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# Electrical conductivity of calcium phosphate ceramics with various Ca/P ratios

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Calcium orthophosphate powders with various Ca/P ratios were prepared by a wet process, employing $CaCO_3$ and $H_3PO_4$ as starting materials. After they were calcined and pressed to form pellets, they were fired at various temperatures ranging from 800 to 1200 °C. The samples at various stages were examined by X-ray diffraction and SEM. The a.c. electrical conductivity was measured for a series of samples. For some of the samples, the d.c. electrical conductivity and electromotive force were also measured. The samples showed relatively high conductivity ($\sim 4 \times 10^{-5}$ S cm$^{-1}$ at 800 °C). With respect to the tricalcium orthophosphate with nearly stoichiometric composition, the predominant charge carrier at 800 °C was presumed to be an ion although it is not identified at the moment.

## 1. Introduction

Calcium orthophosphates such as hydroxyapatite (HAp) and tricalcium orthophosphate (TCP) have attracted a great deal of interest, mainly due to their potential use as bioceramics. Since TCP was found to be bioactive and biodegradable, it has been utilized in the medical field [1].

There have been many reports on calcium orthophosphates concerning their fabrication, characterization and properties [2–8]. Many reports are related to the biological or mechanical properties of these orthophosphates [5–8], and a few concern their electrical properties [9–11]. However, the structural similarity of TCP to HAp suggests that TCP may be a good ionic conductor at elevated temperatures, because HAp is known as an intermediate ionic conductor at such temperatures [10, 11]. Furthermore, it is suggested that even divalent ions in some phosphates may move rapidly at elevated temperatures [9]. If ionic conductors at elevated temperatures are found in this system, they may be utilized as sensors and electrochemical cells.

In this study, calcium orthophosphates with various Ca/P ratios were prepared by a wet process, and the electrical conductivity was measured. A possible charge carrier is discussed on the basis of the results of the characterization and electrical measurements.

## 2. Experimental procedure

The preparation procedure for calcium phosphate powders is shown in Fig. 1. High-purity $CaCO_3$ and $H_3PO_4$ (Wako Pure Chemical Co.) were employed as starting materials. The powders with various Ca/P ratios as a precursor of TCP were prepared by a wet process. The ratio was controlled by changing the ripening period and pH of the solution. After the precipitates were filtered and dried, they were calcined at 800 °C for 3 h to form TCP or HAp-containing TCP. The samples at various stages were analysed with respect to Ca and P using ion chromatography (Yokogawa Electric Co. IC-500).

The resulting powders were pressed uniaxially at 200 kg cm$^{-2}$ to form pellets with a diameter of 20 mm. Subsequently, they were fired at temperatures ranging from 800 to 1200 °C with an interval of 100 °C. The samples were examined by powder X-ray diffraction (Philips PW 1729) and scanning electron microscopy (Jeol Co. JXA-840). The electrical conductivity was measured for the samples selected on the basis of the Ca/P ratio. The samples were cut to form rectangular bars with dimensions of $10 \times 5 \times 1$ mm$^3$ using a low-speed cutting machine (Buehler Ltd, 11-1180). After electrodes were coated on both sides of the pellets with a Pt paste, they were heated at 800 °C for 15 min. For all of the samples, electrical conductivity was measured from room temperature to 800 °C adopting the a.c. two-probe method. The measuring system is described in the previous paper [12]. The d.c. measurements were also conducted on the samples to examine the polarization behaviour. The current under a constant voltage (1 V) was continuously measured by a digital multi-meter (Advantest Co. TR211 4H). Additionally, an oxygen concentration cell was constructed

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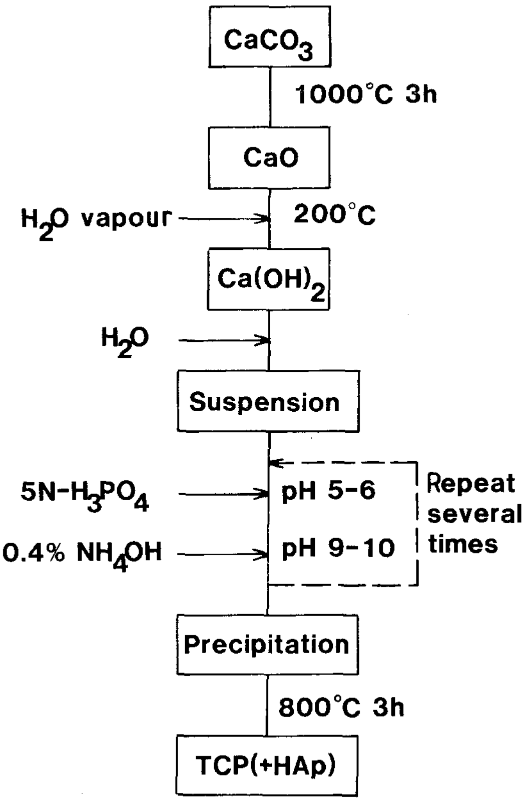

*Figure 1* Procedure for preparing TCP powders with various Ca/P ratios. The ratio was controlled by changing the ripening period.

to measure the electromotive force (e.m.f.) and examine the charge carrier at elevated temperatures. The atmosphere of the measuring electrode was changed from air to $N_2$ or $O_2$ and vice versa employing air as the reference electrode and the e.m.f. was repeatedly measured by the multi-meter.

## 3. Results and discussion

The Ca/P ratio determined by ion chromatography ranged from 1.49 to 1.60, which depended mainly on the ripening period. Among them, the samples with the Ca/P ratios of 1.51 (S-1), 1.56 (S-2) and 1.60 (S-3) were employed for further investigation. The density and phases identified by X-ray for these samples are summarized in Table I. The density increased with an increase in the firing temperature, except for 1200 °C. This is considered due to the phase transition on cooling from the α to β phase which is reported to take place at the temperature between 1120 and 1180 °C [13–17]. The difference in the density of each phase is so large (α; 2.86 g $cm^{-3}$, β; 3.07 g $cm^{-3}$) that microcracks were formed inside the sample owing to the internal stress caused by the volume change.

The microstructures of S-1, S-2 and S-3 are seen in Fig. 2. It is clear that the morphology depended on both the firing temperature and Ca/P ratio, although S-2 exhibited a similar texture to S-3. Since S-3 mostly consisted of HAp, it possessed a fine-grained microstructure which is reported [18] for pure HAp ceramics fabricated by a wet process similar to the present method.

The temperature dependence of the conductivity at 1 kHz for S-1, S-2 and S-3, which were fired at various temperatures, is shown in Fig. 3. The remarkable reduction in the conductivity for the samples fired at 1200 °C is clear compared with those fired at other temperatures. This is thought to be due to the formation of microcracks. The bulk conductivity is usually determined from the complex impedance plot, to distinguish it from the interfacial or electrode impedance. In this case, this method was not adopted because systematic measurement was necessary to learn when the temperature and Ca/P ratio were changed. It should be noted that all the samples showed relatively high conductivity compared with the previously reported values for calcium phosphate [9–11], not much lower than stabilized zirconia ($10^{-2}$–$10^{-3}$ S $cm^{-1}$ at 800 °C).

The polarization behaviour was examined for S-1, S-2 and S-3 fired at 1100 °C. The results are summarized in Table II. Since the current reduced gradually for quite a long time, the resistance 90 min after the first application of the electric field was adopted, although the current still slowly decreased. It is noteworthy that S-3 at room temperature had lower resistance than the others, because the predominant phase of S-3 is HAp which contains a hydrophilic hydroxy group in the lattice and is thought to exhibit protonic conduction due to the adsorbed water [19]. As the current at 90 min is mainly due to the electronic conduction, the resistance drop is thought roughly to reflect the transported number of ions. Therefore it is presumed that the predominant charge carriers at 800 °C may not be electrons but ions for S-1 and S-3. This coincides with the report that the charge carrier

TABLE I Density (g $cm^{-3}$) and identified phases for S-1, S-2 and S-3

| | Firing temperature (°C) | | | | |
|---|---|---|---|---|---|
| Sample | 800 | 900 | 1000 | 1100 | 1200 |
| S-1 | 1.64<br>β-TCP | 1.92<br>β-TCP | 2.03<br>β-TCP | 2.54<br>β-TCP | 2.47<br>α-TCP<br>β-TCP |
| S-2 | 1.71<br>β-TCP | 1.83<br>β-TCP | 2.45<br>β-TCP | 2.45<br>β-TCP | 2.47<br>α-TCP<br>β-TCP |
| S-3 | 1.57<br>β-TCP<br>HAp | 1.74<br>β-TCP<br>HAp | 2.01<br>β-TCP<br>HAp | 2.87<br>β-TCP<br>HAp | 2.76<br>α,β-TCP<br>HAp |

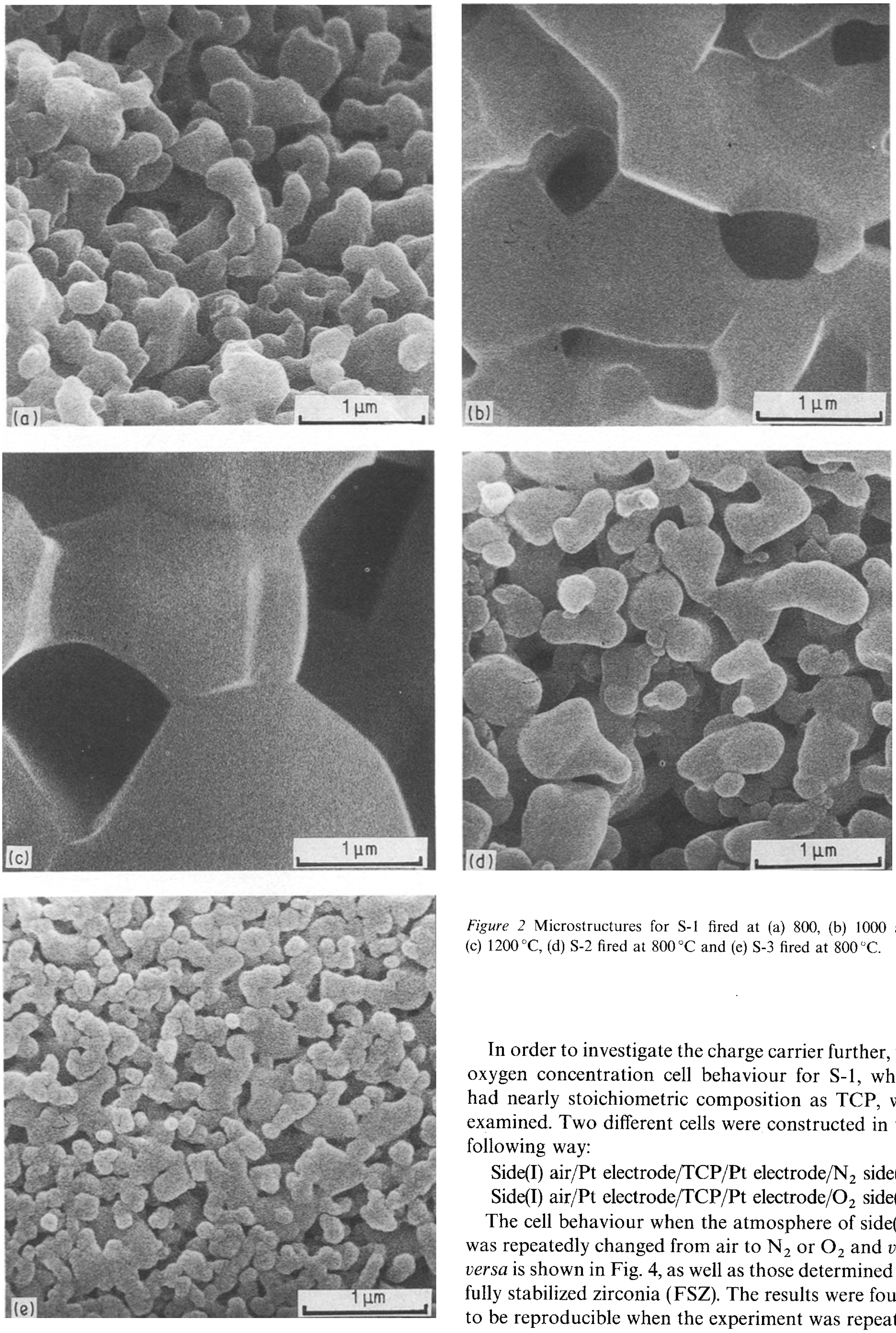

*Figure 2* Microstructures for S-1 fired at (a) 800, (b) 1000 and (c) 1200 °C, (d) S-2 fired at 800 °C and (e) S-3 fired at 800 °C.

was a proton at 900 °C [20] with respect to S-3. However, it is not clarified completely for TCP (S-1) although calcium ions are suggested to be the carriers at higher temperatures [9].

In order to investigate the charge carrier further, the oxygen concentration cell behaviour for S-1, which had nearly stoichiometric composition as TCP, was examined. Two different cells were constructed in the following way:

Side(I) air/Pt electrode/TCP/Pt electrode/$N_2$ side(II)
Side(I) air/Pt electrode/TCP/Pt electrode/$O_2$ side(II)

The cell behaviour when the atmosphere of side(II) was repeatedly changed from air to $N_2$ or $O_2$ and *vice versa* is shown in Fig. 4, as well as those determined by fully stabilized zirconia (FSZ). The results were found to be reproducible when the experiment was repeated several times. The polarity and response behaviour can be explained on the basis of the model that the charge carrier is an oxide ion. However, the e.m.f. value was much less than that measured by FSZ, especially for the air/TCP/$O_2$ system, which suggested that it would depend on the oxygen partial pressure. Even if the charge carrier is not an oxide ion but a calcium ion or a proton, the same oxygen partial

TABLE II $R_0$ (resistance at 0 min) and $R_{90}$ (resistance at 90 min) for S-1 fired at 1100 °C under d.c. electric field[a]

| Sample | Temperature (°C) | $R_0$ (M Ω) | $R_{90}$ (M Ω) | $[(R_0 - R_{90})/R_{90}) \times 100]$ (%) |
|---|---|---|---|---|
| S-1 | RT | 76 | 232 | 67 |
| | 400 | 31 | 45.5 | 32 |
| | 800 | $1.7 \times 10^{-4}$ | $1.4 \times 10^{-3}$ | 88 |
| S-2 | RT | 280 | 550 | 49 |
| | 400 | 13 | 21 | 38 |
| | 800 | $4.2 \times 10^{-4}$ | $1.2 \times 10^{-3}$ | 65 |
| S-3 | RT | 48 | 365 | 87 |
| | 400 | 196 | 283 | 31 |
| | 800 | $2.4 \times 10^{-4}$ | $1.3 \times 10^{-3}$ | 82 |

[a] The applied voltage was less than decomposition value (1 V).

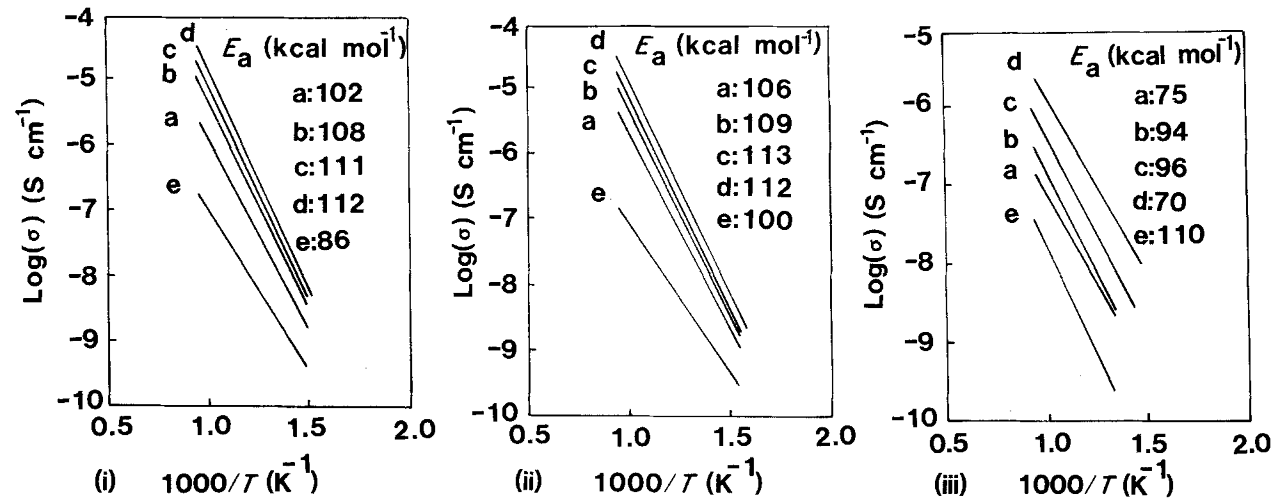

*Figure 3* Temperature dependence of the conductivity for (i) S-1, (ii) S-2 and (iii) S-3 fired at (a) 800, (b) 900, (c) 1000, (d) 1100 and (e) 1200 °C.

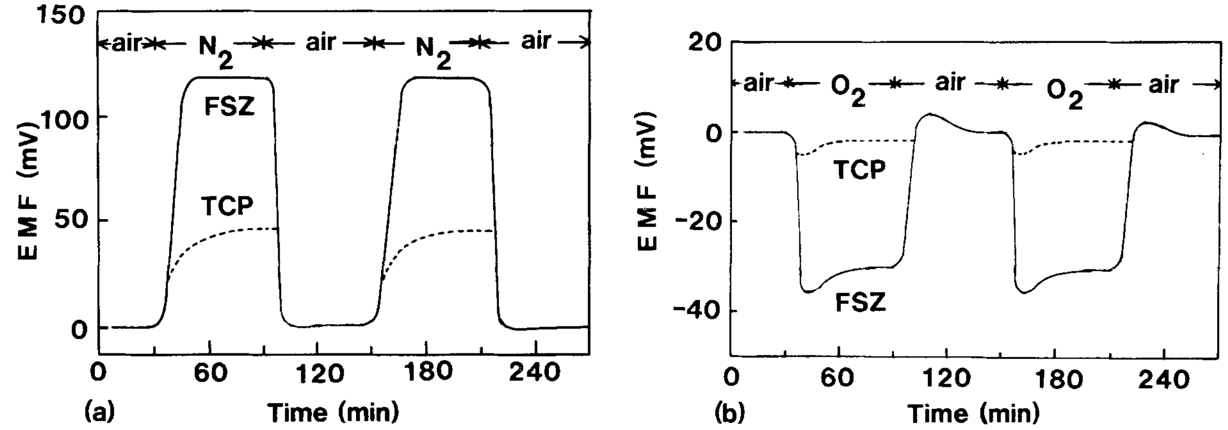

*Figure 4* Oxygen concentration cell behaviour of S-1 fired at 1100 °C for (a) air-$O_2$ system and (b) air-$N_2$ system.

pressure dependence as for an oxide ion can be explained assuming the following overall reaction:

Oxide ion $\frac{1}{2}O_2 + 2e \rightarrow O^{2-}$

Calcium ion $Ca^{2+} + 2e + \frac{1}{2}O_2 \rightarrow CaO$

Proton $2H^+ + 2e + \frac{1}{2}O_2 \rightarrow H_2O$

As the sample powders were prepared by the wet process, a hydroxy group or other proton containing chemical species may exist in the lattice, although the firing process was completed. Therefore the third case cannot be excluded from the possible models. In these three cases, the polarity and e.m.f. coincide with each other if the equilibrium state is realized. The e.m.f. value $E$ for these cases is given by;

$$E = (RT/4F)\ln[p_{O_2}(I)/p_{O_2}(II)]$$

where $R$, $T$, $F$ and $p_{O_2}$ denote gas constant, absolute temperature, Faraday constant and oxygen partial pressure, respectively. Consequently it is not possible to determine the charge carrier from these results. Measurements to clarify the charge carrier and transport number are now in progress using oxygen and hydrogen concentration cells under various conditions. The results will be reported separately in the near future.

## 4. Conclusions

Electrical measurements of calcium phosphate with various Ca/P ratios were carried out. The calcium phosphate ceramics exhibited relatively high conductivity at elevated temperatures. The predominant charge carriers are most likely to be ions at 800 °C. The e.m.f. was observed for the oxygen concentration cell, but the value was much less than that determined by FSZ.

## References

1. T. KANAZAWA, in " Inorganic Phosphate Materials" (Elsevier, Tokyo, 1989) p. 89.
2. H. MONMA, S. UENO and T. KANAZAWA, *J. Chem. Tech. Biotechnol.* **31** (1981) 15.
3. H. MONMA, M. TSUTSUMI, M. GOTO, T. UMEGAKI and T. KANAZAWA, *Yogyo-Kyokai-Shi* **92** (1984) 157.
4. B. DICKENS, L. W. SCHROEDER and W. E. BROWN, *J. Solid State Chem.*. **10** (1974) 232.
5. M. MATHEW, L. W. SCHROEDER, B. DICKENS and W. E. BROWN, *Acta Crystallogr.* **B33** (1976) 1325.
6. A. A. DRIESSEN, C. P. A. P. KLEIN and K. de GROOT, *Biomaterials* **3** (1982) 113.
7. M. AKAO, N. MIURA and H. AOKI, *J. Ceram. Soc. Jpn* **92** (1984) 672.
8. M. JARCHO, R. L. SALSBURY, M. B. THOMAS and R. H. DOREMUS, *J. Mater. Sci.* **14** (1979) 142.
9. H. FUJIWARA, H. YAMAZOE, H. ABE, E. ICHINOSE and M. IWASE, *CAMP-ISIJ* **2** (1989) 1057.
10. T. TAKAHASHI, S. TANASE and O. YAMAMOTO, *Electrochim. Acta.* **23** (1978) 369.
11. K. YAMASHITA, H. OWADA, T. UMEGAKI, T. KANAZAWA and T. FUTAGAMI, *Solid State Ionics* **28–30** (1988) 660.
12. M. NAGAI, T. NISHINO and T. SAEKI, *Sensors and Actuators* **15** (1988) 145.
13. G. TROMEL, H. J. HARKORT and W. HOTOP, *Z. Anorg. Allgem. Chem.* **256** (1948) 253.
14. J. H. WELCH and W. GUTT, *J. Chem. Soc.* **1961** (1961) 4442.
15. W. FIX, H. HAYMANN and R. HEINKE, *J. Amer. Ceram. Soc.* **52** (1969) 346.
16. D. E. C. CORBRIDGE, in "The Structural Chemistry of Phosphorus" (Elsevier, Amsterdam, 1974) p. 99.
17. H. MONMA and M. GOTO, *J. Ceram. Soc. Jpn* **91** (1983) 473.
18. T. KANAZAWA, in "Inorganic Phosphate Materials" (Elsevier, Tokyo, 1989) p. 20.
19. M. NAGAI and T. NISHINO, *Solid State Ionics* **28–30** (1988) 1456.
20. H. OWADA, K. YAMASHITA, T. UMEGAKI and T. KANAZAWA, *Gypsum and Lime* **217** (1988) 401.

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