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Characterization of $MgSiO_3$, $CaMgSi_2O_6$ and $CaSiO_3$ Precursor Powders by ^{29}Si MAS NMR

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Abstract

$MgSiO_3$, $CaMgSi_2O_6$, and $CaSiO_3$ precursor powders were characterized by ^{29}Si MAS NMR spectroscopy and the relation between the spectra and the crystallization reactions on firing was investigated. Samples were synthesized by a coprecipitation method and a slow hydrolysis method. They were fired at 500–900°C and the crystallization process was examined by XRD and NMR. Homogeneity of the samples prepared by the coprecipitation method was better than for those prepared by the hydrolysis method. Homogeneity of the samples became worse in the sequence $MgSiO_3$, $CaMgSi_2O_6$, $CaSiO_3$ for samples made by the same preparation method. Good correlation between a decreasing number of NMR peaks and a higher homogeneity of the samples was found.

$MgSiO_3$-, $CaMgSi_2O_6$- und $CaSiO_3$-Precursor-Pulver wurden mittels der ^{29}Si MAS NMR Spektroskopie untersucht und die Beziehung zwischen den Spektren und den Kristallisationsreaktionen beim Feuern ermittelt. Die Herstellung der Proben erfolgte mittels einer Koausscheidungsmethode und einer langsamen Hydrolysemethode. Die Proben wurden bei 500–900°C gefeuert und der Kristallisationsprozeß mit Hilfe von XRD und NMR untersucht. Die Homogenität der durch Koausscheidung hergestellten Proben war besser als die der mittels Hydrolysemethode hergestellten Proben. Die Homogenität der Proben verschlechterte sich in der Reihenfolge $MgSiO_3$, $CaMgSi_2O_6$, $CaSiO_3$ für Proben, deren Herstellung in gleicher Weise erfolgte. Es ergab sich eine gute Korrelation zwischen der Abnahme der Zahl der NMR Spitzen und einer höheren Homogenität der Proben.

Des poudres précurseurs de $MgSiO_3$, $CaMgSi_2O_6$ et $CaSiO_3$ ont été caractérisées par spectroscopie RMN MAS du ^{29}Si et la relation entre les spectres et les réactions de cristallisation durant le traitement thermique a été étudiée. L'homogénéité des échantillons qui ont été préparés par les méthodes de coprécipitation s'avère meilleure que par la méthode d'hydrolyse. En outre, il est apparu que l'homogénéité des échantillons se dégrade suivant la séquence $MgSiO_3$, $CaMgSi_2O_6$, $CaSiO_3$ pour une même méthode de préparation. Une bonne corrélation entre le nombre décroissant des pics en RMN et une homogénéité des échantillons plus élevée a pu être obtenue.

1 Introduction

It is well known that powder synthesis through a liquid phase[1] is suitable for the preparation of fine, active and homogeneous powders. In the preparation of multicomponent compounds, it is very important to find appropriate conditions for the preparing of a good precursor, which has a high degree of homogeneity and the ideal composition. In order to find such conditions, it is important to characterize the precursor as much as possible by various methods.

^{29}Si MAS NMR is an effective method for characterizing silicates, especially for amorphous substances such as glass or gel (it is difficult to get

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satisfactory structural information by X-ray diffraction methods[2,3]). The local environment around Si atoms can be examined by ^{29}Si MAS NMR from their chemical shift values. Polymerization structures of silicate ions are usually described by the Q^n notation,[4] in which the superscript n ($n = 0$–4) means the number of bridging oxygens per Si tetrahedron. The NMR chemical shift values distribute in a certain range due to the influence of geometrical differences and also the higher ordered coordination environment around the Si atoms. They distribute within a range of about 10 ppm for each Q^n group.[5] The NMR peaks of amorphous materials are reported to be broad compared with those of crystalline materials, but the chemical shift values are almost identical in both cases.[6] Homogeneity of local structures of amorphous silicates can, therefore, be investigated by ^{29}Si MAS NMR spectroscopy.

In this paper, the local environment around Si atoms for $MgSiO_3$, $CaMgSi_2O_6$ and $CaSiO_3$ precursor powders prepared by liquid-phase synthesis methods and also their crystallization process were investigated by ^{29}Si MAS NMR.

2 Experimental

2.1 Sample preparation

Precursor powders of $MgSiO_3$, $CaMgSi_2O_6$ and $CaSiO_3$ samples were prepared. Chemicals used were magnesium nitrate hexahydrate, calcium nitrate tetrahydrate and tetraethyl orthosilicate (TEOS). They were dissolved in ethanol and used as the starting solution. The concentration of TEOS in all the samples was adjusted to be 0·4 mol/litre and the H_2O/TEOS ratio was adjusted to be 6. Iron (III) nitrate enneahydrate, with a concentration of 1 wt% in Fe, was added to $CaMgSi_2O_6$ and $CaSiO_3$ samples in order to reduce their long spin-lattice relaxation time in the ^{29}Si MAS NMR measurements.

Gel precipitates were obtained by adding 25% NH_4OH to the starting solution; these samples are designated as the coprecipitation samples. Gels were also obtained by slow hydrolysis of TEOS while keeping them in an air bath at 60°C covered with pin-holed Al foil. They are designated as the slow hydrolysis samples. These gels were dried to powders by the water bath and the air bath at 110°C. They were calcined at 500°C for 2 h and used for the starting materials. The starting materials were fired at various temperatures from 500 to 900°C for 2 h in air.

2.2 Characterization

Crystalline phases in the samples fired at various temperatures were identified by powder X-ray diffractometry (XRD, Rigku Co., Geigerflex diffractometer) with a monochromated CuK_α radiation.

Differential thermal analysis (DTA, Rigaku Co., Microtype) was performed on the calcined samples. The heating rate was 10°C/min and the amount of sample was about 20 mg.

^{29}Si MAS NMR measurements were performed using JNM GSX-270 spectrometer (4·3 tesla and the observation frequency of 53·54 MHz). The sample was placed in a zirconia sample tube, and spun at 3500–4000 Hz around the axis tilted at an angle of 54°44' (magic angle). In the measurements, the conventional method with 2 μs pulses and 60 s time intervals was used. Signals were accumulated for 200–240 times. Polydimethylsilane was used as a secondary standard of ^{29}Si chemical shift, for which the value was $-33{\cdot}8$ ppm.

3 Results and discussion

Table 1 shows the crystalline phases detected in the samples fired at various temperatures. All the coprecipitation samples calcined at 500°C were nearly amorphous irrespective of their composition, and the objective crystalline phases, $MSiO_3$, appeared by firing at 800°C. On the other hand,

Table 1. Crystalline phases in the samples fired at various temperatures

Sample	*Preparation method*	*Temperature (°C)*			
		500	*700*	*800*	*900*
$MgSiO_3$	Coprecipitation	Amorphous	Amorphous	$MgSiO_3$	$MgSiO_3$
	Hydrolysis	Amorphous	Mg_2SiO_4	$MgSiO_3$, Mg_2SiO_4	$MgSiO_3$, Mg_2SiO_4
$CaMgSi_2O_6$	Coprecipitation	Amorphous ($CaCO_3$)	Amorphous	$CaMgSi_2O_6$	$CaMgSi_2O_6$
	Hydrolysis	Amorphous ($CaCO_3$)	$Ca_3MgSi_2O_8$	$CaMgSi_2O_6$, $Ca_3MgSi_2O_8$, $Ca_2MgSi_2O_7$	$CaMgSi_2O_6$, $Ca_3MgSi_2O_8$, $Ca_2MgSi_2O_7$
$CaSiO_3$	Coprecipitation	Amorphous (unidentified)	Amorphous (unidentified)	β-$CaSiO_3$	β-$CaSiO_3$
	Hydrolysis	Unidentified	α'-Ca_2SiO_4, CaO	β-Ca_2SiO_4, CaO	β-Ca_2SiO_4, CaO, β-$CaSiO_3$

(): Trace amount.

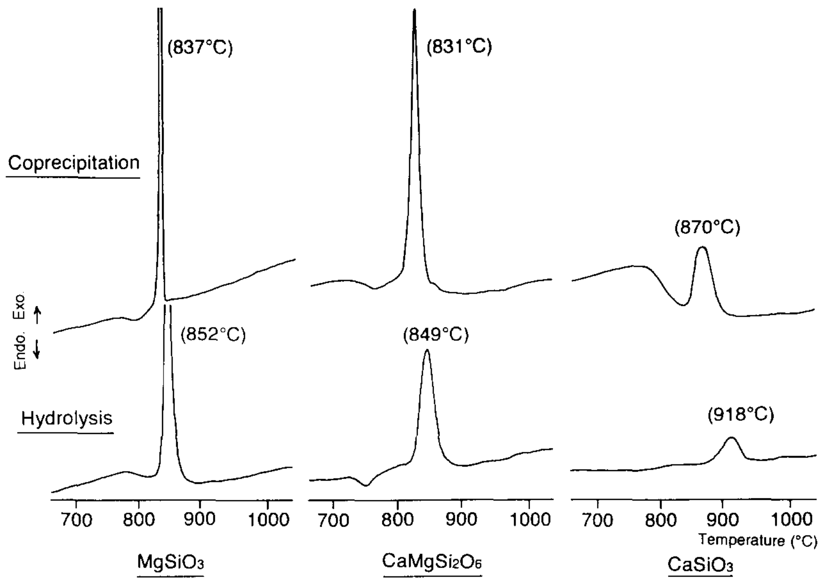

Fig. 1. DTA curves of the samples.

the slow hydrolysis samples fired at higher than 700°C contained crystalline phases, which were other than the objective phases. Especially, the $CaSiO_3$ sample did not contain the objective phase, $CaSiO_3$ (wollastonite), even when fired at 800°C.

Figure 1 shows the DTA curves of the samples. The exothermic peak appearing at around 800–900°C is attributed to the crystallization of the amorphous precursor. The exothermic peak temperatures of the coprecipitation samples were always lower than those of the hydrolysis samples and the peak widths were narrower. Comparing the exothermic peaks of the coprecipitation samples, they apparently became sharper and stronger in the order $CaSiO_3$, $CaMgSi_2O_6$, $MgSiO_3$. The same trend for exothermic temperature and peak width was observed for the hydrolysis samples.

The NMR spectra of the samples fired at 500°C for 2 h are shown in Fig. 2. The spectra are apparently formed by overlapping of a number of peaks and are separated into two to five peaks by assuming the Gauss function. The calculated peaks are shown by the broken lines in Fig. 2. The area and chemical shift of each peak in the coprecipitation samples and those in the hydrolysis samples are listed in Tables 2 and 3, respectively. Each separated peak is assigned to the respective Q^n structures referring to the chemical shift data reported for the crystalline phases.[5] This assignment is hypothetical because the accurate peak positions of Q^n for amorphous components are not clarified yet.

In the $MgSiO_3$ samples, the spectra of the coprecipitation samples differ distinctly from those of the hydrolysis samples, as shown in Fig. 2. The

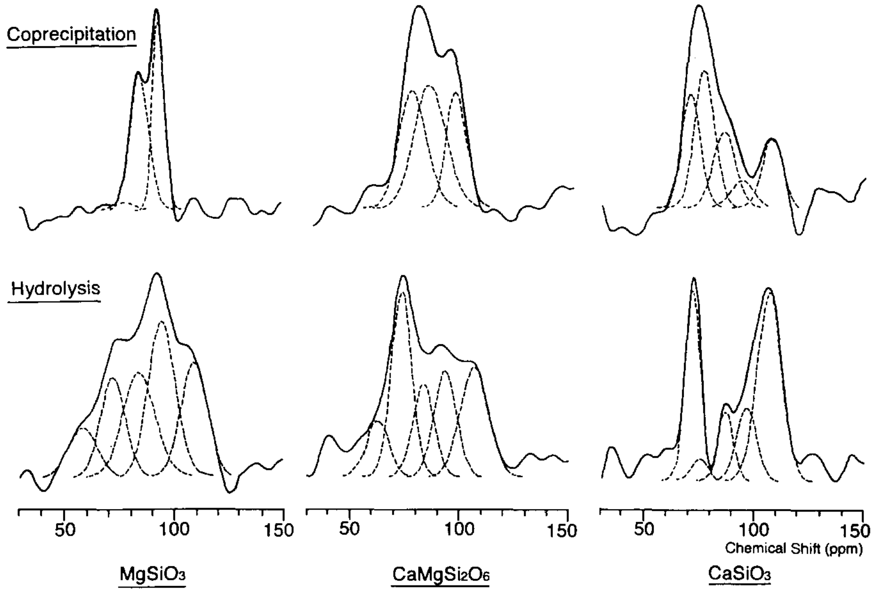

Fig. 2. ^{29}Si MAS NMR spectra of the samples fired at 500°C.

Table 2. Q^n peak areas and chemical shifts of ^{29}Si MAS NMR spectra of the samples prepared by the coprecipitation method

		Temperature (°C)			
		500	*700*	*800*	*900*
$MgSiO_3$	Q^0	0	0	0	0
		(—)*	(—)	(—)	(—)
	Q^1	2·8	0	0	0
		(−77·4)	(—)	(—)	(—)
	Q^2	50·8	70·5	100	100
		(−84·9)	(−84·0)	(−82·3)	(−82·3)
	Q^3	46·3	29·5	0	0
		(−93.8)	(−91·8)	(—)	(—)
	Q^4	0	0	0	0
		(—)	(—)	(—)	(—)
$CaMgSi_2O_6$	Q^0	0	0	0	0
		(—)	(—)	(—)	(—)
	Q^1	34·3	41·2	7·9	29·6
		(−76·0)	(−75·0)	(−72·0)	(−73·0)
	Q^2	41·2	34·0	68·9	70·4
		(−83·9)	(−83·0)	(−84·5)	(−83·4)
	Q^3	24·5	20·4	10·6	0
		(−95·7)	(−96·0)	(−99·0)	(—)
	Q^4	0	4·4	12·5	0
		(—)	(−107·0)	(−111·0)	(—)
$CaSiO_3$	Q^0	24·3	19·9	17·3	13·1
		(−70·8)	(−70·5)	(−70·3)	(−70·7)
	Q^1	32·5	20·3	17·3	0
		(−77·0)	(−76·0)	(−74·5)	(—)
	Q^2	19·7	42·6	27·9, 33·4	73·9
		(−86·0)	(−82·3)	(−83·5, −88·6)	(−88·0)
	Q^3	7·2	17·2	4·1	0
		(−94·1)	(−94·3)	(−93·3)	(—)
	Q^4	16·4	0	0	13·1
		(−107·8)	(—)	(—)	(−110·8)

* Numbers in parentheses are chemical shifts (ppm).

Table 3. Q^n peak areas and chemical shifts of ^{29}Si MAS NMR spectra of the samples prepared by the hydrolysis method

		Temperature (°C)			
		500	*700*	*800*	*900*
$MgSiO_3$	Q^0	9·5	8·5	12·0	16·9
		(−58·5)*	(−62·2)	(−61·6)	(−62·1)
	Q^1	16·8	20·4	0·0	7·1
		(−72·0)	(−73·0)	(—)	(−70·1)
	Q^2	23·2	20·0	58·6	45·2
		(−84·0)	(−84·0)	(−81·7)	(−82·5)
	Q^3	29·6	29·1	2·7	10·1
		(−94·4)	(−94·8)	(−98·0)	(−97·7)
	Q^4	20·8	22·1	26·6	20·7
		(−109·0)	(−110·8)	(−105·5)	(−108·8)
$CaMgSi_2O_6$	Q^0	10·0	11·0	6·7	6·9
		(−63·0)	(−62·8)	(−59·4)	(−59·9)
	Q^1	30·7	34·7	32·3	34·4
		(−74·0)	(−72·8)	(−72·2)	(−71·6)
	Q^2	15·6	18·4	26·6	30·7
		(−84·0)	(−84·0)	(−84·4)	(−83·9)
	Q^3	19·1	17·5	4·1	3·7
		(−93·0)	(−94·4)	(−96·6)	(−97·0)
	Q^4	24·7	18·4	30·2	24·3
		(−106·8)	(−106·2)	(−109·0)	(−108·6)
$CaSiO_3$	Q^0	27·8	43·9	39·8	39·8
		(−72·2)	(−70·1)	(−71·0)	(−70·3)
	Q^1	3·8	0	0	0
		(−77·0)	(—)	(—)	(—)
	Q^2	9·8	9·0	5·4	16·1
		(−87·5)	(−87·5)	(−84·8)	(−88·5)
	Q^3	13·8	12·5	4·0	0
		(−97·2)	(−98·0)	(−94·3)	(—)
	Q^4	45·2	34·6	50·9	44·1
		(−107·5)	(−109·0)	(−110·3)	(−109·5)

* Numbers in parentheses are chemical shifts (ppm).

spectrum of the coprecipitation sample fired at 500°C is separated into Q^2 and Q^3 peaks as well as a very small Q^1 peak. The intensity ratio of the Q^2 and Q^3 peaks was almost 1:1. As the firing temperature was elevated, the Q^3 peak decreased and disappeared in the samples fired above 800°C. The objective phase, $MgSiO_3$, has a chain silicate structure and it corresponds to Q^2 structure. It is, therefore, considered that a $MgSiO_3$-like local arrangement is already formed in the amorphous state and easily crystallizes to form $MgSiO_3$ crystals on firing in this case.

On the other hand, the spectra of the hydrolysis samples were complex and were separated into five peaks corresponding to Q^0–Q^4. Their intensity ratios showed little change even when fired to 900°C. Q^0 and Q^2 peaks can be assigned to Mg_2SiO_4 and $MgSiO_3$ crystals, respectively. Since Q^3 and Q^4 peaks can not be assigned to any crystalline phases observed in the XRD pattern, they are assigned to the amorphous phase, which is considered to be rich in SiO_2. If starting materials have various local arrangements, they tend to form their respective crystalline phases by firing. Once each phase forms, it remains present up to high temperatures and hinders the formation of the objective phase. The importance of homogeneity in the starting materials is stressed from these results.

In the $CaMgSi_2O_6$ samples, the spectrum of the coprecipitation sample fired at 500°C was separated into three peaks corresponding to Q^1, Q^2 and Q^3. On the other hand, the spectrum of the hydrolysis sample contained five peaks corresponding to Q^0–Q^4, similar to that of the $MgSiO_3$ sample, although their proportions were slightly different. The Q^1 peak was larger than the other peaks in this case. As the firing temperature was increased, the Q^1 and Q^3 peaks decreased greatly in the coprecipitation sample. The Q^1 peak, however, still remained after firing at 900°C. In the hydrolysis sample, the Q^3 peak decreased with increasing firing temperature but showed little change for the other peaks. Here, the crystalline phases detected by XRD correspond to the following Q^n structures, respectively: $CaMgSi_2O_6$ (diopside) is Q^2, $Ca_2MgSi_2O_7$ (Akermanite) is Q^1 and $Ca_3MgSi_2O_8$ (merwinite) is Q^0.

In the $CaSiO_3$ samples fired at 500°C, five peaks corresponding to Q^0–Q^4 appeared not only in the hydrolysis sample but also in the coprecipitation sample. As the firing temperature increased, the Q^2 peak in the coprecipitation sample increased gradually. However, the Q^0 and Q^1 peaks still remained at 800°C and the Q^0 peak was observed even at 900°C. Since only $CaSiO_3$ phase was detected in these samples by XRD, NMR is found to be more effective than XRD in allowing more detailed information to be obtained about local structure around Si atoms, i.e. homogeneity of the sample. A curious point in this sample is that Q^4 peak appeared again in the sample fired at 900°C but the reason is uncertain. The spectrum of the hydrolysis sample was similar to those of $MgSiO_3$ and $CaMgSi_2O_6$ samples; however, the Q^1 peak was very small and the Q^0 and Q^4 peaks were very large. The Q^0 in this sample corresponds to Ca_2SiO_4 crystals while Q^4 corresponds to amorphous SiO_2. The Q^2 peak increased and the Q^3 peak decreased in the sample fired at 900°C; however, the Q^0 and Q^4 peaks did not decrease, even at this temperature. The area of the Q^2 peak of this sample was the smallest among those of all the samples and the formation amount of the objective crystalline phase was the smallest.

These obtained results can be understood by the difference of homogeneity of the components in the samples, i.e. local distribution and variation of the components. The DTA and XRD experiments show that the crystallization reaction in the coprecipitation samples proceeds more rapidly and homogeneously than that in the hydrolysis samples. The exothermic peak of the DTA curve showed that the crystallization temperature range became wider in the order $MgSiO_3$, $CaMgSi_2O_6$, $CaSiO_3$ for the same preparation method. If the kind and the proportion of polymerized structures estimated from the NMR spectra are defined as a measure of homogeneity, the coprecipitation samples are always more homogeneous than the hydrolysis samples in the as-prepared state. When comparing the homogeneity of the samples among three compounds, their homogeneity decreased in the order $MgSiO_3$, $CaMgSi_2O_6$, $CaSiO_3$. This interpretation is compatible with the results of the DTA and XRD measurements. Grimer *et al.*[6] report that the ^{29}Si NMR spectra of silicate glasses are similar to those of the respective crystals except for broadening of the peak. If there is chemical inhomogeneity in an amorphous silicate material, several Q^n structures corresponding to each local composition occur and they can be distinguished by ^{29}Si MAS NMR.

As already mentioned, the inhomogeneity of the local structure around Si atoms in the samples is reflected in the NMR spectra. However, the ratio of peak area does not always coincide accurately with the proportion of Q^n species actually in the samples. For example, the NMR spectrum of the $CaMgSi_2O_6$ coprecipitation sample fired at 900°C was composed of the Q^2 and Q^1 peaks, as shown in Table 2. When there are Q^n structures with $n < 2$ in $MSiO_3$, those with $n>2$ have to exist in the sample to maintain the stoichiometry. No plausible explanation is, therefore, possible to explain this observation data, except by considering the inhomogeneity of components in the sample. Two reasons are considered for this contradiction. One is the existence of OH groups in the sample. If the sample contains OH groups and they form silanol bonds, Si–OH, the number of Ca and Mg ions around a Si atom can be fewer than the one predicted from the Q^n structure, satisfying the local charge balance. The other reason is related to the experimental conditions. If SiO_4 tetrahedra polymerize to a Q^4 structure with considerable molecular weight, a very long relaxation time is required to observe the NMR spectrum and it is difficult to observe it under the present experimental conditions. It is unlikely that a large amount of OH groups exist in the $CaMgSi_2O_6$ sample fired at 900°C. The latter reason may be plausible in this case. If the NMR data are examined more precisely, those of several of the samples do not satisfy the stoichiometry and they always deviate to a SiO_2-poor composition. These discrepancies can be also explained by this reason.

Although the $MgSiO_3$ coprecipitation sample showed the most rapid and homogeneous crystallization reaction among the samples, a couple of different SiO_4 polymerization structures were found in the sample. Since local structural regions in the Mg-poor composition (Q^3 structure) as well as that in the desirable composition (Q^2 structure) were observed from the NMR spectrum, it should contain the region in the Mg-rich composition, although it is not detected in the NMR spectrum. Such a compositional fluctuation of this sample is smaller than those of the other samples. Therefore, the crystallization reaction occurs rapidly and homogeneously and little subsidiary phase is formed during the thermal reaction.The same considerations can be applied to the other samples. The fluctuation of composition in the $CaMgSi_2O_6$ and the $CaSiO_3$ samples is considered to be larger than that in the $MgSiO_3$ sample from the NMR spectra. It is compatible with the data of the width of exothermic peaks in the DTA. The distribution of components in $CaMgSi_2O_6$ powders, prepared by the same methods as used in this paper, was measured by analytical electron microscopy.[7] The powders prepared by the coprecipitation method were always chemically more homogeneous than those prepared by the hydrolysis method. The degree of mixing between Mg and Si components in the $MgSiO_3$ samples was better than that between Ca and Si components in the $CaSiO_3$ samples. These results are consistent with those obtained in this study.

4 Conclusions

$MgSiO_3$, $CaMgSi_2O_6$, and $CaSiO_3$ precursor powders were characterized by ^{29}Si MAS NMR spectra, XRD and DTA methods, and the relation between chemical homogeneity of precursor powders and their crystallization reactions were investigated. The results are summarized as follows:

(1) The coprecipitation samples are always more homogeneous than the hydrolysis samples.
(2) The crystallization reaction occurred more rapidly and homogeneously in the sequence $MgSiO_3$, $CaMgSi_2O_6$, $CaSiO_3$.
(3) ^{29}Si MAS NMR spectra showed that the variety of the SiO_4 polymerization structure decreased as the homogeneity of the samples increased, and the crystallization reaction occurred more rapidly and homogeneously in these samples.

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