

Optical Properties of Pb^{2+} -exchanged Sulfide Cancrinite

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Pb^{2+} -exchanged cancrinites were prepared with the aim of synthesizing PbS loaded cancrinites. We observed a significant difference in the UV-vis diffuse reflectance absorption spectra between the Pb^{2+} -exchanged cancrinite containing S^{2-} and those containing OH^- , CO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} . The samples so obtained were stable upon exposure to atmospheric moisture. It was suggested that lead lies in the vicinity of sulfur in S^{2-} bearing cancrinite, the bond state and interaction intensity between sulfur and lead in S^{2-} bearing cancrinite are different from those in $\text{S}_2\text{O}_3^{2-}$ or SO_4^{2-} bearing cancrinites after ion exchange.

Key words: Cancrinite, hydrothermal synthesis, ion-exchange, absorption spectrum

1. INTRODUCTION

Quantum size effects in small semiconductor particles have been known for three decades [1]. They can be observed as a blue shift in the absorption edge relative to that of the bulk, of which the extent is strongly dependent upon the particle size [2]. Synthesis and properties of small semiconductor clusters have thus attracted much interest and are currently under intensive investigation [3]. However, the synthesis of quantum-confined clusters is often plagued by the tendency of the extremely small particles to rapidly agglomerate and grow to diameters which are well outside the regime of quantum confinement. For this reason, the synthesis of quantum-size clusters necessitates the use of stabilizing media to prevent agglomeration. The stabilizers which are commonly employed include micelles, colloids, polymers, glasses, and zeolites [3]. Zeolites, which impose size and geometry constraints on encapsulated materials, have been shown to be useful hosts for stabilizing small semiconductor clusters. Extensive theoretical and experimental work focused on the synthesis and characterization of zeolites A, X, Y, L and mordenite-entrapped CdS or PbS clusters [3]. Traditional synthetic routes lie in the preparation from Cd or Pb-exchanged zeolites after exposure to H_2S .

However, the products so obtained are very moisture sensitive, precluding their technical applications.

Cancrinite is found in nature as a porous mineral with the composition $[\text{Na}_6\text{Ca}(\text{Al}_6\text{Si}_6\text{O}_{24})\text{CO}_3 \cdot 2\text{H}_2\text{O}]$ [4], being a low-silica zeolite ($\text{Si}/\text{Al}=1$) that can be prepared synthetically from gels containing anions such as CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, S^{2-} , OH^- [5]. The study on cancrinite was restricted to its hydrothermal synthesis and characterization of contained polyatomic anion states [4-6]. Therefore, if we can fully utilize the merit of cancrinite structure, synthesize firstly cancrinite containing sulfur and then proceed cation exchange for introducing Cd^{2+} or Pb^{2+} , it will be a convenient way to obtain CdS or PbS encapsulated cancrinite.

The aim of our research is to open up the possibilities for synthesizing PbS loaded cancrinites. The introduction of Pb^{2+} into S^{2-} bearing cancrinite was thus explored. S^{2-} bearing cancrinites, $[\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{S} \cdot 4\text{H}_2\text{O}]$, were first synthesized by hydrothermal treatments. Cation exchange reaction of these cancrinites to lead aqueous solutions was then proceeded. Thermal curing was also conducted for the Pb^{2+} -exchanged cancrinite samples under N_2 atmosphere. The samples so obtained were characterized by UV-vis diffuse reflectance absorption spectra.

2. EXPERIMENTAL

2.1. Preparation

The molar gel compositions used to synthesize S^{2-} bearing cancrinites are $xNa_2O:Al_2O_3:2SiO_2:xNa_2S:100H_2O$ ($2 \leq x \leq 3.5$) and $yNa_2O:Al_2O_3:2SiO_2:(5-y)Na_2S:100H_2O$ ($0 \leq y \leq 4$). The following reagents were used to prepare the gels: sodium hydroxide (96%, Nacalai Tesque), aluminum hydroxide (Koso Chemical), colloidal silica (40 wt.%, Nissan Chemical) and sodium sulfide nonahydrate (98%, Kanto Chemical).

Granular sodium hydroxide was first added to deionized water until complete dissolution. Aluminum hydroxide, colloidal silica, and sodium sulfide nonahydrate were then added to the sodium hydroxide aqueous solution and stirred vigorously for 2 h. The gel was then placed in a Teflon-lined autoclave and heated at 110°C at autogenous pressure for 5 days. The product mixture was filtered and washed extensively with deionized water and then dried at 60°C . As a comparison, OH^- , CO_3^{2-} , $S_2O_3^{2-}$, SO_4^{2-} -containing cancrinites were also synthesized. The molar gel compositions were $4Na_2O:Al_2O_3:2SiO_2:X:100H_2O$ with X being Na_2O , Na_2CO_3 , $Na_2S_2O_3$, Na_2SO_4 , respectively. The other reactants used were sodium carbonate (99.5%, Kanto Chemical), sodium thiosulfate pentahydrate (99.0%, Wako Pure Chemical Industries), sodium sulfate (99.0%, Kanto Chemical). The fully same procedure was conducted for their hydrothermal synthesis.

For ion exchange experiment, 0.5 g of the synthesized cancrinite was slurried in 30 g of deionized water. A total of 5 g of lead (II) nitrate (99%, Nacalai Tesque) was then added and the mixture stirred at room temperature for 2 days. The product so obtained was also filtered and washed with deionized water and then dried at 60°C . Thermal curing of samples was proceeded at different temperatures under N_2 atmosphere, without decomposition of the cancrinite framework.

2.2. Characterization

Powder x-ray diffraction data were collected on a Shimadzu XD-3 diffractometer with $CuK\alpha$ radiation. The elemental analyses were performed by Rigaku RIX-3000 x-ray fluorescence spectrometer. UV-vis diffuse reflectance absorption spectra were recorded with a

Shimadzu UV-2100PC UV-vis scanning spectrophotometer. All spectral measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

The x-ray diffraction pattern exhibits clearly that the as-synthesized solid has the structure of S^{2-} cancrinite (JCPDS, 38-0515). The formation of S^{2-} cancrinite as the sole crystalline phase was identified in all samples studied. Cation exchange reaction in lead aqueous solution does not result in any change of the positions and relative intensity ratios of those diffraction peaks, indicating that cancrinite crystallinity is maintained through the ion exchange process.

The elemental analyses reveal that the products synthesized from different gel compositions are of the same chemical compositions. Table I evidences, as an example, the composition analysis result of the product synthesized from certain gel composition, stated as atomic ratio to silicon. After ion exchange, the amounts of aluminium and sulfur are unvaried and that of lead is half as much as decrement of sodium.

Table I. Composition analysis of synthesized products (atomic ratio to silicon).

	Na	Al	S	Pb
Ideal*:	1.33	1	0.17	/
Unexchanged:	1.26	0.99	0.15	/
Exchanged:	0.78	0.98	0.14	0.24

*: calculated from the ideal formula of S^{2-} cancrinite: $Na_8(Al_6Si_6O_{24})S \cdot 4H_2O$.

Figure 1 is the absorption spectra of synthesized S^{2-} cancrinite samples. After ion exchange, a sharp peak appears around 230 nm, accompanied by a weak shoulder at about 270 nm. Also shown in Fig.2 is the absorption spectra of S^{2-} , CO_3^{2-} and OH^- bearing cancrinites (hereafter referred to as simply CAN in figures). As a comparison, those of the unexchanged CO_3^{2-} and OH^- bearing cancrinites are represented on the left of the figure. The spectra of exchanged samples all display the absorption peaks at about 230 nm while those of unexchanged ones show no the absorption peak,

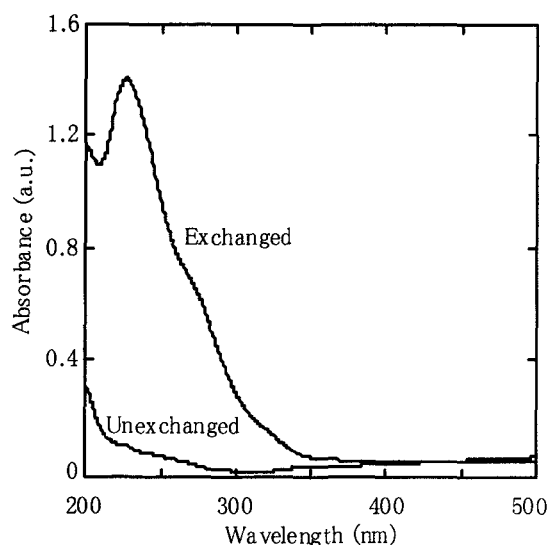


Fig.1. Absorption spectra of synthesized S^{2-} -cancrinite samples.

implying that the absorption peak at about 230 nm is related to Pb^{2+} .

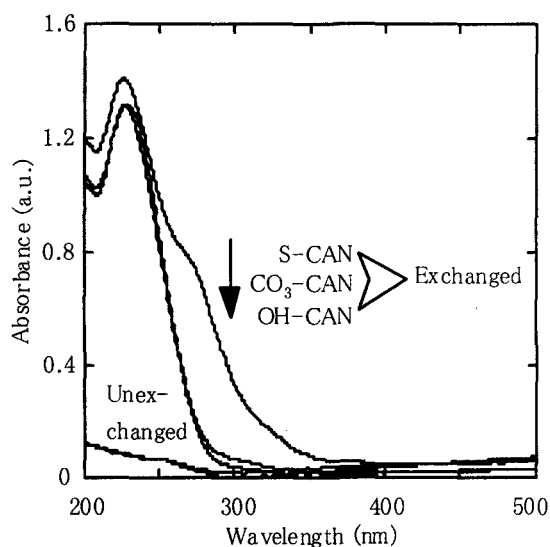


Fig.2. Absorption spectra of various cancrinite samples.

Thermal treatment was also conducted for these Pb^{2+} -exchanged cancrinite samples since heating can eliminate the effect of $Pb(OH)^+$ and other radicals likely present, arising from the hydrolysis of Pb^{2+} , and render the coordination states of sulfur more clear. Figure 3 manifests the absorption spectra of these cancrinite samples heated at $400^{\circ}C$ for 2 h. Besides the peak at about 230 nm, a broad band located at 300 nm also presents in the absorption spectrum of S^{2-} bearing

cancrinite sample, whereas the band does not appear in the absorption spectra of the other cancrinite samples, suggesting that a stronger interaction between sulfur and lead exists in the S^{2-} bearing cancrinite following the dehydrolysis, compared with the other cancrinites.

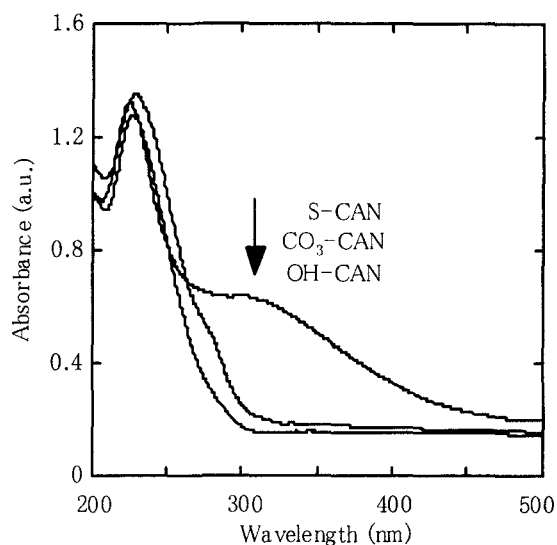


Fig.3. Absorption spectra of ion-exchanged cancrinite samples heated at $400^{\circ}C$ for 2 h under N_2 atmosphere.

In addition, $S_2O_3^{2-}$ and SO_4^{2-} bearing cancrinites were also synthesized hydrothermally. Figure 4 gives their absorption spectra after ion exchange, together with that of S^{2-} bearing cancrinite. A distinct shoulder at about 270 nm can be observed in the $S_2O_3^{2-}$ bearing sample and a weak shoulder in the S^{2-} bearing sample, while the shoulder does not appear totally in the SO_4^{2-} -bearing sample, inferring that the bond state between sulfur and lead in S^{2-} bearing cancrinite is different from those in $S_2O_3^{2-}$ and SO_4^{2-} bearing cancrinites. Furthermore, the shoulder at about 270 nm shifts to around 300 nm when $S_2O_3^{2-}$ bearing sample was treated at $400^{\circ}C$ for 2 h (Fig.5), in line with that observed in S^{2-} bearing sample after the same thermal treatment. Accordingly, the interaction between sulfur and lead contributes to the shoulders at about 300 nm in Figs.3 and 5, as well as those at about 270 nm in Figs.1, 2 and 4.

Above observations also suggest that lead lies in the vicinity of sulfur in S^{2-} bearing cancrinite after ion exchange, thermal curing probably varies the bond state and interaction intensity between sulfur and lead, giving rise to the absorption shoulder at about 270 nm shifting

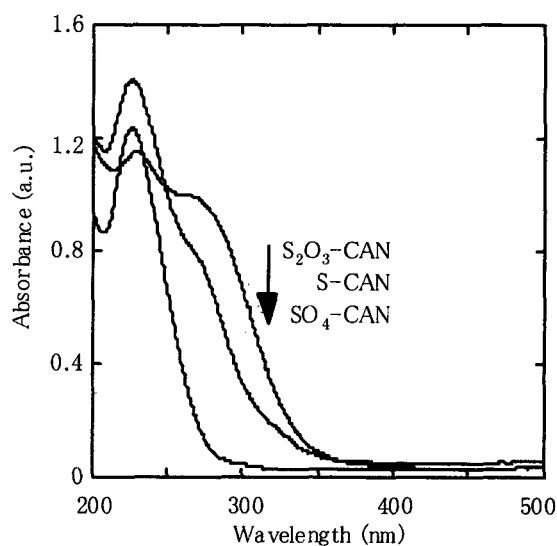


Fig.4. Absorption spectra of ion-exchanged cancrinite samples.

towards the long wavelength side. Moreover, the absorption spectrum of the exchanged cancrinite containing S^{2-} in this study illustrates a remarkable blue shift in the absorption edge relative to that of bulk PbS (ca. 3200 nm) [7], reflecting that some sulphocompound clusters different than bulk PbS generate in the cancrinite channel [4]. Further study is surely necessary in order to confirm the speculation.

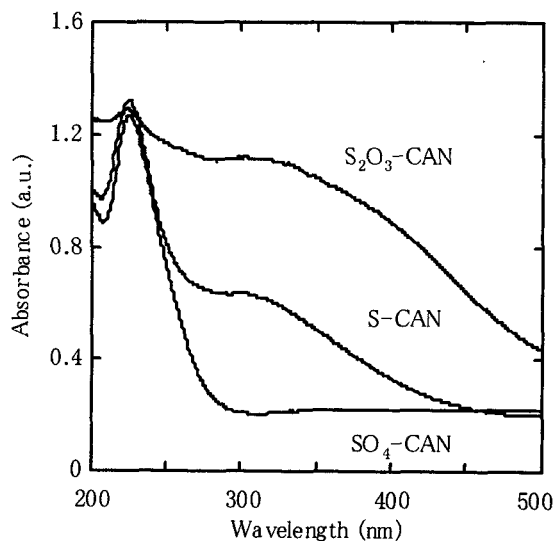


Fig.5. Absorption spectra of ion-exchanged cancrinite samples heated at 400°C for 2 h under N_2 atmosphere.

On the other hand, the Pb^{2+} -exchanged cancrinite samples obtained were stable upon exposure to

atmospheric moisture. This may be due to the formation feature of cancrinite structure: anions or anion groups function as the template and are indispensable to the formation of three-dimensional frameworks [8]. The migration and aggregation of those anions or anion groups will turn out the collapse of cancrinite structure. It follows that once the sulfide is formed in the cancrinite structure, it will be chemically stable unless the structure frameworks of cancrinite are destroyed.

4. CONCLUSIONS

Cation exchange reaction of S^{2-} containing cancrinite to lead aqueous solution was proceeded for synthesizing PbS loaded cancrinite. We observed a significant difference in the UV-vis diffuse reflectance absorption spectra between the Pb^{2+} -exchanged cancrinite containing S^{2-} and those containing OH^- , CO_3^{2-} , $S_2O_3^{2-}$, SO_4^{2-} . The samples so obtained were stable upon exposure to atmospheric moisture. It was suggested that lead lies in the vicinity of sulfur in S^{2-} bearing cancrinite, the bond state and interaction intensity between sulfur and lead in S^{2-} bearing cancrinite are different from those in $S_2O_3^{2-}$ or SO_4^{2-} bearing cancrinites after ion exchange.

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