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Synthesis and thermal properties of zirconium ortho- and diphosphates

MAKOTO WATANABE, MAKOTO SAKURAI, TETSUYA YAMADA, HIDEHIKO MORI
Department of Industrial Chemistry, College of Engineering, Chubu University, Matsumoto-cho, Kasugai, Aichi 487, Japan

Single phase sodium zirconium orthophosphates [$NaZr_2(PO_4)_3$ and $Na_2Zr(PO_4)_2$] and zirconium diphosphate (ZrP_2O_7) have been synthesized. The measured linear expansion coefficient of $NaZr_2(PO_4)_3$ was rather small only reaching a value of 0.16% at 800 °C. The expansion coefficients of $Na_2Zr(PO_4)_2$ and ZrP_2O_7 were also rather small and were 1.4 and 1.0% respectively at 800 °C. These phosphates showed different behaviour depending on the type of thermal pretreatment before the measurement of the expansion coefficient.

1. Introduction

Phosphates are well known compounds and have been studied in many pure and applied chemical fields. They are used as food additives, detergents, chemical fertilizers, flame retardants and in chemical manufacturing and as ceramic industrial materials, [1–4]. Zirconium orthophosphates are used as inorganic ion exchangers. They also have a high resistance to thermal shock [5–8]. There are two kinds of sodium zirconium orthophosphate. One is $NaZr_2(PO_4)_3$ and the other is $Na_2Zr(PO_4)_2$. These compounds are usually produced by conventional powder processes and it is difficult to synthesize a single phase product. This paper describes a solution process to obtain single phase monosodium or disodium zirconium orthophosphates and zirconium diphosphate. The thermal expansion behaviour of the compounds is also discussed in this work.

2. Experimental procedure

2.1. Preparation

2.1.1. Sodium zirconium orthophosphate

Phosphoric acid (85%), zirconium oxide, and sodium carbonate were carefully mixed with stirring by a glass rod. The mixture was gently heated by a burner in order to remove water. The resulting white substance was ground in a mill into a fine powder. The powder was then heated at 200 °C for 90 min and the product was then reground. The same treatment was successively performed at 400, 600, 800, and 1000 °C. The product at each temperature was analysed in order to obtain information on the progress of the reaction. The final product was washed with hot water in order to remove any water-soluble impurities and dried by heating at 110 °C.

2.1.2. Zirconium diphosphate

Zirconium diphosphate was obtained as a component of the reaction products produced by the above treatment however it proved impossible to isolate single phase zirconium diphosphate from the H_3PO_4–ZrO_2–Na_2CO_3 system. In order to obtain single phase zirconium diphosphate, a mixture of 85% phosphoric acid and zirconium oxide was treated in a similar manner to that used in the H_3PO_4–ZrO_2–Na_2CO_3 system. If the final product contained free zirconia, extra 85% phosphoric acid was added to the reaction. The process was repeated until a Zr/P molar ratio was found from which no free zirconia was detectable in the X-ray diffraction pattern of the final product. The following process was also studied in an attempt to find a simpler reaction to synthesize zirconium diphosphate. Zirconium chloride was dissolved in water and then 20% phosphoric acid was mixed in the solution with stirring. The resulting mixture was filtered off and the residue was washed with water until chloride ions were undetectable in the filtrate. The residue was then dried by heating at 100 °C and the same thermal treatment other than the heating time as that in the H_3PO_4–ZrO_2–Na_2CO_3 system was carried out. In this case the heating time at each temperature was 60 min.

2.2. Chemical analysis

The zirconium phosphates were dissolved in a hot sulfuric acid solution. The determination of sodium, zirconium, and phosphorus in the solution was carried out by atomic absorption analysis (Shimazu atomic absorption photometer, AA–680), EDTA volumetric analysis, and the molybdenum blue colorimetric method.

2.3. X-ray diffractometry (XRD)

An XRD pattern of a powder sample was taken with nickel-filtered CuK_α radiation using a Rigaku X-ray diffractometer (RAD-1B).

2.4. Thermogravimetric–differential thermal analysis (TG–DTA)

The TG–DTA measurement of a powder sample was run at a heating rate of $10°C\,min^{-1}$ in air using a Rigaku and/or Seiko TG–DTA apparatus.

2.5. Thermomechanical analysis (TMA)

A pellet was made by pressing the powder at $500\ kg\,cm^{-2}$ and the linear thermal expansion coefficient of the sample was measured up to 800 °C at a heating rate of $10\ °C\,min^{-1}$ using a Shimazu TMA apparatus.

3. Results and discussion

3.1. Composition

Table I shows the mixing molar ratios of the phosphoric acid, zirconium oxide, and sodium carbonate. The phase composition of the sample batches at each heating temperature is listed in Table II. A circle in the

TABLE I Mixing molar ratio of phosphoric acid, zirconium oxide, and sodium carbonate.

Sample no.	H_3PO_4	ZrO_2	Na_2CO_3	Sample no.	H_3PO_4	ZrO_2	Na_2CO_3
1	2	2	1	18	7	3	0
2	9	5	6	19	17	8	0
3	12	5	3	20	6	2	3
4	10	9	1	21	3	2	1
5	1	1	0	22	5	3	2
6	2	1	0	23	55	28	18
7	3	3	4	24	11	5	4
8	3	4	3	25	55	22	23
9	4	3	3	26	2	1	1
10	2	5	3	27	10	3	7
11	3	5	2	28	12	3	5
12	1	3	1	29	9	5	7
13	8	4	1	30	2	1	2
14	6	4	1	31	8	2	5
15	3	1	1	32	3	2	5
16	5	2	3	33	2	1	7
17	5	4	1				

TABLE II Composition of the thermal products determined from the XRD patterns. (2 = 200, 4 = 400, 6 = 600, 8 = 800, 10 = 1000 °C).

Sample no.	$NaZr_2(PO_4)_3$					$N_2Zr(PO_4)_2$					ZrP_2O_7					ZrO_2					Na_3PO_4					Na_2ZrO_3					Unknown				
	2	4	6	8	10	2	4	6	8	10	2	4	6	8	10	2	4	6	8	10	2	4	6	8	10	2	4	6	8	10	2	4	6	8	10
1	0	0	0	0	0	–	–	–	–	0	–	–	–	–	–	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0
2	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0
3	0	0	0	0	0	–	–	–	–	–	0	0	0	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
4	–	–	0	0	0	–	–	–	–	–	0	0	0	0	0	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
5	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
6	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
7	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–
8	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	–	–	–	–	0	–	–	–	–	–	–	–	–	–	0
9	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0
10	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	–	–	–	0	0	–	–	–	–	–	–	–	–	–	–
11	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0
12	–	–	–	–	0	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0
13	–	–	0	0	0	–	–	–	–	–	0	0	0	0	–	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
14	0	0	0	0	0	–	–	–	–	–	0	0	0	0	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
15	0	0	0	0	0	–	–	–	–	–	0	0	0	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
16	0	0	0	0	–	–	–	–	–	0	–	–	–	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
17	0	0	0	0	0	–	–	–	–	–	0	0	0	–	–	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
18	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
19	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
20	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
21	0	0	0	0	0	–	–	–	–	–	0	0	–	–	–	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
22	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
23	0	0	0	0	0	–	–	–	–	–	0	0	–	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
24	0	0	0	0	0	–	–	–	–	–	0	0	0	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
25	0	0	0	0	0	–	–	–	–	–	0	0	–	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
26	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0
27	0	0	0	0	0	–	–	–	0	0	–	–	–	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0
28	–	–	0	0	0	–	–	–	–	–	0	0	0	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
29	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0
30	0	0	0	0	0	–	–	–	0	0	–	–	–	–	–	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
31	0	0	0	0	0	–	–	–	–	–	–	–	–	–	–	0	0	0	–	–	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0
32	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	0	0	0	0	0	–	–	–	–	0	–	–	–	–	–
33	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0	0	0	0	0	0	0	0	0	0	–	–	–	0	0	0	0	0	0	0

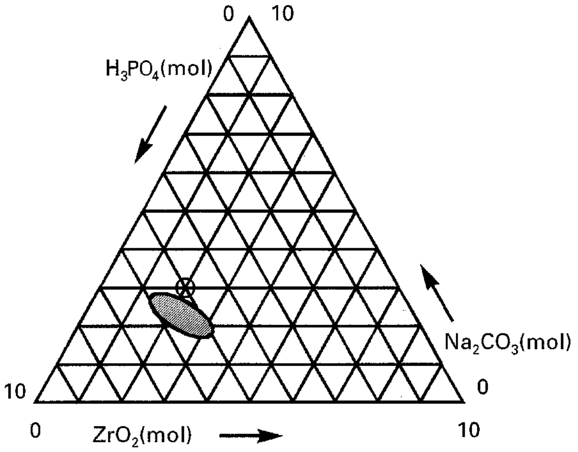

Figure 1 Formation region of; (◍) $NaZr_2(PO_4)_3$ and (O) $Na_2Zr(PO_4)_2$ as a single phase product at 1000 °C.

table indicates that a phase was present in the reaction product. Sodium dizirconium tris(orthophosphate) and zirconium diphosphate were formed in a wide composition and temperature range. The diphosphate tends to decompose to the orthophosphate at 800–1000 °C. Accordingly, sodium dizirconium tris(orthophosphate) was obtained as a single phase product over a relatively wide mixing ratio at 800–1000 °C. On the other hand, disodium zirconium bis(orthophosphate) was produced from only one sample (No. 16) at 1000 °C. Zirconium diphosphate was observed over a relatively wide mixing ratio and temperature range, but it could not be isolated as a single phase. The molar ratios in the H_3PO_4–ZrO_2–Na_2CO_3 system that form single phase $NaZr_2(PO_4)_3$ or $Na_2Zr(PO_4)_2$ at 1000 °C are shown in Fig. 1. A zirconium diphosphate single phase was obtained by heating the product of mixtures of phosphoric acid and zirconium dioxide at varying molar ratios at 1000 °C until all of the zirconium dioxide had reacted. The results of elemental analysis of the samples were as follows: (1) $NaZr_2(PO_4)_3$, obtained; Na 5.0, Zr 36.9, P 18.7%, calculated; Na 4.7, Zr 37.2, P 18.9%, (2) $Na_2Zr(PO_4)_2$, obtained; Na 13.8, Zr 28.2, P 18.1%, calculated; Na 14.1, Zr 27.9, P 18.9%, (3) ZrP_2O_7, obtained; Zr 33.9, P 22.8%, calculated; Zr 34.4, P 23.4%.

3.2. TG–DTA measurement

TG and DTA curves of $NaZr_2(PO_4)_3$, $Na_2Zr(PO_4)_2$, and ZrP_2O_7 were recorded up to 1000 °C. No detectable thermal change except for the removal of adsorbed water was observed.

3.3. TMA measurement

The samples obtained by the processes described in Section 3.1 were preheated as follows: (1) gradual heating from room temperature to 800 °C, (2) at 800 °C for 1 h, and (3) at 1000 °C for 1 h. The linear expansion coefficients of the preheated $NaZr_2(PO_4)_3$, $Na_2Zr(PO_4)_2$, and ZrP_2O_7 are shown in Figs 2–5.

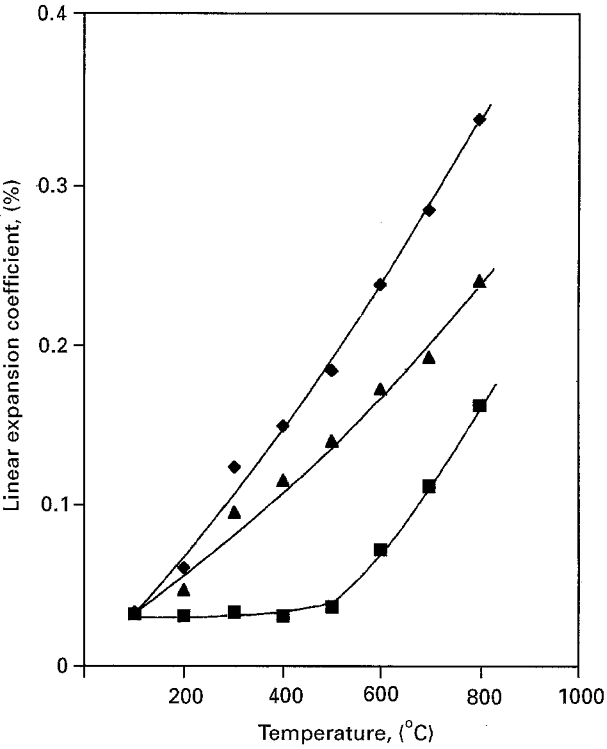

Figure 2 Linear expansion coefficient of $NaZr_2(PO_4)_3$. The symbols on the figure are (■) gradual heating from room temperature to 800 °C, (◆) heating at 800 °C for 1 h and (▲) heating at 1000 °C for 1 h.

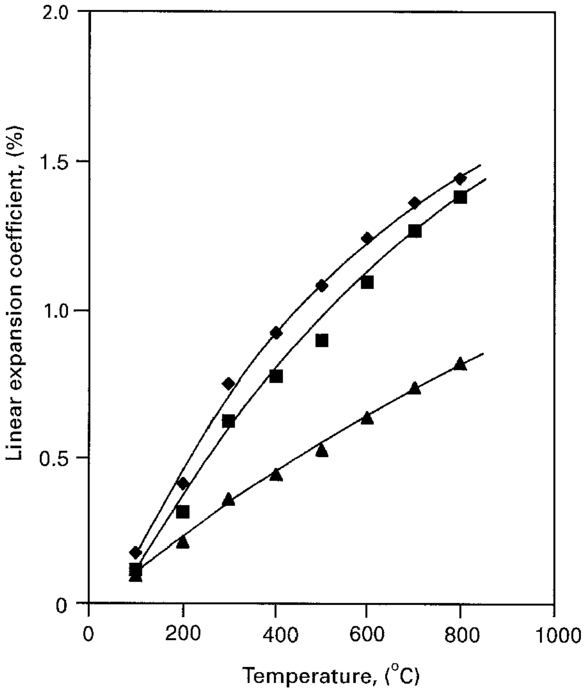

Figure 3 Linear expansion coefficient of $Na_2Zr(PO_4)_2$. The symbols on the figure are (■) gradual heating from room temperature to 800 °C, (◆) heating at 800 °C for 1 h and (▲) heating at 1000 °C for 1 h.

3.3.1. $NaZr_2(PO_4)_3$

The sample preheated by process (1) showed the smallest expansion coefficient of 0.16% at 800 °C. The expansion coefficient of the sample between 100–500 °C was especially small at about 0.03%. The expansion coefficient of the samples treated by

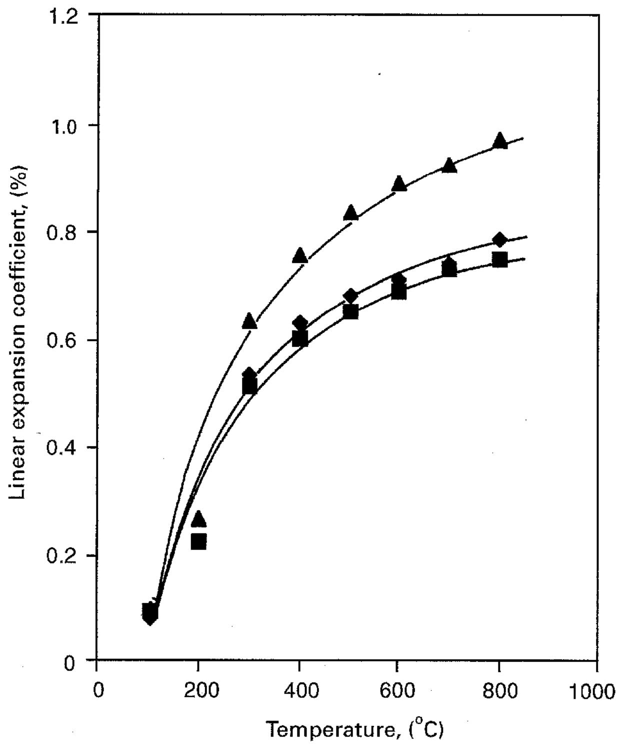

Figure 4 Linear expansion coefficient of ZrP_2O_7 obtained from the H_3PO_4–ZrO_2 system. The symbols on the figure are (■) gradual heating from room temperature to 800 °C, (◆) heating at 800 °C for 1 h and (▲) heating at 1000 °C for 1 h.

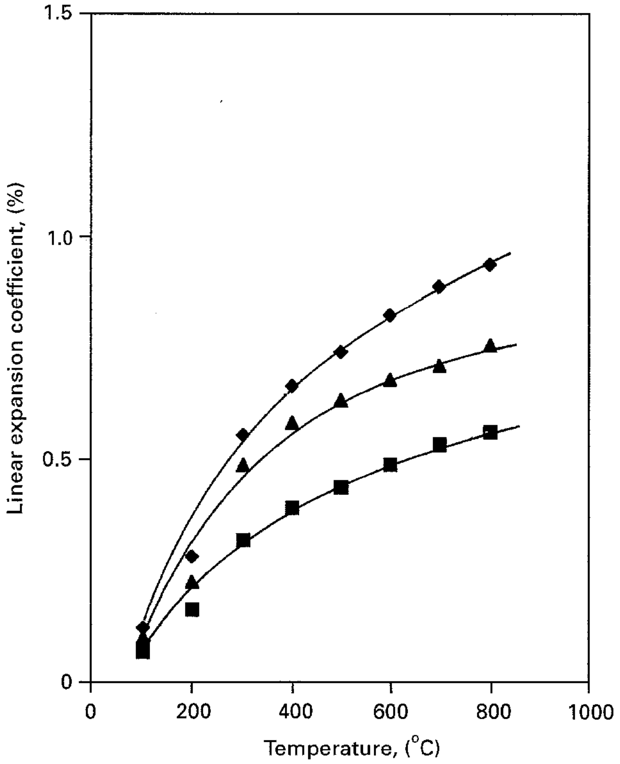

Figure 5 Linear expansion coefficient of ZrP_2O_7 obtained from the H_3PO_4–$ZrCl_4$ system. The symbols on the figure are (■) gradual heating from room temperature to 800 °C, (◆) heating at 800 °C for 1 h and (▲) heating at 1000 °C for 1 h.

processes (2) and (3) linearly increased as the temperature increased. The expansion coefficient of the sample measured after heating by process (3) was smaller than that measured after the heating pretreatment of process (2).

3.3.2. $Na_2Zr(PO_4)_2$

The sample pretreated by process (3) showed the smallest expansion coefficient at all temperatures. The expansion coefficient of the sample was 0.83% at 800 °C. The samples treated by processes (1) and (2) gave almost the same thermal expansion behaviour and the expansion coefficient was about 1.4% at 800 °C. In every case, the coefficient linearly increased with an increase in heating temperature.

3.3.3. ZrP_2O_7

3.3.3.1. Product obtained from H_3PO_4–ZrO_2 system. The samples preheated by processes (1) and (2) showed the same expansion coefficient at every temperature and the coefficient was about 0.7% at 800 °C. The sample treated by process (3) exhibited a larger expansion coefficient at every temperature with a value of about 1.0% at 800 °C. The expansion coefficients of all these samples increased rapidly at temperatures lower than 400 °C and the increase in the coefficient at higher temperatures was small.

3.3.3.2. Product obtained from H_3PO_4–$ZrCl_4$ system. The sample preheated by process (1) gave the smallest expansion coefficient at every heating temperature. The value was very small at about 0.5% at 800 °C. The expansion coefficients of the samples preheated by processes (2) and (3) were 0.94 and 0.75% respectively at 800 °C. These values were smaller than those of the samples obtained from the H_3PO_4–ZrO_2 system. The rapid increase in the coefficient of the samples of this system at temperatures lower than 400 °C and the small change at temperatures higher than 400 °C were the same as those obtained with the H_3PO_4–ZrO_2 system.

3.3.4. Differences in thermal behaviour due to pretreatment conditions

As mentioned above, $NaZr_2(PO_4)_3$, $NaZr_2(PO_4)_2$, and ZrP_2O_7 showed different thermal behaviour according to the pretreatment of the samples. This can be responsible for the difference of the residual stress by the pretreatment.

References

1. J. R. van WAZER, "Phosphorus and its compounds", Vols. I and II (Interscience Publishers, New York 1961).
2. D. E. C. CORBRIDGE, "Phosphorus" (Elsevier, Amsterdam, Oxford, New York, 1980).
3. A. D. F. TOY and E. N. WALSH, "Phosphorus chemistry in everyday living" (Amer. Chem. Soc., Washington, DC, 1987).
4. T. KANAZAWA, "Inorganic phosphate materials" (Elsevier, Amsterdam, Oxford, New York, Tokyo, 1989).
5. J. ALAMO and R. ROY, *J. Mater. Sci.* **21** (1986) 444.
6. G. E. LENAIN, H. A. McKIMSTRY, J. ALAMO, and D. K. AGRAWAL, *ibid.* **22** (1987) 17.
7. T. OTA and I. YAMAI, *J. Amer. Ceram. Soc.* **69** (1986) 1.
8. N. KATAGIRI, Y. HATTORI, T. OTA, and I. YAMAI, *J. Ceram. Soc. Jpn.* **102** (1994) 69.

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