Synthesis of liebenbergite nano-crystallites from silicate precursor gels prepared by geopolymerization

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Silicate precursor gels containing Ni ions were prepared from sodium metasilicate and nickel nitrate solutions by geopolymerization at room temperature. Caustic soda solution was introduced as pH stabilizer. The gels obtained were heat-treated at 700–1400°C for 1 hour. Crystalline phases as well as raw gels were characterized by XRF, TG-DTA, XRD and FE-SEM techniques. NiO contents of the gels increased with increasing pH values. Gels having stoichiometric composition of liebenbergite, Ni_2SiO_4 were obtained at pH 12.8 with slight Na_2O contamination. Na_2O contents of the gels also increased gradually with increasing pH values up to 5.87% at pH 12.1 and finally decreased abruptly down to 1.5–2% levels, when exceeding pH 12.6. This trend was very convenient to obtain stoichiometric liebenbergite gels having less Na_2O contamination. Two categories of gels were found by TG-DTA in respect to exothermic peaks. Gels prepared at low pH region, ca. 0–5, and high pH region, ca. 13–14, showed no exothermic peaks, indicating that the gels were composed of not inorganic polymers but of simple aggregates of coprecipitates. On the contrary, gels prepared at intermediate pH region, ca. 5–13, showed a sharp exothermic peak, indicating that the gels were composed of inorganic polymers in which atomic order mixing took place due to polycondensation of metal-bearing silica complexes. Accordingly, crystallization temperatures of the gels were lower for the latter that was around 800°C than for the former that was around 1100°C. When heating the gels at elevated temperature, liebenbergite precipitations were observed almost in all gels associated with cristobalite and/or bunsenite according to pH values of gel preparation. The crystalline phases were in nanometer order in size, generally less than 70 nm. The obtained liebenbergite crystallites were platy flakes and 2-dimensionally developed in morphology.

Keywords: Geopolymer, Sol-gel process, Liebenbergite, Nanocrystals, Cristobalite, Bunsenite

INTRODUCTION

In recent years nanometer-scale materials have received considerable interests in various scientific disciplines due to their remarkable catalytic, electronic, magnetic, optical, and mechanical properties, which are different from the micrometer-scale materials. Specifically, liebenbergite, Ni_2SiO_4 which belongs to olivine group and melts incongruently at 1545°C into bunsenite and cristobalite (Levin et al., 1969), has attracted considerable attention as catalysts for disintegrating chlorofluorocarbons (Yatabe et al., 1995) and carbon dioxide (Ikeda, 2004) relevant to the ozone layer destroying and the green house effect problems, respectively. Preparation of liebenbergite from different starting materials has been extensively attempted so far (Tamada, 1984; Wolfenstine et al., 1985, 1994; Jacob and Shukla, 1987; Yatabe et al., 1995; Ikeda et al.,

2001). Some authors (Wolfenstine et al., 1985, 1994; Jacob and Shukla, 1987) worked on kinetic decomposition of liebenbergite into metallic Ni and quartz.

The term “geopolymers” was introduced by Davidovits to designate a new class of three dimensional silico-aluminate inorganic polymers (Davidovits, 1982). Since then, interest in geopolymers has steadily grown up to now. The geopolymer process for preparing monolithic materials (Palomo et al., 1992; Ikeda and Nakamura, 1996; Ikeda 1997; Ikeda et al., 1998) at room temperature has currently being made a great progress as a materials recycling technique for industrial wastes. This technique has diversified applications other than the monolith preparation as binders. That is the immobilization of hazardous heavy metals including radio active elements. The other is the synthesis of nanometer sized silicate crystals at relatively low temperatures similar to the sol-gel technique (Vallepu et al., 2005; Iwahiro et al., 2001, 2002). Generally, there is not so distinct discrimination between these

two techniques. In the sol-gel technique, costly tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) is used as SiO_2 -source, but in the geopolymer technique inexpensive sodium or potassium silicate is used as SiO_2 -source. The latter technique is superior to the former technique from economic point of view, if tremendous demand is expected in practical applications. The geopolymerization is frequently seen in terrestrial sedimentary rocks, which is well-known in terms of "diagenesis" in geology (Manning, 1995). Readers are kindly requested to see the literatures on geopolymerization (Ikeda, 1998; Ikeda et al., 2005), if necessary.

In this paper, chemical compositions of Ni-bearing precursor gels prepared by geopolymerization will be primarily studied as a function of pH and then, synthetic conditions of nanometer sized liebenbergite will be studied on the basis of polycondensations of Ni-bearing silicate complexes as a function of heating temperature.

EXPERIMENTAL

Reagent grade $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were

used for SiO_2 and NiO sources, respectively. Sodium metasilicate solution was prepared by diluting the reagent with deionized water to show 1.09 S.G., which is almost saturated value corresponding to 0.74 mol/L as SiO_2 . Nickel nitrate solution with the same concentration of 0.74 mol/L as NiO was also prepared. Caustic soda solution of 0.5 mol/L concentration labeled S was generally introduced to regulate pH values of mixed solutions. For low and high pH regions, however, extra solutions of nitric acid of 0.74 mol/L concentration labeled N and caustic soda of 5 mol/L concentration labeled SS were also introduced. The starting amount of the sodium silicate solution was 50mL, which were primarily taken in a 500 mL plastic beaker and secondly added with appropriate amount of the pH regulating solution that was 0–100 ml according to objective pH values. Then, the nickel nitrate solution was slowly added dropwise into the beaker taking 2 hour period from a burette, agitating with a laboratory magnetic stirrer. After pH measurements precipitates were filtrated and washed with deionized water sufficiently. Finally, pale green gels were obtained by drying the filtrates at ambient temperature for 3 days. The gels are

Table 1. Chemical and normative mineral compositions of gels as a function of pH and Na_2O contamination

No.	Volume ratio*	pH	Composition (mass %)				NiO/ SiO_2 (Molar ratio)
			NiO	SiO_2	Na_2O	Total	
1	1-1-0.4N	0.1	00.28	99.52	0.19	99.99	0.00
2	1-1-0.3N	2.5	20.14	78.59	1.29	100.02	0.20
3	1-1-0.2N	4.4	40.61	59.17	0.20	99.98	0.55
4	1-1-0S	6.5	60.01	37.18	2.78	99.97	1.29
5	1-1-0.5S	8.5	61.01	35.53	3.47	100.01	1.38
6	1-1-0.75S	10.3	61.55	34.12	4.31	99.98	1.45
7	1-1-1S	12.1	62.15	31.96	5.87	99.98	1.56
8	1-1-1.5S	12.6	63.54	31.29	5.21	100.04	1.63
9	1-1-2S	12.8	69.72	28.75	1.52	99.99	1.95
10	1-1-0.5SS	13.3	76.15	21.74	2.09	99.98	2.81
11	1-1-1SS	13.8	78.01	20.45	1.52	99.98	3.06
Normative mineral composition (mass %)**							
No.	SiO_2		Ni_2SiO_4		NiO		
1	99.51		-		-		
2	72.07		27.92		-		
3	43.05		56.94		-		
4	13.65		86.34		-		
5	11.40		88.59		-		
6	9.80		90.19		-		
7	7.48		92.51		-		
8	6.10		93.89		-		
9	0.72		99.27		-		
10	-		77.40		22.59		
11	-		72.18		27.81		

* N, S and SS denoting nitric acid, low concentration caustic soda and high concentration caustic soda solutions used for pH regulating agents, also see the text.

** Disregarding Na_2O .

Figure 1. Variation curve of NiO/SiO₂ molar ratio of gels as a function of pH.

numerically labeled in the order of the sodium metasilicate, the nickel nitrate and the pH regulating solutions, N, S and SS as designated in volume ratios, e.g., 1-1-0.3N, 1-1-1S, 1-1-0.5SS and so on together with sequential Nos. as seen in Table 1.

Chemical compositions of the gels were determined by X-ray fluorescence spectrometer (XRF), Rigaku ZSX-101e. Sample gels were dehydrated completely by firing at 1000°C beforehand, and then, were preformed into bead sample disks mixed the gel powders with anhydrous lithium tetra borate in 1:10 proportion according to conventional method. Thereby, a few drops of 0.75 M lithium iodide solution were added for easy removal of the disks from a platinum crucible.

Thermogravimetric and differential thermal analysis (TG-DTA) of the precursor gels was performed by employing MAC Science TG-DTA 2000S at heating rate of 10°C/min in air. The gels prepared were heat-treated at 700–1400°C for 1 h in various intervals of temperature, using a Pt-crucible and an electric resistance furnace to obtain crystalline phases. X-ray diffraction (XRD) analysis was carried out, employing Mac Science MXP3 for identifying the crystalline phases under Ni-filtered CuK α radiation and 40 kV–20 mA conditions. Crystallite sizes were determined by the Schirrer equation. Gels and crystalline shapes were observed by field emission type scanning electron microscope (FE-SEM), JEOL-JSM-7000F.

RESULTS AND DISCUSSION

Chemical composition

Chemical compositions of the gels are represented in

Table 1 and the variation of NiO/SiO₂ molar ratio in Figure 1 together with Na₂O contamination levels. Analytical errors are estimated to be $\pm 0.05\%$ at most. It was noted that NiO contents increased with increasing pH. In order to obtain only liebenbergite, the NiO/SiO₂ molar ratio should be exactly 2, which were reached at pH 12.8. It is desirable that sodium contamination should be as small as possible. Nevertheless, it was detected despite sufficient washing the gels. It is convenient to divide the pH range into 4 regions in respect of Na₂O contamination levels, i.e., ultra low, ca. 0–5, low ca. 5–9, high ca. 9–12.7, and ultra high ca. 12.7–14. In ultra low pH region, the contamination level was very small, showing less than 1% as Na₂O. In low pH region, the level increased up to around 3%. In high pH region, the level increased much more, showing around 5%. In ultra high pH region, however, the level decreased down markedly, showing around 1.5–2%. This ultimate decreasing of contamination level is advantageous to obtain useful liebenbergite gels for applications. The small contaminations found in ultra low and ultra high pH regions are considered due to simple absorption in void and surface of the gels rather than incorporation. However, the high contaminations detected in the gels prepared at low and high pH regions are considered due to incorporation into polycondensed gels as mentioned in the next section, terminated with -O-Si-O-Na of siloxane groups. Sample No. 9 had exceptionally low Na₂O contamination despite belonging to the category of polycondensed gels as mentioned later. At the moment, -O-Si-O-H terminations are preferentially considered rather than -O-Si-O-Na terminations.

Figure 2. Typical TG-DTA curves of precursor gels.

TG-DTA and XRD analyses

Typical TG-DTA results of the as-prepared gels are shown in Figure 2. XRD results as well as exothermic peak positions of all the gels are tabulated in Table 2. Every DTA curve exhibited an endothermic peak centered around 80°C irrespective of samples due to dehydration of absorbed water. Importance is exothermic peaks whose presence can be regarded as a measure of polycondensation of the gels, when it appears generally below 1000°C. It is well-known that gels precipitate generally some crystalline phases so instantly, generating a sharp exothermic peak in TG-DTA charts with elevation of heating temperature, if the gels are polymerized.

Samples from Nos. 4 to 9 prepared in low to high pH regions showed an exothermic peak located below 1000 °C, ranging from 770°C to 950°C as seen in Table 2. Sample No. 9 was an exception, which was prepared in ultra high pH region, and showed an exothermic peak centered at 950°C that was highest among present samples. No double exothermic peak was encountered in this study, which was previously reported in case of silica-rich liebenbergite gels (Ikeda et al., 2001). These results indicate that obtained gels from Nos. 4 to 9 were not diphasic character but monophasic character.

When heated other precursor gels prepared in both ultra low and ultra high pH regions, no exothermic peaks were encountered. Therefore, simple aggregates of coprecipitates are estimated for the gel structures (Iwahiro et al., 2001). Consequently, crystallization temperatures of the gels were much higher, exceeding 1000°C as seen in Table 2.

XRD results are represented in Figures 3 to 6 in terms of heating temperature. Starting gels all exhibited pale green in colour. On heating, the gels turned black in color first generally and some yellowish green spots appeared. Then, they finally became yellowish green, indicating entire crystallization of the gels.

Evolution of crystalline phases as a function of temperature should be discussed in the 4 categories of pH region as mentioned above: ultra low, low, high and ultra high. For precursor gels prepared at ultra low pH regions, formation of liquid at elevated temperature was unclear due to very small Na₂O contamination. However, some influence of contaminated Na₂O was encountered in other gels. For those prepared at low pH regions, some formation of liquid was estimated from alteration of identified phases with elevation of temperature. For those prepared at high pH region, actual formation of liquid was found at very high temperature. For those prepared at ultra high

Table 2. Identified crystalline phases as a function of heating temperature and exothermic peaks

No.	pH region	Top of exothermic peak of DTA (°C)	Heating temperature (°C) and crystalline phase							
			700	800	900	1000	1100	1200	1300	1400
1	Ultra	—	-	-	-	-	(C)	C	C	C
2	low	—	-	-	-	-	C,(L),B	C,L,B	C,L,B	C,L,B
3		—	-	-	-	-	C,L,B	C,L,B	C,L,B	C,L,B
4	Low	770	-	(L)	L, C	L, C	L, C	L, C	L, C	L
5		840	-	(L)	L, C	L	L	L	L	L, B
6	High	880	-	L, (B)	L, (B)	L, (B)	L, (B)	L, B	B, (L)	B + melt
7		820	-	L, (B)	L, (B)	L, (B)	L, (B)	L, B	B, (L)	B + melt
8		870	-	(L)	L, (B)	L, B	L, B	L, B	B, (L)	B + melt
9	Ultra	950	-	-	-	L, B	L, B	L, B	L, B	B, (L)
10	high	—	-	-	-	-	L, B	L, B	L, B	L, B
11		—	-	-	-	-	(L,B)	L, B	L, B	L, B

L, liebenbergite; C, cristobalite; B, bunsenite; -, amorphous; Brackets, low crystalline or minor.

Figure 3. X-ray diffraction results of heat-treated samples prepared in ultra low pH region. All peaks in sample No.1 are characteristic of cristobalite and peaks in samples Nos. 2 and 3 are characteristic of liebenbergite except C, cristobalite and B, bunsenite.

pH region, formation of liquid was estimated from disintegration of liebenbergite at elevated temperature. Details are as follows.

For the samples Nos. 1, 2 and 3 prepared in ultra low pH region, cristobalite was identified as major phase (Fig.3). With increasing contents of NiO-component, some liebenbergite formed associated with appreciable amount of bunsenite irrespective of heating temperature over 1000°C. The present gel compositions can be interpreted in the system NiO-SiO₂ (Levin et al., 1969), neglecting the small Na₂O contaminations, in which liebenbergite, Ni₂SiO₄ is regarded as an only intermediate

Figure 4. X-ray diffraction results of heat-treated samples prepared in low pH region. All peaks are characteristic of liebenbergite except C, cristobalite and B, bunsenite.

phase. In this respect, presence of bunsenite is too strange to explain, since the gel compositions are located on SiO₂-rich side as seen in Table 1, where there is no potential of bunsenite. If the starting gels are polycondensed, atomic order mixing takes place and the gels may precipitate only cristobalite and liebenbergite. Therefore, this bunsenite is regarded as metastable phase due to not polycondensed but the co-precipitated aggregate nature of starting gels as suggested by the DTA results in which no exothermic peaks were detected below 1000°C range.

For the samples Nos. 4 and 5 prepared at low pH region (Fig. 4), liebenbergite associated with minor cristobalite or liebenbergite associated with minor bunsenite was noted. The precursor gel No. 4 precipitated trace liebenbergite at 800°C. Then, at 900°C, precipitation of liebenbergite developed, associated with small amount of cristobalite up to 1300°C. Finally, the cristobalite diminished and only liebenbergite was identified at 1400°C. This diminish is probably attributed to some formation of liquid phase due to the considerably high Na₂O contamination in the starting gel. The precursor gel No. 5 showed trace liebenbergite at 800°C. Then, at 900°C, trace cristobalite was detected other than main phase liebenbergite. At 1000°C, the cristobalite diminished probably due to formation of trace liquid and this state continued up to 1300°C. At 1400°C, bunsenite appeared other than lieben-

Figure 5. X-ray diffraction results of heat-treated samples prepared in high pH region. All peaks are characteristic of liebenbergite except B, bunsenite.

bergite. This is probably attributed to the partial melting of liebenbergite into bunsenite and liquid due to the considerably high Na_2O contamination.

For the samples Nos. 6, 7, and 8 prepared at high pH region (Fig. 5), liebenbergite was identified mostly accompanied with bunsenite. For the precursor gels Nos. 6, 7 and 8, the intensity of XRD peaks of bunsenite markedly increased and liebenbergite decreased at 1200°C and over, suggesting a large amount of liquid formation due to the very high Na_2O contaminations. Finally at 1400°C, clear melting of the charge in the crucible was observed (Table 2) and no liebenbergite was identified any more. The run products consisted of bunsenite and large amount of liquid, ultimately.

For the samples Nos. 9, 10 and 11 prepared at ultra high pH region (Fig. 6), sample No. 9 having nearly stoi-

Figure 6. X-ray diffraction results of heat-treated samples prepared in ultra high pH region. All peaks are characteristic of liebenbergite except B, bunsenite.

chiometric composition of liebenbergite showed a peculiar character as mentioned in TG-DTA and this gel could be classified into Nos. 4 to 8 category in respect to showing an exothermic peak. For the precursor gel No. 9, the amount of bunsenite increased at 1300°C and over probably due to a slight formation of liquid, although no visual melting was observed due to the abrupt decreasing Na_2O contamination. For samples Nos. 10 and 11 liebenbergite precipitated together with bunsenite at 1000°C and over. This phase assemblage was exactly the same expected from NiO-SiO_2 system. However, formation of bunsenite increased at 1300°C and 1400°C for the precursor gels Nos. 10 and 11, respectively. Some liquid is estimated to form due to the effect of the contaminated Na_2O -component at high temperature and partial melting of the liebenbergite into bunsenite and liquid might take place.

Table 3. Crystallite sizes of liebenbergite perpendicular to (112) determined by the Scherrer equation

No.	Volume ratio	pH	Heating temperature (°C) and Crystallite size (nm)						
			800	900	1000	1100	1200	1300	1400
2	1-1-03N	2.5	-	-	-	-	38	41	41
3	1-1-0.2N	4.4	-	-	-	39	46	41	41
4	1-1-0S	6.5	38	46	46	46	46	46	46
5	1-1-0.5S	8.5	46	46	46	46	46	46	46
6	1-1-10.75S	10.3	38	40	46	45	46	68	-
7	1-1-1S	12.1	41	41	46	43	41	69	-
8	1-1-1.5S	12.6	32	32	32	40	43	68	-
9	1-1-2S	12.8	-	-	40	40	45	45	64
10	1-1-0.5SS	13.3	-	-	-	46	46	52	60
11	1-1-1SS	13.8	-	-	-	38	46	52	59

Figure 7. FE-SEM microphotographs of No.5 precursor gel and obtained liebenbergite as exemplified.

Although there is Na_2O contamination problem in present precursor gels, the formation temperature of liebenbergite is much lower than that of conventional methods studied so far: $>1500^\circ\text{C}$ for mechanical oxide mixtures (Tamada, 1984), $\sim 1400^\circ\text{C}$ (Wolfenstine et al., 1985, 1994; Jacob and Shukla, 1987) for TEOS hydroly-

sis and $\sim 1200^\circ\text{C}$ (Yatabe et al., 1995) for Na-metasilicate coprecipitation. So far as catalytic applications are concerned, the contamination is not a serious problem, since catalyzers work generally below 1000°C and mostly $300\text{--}600^\circ\text{C}$.

Crystallite size and FE-SEM observation

Crystallite sizes encountered in this study were calculated on liebenbergite, cristobalite and bunsenite from FWHM of (112), (101) and (200) diffraction peaks, respectively, applying the Scherrer equation. Nanometer sized crystallites were obtained irrespective of mineral species, but only liebenbergite results are shown in Table 3.

The XRD crystallite size was ranging from 32 to 69 nm and some grain growth was generally detected according to elevation of heating temperature. However, no appreciable change was noted in some samples such as Nos. 4 and 5. This suggests the thickness of crystallite size was maintained almost constant irrespective of heating temperature as mentioned later. Incidentally, the [001] thickness becomes nearly the twice of [112] thickness listed in Table 3.

FE-SEM photomicrographs of sample No. 5 are shown in Figure 7 as an exemplified case, in which nearly single phase liebenbergite was identified from 1000 to 1300°C. Normative potential of liebenbergite was 88.59% as seen in Table 1. As-prepared gel showed spawn-like aggregates of gels similar to forsterite precursor gels as reported in literature (Vallepu et al., 2005). On heating, the precursor gels precipitated nanometer sized platy crystallites at 900°C. Grain growth was observed according to elevation of heating temperature. Specifically, on heating at 1300°C, the platy size reached up to nearly 3 μm . This seems in contradiction with the results determined by the Scherrer equation. However, this equation only measures the thickness perpendicular to crystallographic planes concerned. The obtained liebenbergite developed 2-dimensionally, probably a $\times$ b directions. Accordingly, XRD crystallites sizes are not in contradiction with FE-SEM results. The grain growth is attributed to some formation of liquid phase. Although the liquid presence was not clearly observed even under FE-SEM, the presence can be estimated from the chemical composition and XRD pattern changes with elevation of heating temperature as mentioned in preceding section.

CONCLUSION

Preparation of Ni-bearing silicate gels was carried out by mixing Na-metasilicate, caustic soda and Ni-nitrate solutions. Then, the obtained precursor gels were heat-treated at high temperatures up to 1400°C. Following items were drawn as conclusion.

(1) NiO-content of silicate gels increases with increasing pH. Na_2O contamination also increases with increasing pH up to 5.8% at pH 12.1 and then, decreases rapidly down to 1.5–2 levels, when exceeding pH 12.6 Precursor

gels having exactly liebenbergite composition can be obtained under pH 12.8 condition with slight Na_2O contamination, that is 1.52%.

(2) Polymerized precursor gels are obtained, when prepared in intermediate pH conditions designated as low and high pH in the text, ranging from approximately 5 to 12.7, while non-polymerized gels are obtained, when prepared in extremely high and low pH conditions, ranging from approximately 0 to 5 and approximately 12.7 to 14. Only one exception is the gel prepared at pH 12.8 (No. 9), which is polymerized, judging from TG-DTA results.

(3) The polymerized gels show a sharp exothermic peak in TG-DTA charts at temperatures ranging from 770°C to 950°C to yield crystalline phases below 1000°C, while the non-polymerized gels show no such a peak to yield crystalline phases.

(4) Present gel compositions are located in the system SiO_2 -NiO, when disregarded the contaminated Na_2O . Accordingly, cristobalite, SiO_2 and liebenbergite, Ni_2SiO_4 or liebenbergite and bunsenite, NiO should be precipitated from the precursor gels according to gel compositions and heating temperature. However, metastable formation of bunsenite has been encountered with stable cristobalite and liebenbergite minerals in the gels prepared in ultra low pH region. Some liquid formation is estimated specifically at elevated temperatures due to the contaminated Na_2O .

(5) Crystalline phases encountered are nanometer sized crystallites irrespective of mineral species. Specifically, the liebenbergite is platy in morphology and is also in nanometer size at low temperatures. However, grain growth has been noted on liebenbergite crystallites at elevated temperatures due to some formation of liquid phase caused by the influence of contaminated Na_2O . The nanometer sized liebenbergite crystallites exhibit two-dimensional flaky platelets at low temperatures and finally grow 2-dimensionally up to nearly 3 μm platelets at high temperatures still keeping nanometer thickness.

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Manuscript received October 13, 2004

Manuscript accepted April 6, 2005

Manuscript handled by Tsutomu Sato