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Synthesis of nanometer enstatite from precursor gels prepared by the geopolymer technique

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Abstract

The geopolymer technique is one of the methods making inorganic polymers which can be prepared by polycondensation of silicic acids complexes containing foreign metal ions. Sodium silicate solutions prepared from $Na_2O\cdot SiO_2\cdot 9H_2O$ was applied as host solutions. Anhydrous silicate consisting of MgO and SiO_2 components were synthesized by heat treatment of gel precursors prepared by mixing sodium metasilicate solution with Mg–nitrate solution in various molar ratio. Amorphous and crystalline characters were discussed on the basics of DTA and XRD results. The XRD results showed that gels began to crystallize enstatite at about 900 °C.

Keywords: Enstatite; Geopolymer; Sodium silicate; Water glass; Nanocrystal

1. Introduction

Enstatite is known as a terrestrial mineral classified into a mineral family called pyroxene group. This mineral has chemical formula of $MgSiO_3$ for pure end-member and has some modifications which are orthoenstatite, clinoenstatite and protoenstatite belonging to orthorhombic, monoclinic and orthorhombic systems, respectively. Orthoenstatite, simply called enstatite, generally is stable at low temperature and transforms to protoenstatite at about 1200 °C and protoenstatite is stable up to its melting point of 1557 °C. Clinoenstatite and orthoenstatite have been believed to be metastable and transform to protoenstatite at about 1200 °C, which is stable up to the melting point at atmospheric pressure.

Geopolymer technique is a kind of sol–gel technique considered to have diversified applications in future [1–5]. The first one is consolidation of waste powders into monolithic materials. The second is immobilization of hazardous elements. The third is synthesis of nanometer sized silicate crystals. To prepare enstatite, different procedures were described in literatures [6–9]. In this paper, synthesizing technique of nanometer-sized enstatites will be studied by the geopolymer technique in view of potential applications to ceramics and catalyzers.

2. Experimental

Host solution was primarily prepared from reagent grade $Na_2O\cdot SiO_2\cdot 9H_2O$ by dissolution with deionized water to show 1.09 S.G., corresponding to 0.74 mol/L concentration as $Na_2O\cdot SiO_2$ (MS). Then, guest solution was prepared from reagent grade $Mg(NO_3)_2\cdot 9H_2O$ to show 1 mol/L concentration as $Mg(NO_3)_2$ (NM). This guest solution was slowly added to the host solution dropwise from a burette in variable molar ratio with continuous stirring by a laboratory magnetic stirrer. The departure amount of the host solution was 50 mL taken in a 500 mL plastic beaker and then the guest solution was added in desired proportion that were 1:4 to 3:1 in terms of $MgO{:}SiO_2$ molar ratio to obtain silicate precursor gels. The molar ratios were adjusted by volumetry. After pH measurements of supernatants, precipitates were three times filtrated and washed in sufficient amount of deionized water. Finally, precursors were obtained by air-dry at room temperature for 3 days. Chemical compositions of the gels were determined by fluorescent X-ray technique, making vitrified disks of borate. Gel samples were fired at 1000 °C for 1 h. Dynamic crystallization behavior of the gels was studied by TG–DTA

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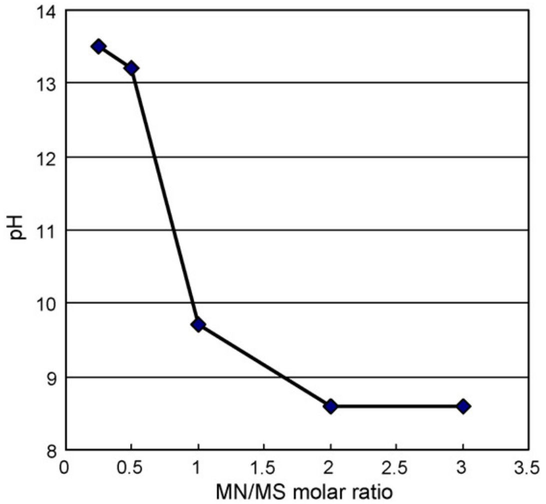

Fig. 1. Diagram showing variation of pH vs. mixing molar ratio.

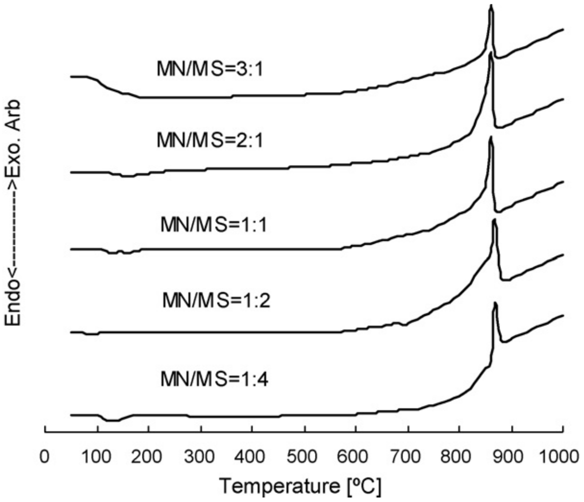

Fig. 2. DTA curves of gels.

technique. Then, the gels were heat-treated from 800 °C to 1400 °C for 1 h with 100 °C intervals in order to study static crystallization behavior of the gels, employing a Pt-crucible and an electric resistance furnace. Obtained crystalline phases were identified by XRD technique. Crystallite sizes were determined by Scherrer equation.

3. Results and discussion

3.1. Variation of pH

Measured pH values of supernatant liquid after gel precipitation are represented in Fig. 1 as well as in Table 1. Marked decreasing of pH values was noted with increasing mixing molar ratio of the solutions due to increasing acidic component. The initial pH around 13.2 observed in the mix of 0.5 (1:2) decreased down to around 10 with increasing mixing ratios via steep change observed between 0.5 (1:2) and 1.0 (1:1) mixing ratios and finally showed nearly constant pH around 8.6. As the results, all runs were plotted in alkali region in this experiment.

3.2. Chemical composition

As tabulated in Table 1, the obtained gels had some contaminated Na_2O-component, around 0.5 mass%. Disregarding this contamination, the chemical compositions of gels indicated very close to enstatite composition. Irrespective of pH values or mixing molar ratios of the stirring solutions except 1:4 (0.25) and 1:2 (0.5) gels prepared at extremely high pH region, in which slightly high MgO/SiO_2 molar ratio was obtained, the prepared gels have composition nearly equals to 1 in terms of MgO/SiO_2 molar ratio.

3.3. Thermal analysis

As shown in Figs. 2 DTA curves of the gels were characterized by the unclear endothermic peak of dehydration at 130–170 °C and the sharp exothermic peak at 850–860 °C for all gels. Presence of exothermic peak is the measure of polycondensation of $[Si(OH)_4]$ complexes bridged with foreign metallic ions as generally seen in glasses and clay minerals. Accordingly, the gels crystallized so instantly to yield enstatite after reaching the exothermic peak temperatures. At the moment, however, it is unclear whether the gels have the polymerized domains or not from the beginning in the gels as prepared at room temperature. It is very natural to consider, that some polymerization took place even at room temperature and the OH–OH polycondensation advanced more with elevation of heating temperature accompanied with gradual dehydration. In order to identified crystalline phase were cause of exothermic peak, experiments of instant crystallization using DTA apparatus by cut off and raising furnace immediately the exothermic peak we performed.

Table 1
Dry base chemical compositions of gels

Mix	Mixing molar ratio, MgO/SiO_2	pH value	Mass%			Total	Mole%			Resulted molar ratio MgO/SiO_2
			SiO_2	MgO	Na_2O		SiO_2	MgO	Na_2O	
1	1:4 (0.25)	13.5	56.90	41.80	1.35	100.05	47.26	51.74	0.99	1.09
2	1:2 (0.5)	13.2	59.22	39.50	1.29	99.99	49.75	49.24	1.01	0.99
3	1:1 (1.0)	9.7	59.21	39.41	1.39	99.99	49.75	49.24	1.01	0.99
4	2:1 (2.0)	8.6	59.11	39.71	1.17	99.97	49.29	49.79	0.91	1.01
5	3:1 (3.0)	8.6	59.20	39.51	1.25	99.95	49.75	49.24	1.01	0.99

Table 2
Preparation conditions of gels and identified phases as a function of heating temperature

Mix	MN/MS	Heating temperature (°C)						
		800	900	1000	1100	1200	1300	1400
1	1:4	Am	O-En, (Fo)	O-En, (Fo)	O-En, (Fo)	P-En, (Fo)	P-En, (Fo)	P-En, (Fo)
2	1:2	Am	O-En, (Fo)	O-En, (Fo)	O-En, (Fo)	P-En, (Fo)	P-En, (Fo)	P-En, (Fo)
3	1:1	Am	O-En, (Fo)	O-En, (Fo)	O-En, (Fo)	P-En, (Fo)	P-En, (Fo)	P-En, (Fo)
4	2:1	Am	O-En, (Fo)	O-En, (Fo)	O-En, (Fo)	O-En, (Fo)	P-En, (Fo)	P-En, (Fo)
5	3:1	Am	O-En, (Fo)	O-En, (Fo)	O-En, (Fo)	O-En, (Fo)	P-En, (Fo)	P-En, (Fo)

O-En: orthoenstatite, P-En: protoenstatite, ( ): very minor phase, Am: amorphous.

Table 3
Crystallite sizes of obtained enstatite calculated by Scherrer equation

MN/MS	Heating-temperature (°C)					
	900	1000	1100	1200	1300	1400
1:4	24.9	29.4	32.7	37.7	42.9	50.1
1:2	27.1	29.6	31.4	39.9	44.1	49.6
1:1	26.3	28.8	31.8	38.3	43.5	47.9
2:1	26.7	29.0	32.9	39.7	43.2	50.6
3:1	26.1	28.9	33.9	37.8	42.6	48.6

3.4. Powder X-ray diffraction

XRD results are summarized in Table 2 as well as Fig. 3. The as-prepared samples were amorphous. Crystalline phases were encountered, when heat-treated at 900 °C and over as suggested by the DTA results and crystallinity was enhanced with rising temperature.

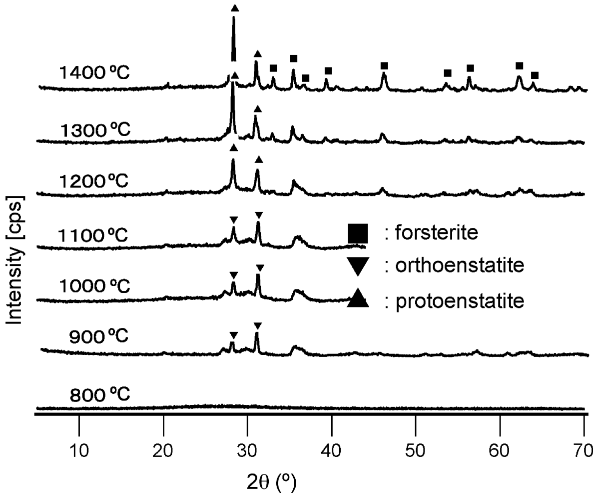

Fig. 3. An exemplified X-ray diffraction results of MN/MS = 1 gel after heat treatment.

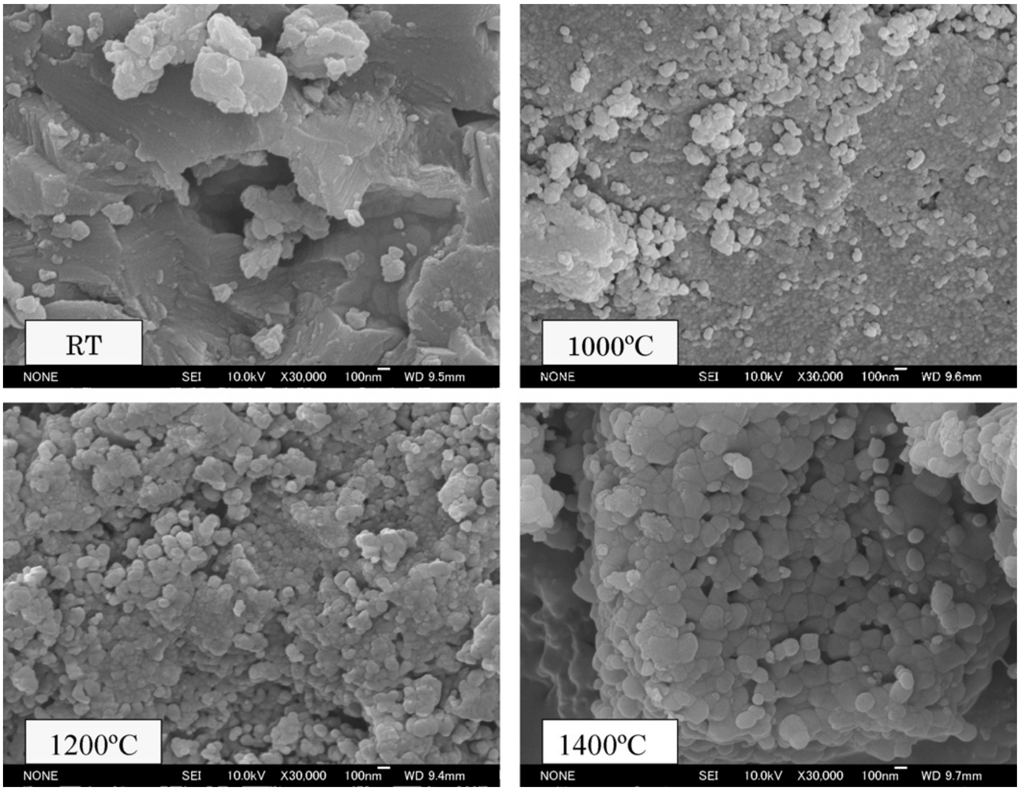

Fig. 4. Field emission scanning electron photomicrographs of MN/MS = 1 precursor gel and obtained enstatite crystallites.

The gel having 1.0 mixing molar ratio is preferentially mentioned first for convenience. This gel crystallized into orthoenstatite at 900 °C. When heat-treated at 1200 °C, protoenstatite formed instead of orthoenstatite. The other samples showed nearly the same trend. However, it should be stressed, that protoenstatite precipitated, when heat-treated at 1300 °C cause of exothermic peak, as it for the gels having higher mixing ratios, 2.0 and 3.0. Generally that orthoenstatite, protoenstatite transformation point becomes around 1100 °C at atmospheric pressure, end when experimental results performed at high pressure. The presence of associated forsterite when the gels heat-treated at 1200 °C for the case of the gels having 1:4 and 1:2 mixing molar ratio and at 1300 °C for the others were observed. The small formation of this mineral is considered due to a slight deviation of gel compositions from stoichiometric composition of enstatite to MgO-rich side. Influence of contaminated Na_2O can be also considered.

The XRD results of gels obtained by immediately after stop heating the end of exothermic peak show all only orthoenstatite phase.

3.5. Crystallite size

The crystallite size of the enstatite was calculated by the Scherrer equation. As tabulated in Table 3, nanometer sized crystallites were obtained irrespective of the starting gels. The dimension of the orthorhombic enstatite was in the range of 24.9–39.7 nm, when measured by (6 1 0) reflection, while that of protoenstatite was in the range of 37.7–50.6 nm, when measure by (1 2 1) reflection. FE-SEM photomicrographs of MN/MS = 1 precursor gel and obtained enstatite crystallites are presented in Fig. 4. Precursor gel showed aggregates of gels. The gels became crystalline on heating. With elevation of heating temperature, dimensional growth of crystallite was observed due to probable grain growth.

4. Conclusion

(1) Enstatite can be prepared by the geopolymer technique and transformation from orthoenstatite to protoenstatite has been also detected by XRD.

(2) Gels crystallize at temperature as low as at 860 °C, which facilitates nanometer-sized crystallization of gels, ranging from 20 s to 50 s nm in size depending on temperature of formation.

(3) Gels compositions are independent of stirring proportion of solutions, always showing nearly $MgO:SiO_2 = 1:1$ proportion, except the gels prepared at extremely high pH region. Finally single phase enstatite can be prepared associated with very minor forsterite presence.

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