JOURNAL OF MATERIALS SCIENCE **34** (1999) 1471–1475

Preparation of silica particles by sol-gel process in reverse suspension

I. KIMURA
Centre for Cooperative Research, Niigata University, Niigata 950-2181, Japan
Y. TAGUCHI, M. TANAKA
Faculty of Engineering, Niigata University, Niigata 950-2181, Japan

Sol-gel process of silicon alkoxide was performed in reverse suspension to limit the sites of hydrolysis and dehydration-condensation of alkoxide to the inside of the dispersed droplets and to prepare silica particles of tens μm in diameter. Acetic acid aqueous solution was used as a dispersed phase, and hexane as a continuous phase. The dispersed phase was poured into the continuous phase, in which silicon alkoxide has dissolved, with stirring to form a reverse suspension. Silica particles of 67 μm in mean diameter were obtained by calcining the gel particles produced. Effects of pH of the dispersed phase and concentration of dispersion stabiliser on the characteristics of the silica particles were discussed. The formation mechanism of the gel particle was inferred with applying Jander's model, which is often used to analyse solid phase reaction of particles.

1. Introduction

In general, sol-gel process was performed in homogeneous systems with using alcohol as a common solvent for metal alkoxide of a raw material and H_2O of a catalyst, because these materials are immiscible each other. This process is used to produce not only massive bodies but also fine particles; e.g. submicron-sized silica particles [1]. The size of tens μm is desired for easy handling when silica is used as particulate materials such a catalyst support. Silica particles with the mean size of 20 to 40 μm can be prepared in a ternary system of tetraethoxysilane (TEOS)-acetic acid-H_2O [2]. It is thought that particles larger than those can be produced, if stabilisation of larger dispersed droplets in reverse suspension is formulated and sol-gel process is performed in those droplets as reaction sites.

The authors have been studying preparation of particulate polymer-based composites and microcapsules by suspension polymerisation [3–5], interfacial reaction [6], and drying-in-liquid method [7–11]. These methods using liquid-liquid suspensions have several advantages of the simple system, the convenient operation, easiness of controlling the structure, and so on. It is significant to investigate application of such methods to the preparation of inorganic materials, also.

Dispersed droplets of tens μm in diameter can be easily produced in reverse suspension. If hydrolysis and subsequent dehydration-condensation of silicon alkoxide dissolved in a continuous phase occurs inside the dispersed droplets, silica particles with size similar to dispersed droplets are expected to be produced.

In the present study, effects of pH of dispersed droplets and the concentration of dispersion stabiliser on the characteristics of the silica particles and the formation mechanism were discussed.

2. Experimental

2.1. Raw materials

TEOS was used as silicon alkoxide, sorbitan monooreate(Span80) of oil-soluble surfactant as dispersion stabiliser, and hexane as a continuous phase media. Deionized and then distilled water was used as a dispersed phase. pH of a dispersed phase was controlled with acetic acid. Grade, purity and manufacturer are listed in Table I. These reagents were selected as ones including no metallic element with exception of TEOS. This aim was to omit the possibility of catalytic poison in the future application of silica particles to catalysis supports.

2.2. Preparation

TEOS and Span80 was dissolved in hexane to prepare a continuous phase. A dispersed phase of which pH has controlled was poured into it with stirring for a fixed duration at 303 K. Wet gel particles produced was washed with hexane and then methanol and dried for 10 h at 298 K in atmosphere to obtain dry gel particles. In order to convert into silica particles, the dry gel particles were calcined for 1 h at 1073 K. The preparation conditions are listed in Table II.

A preparation tank was a separable flask, inner diameter of 85 mm and capacity of 500 cm^3. Disk turbine-type impeller with 6 blades was used as a stirrer and set at a third of the liquid depth from the bottom. To inhibit the air entrainment from the free surface of the dispersion, 4 baffles made of stainless steel were installed.

2.3. Characterisation

The yield y was defined as a ratio of the actually measured weight of silica produced to the theoretical weight

TABLE I Specification of raw materials

	Grade	Purity (%)	Manufacturer[a]
TEOS	3N	99.9	W
Span80	—	97.5	K
Hexane	Primary	95	W
Acetic acid	Extra	99.7	W

[a] W: Wako Pure Chemical Industries Ltd., K: Kanto Chemical Co., Inc.

TABLE II Preparation conditions

Preparation temperature	303 K
Preparation duration, t	3–48 h
Stirring speed	5.0 s^{-1}
Volume fraction of dispersed phase	0.050
Concentration of TEOS	0.34 mol/dm^3
Hydrogen ion exponent of dispersed phase, pH	1–3
Concentration of dispersion stabiliser, C	0–15 mol/m^3

of silica calculated from the amount of TEOS used. The morphologies of the wet gel particles during the preparation and the silica particles obtained were observed with an optical microscope. The particle size distribution was measured by sieving. The mean particle size was calculated as volume-area mean size.

3. Results and discussion

3.1. Morphology

When dispersion stabiliser was not used, the final products were mixtures of plate-shaped ones with bulky ones of hundreds μm to mm in size or tens μm in thickness. Deposition of the product on the stirrer and the baffles was also observed. Stable dispersion was not formed without dispersion stabiliser. Therefore, the dispersed droplets repeatedly coalesce and break up and adhere to walls of the apparatus. It may be thought that the irregular-shaped products were produced in this situation that the dispersed phase cannot keep its shape spherical.

When dispersion stabiliser was used, on the other hand, spherical products were obtained. At a concentration of dispersion stabiliser of $C = 5$ mol/m^3 spherical particles and a small amount of bulky product were obtained, and all the products at $C \geq 10$ mol/m^3 are spherical. Those particles have smooth surfaces shown in Fig. 1. Any linkage between them is not recognised. These results indicate that the dispersion droplets were effectively stabilised by the dispersion stabiliser.

Most of the particles are solid, although some ones contain small bubbles or voids. It is found that the gel was produced in the whole of a dispersed droplet during the preparation for 48 h. The particle size is observed to be almost uniform, 60 to 80 μm.

Fig. 2 shows an optical micrograph of the specimen, which was withdrawn after a lapse of 3 h and ruptured with a needle. It seems to be a thin film-like product. This must be a piece of evidence that a shell-shaped gel layer was formed on the surface of the dispersed phases in the earlier state of the preparation.

3.2. Yield

Fig. 3 shows change in the yield y at pH = 1 and a concentration of dispersion stabiliser of $C = 10$ mol/m^3 with the duration of the preparation t. The yield was 44% for 6 h and increased as time elapsing to reach 95% for 48 h.

Fig. 4 shows effect of pH of the dispersed phase on the yield y of the silica particles prepared for 48 h at a concentration of dispersion stabiliser of $C = 10$ mol/m^3. The yield decreased with increasing pH, from $y = 95\%$ at pH = 1 to $y = 20\%$ at pH = 3.

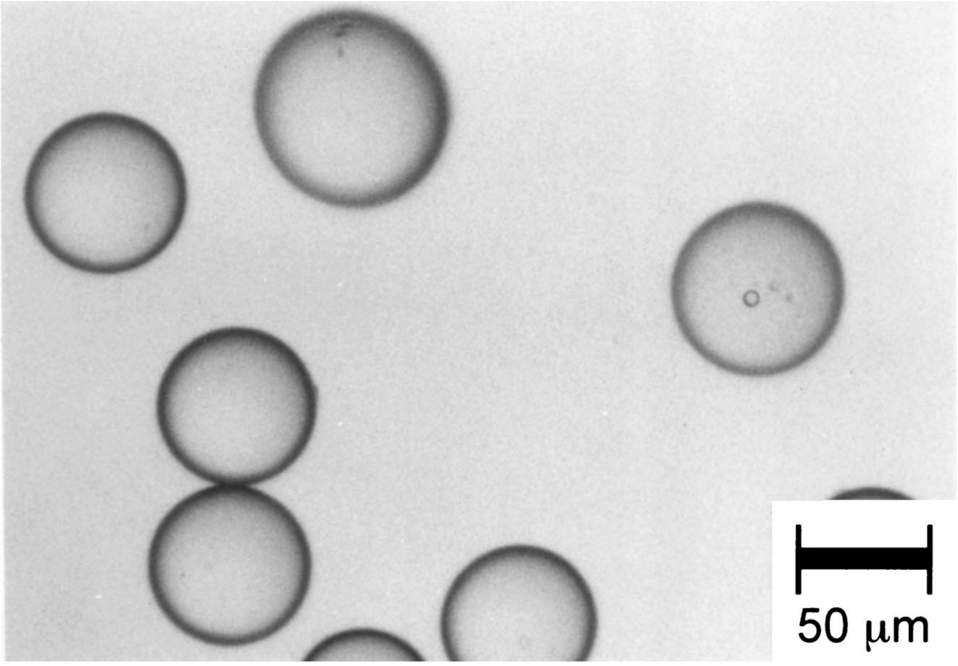

Figure 1 An optical micrograph of silica particles prepared for 48 h at pH = 1 and $C = 10$ mol/m^3.

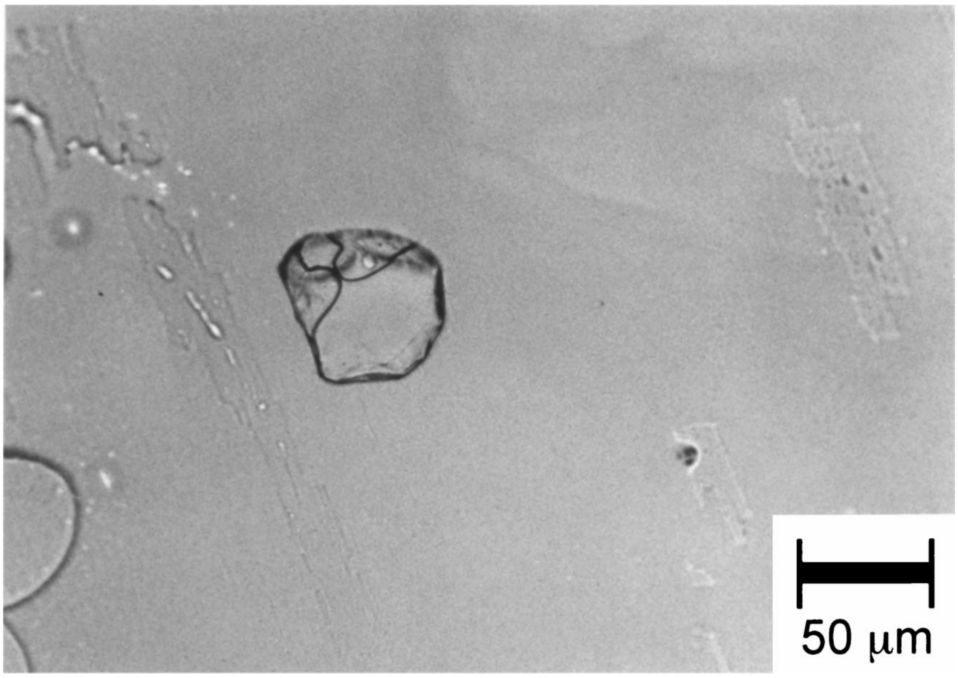

Figure 2 An optical micrograph of the product withdrawn after 3 h and ruptured with a needle.

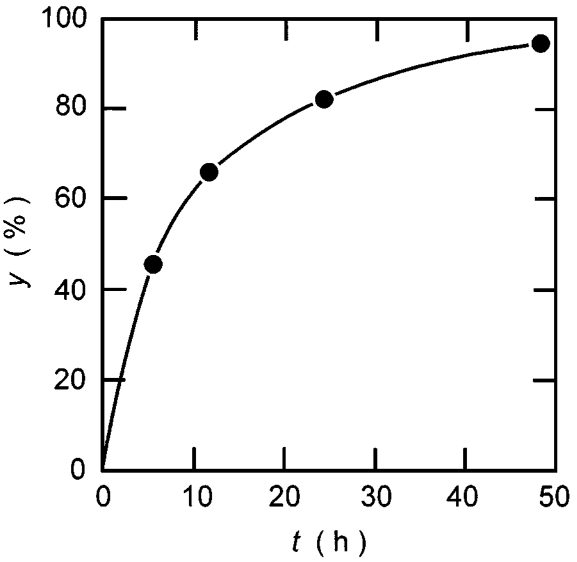

Figure 3 Change in the yield with the duration of reaction at pH = 1 and $C = 10$ mol/m^3.

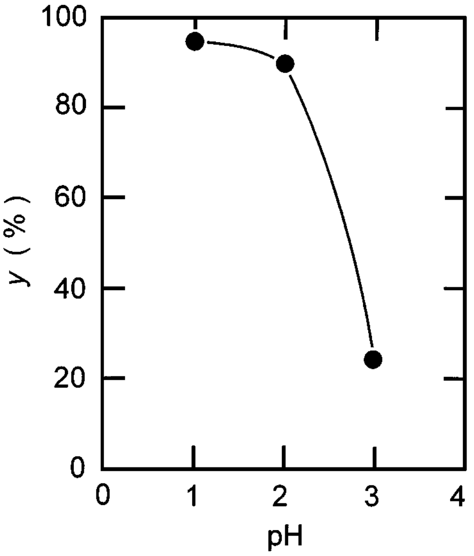

Figure 4 Effect of pH of the dispersed phase on the yield of the silica particles prepared for 48 h at $C = 10$ mol/m^3.

TEOS can be hydrolysed through following four steps:

1. $Si(OC_2H_5)_4 + H_2O \rightarrow Si(OC_2H_5)_3(OH) + C_2H_5OH$
2. $Si(OC_2H_5)_3(OH) + H_2O \rightarrow Si(OC_2H_5)_2(OH)_2 + C_2H_5OH$
3. $Si(OC_2H_5)_2(OH)_2 + H_2O \rightarrow Si(OC_2H_5)(OH)_3 + C_2H_5OH$
4. $Si(OC_2H_5)(OH)_3 + H_2O \rightarrow Si(OH)_4 + C_2H_5OH$

Under acidic conditions, these hydrolysis reactions are initiated by electrophilic attack of hydrogen ion upon oxygen atom of ethoxy group to promote nucleophilic attack of H_2O upon silicon atom. When the step 1 occurs, the number of both attacking hydrogen ion and ethoxy group to be attacked decreases. It is known that the step 1 is very rapid and the steps 2 to 4 are slower [12]. Products hydrolysed through the steps 2 to 4 can polymerise by subsequent dehydration-condensation to produce gel. Most product hydrolysed only through the step 1 can not be incorporated into the gel. Furthermore, it is hydrophobic. Therefore, it will be lost together with the continuous phase in a washing process. The hydrolysis through the steps 2 and more is still slower at higher pH, so that the yield may decrease in this way.

With changing the concentration of dispersion stabiliser, the yield after 48 h was not significantly changed.

3.3. Particle size distribution and mean particle size

Fig. 5 shows the particle size distribution of the silica particles prepared for 48 h at pH = 1. When dispersion

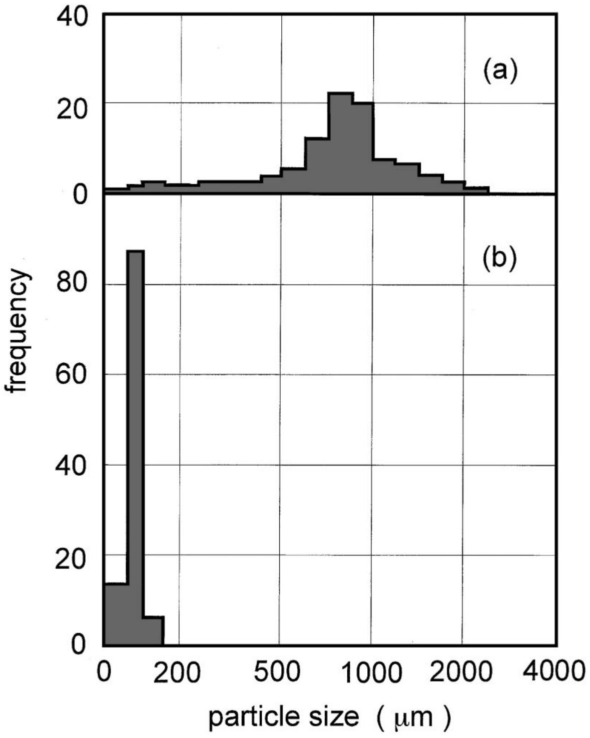

Figure 5 Particle size distribution of the silica particles prepared for 48 h at pH = 1. The concentrations of dispersion stabiliser are (a) 0 and (b) 10 mol/m^3.

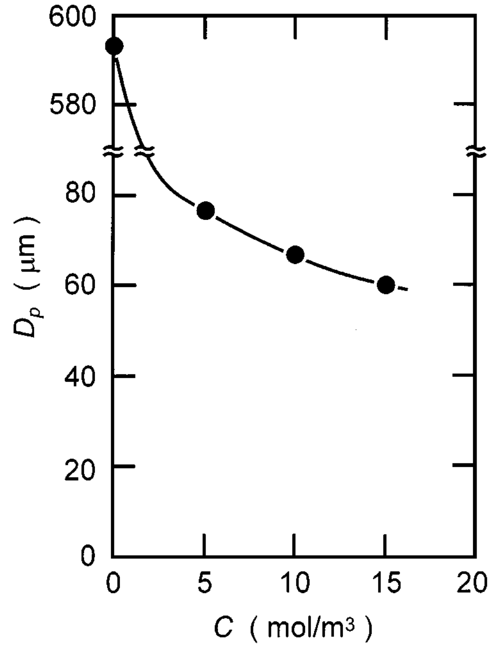

Figure 6 Change in the mean particle size of the silica particles prepared for 48 h at pH = 1 with the concentration of dispersion stabiliser.

stabiliser was not used, the distribution was so broad as to spread over wide range. This is owing to the irregular shape of the product. In the case of a concentration of dispersion stabiliser of $C = 10$ mol/m^3, the distribution was very narrow. This may be owing to the formation of the gel particles with keeping the morphology of the dispersed droplets.

Fig. 6 shows change in the mean particle size D_p of the silica particles prepared for 48 h at pH = 1 with the concentration of the dispersion stabiliser C. The mean particle size decreases with increasing the concentration of the dispersion stabiliser. This reflects the reduction of the size of the dispersed droplets with the dispersion stabiliser.

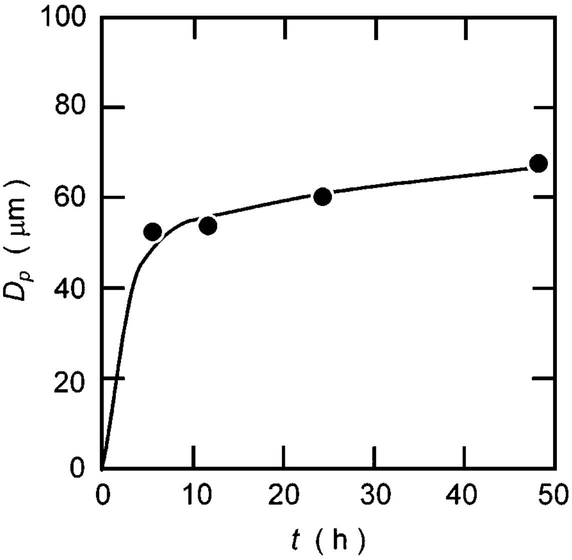

Figure 7 Change in the mean particle size of the silica particles prepared for 48 h at $C = 10$ mol/m^3 pH = 1 and with the duration of the reaction.

The size of the dispersed droplets was not significantly changed during the preparation at a fixed concentration of the dispersion stabiliser, about 60 to 100 μm, but that of final silica particles was changed. Fig. 7 shows change in the mean particle size D_p of the silica particles prepared at pH = 1 and a concentration of dispersion stabiliser of $C = 10$ mol/m^3 with the duration of the preparation t. The mean particle size was 53 μm for 6 h and slightly increased with time elapsing to reach 67 μm for 48 h. This tendency of the change is not in accordance with that of the yield. This may suggest that the gel particles formed in the early stage of the preparation were hollow, and ones prepared in the earlier stage shrink larger on drying the wet gel.

3.4. Formation mechanism of gel particle

Following Jander's equation [13] is often utilised to analyse solid phase reactions of particles:

$$\{1 - (1 - x)^{1/3}\}^2 = kt,$$

where x is conversion, k reaction rate constant, and t reaction duration. This is based on some assumptions that (i) particulate reactant A is surrounded with another reactant B and completely contacted each other, (ii) particle size of reactant A is uniform and constant during reaction, (iii) reaction proceeds spherically from the surface toward the centre of reactant A, (iv) the rate-controlling step is diffusion of reactant B though the product layer, and so on. The authors attempted to apply the results of the yield to Jander's model, although the present system was not just solid phase reaction.

Fig. 8 was obtained by redrawing the results in Fig. 3 with substituting the yield y for the conversion x. It gives a straight line, indicating that application to Jander's model is valid. From considering how the above assumptions are interpreted in the present

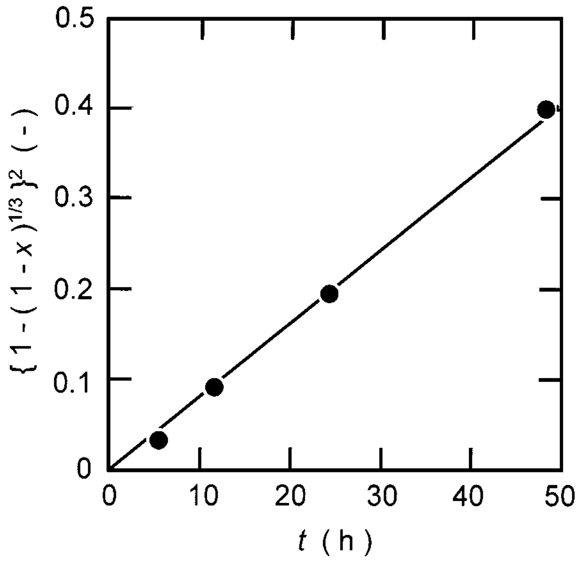

Figure 8 Jander plot of the result in Fig. 3.

system, the formation mechanism of the gel particle can be inferred as follows.

Particulate reactant A corresponds to the dispersed droplet. Reactant B should be the primary hydrolysis product, not TEOS itself, because one ethoxy group of TEOS is hydrolysed as soon as contacting a dispersed droplet. That is, the assumption (i) means that the dispersed droplet is surrounded with the primary hydrolysis product.

The assumptions (ii) and (iii) are supported by Fig. 5 showing narrow particle size distribution and Fig. 2 showing a shell-shaped product, respectively.

The primary hydrolysis product diffuses through the gel layer toward the centre of a dispersion droplet, and ethanol of by-product diffuses backwards. The assumption (iv) means that the rate-controlling step is diffusion process of these substances. Therefore, it can be inferred that the primary hydrolysis product is secondarily and more hydrolysed during the diffusion, so that dehydration-condensation occurs to grow the gel layer when the hydrolysis product reaches its inner surface.

4. Conclusion

Spherical silica particles of 67 μm in mean diameter were prepared by sol-gel process in reverse suspension without using a common solvent. It was confirmed that the gel grows toward the centre of the dispersed droplet. This implies that the structure of a microcapsule is constructed during the preparation process. Therefore, this method is expected to be applicable to the preparation of particulate inorganic composites with controlling the core-shell structure.

References

1. W. STÖBER, A. FINK and E. BOHN, *J. Colloid Interface Sci.* **26** (1968) 62.
2. B. KARMAKAR, G. DE, D. KUNDU and D. GANGULI, *J. Non-Cryst. Solids* **135** (1991) 29.
3. M. TANAKA, A. SAITO, K. HOSOGAI and I. KIMURA, *Kagaku Kogaku Ronbunshu* **18** (1992) 330.
4. M. TANAKA, K. HOSOGAI, T. YUDA, I. KIMURA and N. SAITO, *J. Japan Soc. Colour Mater.* **65** (1992) 484.
5. I. KIMURA, H. YOSHII, N. SAITO and M. TANAKA, *J. Soc. Powder Technol. Japan* **32** (1995) 229.
6. I. KIMURA, S. IKARASHI, N. SAITO and M. TANAKA, *Adv. Powder Technol.* **8** (1997) 1.
7. M. TANAKA, K. INABA and I. KIMURA, *J. Japan Soc. Colour Mater.* **64** (1991) 64.
8. M. TANAKA, K. SATO and I. KIMURA, *ibid.* **64** (1991) 140.
9. M. TANAKA, H. SATO, I. KIMURA and N. SAITO, *ibid.* **66** (1993) 449.
10. M. TANAKA, I. KIMURA, N. SAITO and H. TOMINAGA, *ibid.* **67** (1994) 624.
11. I. KIMURA, A. SOUMA, N. SAITO and M. TANAKA, *Adv. Powder Technol.* **6** (1995) 221.
12. M. YAMANE, S. INOUE and A. YASUMORI, *J. Non-Cryst. Solids* **63** (1984) 13.
13. W. JANDER, *Z. Anorg. Chem.* **163** (1927) 1.

Received 29 July
and accepted 11 November 1998