

## Fine structure in photoluminescence spectrum of $S_2^-$ center in sodalite

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**Abstract** The photoluminescence and excitation spectra of sodalites from Greenland, Canada and Xinjiang (China) are observed at 300 and 10 K in detail. The features of the emission and excitation spectra of the orange-yellow fluorescence of these sodalites are independent of the locality. The emission spectra at 300 and 10 K consist of a broad band with a series of peaks and a maximum peak at 648 and 645.9 nm, respectively. The excitation spectra obtained by monitoring the orange-yellow fluorescence at 300 and 10 K consist of a main band with a peak at 392 nm. The luminescence efficiency of the heat-treated sodalite from Xinjiang is about seven times as high as that of untreated natural sodalite. The emission spectrum of the  $S_2^-$  center in sodalite at 10 K consists of a band with a clearly resolved structure with a series of maxima spaced about  $560\text{ cm}^{-1}$  (20–25 nm) apart. Each narrow band at 10 K shows a fine structure consisting of a small peak due to the

stretching vibration of the isotopic species of  $^{32}S^{34}S^-$ , a main peak due to that of the isotopic species of  $^{32}S_2^-$  and five peaks due to phonon sidebands of the main peak.

**Keywords** Sodalite · Photoluminescence ·  $S_2^-$  center · Heat treatment · Fine structure

### Introduction

Natural sodalite represented by the ideal formula  $Na_8Al_6Si_6O_{24}Cl_2$  or  $3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2) \cdot 2NaCl$  is a well-known fluorescent mineral emitting orange-yellow fluorescence under ultraviolet (UV) light. Results of early investigations were reviewed by Kirk (1954, 1955). Kirk (1954) observed the emission and excitation spectra of the synthetic sodalite  $3(Na_2O \cdot Al_2O_3 \cdot 2SiO_2) \cdot 1.0NaCl \cdot 0.25Na_2S \cdot 0.25Na_2SO_4$  at 293 and 77 K under 365 nm excitation. The emission spectra extended from about 500 to beyond 700 nm. The emission spectrum at 293 K showed a small amount of structure with a most intense peak located at 658 nm, whereas the emission spectrum at 77 K showed a clearly resolved structure with a series of maxima spaced about 20 nm apart with a most intense peak located beyond 700 nm. The excitation spectrum consisted of a structureless band with a peak at 400 nm (Kirk 1954). Kirk (1955) concluded that the orange-yellow fluorescence is due to the presence of sodium polysulfide. Later, the orange-yellow fluorescence has been assigned to  $S_2^-$  molecule ions in sodalite. The optical spectra of the  $O_2^-$ ,  $S_2^-$  and  $Se_2^-$  centers in natural and synthetic sodalites have been reported by some researchers (Hodgson et al. 1967; Taylor et al. 1970; van Doorn and Schipper 1971; Chang and Onton 1973; Tarashchan 1978; Schlaich et al. 2000; Gaft et al. 2005). Taylor et al. (1970) observed the emission and excitation

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spectra of the  $S_2^-$  center in synthetic chloro-sodalite at 110 K. The emission spectrum with the most intense peak at about 670 nm consisted of a band structure with a separation of  $556\text{ cm}^{-1}$ . The excitation spectrum obtained by monitoring the emission at 600 nm consisted of a structureless band with a peak at about 394 nm (Taylor et al. 1970). Chang and Onton (1973) synthesized various types of sodalite. The emission spectra of  $3(\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2)\cdot 2\text{NaCl}\cdot\text{Na}_2\text{SO}_3$  under 366 nm excitation consisted of a band at 300 K with a small amount of structure whose peak is located at 677 nm and a band at 78 K with a clearly resolved structure whose most intense peak is located at about 680 nm (Chang and Onton 1973). Tarashchan (1978) observed the emission spectra of the  $S_2^-$  centers in sulfur-containing aluminosilicate minerals, sodalite, hackmanite, vishnevite, hauyne, lazulite and scapolite. The emission band of sodalite showed a small amount of structure with the most intense peak at about 708 nm. Schlaich et al. (2000) obtained the absorption spectrum, which was transformed from the diffuse reflectance spectrum, and emission spectrum of  $\text{Se}_2^-$  in synthetic sodalite at room temperature. The absorption spectrum consisted of three absorption bands with peaks at 20.00, 28.00 and  $40.00\text{ kcm}^{-1}$ . The emission spectrum, which was obtained under  $28.00\text{ kcm}^{-1}$ -band excitation at 364 nm ( $27.47\text{ kcm}^{-1}$ ) with an  $\text{Ar}^+$ -pumped dye laser, consisted of two bands located in red and blue regions. Schlaich et al. (2000) attributed the 20.00 and  $28.00\text{ kcm}^{-1}$  bands to the  ${}^2\Pi_g^- \rightarrow {}^2\Pi_u^-$  and  ${}^3\Sigma_g^- \rightarrow {}^3\Sigma_u^-$  transitions, respectively, within  $\text{Se}_2^-$ , and red and blue emission bands to the  ${}^2\Pi_u^- \rightarrow {}^2\Pi_g^-$  and  ${}^3\Sigma_u^- \rightarrow {}^3\Sigma_g^-$  transitions, respectively. Gaft et al. (2005) observed the laser-induced time-resolved luminescence spectra of the  $S_2^-$  center in natural sodalite at 300 and 77 K.

The optical properties and paramagnetic resonance spectra of  $\text{O}_2^-$ ,  $S_2^-$ ,  $\text{SeS}^-$  and  $\text{Se}_2^-$  ions in various alkali-halide crystals have been reported by some researchers (Rolfe et al. 1961; Rolfe 1964; Kirk et al. 1965; Rolfe 1968; Ikezawa and Rolfe 1973; Rebane and Rebane 1974). The emission spectra of  $\text{O}_2^-$  ions in alkali-halides at low temperatures consist of a series of more than 12 narrow bands at intervals of  $900\text{--}1,100\text{ cm}^{-1}$  in the blue-green region to the red region (Rolfe et al. 1961; Rolfe 1964; Ikezawa and Rolfe 1973). In the emission spectra of  $S_2^-$ ,  $\text{SeS}^-$  and  $\text{Se}_2^-$  ions in alkali halides, the intervals of the narrow bands are about  $600\text{--}640$ , 460 and  $300\text{ cm}^{-1}$ , respectively (Kirk et al. 1965; Rolfe 1968; Ikezawa and Rolfe 1973).

The luminescence properties of the  $\text{O}_2^-$  and  $S_2^-$  centers in minerals are reviewed by Tarashchan (1978), Marfunin (1979) and Gorobets and Rogojine (2002). The crystal structure of the sodalite family is built up from cubooctahedral cages of  $\text{AlO}_4$  and  $\text{SiO}_4$  groups (Taylor et al. 1970; Denks et al. 1976). Molecule ion  $S_2^-$  in sodalite can

substitute for  $\text{Cl}^-$  ion that is incorporated into the cage. The structure on the orange-yellow emission band of sodalite is banded due to the symmetric vibration of the diatomic sulfur molecules (Tarashchan 1978; Marfunin 1979; Gorobets and Rogojine 2002).

The objectives of this investigation are (1) to observe the luminescence spectra of natural sodalites from Greenland, Canada and Xinjiang (China) in detail, (2) to study the effect of heat treatment on the luminescence efficiency of sodalite and (3) to determine fine structures on emission bands at low temperatures.

## Experimental

In this investigation, four natural sodalites from Greenland, Canada and China (Xinjiang; #1 and #2) were analyzed. Two samples from Xinjiang were obtained from the collections of the Xinjiang Geology and Mineral Museum.

The crystal structures of the samples were examined using an X-ray powder diffraction system (Rigaku RAD-1B). The sodalite structure was ascertained by comparing the data with ICDD Card 37-476 for sodalite.

The chemical compositions of the natural sodalites were determined by electron probe microanalysis (EPMA) (JEOL, JXA-8900). Before the measurement by EPMA, the surface of each test piece was polished flat and smooth. The chemical composition in weight % was determined from the mean of the data obtained at ten points of a test piece.

In preparing sulfur-doped sodalite, grains of natural sodalite were sufficiently powdered using an agate mortar. A mixture of powder sodalite and sulfur (10–50 wt%) was heated in a quartz crucible at  $800\text{--}1,100^\circ\text{C}$  for 30 min in air. Powder sodalite without sulfur was also heated under the same conditions for comparison. After the heat treatment, the sample was rapidly quenched to room temperature by placing the crucible on a metal plate at room temperature and using an air blower.

Before the measurement of luminescence spectra, grains of fluorescent sodalite were sufficiently powdered using an agate mortar. The powdered sample was packed into a sample holder with a synthetic quartz-glass cover.

The measuring system of photoluminescence (PL) and excitation spectra was almost the same as that used in previous studies (Aierken et al. 2006a, b). In the measurement of luminescence spectra, a 200 W deuterium lamp (Hamamatsu Photonics L1835), a 500 W xenon short-arc lamp (Ushio UXL-500D) and a 50 W halogen tungsten lamp (Ushio JC12V-50W) were used as excitation light sources.

In the measurement of PL spectra, excitation wavelengths with a bandwidth of 4 nm were selected using a

Ritsu MC-50L grating monochromator. A band-pass glass filter or an interference filter was set in front of the sample to eliminate stray light from the excitation source. Observation wavelengths with a bandwidth of 0.15–1 nm were selected using a Ritsu MC-50 grating monochromator. A suitable glass filter was set in front of the entrance slit of the observation monochromator to eliminate reflected radiation from the excitation source. The PL spectral intensity was converted to an electric signal using a photomultiplier (Hamamatsu Photonics R955). The electric signal was input to a personal computer through a GP-IB cable. The PL spectra were corrected for the spectral sensitivity of the measuring system using a standard tungsten lamp calibrated according to the National Bureau of Standards (NBS), USA.

In the measurement of optical excitation spectra, the same measuring system as that used for the emission spectra was used, except that an excitation bandwidth of 1 nm and an observation bandwidth of 5 nm were used. As excitation light sources, three types of lamp corresponding to the measurement regions were used: a deuterium lamp in the 200–320 nm region, a xenon short-arc lamp in the 280–400 nm region and a halogen tungsten lamp in the 360–480 nm region. The ordinate of the excitation spectra was plotted against the excitation efficiency after optical excitation energy correction. Optical excitation energy was measured using a photomultiplier. For a wavelength region below 320 nm, optical excitation energy was estimated on the basis of the excitation spectrum of sodium salicylate, which has constant quantum efficiency in this wavelength region.

## Results

The chemical compositions of the natural sodalites examined by EPMA are shown in Table 1. The corresponding compositions of sodalite from South Greenland (Markl et al. 2001) are also shown in Table 1. The determined compositions (wt%) of Na<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and Cl are reasonable compared with the theoretical compositions calculated from the ideal formula 3(Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>)·2NaCl of sodalite. The compositions of SO<sub>3</sub> in natural sodalites from Greenland, Xinjiang (#2), Xinjiang (#1) and Canada are 0.59, 0.11, 0.08 and 0.07 wt%, respectively, in the order of concentration.

Figure 1 shows the PL spectra of the natural sodalites from Greenland, Xinjiang (#2), Canada and Xinjiang (#1) at 300 K under 390 nm excitation. When we rewrite the four spectra normalized at maxima, four curves overlap each other. In other words, the feature of the orange-yellow band of sodalite is independent of the locality of the samples. The PL spectrum consists of a broad band with a small amount of structure and a maximum peak at 648 nm. The relative luminescence efficiencies of the orange-yellow fluorescence of the four samples from Greenland, Xinjiang (#2), Canada and Xinjiang (#1) are 100, 37, 8 and 6, respectively.

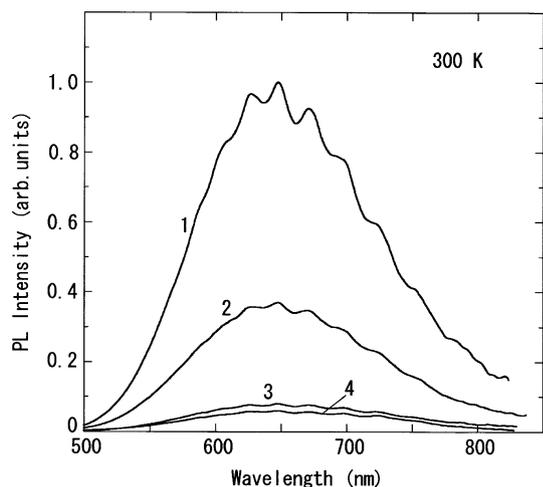
Figure 2a, b shows the emission and excitation spectra of the natural sodalite from Greenland at 300 and 10 K, respectively. The emission spectrum (Em) in Fig. 2a is the same as curve 1 in Fig. 1. The excitation spectrum obtained by monitoring the orange-yellow fluorescence at 300 K consists of a main band (Ex) with a peak at 392 nm and a

**Table 1** Chemical compositions (wt%) of natural sodalites examined by EPMA

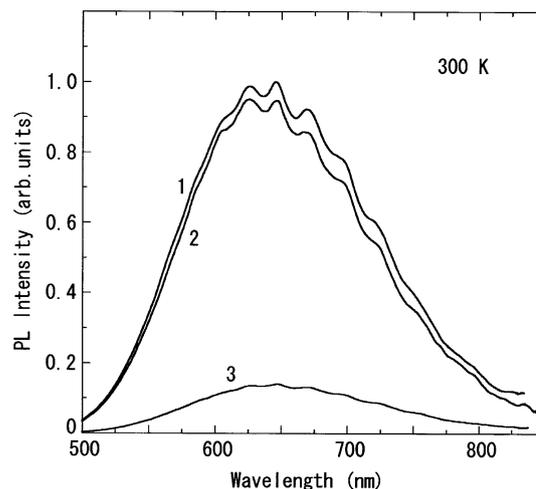
	Greenland	Canada	Xinjiang #1	Xinjiang #2	Greenland <sup>a</sup>	Theoretical
SiO <sub>2</sub>	38.30	37.39	38.92	38.18	36.51	37.20
Al <sub>2</sub> O <sub>3</sub>	31.80	31.32	31.57	31.79	33.69	31.57
Fe <sub>2</sub> O <sub>3</sub>	0.02	0.10	0.05	0.01	0.05	
MnO	0.01	0.02	0.02	0.01		
MgO	0	0	0	0	0.05	
CaO	0.01	0.01	0.03	0.01	0	
PbO	0.03	0.01	0.02	0.03		
ZnO	0.02	0.02	0.04	0.02		
Na <sub>2</sub> O	25.07	24.77	24.16	25.64	24.63	19.18
K <sub>2</sub> O	0.03	0.02	0.07	0	0.02	
SO <sub>3</sub>	0.59	0.07	0.08	0.11	0.12	
Na						4.74
Cl	6.83	7.19	6.75	7.21	7.33	7.32
Br	0.13	0.06	0.11	0.06		
Ce <sub>2</sub> O <sub>3</sub>	0.04	0.06	0.06	0.08		
Eu <sub>2</sub> O <sub>3</sub>	0.04	0.01	0.01	0.05		
P <sub>2</sub> O <sub>5</sub>	0.01	0.01	0	0.01		
Total	102.93	101.06	101.89	103.21	102.40	100.01

Theoretical compositions calculated from the formula 3(Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>)·2NaCl are shown on the right.

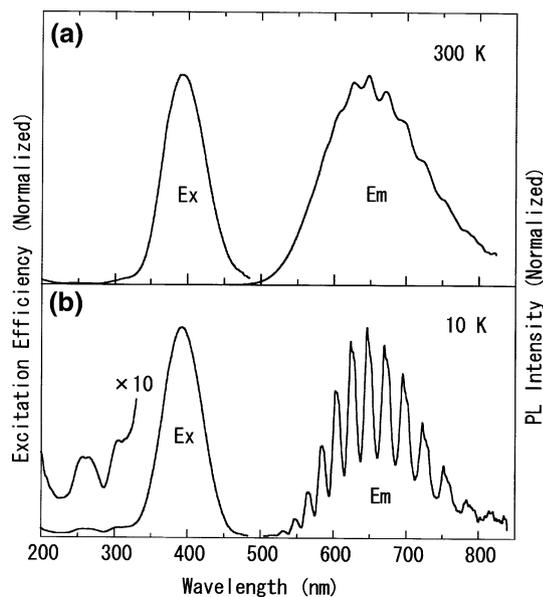
<sup>a</sup> Corresponding compositions of sodalite from South Greenland (Markl et al. 2001)



**Fig. 1** PL spectra of natural sodalites from 1 Greenland, 2 Xinjiang (#2), 3 Canada, and 4 Xinjiang (#1) at 300 K under 390 nm excitation

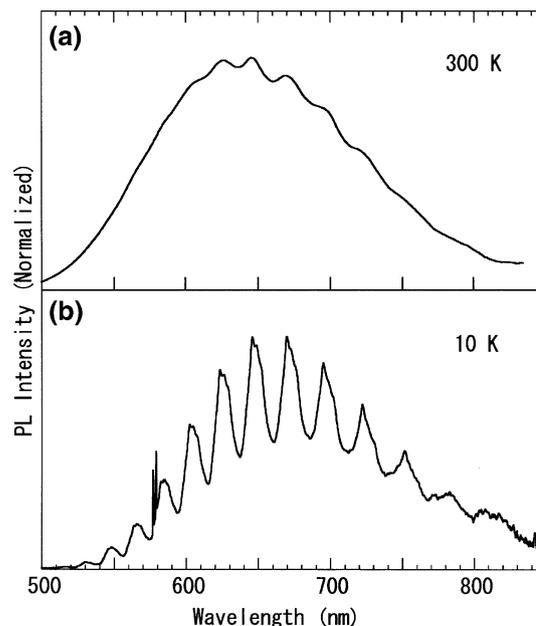


**Fig. 3** PL spectra of 1 sulfur-doped sodalite (30 wt% sulfur, 1,000°C, 30 min), 2 heat-treated sodalite (1,000°C, 30 min), and 3 natural sodalite (Xinjiang #2) at 300 K under 390 nm excitation



**Fig. 2** Optical excitation spectra (Ex) and PL spectra (Em) of natural sodalite from Greenland at **a** 300 K, and **b** 10 K. Ex were obtained by monitoring the orange-yellow fluorescence at 626 nm, and Em were obtained under 390 nm excitation

full width at half maximum (FWHM) of 67 nm. In Fig. 2b, the emission spectrum at 10 K consists of a band (Em) with a clearly resolved structure and a series of maxima spaced about  $560 \text{ cm}^{-1}$  (20–25 nm) apart. Each narrow band shows a fine structure. The excitation spectrum of the orange-yellow fluorescence consists of a main band (Ex) with a peak at 392 nm and an FWHM of 63 nm, and four small bands at 257, 266, 306, and less than 200 nm, as shown in Fig. 2b. The main excitation band (Ex) shows no structure even at 10 K.



**Fig. 4** PL spectra of sulfur-doped sodalite (Xinjiang #2) (30 wt% sulfur, 1,000°C, 30 min) under 390 nm excitation at **a** 300 K, and **b** 10 K. The two narrow spikes at about 578 nm in (b) are Hg 576.595 and 579.065 nm lines introduced as wavelength markers

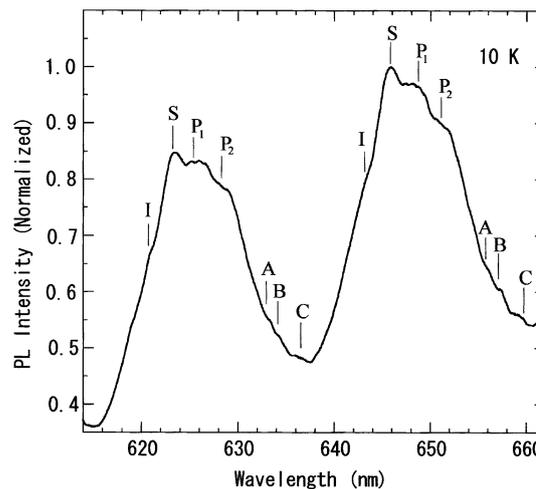
To increase sulfur concentration, we tried to dope sulfur into the natural sodalites by heating the mixture of powder sodalite and sulfur (10–50 wt%) at 800–1,100°C for 30 min in air. Under the optimum conditions of 30 wt% sulfur and 1,000°C, the luminescence efficiencies of the sulfur-doped sodalites from Greenland and Xinjiang (#2) were 2.4 and 7.1 times, respectively, as high as those of the untreated sodalites. The luminescence efficiency of the

**Table 2** Peak wavelengths  $\lambda$  (nm), peak wave numbers  $\lambda^{-1}$  ( $\text{kcm}^{-1}$ ) and intervals ( $\text{cm}^{-1}$ ) of maxima of PL spectrum in Fig. 4b

$\text{S}_2^-$ center in sodalite (this work)			$\text{O}_2^-$ center in synthetic sodalite		
$\lambda$ (nm)	$\lambda^{-1}$ ( $\text{kcm}^{-1}$ )	Interval ( $\text{cm}^{-1}$ )	$\lambda$ (nm)	$\lambda^{-1}$ ( $\text{kcm}^{-1}$ )	Interval ( $\text{cm}^{-1}$ )
546.0	18.315		450.0	22.222	
		569			968
563.5	17.746		470.5	21.254	
		567			1032
582.1	17.179		494.5	20.222	
		568			1009
602.0	16.611		520.5	19.213	
		573			981
623.5	16.038		548.5	18.232	
		556			961
645.9	15.482		579.0	17.271	
		550			918
669.7	14.932		611.5	16.353	
		548			958
695.2	14.384		649.5	15.395	
		541			902
722.4	13.843		690.0	14.493	
		563			920
753.0	13.280		736.5	13.578	
		549			
785.5	12.731				

Corresponding data for the  $\text{O}_2^-$  center in synthetic sodalite (van Doorn and Schipper 1971) are shown on the right

sulfur-doped sodalite from Xinjiang (#2) exceeded that of the sulfur-doped sodalite from Greenland. The heat treatment without sulfur in air also enhanced the luminescence efficiencies of sodalites from Greenland and Xinjiang (#2).



**Fig. 5** Extended part of PL spectrum of sulfur-doped sodalite (Xinjiang #2) (sulfur 30 wt%, 1,000°C, 30 min) at 10 K under 390 nm excitation. The I peak is due to the stretching vibration of the isotopic species of  $^{32}\text{S}^{34}\text{S}^-$ , the S peak is due to that of the isotopic species of  $^{32}\text{S}_2^-$ , and the  $\text{P}_1$ ,  $\text{P}_2$ , A, B and C peaks are due to phonon sidebands of the S peak, as described by Kirk et al. (1965)

Figure 3 shows the PL spectra of the sulfur-doped sodalite (30 wt% sulfur, 1,000°C), heat-treated sodalite (1,000°C) and untreated sodalite (Xinjiang #2) at 300 K under 390 nm excitation; the relative luminescence efficiencies of the orange-yellow fluorescence of the three samples are 100, 95 and 14, respectively. The features of the spectra are almost the same. Note that the luminescence efficiency of the heat-treated sodalite without sulfur is only 5% lower than that of the sulfur-doped sodalite. Brightness of the orange-yellow fluorescence from the heat-treated sodalite under 365 nm excitation is comparable to that of the yellow fluorescence from the well-known phosphor ZnS:Mn under 365 nm excitation.

**Table 3** Peak wavelengths  $\lambda$  (nm) and peak wave numbers  $\lambda^{-1}$  ( $\text{kcm}^{-1}$ ) of fine structures on two narrow bands of the PL spectrum in Fig. 5

	I	S	$\text{P}_1$	$\text{P}_2$	A	B	C
$\text{S}_2^-$ center in sodalite							
$\lambda$ (nm)	621.2	623.5	625.7	628.4	633.0	634.2	636.3
$\lambda^{-1}$ ( $\text{kcm}^{-1}$ )	16.098 (60)	16.038	15.982 (56)	15.913 (125)	15.798 (240)	15.768 (270)	15.716 (322)
$\lambda$ (nm)	643.3	645.9	648.4	651.3	655.9	657.2	659.2
$\lambda^{-1}$ ( $\text{kcm}^{-1}$ )	15.545 (63)	15.482	15.423 (59)	15.354 (128)	15.246 (236)	15.216 (266)	15.170 (312)
$\text{S}_2^-$ center in KCl							
$\lambda$ (nm)	557.5	559.4	561.3	563.3	565.5		
$\lambda^{-1}$ ( $\text{kcm}^{-1}$ )	17.937 (61)	17.876	17.815 (61)	17.752 (124)	17.684 (192)		
$\text{S}_2^-$ center in KBr							
$\lambda$ (nm)	568.6	569.8	571.3	572.7	575.3	577.5	
$\lambda^{-1}$ ( $\text{kcm}^{-1}$ )	17.587 (37)	17.550	17.503 (47)	17.461 (89)	17.382 (168)	17.315 (235)	

Values ( $\text{cm}^{-1}$ ) in parentheses show the separations from the nearest S peak. The lower part shows corresponding data for the  $\text{S}_2^-$  center in KCl and KBr (Kirk et al. 1965)

Figure 4a, b shows the PL spectra of the sulfur-doped sodalite (Xinjiang #2) at 300 and 10 K, respectively, under 390 nm excitation. The PL spectrum in Fig. 4a is the same as curve 1 in Fig. 3. In Fig. 4b, the two narrow spikes at about 577–579 nm are markers for wavelength calibration. The 576.595 and 579.065 nm lines from a low-pressure mercury lamp were introduced into the sample surface. The FWHM of the spikes corresponds to the observation bandwidth of 0.35 nm. As temperature decreases, the structure of the spectrum becomes distinct. The peak positions and intervals of the narrow bands of the PL spectrum in Fig. 4b are listed in Table 2 (left).

Figure 5 shows the extended part of the PL spectrum of the sulfur-doped sodalite (Xinjiang #2) at 10 K, measured at a narrow bandwidth of 0.15 nm under 390 nm excitation. The high luminescence efficiency of the sulfur-doped sodalite enabled us to measure the emission spectra at such a narrow bandwidth. The peak positions of the fine structures on two narrow bands of the PL spectrum in Fig. 5 are shown in Table 3.

## Discussion

The relative luminescence efficiencies of the orange-yellow fluorescence of the natural sodalites from Greenland, Xinjiang (#2), Canada and Xinjiang (#1) are 100, 37, 8 and 6 (Fig. 1), whereas the compositions of  $\text{SO}_3$  in these four natural sodalites are 0.59, 0.11, 0.07 and 0.08 wt%, respectively, (Table 1). This supports the notion that the orange-yellow fluorescence in sodalite is ascribed to  $\text{S}_2^-$  ions, although the relative luminescence efficiency is not proportional to the composition of  $\text{SO}_3$ . The composition of  $\text{SO}_3$  (0.07 wt%) in sodalite from Canada is slightly smaller than that (0.08 wt%) in sodalite from Xinjiang (#1), but the difference between them is insignificant.

As mentioned above, the emission and excitation spectra of the orange-yellow fluorescence of natural and synthetic sodalites have been reported by many investigators. The peak wavelengths of the orange-yellow band, however, do not agree: 658 nm at 293 K and beyond 700 nm at 77 K by Kirk (1954), 629 nm at room temperature by Hodgson et al. (1967), about 670 nm at 110 K by Taylor et al. (1970), 677 nm at 300 K and about 680 nm at 78 K by Chang and Onton (1973), and 708 nm by Trashchan (1978). The peak wavelengths of the excitation band of the orange-yellow fluorescence have been reported: 400 nm at 77 K by Kirk (1954), and about 394 nm at 110 K by Taylor et al. (1970). The main reason for these discrepancies is probably the unsuitable correction of the measured spectra. To obtain reliable spectra, one should make the suitable corrections: (1) the correction of the measured emission spectra for the spectral sensitivity of the

measuring system and (2) the correction of the measured excitation spectra for the optical excitation energy.

As shown in Fig. 2a, b, we obtained the peak wavelengths of the orange-yellow band (648 nm at 300 K and 645.9 nm at 10 K) and excitation band of the orange-yellow fluorescence (392 nm at both 300 and 10 K). We presume that this study gives reliable curves of emission and excitation spectra of the  $\text{S}_2^-$  center in sodalite at 300 and 10 K, because we carefully corrected the measured spectra as described in the above section. The excitation spectrum consists of a main band (Ex) at 392 nm and four small bands at 257, 266, 306, and less than 200 nm, as can be seen in Fig. 2b. This means that the obtained emission spectra reflect the fluorescence only from the  $\text{S}_2^-$  center. If the orange-yellow band includes fluorescence due to other center, we should have another large excitation band in Fig. 2b. The origin of the small excitation band at a wavelength of less than 200 nm may be ascribed to the fundamental absorption of sodalite. The other three small excitation bands at 257, 266 and 306 nm may be ascribed to minor impurities in the sample, the origin of which is unknown. The main excitation band is attributed to the  $^2\Pi_g \rightarrow ^2\Pi_u$  transition within  $\text{S}_2^-$ , and the orange-yellow emission band to the inverse transition. Schlaich et al. (2000) observed the blue emission band with a pronounced vibronic structure, which is attributed to the  $^3\Sigma_u^- \rightarrow ^3\Sigma_g^-$  transition within  $\text{Se}_2^-$  in synthetic sodalite. Any of the small excitation bands in our case cannot be attributed to the  $^3\Sigma_g^- \rightarrow ^3\Sigma_u^-$  transition, because no characteristic emission band with the vibronic structure was observed under 257, 266 or 306 nm excitation.

As shown in Fig. 3, the luminescence efficiency of the orange-yellow fluorescence of the natural sodalite containing sulfur is markedly enhanced by heat treatment without sulfur in air. Two hypotheses for this effect are suggested: One hypothesis is that thermal quenching changes sulfur clusters to  $\text{S}_2^-$  centers in sodalite. In alkali halides activated with copper or lead, activators are quite mobile in the crystal at room temperature, and aggregate to form Cu or Pb clusters, as described by Tsuboi (1980), Burslein et al. (1951), Dryden and Harvey (1969), and Collins and Crawford Jr (1972). In particular, Pb clusters are formed in a few hours after thermal quenching. Researchers of isolated  $\text{Cu}^+$  and  $\text{Pb}^{2+}$  centers in alkali halides, therefore, heated the samples to 400–700°C for 10–60 min, and then rapidly quenched them to room temperature by placing them onto a copper plate at room temperature immediately before optical measurements (Lopez et al. 1980). This heat treatment called “quenching” is effective in resolving Cu and Pb clusters into isolated  $\text{Cu}^+$  and  $\text{Pb}^{2+}$  centers, respectively, in alkali halides. McLaughlan and Marshall (1970) suggested the presence of  $\text{S}_3^-$  radicals in synthetic sulfur-doped sodalite (blue

ultramarine) on the basis of the measurement of the paramagnetic resonance spectrum. From these results, the quenching treatment in this study may change sulfur clusters to  $S_2^-$  centers in sodalite.

Another hypothesis is that the heat treatment of sodalite in air oxidizes  $S_2^{2-}$  to  $S_2^-$ . Hodgson et al. (1967) synthesized sulfur-doped sodalite and heated it in hydrogen atmosphere. The sodalite obtained showed photochromism, that is, upon irradiation with UV light, the sample was colored to deep magenta, and the color was bleached out by visible light. They observed the paramagnetic resonance spectrum of the  $S_2^{2-}$  center in photochromic sodalite and proposed a model of reversible photochromism in which (1) an electron is transferred under the action of UV light from  $S_2^{2-}$  to a chlorine vacancy, (2) the electron trapped at the chlorine vacancy is responsible for the color, and (3) bleaching by visible light releases the electron from the chlorine vacancy reforming  $S_2^{2-}$  (Hodgson et al. 1967). The above conclusion suggests that our sodalite also includes the  $S_2^{2-}$  center, and that the heat treatment of sodalite in air oxidizes  $S_2^{2-}$  to  $S_2^-$  and enhances the luminescence efficiency of the orange-yellow fluorescence.

In our samples, however, the luminescence efficiency of the heat-treated sodalite is stable for 4 months after the thermal quenching. This means that the first hypothesis may be invalid for sodalite. The luminescence efficiency of the heat-treated sodalite from Xinjiang (#2) is comparable to that of the heat-treated sodalite from Greenland, and the component of  $SO_3$  (0.11 wt%) in the untreated sodalite from Xinjiang (#2) is much smaller than that (0.59 wt%) of the untreated sodalite from Greenland. This discrepancy means that the above two hypotheses may be invalid for sodalite. Nevertheless, it is very interesting that the luminescence efficiency of natural sodalite containing sulfur is extremely enhanced by heat treatment in air (Fig. 3). Further experimental study of heat-treated sodalite is required.

As mentioned above, the structure on the orange-yellow band of sodalite is banded due to symmetric vibration of sulfur atoms in  $S_2^-$  centers (Tarashchan 1978; Marfunin 1979; Gorobets and Rogojine 2002). If we apply the diatomic molecule model to  $S_2^-$  and  $O_2^-$  centers in sodalite, the fundamental vibrational frequency  $\omega$  ( $cm^{-1}$ ) is determined by the following equation:

$$\omega = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c} \sqrt{k \left( \frac{1}{m_1} + \frac{1}{m_2} \right)} \quad (1)$$

where  $c$  is the speed of light,  $k$  is the force constant,  $\mu$  is the reduced mass of the diatomic molecule, equal to  $(m_1 m_2)/(m_1 + m_2)$ , and  $m_1$  and  $m_2$  are the masses of the individual atoms.

As shown in Table 2 (left), a series of maxima of the narrow bands in the orange-yellow band due to  $S_2^-$  center in sodalite are spaced about  $560 \text{ cm}^{-1}$  (20–25 nm) apart. van Doorn and Schipper (1971) observed PL spectra of  $O_2^-$ ,  $Mn^{2+}$  and  $Fe^{3+}$  in synthetic sodalite at 77 K. The green emission band due to the  $O_2^-$  center shows a clearly resolved structure. The peak positions and intervals of maxima of the narrow bands in the  $O_2^-$  band in sodalite are also shown in Table 2 (right). The intervals of maxima (about  $560 \text{ cm}^{-1}$ ) in the  $S_2^-$  center are smaller than those (about  $980 \text{ cm}^{-1}$ ) in the  $O_2^-$  center, because the fundamental vibrational frequency in the diatomic molecules depends on the mass of the composed atoms [ $m(^{32}S) > m(^{16}O)$ , see Eq. (1)].

Stuedel (1975) found that the linear relationships between S–S bond distances  $d_{SS}$  and S–S stretching frequencies  $\omega_{SS}$  are expressed by the following empirical equation:

$$d_{SS}(\text{\AA}) = 2.57 - 9.47 \times 10^{-4} \omega_{SS}(\text{cm}^{-1}) \quad (2)$$

and Stuedel (1975) determined  $d_{SS} = 2.00 \text{ \AA}$  for  $\omega_{SS} = 600 \text{ cm}^{-1}$  of  $S_2^-$ . When we apply Eq. (2) to our case,  $\omega_{SS} = 560 \text{ cm}^{-1}$  gives  $d_{SS} = 2.04 \text{ \AA}$  for the  $S_2^-$  center of sodalite in ground state.

Fine structures on narrow bands in the PL spectra of  $O_2^-$  and  $S_2^-$  centers in alkali halides, NaF, NaCl, NaBr, KCl, KI, KBr, and RbBr, have been reported by Rolfe et al. (1961), Rolfe (1964), Kirk et al. (1965), Rolfe (1968), and Ikezawa and Rolfe (1973). Kirk et al. (1965) observed eight peaks, labeled S,  $P_1$ ,  $P_2$ , A, B, I,  $\alpha$  and  $\beta$ , in fine structures on yellow emission bands in KCl:  $S_2^-$  and KBr:  $S_2^-$  at 4 K. The peak positions of fine structures on representative narrow bands are shown in Table 3. Kirk et al. (1965) ascribed the sharp S peak to the isotopic species of  $^{32}S_2^- = (^{32}S-^{32}S)^-$ , the  $P_1$ ,  $P_2$ , A and B peaks to phonon sidebands and the I peak to the isotopic species of  $^{32}S^{34}S^- = (^{32}S-^{34}S)^-$ . The details of the  $^{32}S_2^-$ ,  $^{32}S^{34}S^-$ ,  $^{82}Se_2^-$ ,  $^{80}Se^{82}Se^-$ ,  $^{78}Se^{32}S^-$  and  $^{80}Se^{34}S^-$  centers in KI crystals at 4.2 K were reported by Rolfe (1968).

In this work, the well-corresponding peaks I, S,  $P_1$ ,  $P_2$ , A, B and C are observed as fine structures on narrow bands in the orange-yellow band of sodalite at 10 K (Fig. 5; Table 3). The intensity of the I peak is much smaller than that of the S peak, since the abundances of the isotopic species  $^{32}S-^{34}S$  and  $^{32}S-^{32}S$  are 8.0 and 90.3%, respectively. If we approximate that the force constant  $k(^{32}S-^{34}S)$  in Eq. (1) is equal to  $k(^{32}S-^{32}S)$ , the interval between neighboring I peaks of the  $(^{32}S-^{34}S)^-$  center in sodalite should be slightly smaller (about  $-8 \text{ cm}^{-1}$ ) than that between neighboring S peaks of the  $(^{32}S-^{32}S)^-$  center, because the mass  $m_1(^{34}S)$  is larger than the mass  $m_2(^{32}S)$ . In this case, the former ( $553 \pm 2 \text{ cm}^{-1}$ ) is determined as

smaller than the latter ( $556 \pm 2 \text{ cm}^{-1}$ ) from Table 3. The reliability of the small difference between these values, however, is poor, as the accuracy of the observed wavelength is  $\pm 0.1 \text{ nm}$  ( $\pm 2 \text{ cm}^{-1}$ ). The separations of the  $P_1$ ,  $P_2$ , A, B and C peaks from the nearest S peak, namely, 56–59, 125–128, 236–240, 266–270 and 312–322  $\text{cm}^{-1}$ , respectively, indicate phonon energies with localized modes around the  $S_2^-$  center in sodalite.

### Concluding remarks

Reliable curves of the PL and excitation spectra of the  $S_2^-$  center in sodalite at 300 and 10 K were presented. It was found that the luminescence efficiency of the orange-yellow fluorescence is markedly enhanced by heat treatment in air. The high luminescence efficiency of heat-treated sodalite enabled us to observe the luminescence spectrum in detail. Fine structures on the narrow bands in the orange-yellow band of sodalite at 10 K were shown for the first time.

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