as a detector. Samples were excited using the 514.5-nm line from a Carl Zeiss ILA 120 argon ion laser with power levels of 6 mW incident into the entrance optics. Microsampling (180° backscatter geometry) was accomplished with an Olympus 50× objective with a numerical aperture of 0.75. With this objective, the laser beam focal point diameter was approximately  $2 \mu\text{m}$ . Taking into account scattering losses inside the spectrometer, the power level corresponds to an irradiation density of about  $60 \text{ kW/cm}^2$  at the sample.

The polarization of both the incident and the scattered radiation is either parallel ( $\parallel c$ ) or perpendicular ( $\perp c$ ) to the crystallographic *c*-axis.

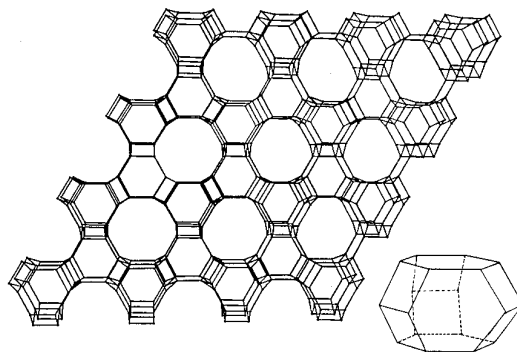


FIG. 1. Structural sketch of the cancrinite framework, built up of *e*-cages; the channels are parallel to the crystallographic *c*-axis (view direction).

## RESULTS AND DISCUSSION

#### Microfocus UV/VIS Spectroscopy

Dichroism of the red-brown Se-cancrinite is observed when the crystals are irradiated with polarized light. They look red if the plane of polarization is parallel to the crystal *c*-axis, while a rotation of the plane of polarization by 90° changes the color to yellow.

Figure 2 shows the polarization-dependent absorption spectra of Se-cancrinite. In the orientation  $\perp c$ , one band at 420 nm is observed and one at  $\leq 300$  nm is suggested. Unfortunately, despite the use of small single crystals, no light is transmitted in the wavelength range smaller than 300 nm, due to an intense absorption in this region. Diffuse reflectance spectra (Fig. 3), however, clearly show an absorption band at 290 nm (7). The latter band superimposes the lower energy slope of a strong band at  $\approx 240$  nm due to the zeolite framework. In the  $\parallel c$  spectrum these two main bands also appear and in addition relatively weak bands at 500 and 355 nm (Fig. 2) appear. The shoulder at about 500 nm is responsible for the red-to-yellow color shift when switching from the  $\parallel c$  to the  $\perp c$  orientation, and for the orange-red color of Se-cancrinite powder material as well. The main bands at 290 and 420 nm are attributed to Se<sub>2</sub><sup>2-</sup>-dianions. The absorption bands at 500 and 355 nm, visible as distinct shoulders, can be assigned to Se<sub>2</sub><sup>-</sup>-radicals by comparison with the spectral results for Se-doped sodalite and Se-ultramarine (Table 1). Moreover these bands exhibit strong polarization dependence—with vanishing intensity for the  $c \parallel$  orientation. Se<sub>2</sub><sup>-</sup>-radicals are found as the only Se species in the by-product sodalite (Se-doped sodalite) (7). By comparing the spectra in Figs. 2 and 3 it is clearly seen that the powder material contains a comparatively higher percentage of Se<sub>2</sub><sup>-</sup>-radicals due to the Se-doped sodalite.

#### Polarized Raman Spectra

The  $\parallel c$  Raman spectrum is dominated by a very strong line at  $\nu = 244 \text{ cm}^{-1}$  ( $2\nu = 488$ ,  $3\nu = 732 \text{ cm}^{-1}$ ) (Fig. 4),

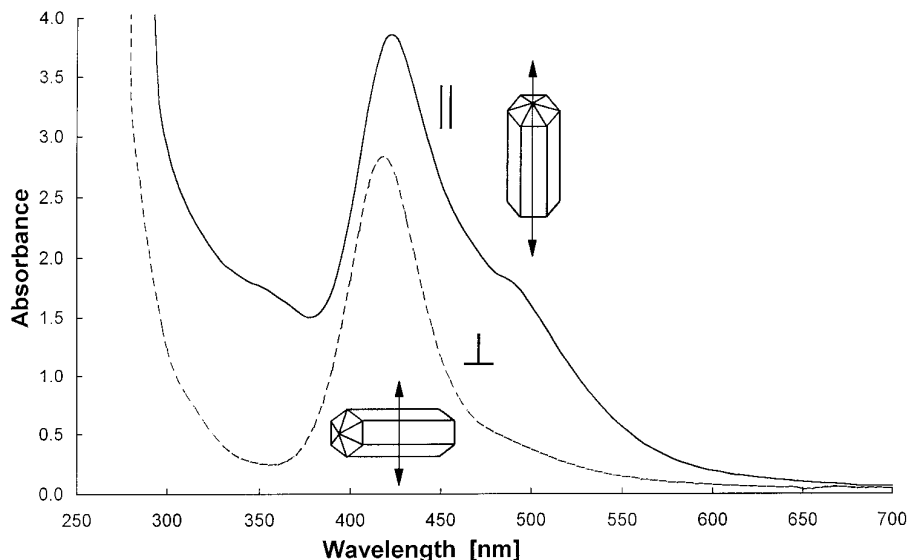


FIG. 2. Polarized UV/VIS spectra of a Se-cancrinite single crystal with the polarization plane parallel and perpendicular to the  $c$ -axis, respectively. Crystal size about  $100\ \mu\text{m} \times 20\ \mu\text{m}$ .

which we assign to the stretching mode of the  $\text{Se}_2^{2-}$  anion. Peaks of much smaller intensity are observed at 92, 181, 270, 284,  $\approx 330$ , 417, and  $499\ \text{cm}^{-1}$ , some of them being more intense in the  $\parallel c$  polarization. These are due to the cancrinite framework with the exception of the very weak  $330\ \text{cm}^{-1}$  band, which is attributed to the  $\text{Se}_2^-$  radical (10) (Table 2). Surprisingly, peaks are also observed, which have to be assigned to vibrations of the  $\text{CO}_3^{2-}$  ion ( $747\ \text{cm}^{-1}$ , deformation;  $969$ ,  $1040$ , and  $1088\ \text{cm}^{-1}$ , stretching; carbo-cancrinite (12), see sample preparation). The polarization of the  $\text{Se}_2^{2-}$ -vibration indicates an orientation of the anion parallel to the  $c$ -axis of the crystal which is identical

with the  $C_3$  axis of the carbonate ion in the carbo-cancrinite. Accordingly, while the vibration of the  $\text{Se}_2^{2-}$  anion has the higher intensity  $\parallel c$  the symmetric stretching mode of the carbonate ion is stronger in the  $c\perp$ -polarization.

### Discussion

The existence of  $\text{Se}_2^{2-}$ -anions in the Se-cancrinite is confirmed by comparison (UV/VIS and Raman) with other  $\text{Se}_2^{2-}$ -containing materials. Reducing red Se-ultramarine (7) (Figs. 5a and 5b), whose color originates from the  $\text{Se}_2^-$  radical anion with two UV/VIS-bands at 500 and 355 nm, by elemental sodium (treatment with sodium dissolved in liquid ammonia at  $-70^\circ\text{C}$ , evaporation of the ammonia and subsequent heating of the resulting product) the color changes to brown-orange. Two new absorptions appear—a strong band at 420 nm and a shoulder around 310 nm. For selenium-doped KI four bands are reported (5) from which two ( $\approx 510$  and  $\approx 350$  nm) are attributed to the  $\text{Se}_2^-$ -radical (5–8). The positions of the other two ( $\approx 430$  and  $\approx 290$  nm) nicely match with those observed here (Table 1). Similarly—using  $\text{Na}_2\text{Se}_4$  as the selenium-donating compound in a hydrothermal synthesis (7)—yellow single crystals with the sodalite structure were obtained, showing only the latter two bands.

Absorption bands at 310 and 420/430 nm (13–15) are ascribed to  $\text{Se}_2^{2-}$  dianions in solution (water)—identical with those just mentioned—and a Raman band is reported for  $\text{Se}_2^{2-}$  in the dialkali metal dichalcogenide  $\text{Na}_2\text{Se}_2$  at  $252\ \text{cm}^{-1}$  (9). Hence, all observations confirm that the color center in the Se-cancrinite is mainly  $\text{Se}_2^{2-}$ .

The  $\text{Se}_2^{2-}$  dianion has an absorption maximum around

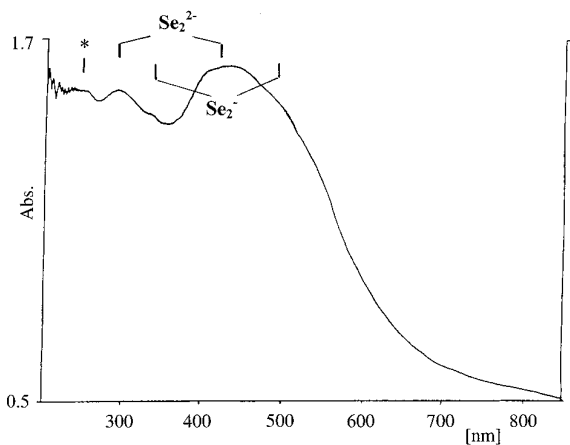


FIG. 3. Diffuse reflectance spectrum of Se-cancrinite. The energetic positions of the bands due to the  $\text{Se}_2^{2-}$  and  $\text{Se}_2^-$  color centers are indicated (\*, onset of host lattice absorption).

TABLE 1  
UV/VIS Bands of Se-Doped KI/Sodalite, Reduced Se-Ultramarine, Se<sub>2</sub><sup>-</sup>/Water, and Se-Containing Cancrinite

Se:KI (5)	Se:SOD (6-8) (red)	Reduced Se-ultramarine (7)	Se:SOD (7) (yellow)	Se <sub>2</sub> <sup>-</sup> /water (14)	Se:CAN	Se-species
510 nm	495 nm	500 nm	—	—	500 nm	Se <sub>2</sub> <sup>-</sup>
430 nm	—	420 nm	410 nm	420 nm	420 nm	Se <sub>2</sub> <sup>-</sup>
350 nm	365 nm	365 nm	—	—	355 nm	Se <sub>2</sub> <sup>-</sup>
290 nm	—	≈320 nm (sh)	≈300 nm (sh)	310 nm	290 nm	Se <sub>2</sub> <sup>-</sup>

250 nm (14) and is therefore not responsible for any UV/VIS band (a Se<sup>-</sup> radical seems to be very unlikely, hence it is a rather unstable radical species).

It is expected that the polarization dependence of the UV/VIS spectra can be understood by assuming the presence of Se<sub>2</sub><sup>-</sup> and Se<sub>2</sub><sup>2-</sup> color centers, being aligned parallel to the *c* channel direction and possessing a symmetry according to the point group  $D_{\infty h}$ . In the case of the radical anion the lowest lying transition at 20000 cm<sup>-1</sup> has to be assigned (16) to  $A^2\Pi_u \leftarrow X^2\Pi_g$  which is indeed allowed only  $\parallel c$ . Recent calculations (16) corroborate this assignment by predicting a vertical excitation energy of 18500 cm<sup>-1</sup> for the  $A^2\Pi_u \leftarrow X^2\Pi_g$  system. The deviation between the maximum of the absorption band and the theoretical prediction is due to matrix effects, Franck-Condon factors, and small intrinsic errors in the chosen theoretical method (relatively corrected multireference configuration interaction).

The UV transition at 28000 cm<sup>-1</sup> has been to Se<sub>2</sub><sup>-</sup> on the basis of photoluminescence excitation spectroscopy by Murata and co-workers (5). However, the same calculations (16) which support the assignment of the 20000 cm<sup>-1</sup> absorption band have cast some doubt on this assignment

since there are no electronic states with Se<sub>2</sub><sup>-</sup> vertical excitation energies at around 28000 cm<sup>-1</sup> from the  $X^2\Pi_g$  ground state, which could be reached in parity-allowed transitions. Moreover, the remaining low-lying spin- and parity-allowed electronic absorptions from the ground state ( $B^2\Delta_u \leftarrow X^2\Pi_g$ ,  $C^2\Sigma_u^- \leftarrow X^2\Pi_g$ ,  $D^2\Sigma_u^+ \leftarrow X^2\Pi_g$ ) should exhibit polarization properties (i.e., vanishing intensity along the *c*-axis) that are the reverse of those observed, even if the host matrices shifted their transition energies from the ground state into the region of the observed UV band. Of course, it is possible that in addition to energetic effects the solid matrix environment lifts spectroscopic selection rules in a way that perturbations between the various electronic states give rise to a new resonance system corresponding to the 28000 cm<sup>-1</sup> band, which would not be present in the isolated Se<sub>2</sub><sup>-</sup> species. However, in the absence of a precise physical picture we refrain from further speculation on this point. In summary, on the basis of its transition energy, polarization behavior, and theory one can presently not give a consistent assignment of the UV band observed at 28000 cm<sup>-1</sup> in selenium-doped host materials.

Unfortunately, quantum-chemical calculations similar to the ones on the singly charged Se<sub>2</sub><sup>-</sup> system are not useful for the assignment of the suspected Se<sub>2</sub><sup>2-</sup> dianion absorption bands: Since the second electron affinity of the Se<sub>2</sub> molecule is negative (i.e., the process  $Se_2^{2-} \rightarrow Se_2 + e^-$  is exothermic), a treatment of the free dianion would have to include continuum states, which is not possible within the standard molecular approach. Thus, all assignments of Se<sub>2</sub><sup>2-</sup> bands made here have to be given with reference to earlier experimental conclusions from the literature. In the case of

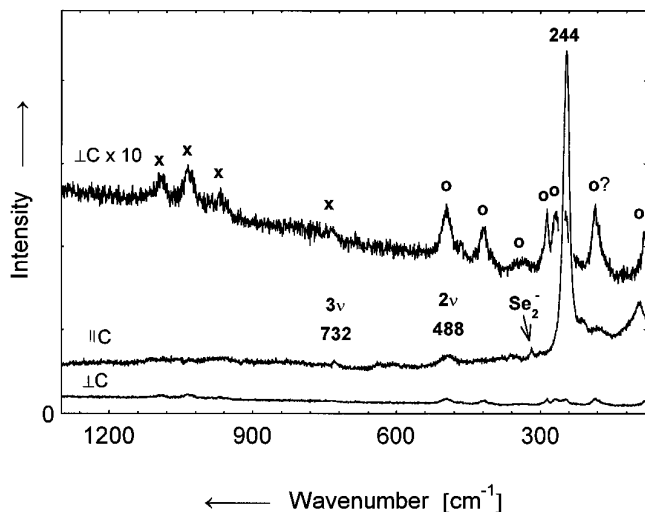


FIG. 4. Polarized Raman spectra of Se-cancrinite with the polarization plane parallel and perpendicular to the *c*-axis, respectively.

TABLE 2  
Raman Frequencies of Diatomic Se-Species

	$\omega_c/\text{cm}^{-1}$	Ref.
Se <sub>2</sub>	390	(7, 11)
Se <sub>2</sub> <sup>-</sup>	330	(7, 10)
Se <sub>2</sub> <sup>2-</sup>	250, 245	(9, this work)

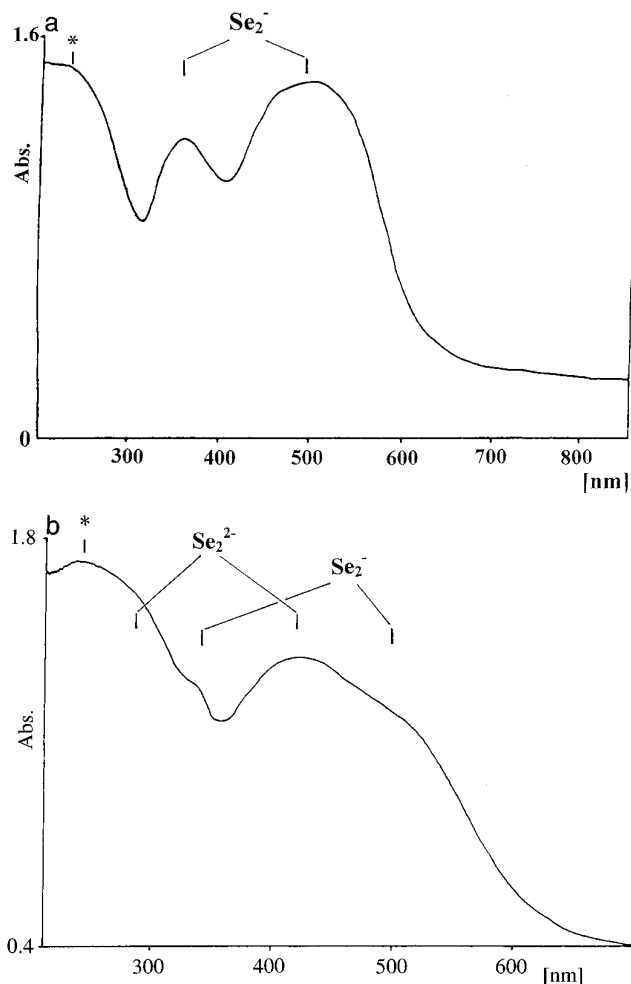


FIG. 5. Diffuse reflectance spectra of a red Se-ultramarine (a) and brown-orange reaction product obtained by reduction with sodium (b). The absorptions due to the  $\text{Se}_2^{2-}$  and  $\text{Se}_2^-$  color centers and to the host lattice (\*) are indicated.

$\text{Se}_2^-$  the lowest lying allowed transition is  ${}^1\Sigma_g^+ \rightarrow {}^1\Pi_u$ , while the next symmetry- and spin-allowed transition is expected to be  ${}^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ . According to the polarization rules the former should be observed only  $\perp c$  and the latter exclusively  $\parallel c$ . A closer inspection of Fig. 2 shows that the intensities of the two bands follow only partly the expectation. The band at 420 nm is of lower intensity  $\parallel c$  than  $\perp c$ , having in mind that the absorption around 500 nm contributes distinctly to the total intensity in the former direction. Also the onset of absorption in the region of the higher energy

transition occurs at a lower energy for  $\parallel c$  compared to  $\perp c$ . We may readily explain this unexpected feature by proposing that part of the  $\text{Se}_2^{2-}$  anions are canted with respect to the channel  $c$ -direction, presumably due to the presence of the strongly polarizing  $\text{Au}^+$  cations on the sodium positions. This is not in contradiction with the Raman spectrum (Fig. 4), which still shows a line at  $245\text{ cm}^{-1}$  with small intensity also  $\perp c$ .

## CONCLUSIONS

The described spectroscopic results, in connection with data from the literature, convincingly demonstrate that one can attribute the UV/VIS bands around 310 and 420 nm as well as the Raman line around 250 nm to the  $\text{Se}_2^-$ -ion as the predominating coloring species in the investigated Se-cancrinite.

## ACKNOWLEDGMENT

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## REFERENCES

1. R. M. Barrer, "Hydrothermal Chemistry of Zeolites," Academic Press, London, 1982.
2. V. M. Bogomolov, A. N. Efimov, M. S. Ivanova, V. V. Poborchii, S. G. Romanov, Yu. I. Smolin, and Yu. F. Shepelev, *Sov. Phys. Solid State* **34**, 916 (1992).
3. N. B. Pahor, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Crystallogr.* **B38**, 893 (1982).
4. V. V. Poborchii, *J. Phys. Chem. Sol.* **55**, 737 (1994).
5. H. Murata, T. Kishigami, and R. Kato, *J. Phys. Soc. Jpn.* **59**, 506 (1990).
6. G.-G. Lindner and D. Reinen, *Z. Anorg. Allg. Chem.* **620**, 1321 (1994).
7. G.-G. Lindner, thesis, Philipps Universität Marburg, July 1994 (Shaker, Aachen 1994).
8. H. Schlaich, G.-G. Lindner, J. Feldmann, D. Reinen, and E. O. Göbel, submitted.
9. P. Böttcher, J. Getzschmann, and R. Keller, *Z. Anorg. Allg. Chem.* **619**, 476 (1993).
10. R. J. H. Clark, T. J. Dines and M. Kurmoo, *Inorg. Chem.* **22**, 2766 (1983).
11. G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed., New York, 1950. Van Nostrand, p. 575/6.
12. N. B. Reshetnyak, T. A. Sosedko, and L. I. Tret'yakova, *Mineral. Zh.* **10**, 69 (1988).
13. M. Schönešhofer, W. Karmann, and A. Henglein, *Int. J. Radiat. Phys. Chem.* **1**, 407 (1969).
14. L. E. Lawrence and T. L. Young, *Aust. J. Chem.* **39**, 511 (1986).
15. A. B. Ellis, S. W. Kaiser, J. M. Bolts, and M. S. Wrighton, *J. Am. Chem. Soc.* **99**, 2839 (1977).
16. C. Heinemann, W. Koch, G.-G. Lindner, D. Reinen, and P.-O. Widmark, *Phys. Rev. A*, in press.