Formation of $MgGeO_3$ from the Hydrate prepared by Hydrolysis of Magnesium and Germanium Oxides

Osamu Yamaguchi,* Katsuji Kawabe, and Kiyoshi Shimizu
Department of Applied Chemistry, Faculty of Engineering, Doshisha University, Kyoto 602, Japan

Magnesium–germanium hydrate, which yields a $MgGeO_3$ powder, has been prepared by the simultaneous hydrolysis of magnesium and germanium alkoxides. Its composition is $MgGeO_3 \cdot 0.25H_2O \cdot nH_2O$, and its structure is similar to that of $Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$ and $4.25MgO \cdot 4GeO_2 \cdot 1H_2O \cdot 5H_2O$ prepared hydrothermally. Magnesium metagermanate, $MgGeO_3$, is slowly crystallized at 660—1 200 °C after the completion of dehydration of the hydrate. The kinetics of crystallization of $MgGeO_3$ have been studied by means of *X*-ray diffraction measurements. The initial stage at each temperature proceeds rapidly. The final stages can be expressed in terms of the contracting cube equation, the activation energy being 198 kJ mol^{-1}.

Magnesium metagermanate, $MgGeO_3$, is generally formed by solid-state reaction of an equimolar mixture of MgO and GeO_2.[1-3] On the other hand, Labbe [4] showed that $MgGeO_3$ is formed by the decomposition of $MgGeO_3 \cdot 2.5H_2O$ prepared from an aqueous solution of GeO_2 and $Mg(O_2CMe)_2 \cdot 4H_2O$. In addition, the i.r. spectrum of the hydrate was compared with that of talc, $Mg_3Si_4O_{10}(OH)_2$.[5,6] However, no other characterization or the thermal behaviour of $MgGeO_3 \cdot 2.5H_2O$, except i.r. and t.g.a. data, were described.

Apart from the formation of $MgGeO_3$, synthetic hectorite, $Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$, was prepared under hydrothermal conditions by Strese and Hofmann.[7] Moreover, Pflugmacher *et al.*[8] reported that $4.25MgO \cdot 4GeO_2 \cdot 1H_2O \cdot 5H_2O$ prepared hydrothermally is similar in structure to $Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$.

In the present study, it was found that the *X*-ray diffraction pattern of magnesium–germanium hydrate derived from the corresponding alkoxides is similar to that of $Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$[7] and $4.25MgO \cdot 4GeO_2 \cdot 1H_2O \cdot 5H_2O$.[8] On the basis of this result, the characterization and thermal behaviour of the hydrate were studied by *X*-ray diffraction, thermal analysis, and i.r. spectroscopy. A kinetic study of $MgGeO_3$ formation was also carried out.

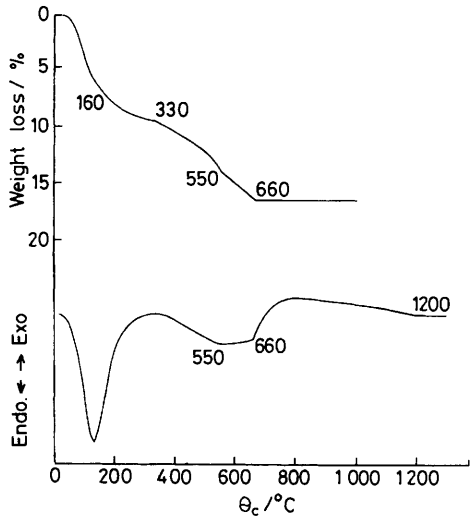

Figure 1. T.g.a. (upper) and d.t.a. (lower) curves of the starting powder. Sample weight = 95 mg

Experimental

Germanium isopropoxide was a pure grade. Magnesium methoxide was synthesized by heating 99.9% magnesium metal foil in dry methanol with a small amount of iodine as a catalyst for 5 h at 64 °C. The mixed alkoxides prepared in the mole ratio Mg : Ge = 1 : 1 were refluxed in an excess of 2-propanol for 10 h at 82 °C and then hydrolyzed by adding aqueous ammonia solution at 25 °C. The temperature was slowly raised to 80 °C, with stirring. The hydrolysis product was separated from the suspension by centrifugation, washed repeatedly with hot water, and dried at 80 °C under reduced pressure. The powder obtained is termed 'starting powder'. Its average particle size, as determined by electron microscopy, was *ca.* 400 Å.

Thermal analyses (t.g.a., d.t.a.) were carried out in air at a heating rate of 10 °C min^{-1}. α-Alumina was used as a standard material in d.t.a. The starting powder and the specimens heated at a rate of 10 °C min^{-1} were examined by means of a standard *X*-ray diffractometer using nickel-filtered Cu-K_α radiation. The goniometer scanning speed of 1/4° min^{-1} was selected so as to achieve accurate *d* spacings. Infrared spectra were obtained for dispersions in potassium bromide, using the pressed disk technique.

Results and Discussion

Thermal Analysis.—Figure 1 shows a t.g.a. curve of the starting powder. The weight loss of 13.9% up to 550 °C is due to loss of ammonia, organic residues from the parent alcohol, absorbed water, and hydrate water.[9] Continued weight loss, 2.6%, was observed between 550 and 660 °C. In view of the *X*-ray diffraction and i.r. data described below, this can be attributed to the release of structural water corresponding to $0.25H_2O$. A d.t.a. curve is also shown in Figure 1. After the completion of dehydration, a large exothermic peak was observed at 660—1 200 °C. The *X*-ray diffraction analysis confirmed that this peak is due to the crystallization of $MgGeO_3$ from an amorphous phase.

Identification of the Starting Powder.—Table 1 shows the *X*-ray diffraction data of the starting powder. Three compounds have been reported previously in the system MgO–

Table 1. *X*-Ray diffraction data

Starting powder $MgGeO_3 \cdot 0.25H_2O \cdot nH_2O$		$MgGeO_3 \cdot 0.25H_2O$ [a]		$Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$ [b]			$4.25MgO \cdot 4GeO_2 \cdot 1H_2O \cdot 5H_2O$ [c]	
d/Å	I/I_0	*d*/Å	I/I_0	*d*/Å	I/I_0	*hk* values	*d*/Å	I/I_0
							5.318	20
4.688	50	4.651	35	4.55	80	11, 02	4.663	60
							3.446	70
2.680	100	2.664	100	2.58	100	13, 20	2.678	100
2.552	65	2.541	60				2.522	70
2.234	15	2.227	20				2.290	20
							2.095	10
1.771	25	1.766	15	1.70	40	24, 31, 15	1.756	40
1.566	50	1.560	65	1.52	100	33, 06	1.563	80
1.413	15	1.409	20				1.419	20
1.348	20	1.344	15	1.31	70	26, 40	1.343	50

[a] Specimen obtained by heating the starting powder to 550 °C. [b] Ref. 7. [c] Ref. 8.

Table 2. Infrared spectral data (cm^{-1})

Starting powder $MgGeO_3 \cdot 0.25H_2O \cdot nH_2O$		$MgGeO_3 \cdot 2.5H_2O$	Talc $Mg_3Si_4O_{10}(OH)_2$		$Mg_3Ge_4O_{10}(OH)_2$	
			3 670w	ν(O–H)	3 620w	ν(O–H)
3 400s,br	ν(O–H)					
1 628m,br	δ(O–H)					
858w (sh)	ν(Ge–O)	865w (sh)	1 080w (sh)			
822s,br	ν(Ge–O)	823s,br	1 020s,br	ν(Si–O)	837s,br	ν(Ge–O)
					717m	ν(Ge–O–Mg)
554w,br	ν(Ge–O)	562w,br 495w,br	668m	ν(Si–O)	561m	ν(Ge–O)
392s,br	δ(Ge–O) ν(Ge–O–Mg)	400s,br	467 451 s,br	δ(Si–O) ν(Si–O–Mg)		
348w (sh)	δ(Ge–O)		435w (sh)	δ(Si–O)		

s = Strong, m = medium, w = weak, br = broad, and sh = shoulder.

GeO_2.[1] In the present study, magnesium germanates other than $MgGeO_3$ and free species were not observed throughout the heating process. From the results the starting powder can be considered to be a compound corresponding to magnesium–germanium hydrate, $MgGeO_3 \cdot 0.25H_2O \cdot nH_2O$, containing ammonia and parent alcohol. As shown in Table 1, the *X*-ray data of the starting powder are very similar to those of $Mg_3Si_4O_{10}(OH)_2 \cdot nH_2O$[7] and $4.25MgO \cdot 4GeO_2 \cdot 1H_2O \cdot 5H_2O$[8] prepared hydrothermally. Therefore, it is thought that $MgGeO_3 \cdot 0.25H_2O \cdot nH_2O$ is structurally analogous with the compounds described above.

Heating Process.—*X*-Ray diffraction analysis showed that the observed *d* values of the starting powder did not change up to 160 °C. However, the diffraction peaks of the specimens in the temperature range of 160—330 °C were shifted step by step to a higher angle with increasing temperature. No significant change was observed between 330 and 550 °C. The specimen heated to 550 °C corresponds in composition to $MgGeO_3 \cdot 0.25H_2O$ (Table 1). The peak intensities of $MgGeO_3 \cdot 0.25H_2O$ decreased with increasing temperature at 550—660 °C. As soon as the peaks of this hydrate had disappeared at 660 °C, those corresponding to $MgGeO_3$ appeared and increased slowly in intensity up to 1 200 °C. A specimen heated at 1 200 °C showed the characteristic *X*-ray diffraction pattern of $MgGeO_3$.

Infrared Spectrum.—The i.r. data for the starting powder are presented in Table 2, and compared with those of $MgGeO_3 \cdot 2.5H_2O$,[4] talc $Mg_3Si_4O_{10}(OH)_2$, and $Mg_3Ge_4O_{10}(OH)_2$[6] prepared hydrothermally. In the region 1 000—200 cm^{-1} the data of the starting powder are in agreement with those of $MgGeO_3 \cdot 2.5H_2O$, although the band in the vicinity of 495 cm^{-1} was absent in the present study. The absorption bands at 3 400 and 1 628 cm^{-1} are due to the O–H stretching and bending vibrations of water, respectively.[10] The O–H stretching vibration at 3 620—3 680 cm^{-1} was not observed in the starting powder, suggesting that hydroxyl groups [6] are absent in the starting powder. The i.r. spectrum of $MgGeO_3 \cdot 0.25H_2O$ heated to 550 °C was the same as that of the starting powder, except that the bands at 3 400 and 1 628 cm^{-1} were of low intensity. Judging from the assignment of the bands of $Mg_3Ge_4O_{10}(OH)_2$,[6] the present bands at 822 and 554 cm^{-1} are due to Ge–O vibrations. According to the $Mg_3Si_4O_{10}(OH)_2$ data,[6] the bands at 467 and 435 cm^{-1} should be assigned to Si–O vibrations. On the other hand, the band at 451 cm^{-1} is due to a Si–O–Mg vibration. Due to the mass effect the absorption bands of $Mg_3Ge_4O_{10}(OH)_2$ are located at lower frequencies than those of $Mg_3Si_4O_{10}(OH)_2$.[6] Thus, the bands at 392 and 348 cm^{-1} of the starting powder correspond to those at 467 and 451 and 435 cm^{-1}, of $Mg_3Si_4O_{10}(OH)_2$; the former must be assigned as overlapping Ge–O and Ge–O–Mg vibrations and the latter as a Ge–O vibration. From the i.r. spectrum, *X*-ray diffraction, and thermal analysis, it is concluded that the starting powder is a magnesium–germanium hydrate.

Kinetics of $MgGeO_3$ *Crystallization.*—The fraction of crystallization was determined as a function of time at different temperatures (Figure 2). The starting powder was pre-heated to 660 °C at a rate of 10 °C min^{-1}. A well crystallized specimen was obtained by heating the starting powder

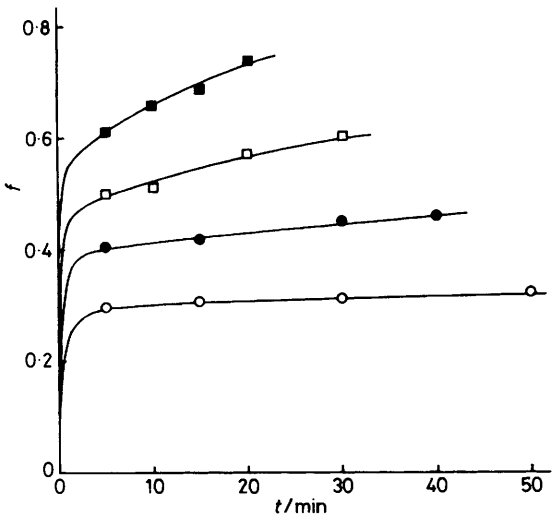

Figure 2. Crystallization of $MgGeO_3$ as a function of time at different temperatures: ○, 900; ●, 980; □, 1 060; ■, 1 140 °C. f = Fraction of $MgGeO_3$ crystallized in time t

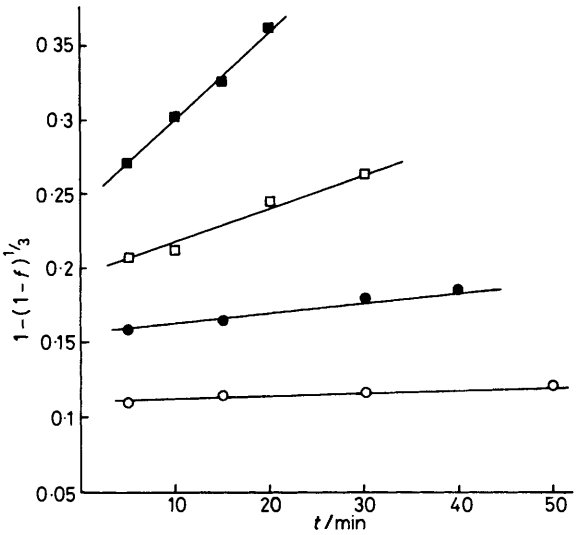

Figure 3. Plots of $1 - (1 - f)^{\frac{1}{3}}$ *vs.* time, t, of the data shown in Figure 2. See Figure 2 for key

for 3 h at 1 300 °C. The fractional crystallization was determined from the ratio of the intensity of the $MgGeO_3$ peak (321) * to that of the ($MgGeO_3$ + CaF_2) peak (220) as an internal standard, using a calibration curve with known compositions. The initial stage of crystallization at each temperature proceeded rapidly and may represent the process of nucleation. The data in the final stage can be interpreted in terms of the contracting cube equation (1) (Figure 3),[11] where

$$1 - (1 - f)^{\frac{1}{3}} = kt \qquad (1)$$

f, t, and k are the fractional crystallization, time, and rate constant, respectively. Equation (1), which has been employed to explain the kinetics of thermal decomposition of solids, is equivalent to one of the limiting forms of the Mampel equation.[12] In the present case, it indicates that crystallization is controlled by the rate of advance of interfacial growth. An Arrhenius plot of the rate constants gave an activation energy of 198 kJ mol^{-1}.

* Similar results were obtained by use of the (121) peak.

References

1 C. R. Robbins and E. M. Levin, *Am. J. Sci.*, 1959, **257**, 63.
2 H. Koelmans and C. M. C. Verhagen, *J. Electrochem. Soc.*, 1959, **106**, 676.
3 L. N. Belonogova, V. N. Kryokova, and N. G. Vyazova, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1973, **16**, 666.
4 J. P. Labbe, *Mikrochim. Acta*, 1964, **2—4**, 298.
5 D. M. Roy and R. Roy, *Am. Mineral.*, 1954, **39**, 957.
6 V. Stubičan and R. Roy, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1961, **115**, 200.
7 H. Strese and U. Hofmann, *Z. Anorg. Allg. Chem.*, 1941, **247**, 65.
8 A. Pflugmacher, D. Schorning, and R. Schwarz, *Z. Anorg. Allg. Chem.*, 1958, **295**, 92.
9 O. Yamaguchi, T. Kanazawa, and K. Shimizu, *J. Chem. Soc., Dalton Trans.*, 1982, 1005.
10 M. L. Hair, 'Infrared Spectroscopy in Surface Chemistry,' Marcel Dekker, New York, 1967, p. 198.
11 See, for example, R. B. Fahim and G. A. Kolta, *J. Phys. Chem.*, 1970, **74**, 2502.
12 K. L. Mampel, *Z. Phys. Chem., Abt. A*, 1940, **43**, 235.

Received 8th November 1982; *Paper* 2/1877