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Effects of precursor pH and sintering temperature on synthesizing and morphology of sol–gel processed mullite

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Abstract

Needlelike mullite, which shows high aspect ratios, has been synthesized by coprecipitation from aluminum nitrate enneahydrate and colloidal silica sols. The effects of precursor pH and sintering temperature on the synthesizing behavior and the morphology of the needlelike mullite have been investigated. The equilibrium mullite phase appeared in the samples, which had been sintered at and above 1200 °C for each precursor pH. Crystallization of cristobalite from excessive SiO_2 occurred during sintering from 1200 °C, and the amount of cristobalite increased with sintering temperature up to 1400 °C. However, resorption of cristobalite into mullite decreased the amount of the phase from 1500 °C. The mullite synthesized with precursor pH $\leqslant 2$ (acidic sample) displayed high aspect ratios at high sintering temperature. However, morphology of the mullite synthesized with precursor pH $\geqslant 8$ (basic sample) transformed to rodlike or granular shape with increasing sintering temperature.

Keywords: A. Sol–gel processes; B. Microstructure; D. Mullite; Synthesis; Morphology

1. Introduction

Needlelike or fibrous mullite particles are attractive to high temperature application such as reinforcement in high-temperature structural components, owing to high creep resistance, chemical stability, mechanical strength, relatively low thermal expansion coefficient and electrical properties [1–3]. There have been many attempts to synthesize needlelike mullite particles as well as mullite whiskers or fibers with various starting materials by sol–gel method, because sol–gel method has advantage on synthesizing high purity mullite phase at relatively low temperatures range from 850 to 1250 °C [4–10].

Mullite can be synthesized from monophasic and diphasic gels obtained either by sol–gel or coprecipitation methods [6–9] leading to the different precursor types described by Schneider et al. [10]. They also reported that crystallization occurs around 980 °C for the monophasic gel [6,9], and above 1250 °C for the diphasic gel [6–9]. The synthesis of needlelike mullite particles as well as mullite fibers or whiskers is strongly dependent upon starting materials and methods [4,11–13]. Moreover, it is necessary to adjust precursor pH for controlling the morphology of the mullite synthesized using sol–gel methods, including sintering temperature with precursor pH [5].

The present work describes the process to synthesize fine needlelike mullite through coprecipitation of aluminum nitrate enneahydrate and colloidal silica sols. Effects of precursor pH and sintering temperature on synthesizing behavior and morphology of sol–gel processed mullite have been extensively investigated.

2. Experimental procedure

Aluminum nitrate enneahydrate [$Al(NO_3)_3 9H_2O$, 98%, Junsei Chemical Co., Japan] and colloidal silica (Nalcoag 1130, 30%, USA) were used as starting materials. Mullite precursor sols with non-stoichiometirc composition ($0.35Al_2O_3$–$2SiO_2$) were prepared by mixing of aluminum nitrate enneahydrate and colloidal silica in an

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aqueous solution at 70 °C. Precursor pH of the sols was controlled to pH $\leqslant$ 2 (hereinafter acidic sample) and pH $\geqslant$ 8 (hereinafter basic sample), by the addition of NH_4OH. Mullite precursor gels were prepared by drying of the sols at 120 °C for 24 h.

Thermal analysis of the gels has been carried out up to 1300 °C in air at a constant heating rate of 7 °C by TGA/DTA (TG/DTA, SDT2960, TA Instrument, USA). The dried gels were calcined (heating rate: 10 °C/min) in the temperature range of 900~1600 °C for 2 h. X-ray diffraction (XRD, Rigaku Co., D/MAX-III, Japan) has revealed the developed phases during heat treatment of the powders.

The dried powders, which were wet milled from the calcined powders in aqueous solution, were compacted to disk shape with the pressure of 20 MPa. Sintering of the green compacts has been carried out in the temperature range of 1200~1600 °C for 2 h, where the heating rate was fixed with 7 °C/min. The morphology of the synthesized particles has been observed by scanning electron microscopy (SEM, S2400, Hitachi, Japan) with the specimens prepared by the polished and then chemically etched with 40% HF solution.

3. Results and discussion

In the acidic sample, transparent and uniform gelation, whose rate was relatively slow, has occurred. However, in the basic sample, gelation rate was relatively fast and the nature of the gel was opaque. There results mean that the rate of gelation and physicochemical nature of the synthesized gels were very dependent upon the precursor pH. The results are similar to those of Anilkumar's [5].

Fig. 1 shows the TGA/DTA analyses of the as-dried gels. The total weight loss in the acidic sample (≈28%) was less than that of the basic sample (≈51%). DTA curves displayed broad and small endothermic peaks around 480~490 °C, considering as dehydration of aluminum hydrate and low-temperature phase transformation (η-Al_2O_3) [14]. The broad endothermic peaks in the temperature range of 500~1000 °C indicate that there have been reactions between η-Al_2O_3 and amorphous silica before crystallization. Small but sharp exothermic peak appeared around 990 °C for the acidic samples, but the relatively broad peak for the basic samples appeared around 1082 °C. The peaks are related to the phase transformation from η-Al_2O_3 to θ-Al_2O_3 [1,14] or to the formation of mullite [13,15].

Crystallization of mullite for all samples has been detected above 1200 °C by the broad exothermic peaks. Generally exothermic peak for the diphasic gel does not appear up to 1250 °C [6–9], while the acidic sample has a sharp exotherm around 990 °C. The exotherm is attributed to the formation of mullite or spinel phases [6,9], also indicates that the gel in the acidic sample is monophasic mullite precursor. The broad peak around 1082 °C for the basic sample indicates the formation of intermediate phases, such as cubic mullite or Al–Si spinel. The shape of the exothermic peaks (at 1082 and 1250 °C) in the basic sample is closely related to the homogeneity of Al–Si components in the gel [8]. The peak also indicates homogeneous mixing of Al–Si components in the gel. However, the broad peaks mean less homogeneous mixing of the components. TGA/DTA analyses revealed that the formation of mullite phase during sintering was not dependent upon the precursor pH.

Fig. 2 shows the XRD patterns of the calcined mullite precursors. A meta-stable alumina (θ-Al_2O_3) and amorphous SiO_2 phases exist in the both samples calcined below 1100 °C. Through calcinations at 1200 °C, θ-Al_2O_3 does not exist in the acidic sample, while the phase still exists in the basic sample. XRD results of the samples (acidic and basic) calcined at 1200 °C show coexistence of mullite and cristobalite phases, indicating that the mullitization temperature of the acidic sample is lower than that of the basic sample. Peak intensity of mullite in the XRD results increases with increasing sintering temperature for each sample. Figs. 3 and 4 display the evolution of mullite morphology with sintering temperature for each sample. The amount of cristobalite increased with increasing sintering temperature above 1200 °C and showed maximum condition in the samples (acidic and basic) sintered at 1400 °C. Because aluminosilicate glassy phase re-absorbed the cristobalite above 1400 °C, cristobalite phase did not appear in the samples (acidic and basic) sintered above 1600 °C.

In the present study, it is found that the mullitization temperature is an important criterion to evaluate the degree of mixing of the constituents such as Al, Si in the gel. Sacks et al pointed out that the temperature of 1600~1700 °C is required to achieve complete mullitization when alumina and silica particles are mixed in the micrometer size range [16]. If the mixing scale is at molecular level, mullitization can be achieved at the temperature of 1000~1100 °C. Schneider et al. classified the sequence of mullite formation depending on the particle size or bonding form: type I: atomic level; type II: molecular level or cluster; and type III: for the oxides [10]. Okada et al. also classified four types of transformation sequences depending on the mixture homogeneity of the oxides of the particle size as follows: type A: mixtures of sols and/or oxides; type B: precipitates; type C: clay minerals; type D: glassy states [3]. In the present study, the mullite phase has appeared in the gel heat treated in the temperature range of 1200~1300 °C, depending on the pH condition. The broad peaks in the TGA/DTA curves indicate the existence of the mullite phase and mean the heterogeneous mixing of the aluminosilicate sol. Therefore, the sequence found by this

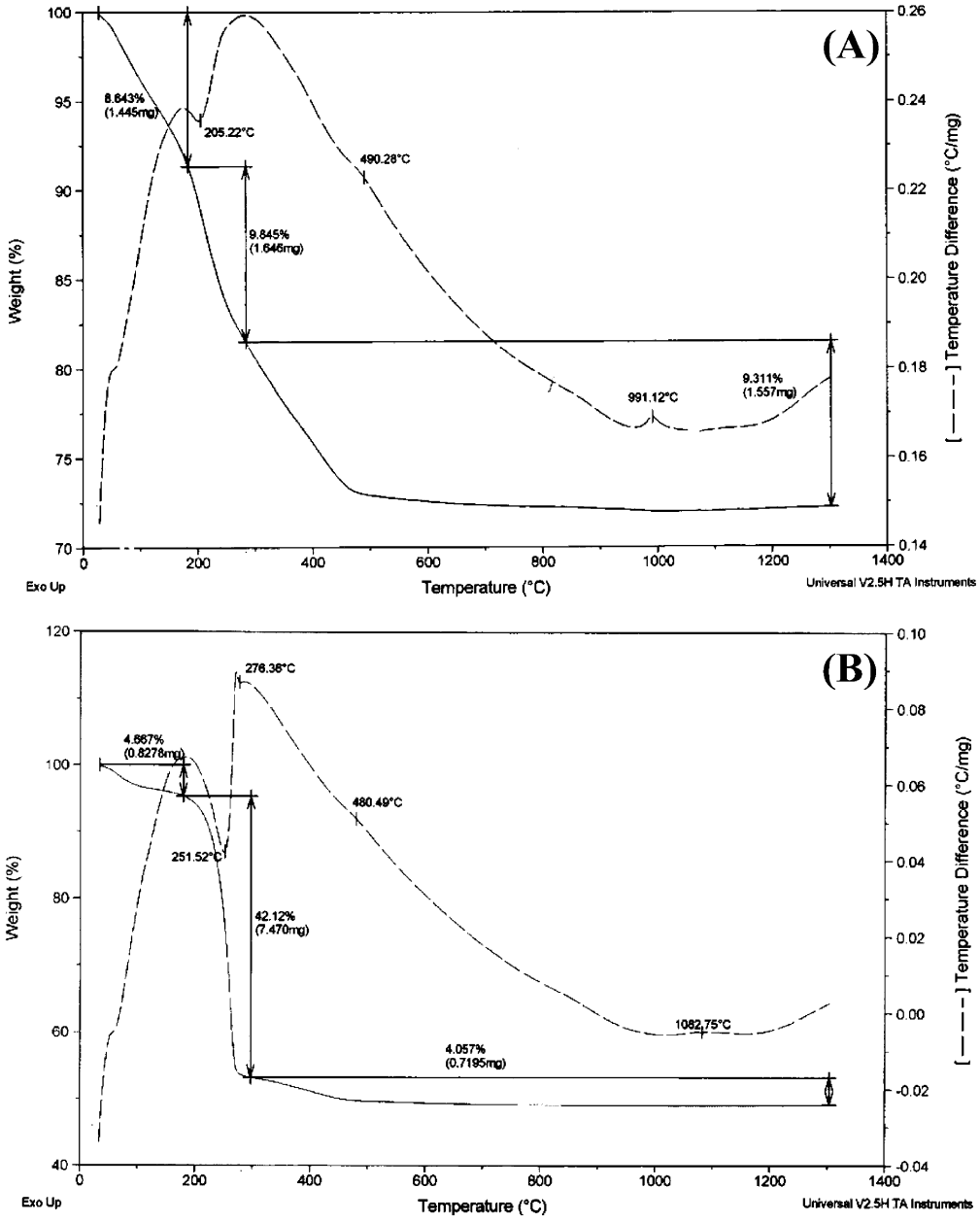

Fig. 1. TGA–DTA curves of mullite precursors with (A) acidic sample (pH $\leqslant$ 2) and (B) basic sample (pH $\geqslant$ 8).

study can be considered as type II of Schneider's classification or an admixture of type A and B of Okada's.

Figs. 3 and 4 show the mullite phase synthesized at various conditions. Fig. 3(A) displays the morphology of the mullite, which was synthesized from the acidic sample at 1200 °C for 2 h, showing fine rodlike mullite particle (approximately 0.5 μm in length). Sintering at 1300 °C generated needlelike mullite particles (1∼2 μm in length and 0.1∼0.3 μm in width) as shown in Fig. 3(B). Increasing the sintering temperature assisted growth of the mullite particles, for instance, the mullite phase synthesized at 1600 °C, has 10∼20 μm in length and 1∼2 μm in width as shown in Fig. 4(B). In the acidic sample, the morphology developed from rodlike to needlelike with increasing the sintering temperature. In the basic sample [Figs. 3(D) and 3(E)], increasing sintering temperature up to 1300 °C assisted growth of the needlelike mullite phase (sintering at 1200 °C: about 1∼2 μm in length, sintering at 1300 °C: about 4∼5 μm in length). However, sintering at high temperature of 1500 and 1600 °C made the morphology relatively coarse granule or rodlike as shown in Figs. 4(D) and 4(E).

The difference in the gelation of each pH condition can be considered as the reason why the precursor pH affects the morphology of the mullite grain [17]. Aluminosilicate hydrate compound with alumina and silica precursors forms mullite rapidly in the acidic condition

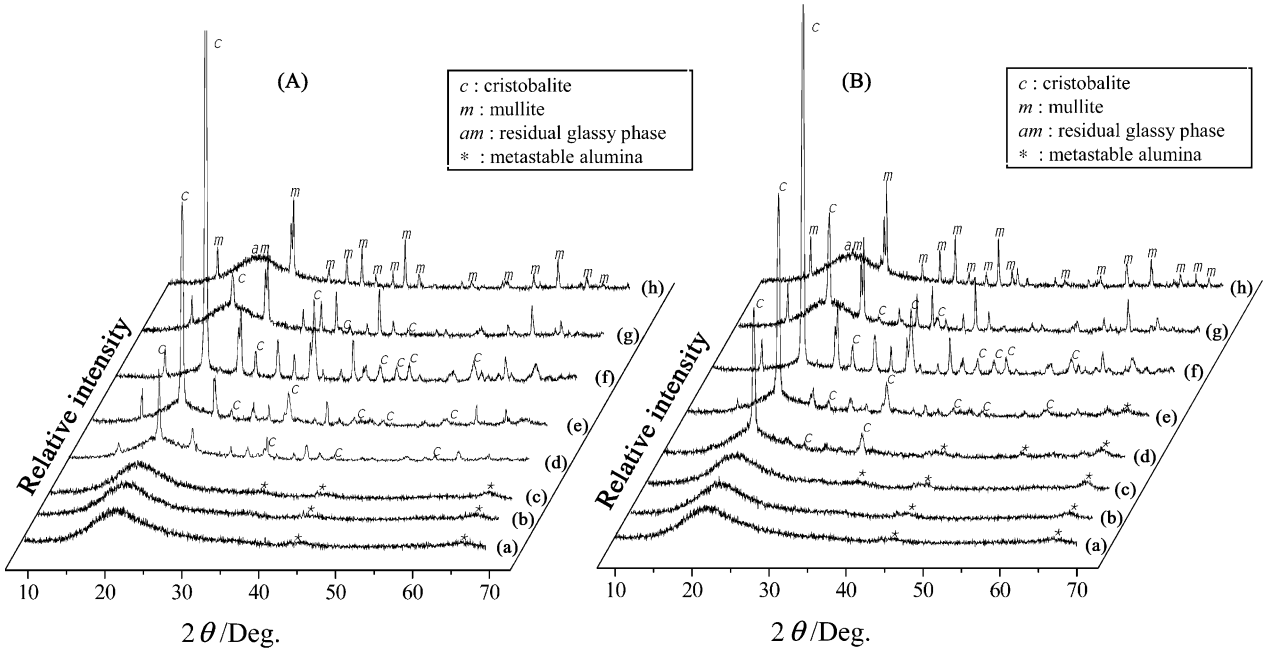

Fig. 2. XRD patterns of mullite precursor calcined at different temperature: (A) acidic sample (pH $\leqslant$ 2) and (B) basic sample (pH $\geqslant$ 8): (a) 900 °C, (b) 1000 °C, (c) 1100 °C, (d) 1200 °C, (e) 1300 °C, (f) 1400 °C, (g) 1500 °C, and (h) 1600 °C.

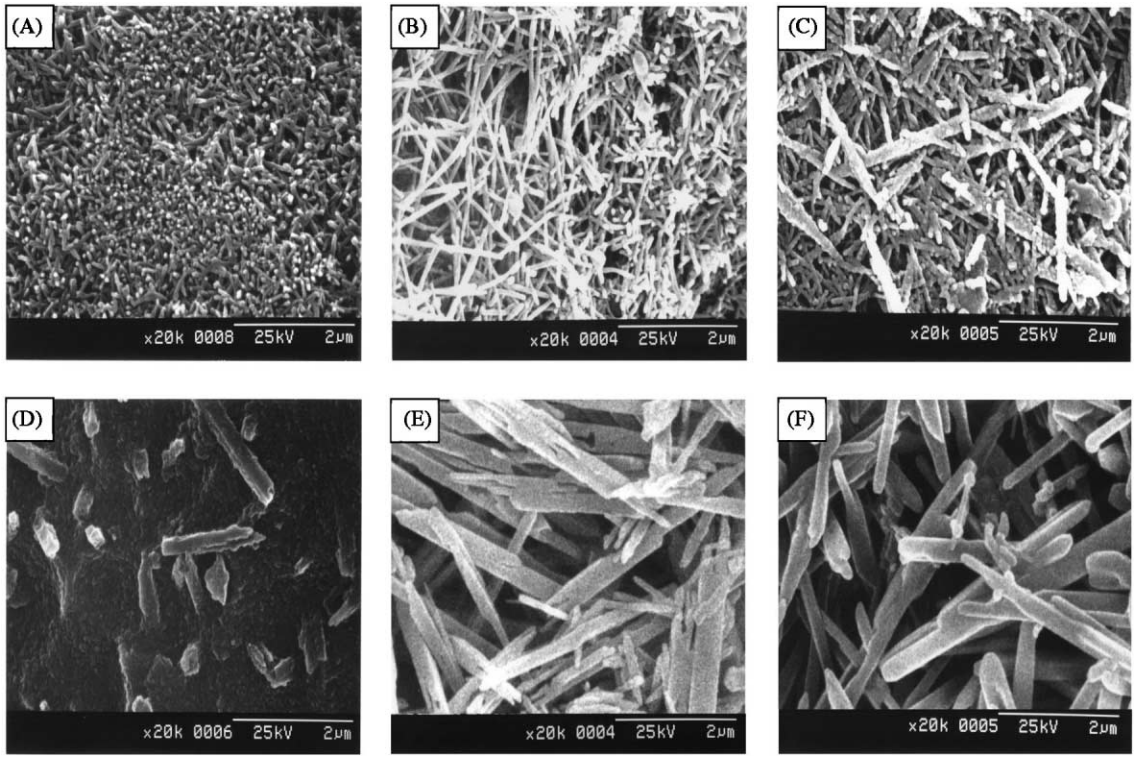

Fig. 3. SEM photographs of samples obtained by sintering green bodies at 1200~1400 °C for 2 h and then treating with 40% HF solution: (A) 1200 °C (acidic sample), (B) 1300 °C (acidic sample), (C) 1400 °C (acidic sample), (D) 1200 °C (basic sample), (E) 1300 °C (basic sample), and (F) 1400 °C (basic sample).

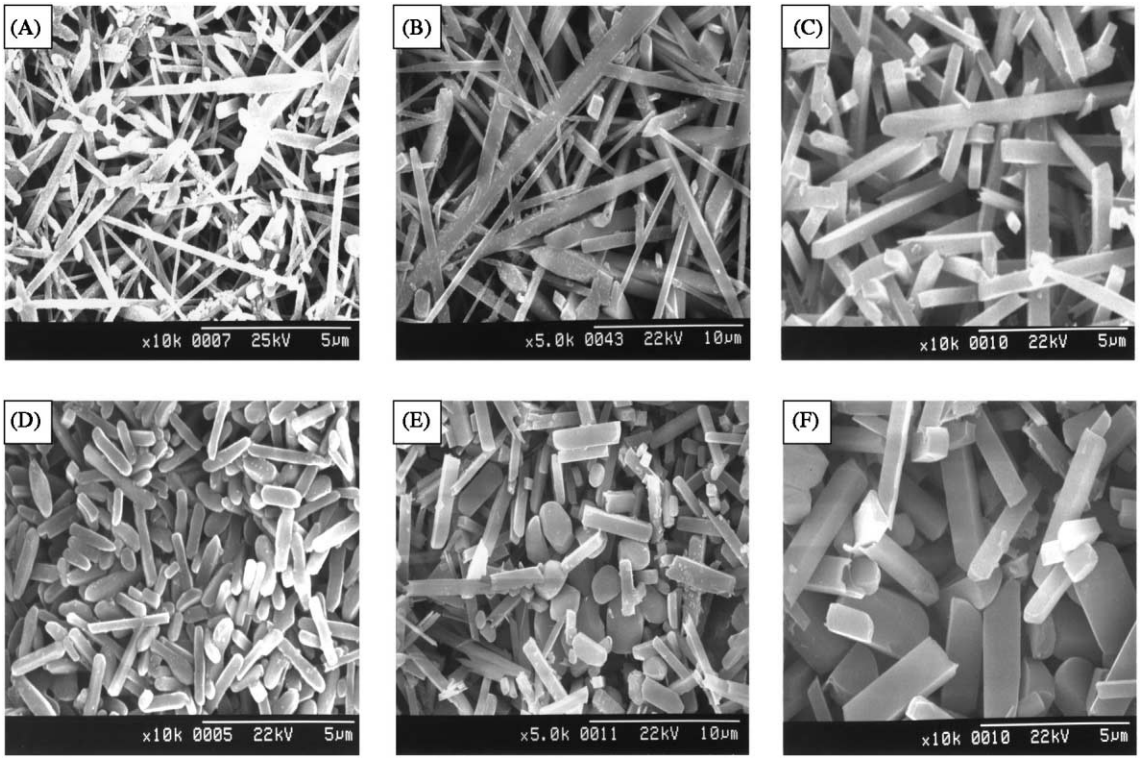

Fig. 4. SEM photographs of samples obtained by sintering the green bodies at 1500 and 1600 °C for 2 h and then treating with 40% HF solution: (A) 1500 °C (acidic sample), (B) 1600 °C (acidic sample), (C) 1600 °C (acidic sample, fracture surface) (D) 1500 °C (basic sample), (E) 1500 °C (basic sample), and (F) 1600 °C (basic sample, fracture surface).

($pH \leqslant 2$). Meanwhile, aluminosilicate sol can be flocculated in the basic condition ($pH \geqslant 8$). This means that aluminosilicate sol can form relatively less network and larger primary particle in higher pH. However, it is not clear how much affects on the morphology of the mullite grain. Studies of this effect are underway and will be reported later.

From the above results the effects of the precursor pH and the sintering temperature on the synthesizing and the morphology of the mullite can be summarized as follows. Long needlelike mullite can be obtained by heating the gel prepared with low pH at high temperature, and granule or rodlike mullite by heating the gel prepared with high pH at high temperature. Additionally the gel prepared at high pH can offer needlelike mullite at low temperature below 1400 °C.

4. Conclusions

Needlelike mullite has been obtained from the gels of aluminum nitrate enneahydrate and colloidal silica through coprecipitation. The gel in the acid sample was transparent and the gel in the basic sample was opaque, indicating that the rate of gelation and physicochemical nature of the gels were dependent upon the precursor pH. The precursor pH did not affect the reactivity and the phase formation in the mullite, showing the mullitization temperature of the gels was about 1200 °C for the acidic sample and above 1200 °C for the basic sample. On the other hand, cristrobalite was crystallized from 1200 °C and the peak intensity increased up to 1400 °C, showing resorption into mullite from 1500 °C. The mullite of high aspect ratio has been synthesized from the acidic sample, which morphology developed from rodlike to needlelike with increasing the sintering temperature. However, the morphology of the mullite from the basic sample generated rodlike or granular type with increasing the sintering temperature, especially at the high temperature above 1400 °C. The importance of the initial pH condition, which prominently affected the formation of needlelike mullite, was emphasized.

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