JOURNAL OF MATERIALS SCIENCE 19 (1984) 396–402

Low temperature synthesis of glassy solids of the system Al_2O_3–P_2O_5–SiO_2

H. SUZUKI, H. SAITO
Department of Mechanical System Engineering, Toyota Technological Institute, 2-12-1, Hisakata, Tenpaku-ku, Nagoya-shi, Aichi-ken, Japan

T. HAYASHI
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ky, Nagoya-shi, Aichi-ken, Japan

Glassy solids of the system Al_2O_3–P_2O_5–SiO_2, which have not been obtainable because of the devitrification of glass during the cooling process after melting, were obtained by the gel method. After the gels of the system Al_2O_3–P_2O_5–SiO_2 were prepared from $AlCl_3 \cdot 6H_2O$, H_3PO_4 and $Si(OC_2H_5)_4$, they were heat treated up to 800° C to obtain glassy solids. In SiO_2 concentrations ranging from 75 to 82 mol % in batch compositions, non-porous transparent solids were obtained, while in SiO_2 concentrations above 87 mol %, porous transparent solids were obtained. Tridymite was precipitated because of the crystallization of glassy solids during heat treatment above 800° C. It depended upon the microstructure of the gels whether non-porous glassy solids were obtained or not. The thermal expansion coefficients of the glassy solids were greatly dependent upon the concentration of P_2O_5, ranging from 1.7×10^{-6} to 4.2×10^{-6} (1/° C).

1. Introduction

Low temperature synthesis of glass by the gel method has several advantages over the conventional melting method. The gel method is particularly suitable for the preparation of glass having a high melting point or a composition within an immiscible region, and with high purity and homogeneity. Recently, many glasses have been prepared by this method [1–11].

In the present work, glasses in the system Al_2O_3–P_2O_5–SiO_2, which have been unobtainable because of the devitrification of glasses during the cooling process after melting, were synthesized by the gel method. In the system Al_2O_3–SiO_2–P_2O_5, Eiduk *et al.* [12] suggested that glasses consisted of weakly bonded $[PO_4]$, $[AlPO_7]$ and $[SiO_4]$ groups, and that the amount of the $[AlPO_7]$ group, containing stable bound P_2O_5, appeared to increase with increasing Al_2O_3 concentration. The glass formation diagram in the system Al_2O_3–SiO_2–P_2O_5 shows that the glass formation region was narrowly restricted.

However, it is known that chemical reactions to form non-crystalline solids are particularly effective in the case of hydrogen-bonded structures in aqueous media [13]. For example, the reaction

$$Al_2O_3 + 6H_3PO_4 \rightarrow 2Al(H_2PO_4) + 3H_2O \quad (1)$$

forms a non-crystalline gel in which hydrogen bonding predominates. The same reaction occurs in the case of the substitution of $Al(OH)_3$ for Al_2O_3 [14, 15]. Hence, in the present work, $AlCl_3 \cdot 6H_2O$, H_3PO_4 and $Si(OC_2H_5)_4$ were used as raw materials to obtain glasses of the system Al_2O_3–P_2O_5–SiO_2 by the gel method. It is well known that metal phosphate coatings have advantages of a much lower curing temperature, good adhesion and burning resistance compared with silicate coatings [16–19]. Therefore, glasses in this system are thought suitable for use as glass-coatings.

2. Experimental details

2.1. Preparation of gels

$AlCl_3 \cdot 6H_2O$, H_3PO_4 and $Si(OC_2H_5)_4$ prepared by Wako Chemicals were used as raw materials. The

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TABLE I Gelation time for the solutions of various composition

Sample	Calculated composition SiO_2 (mol%)	$HCl/Si(OC_2H_5)_4$ (molar ratio)	Gelation $H_2O = 16$	Time (days) $H_2O = 32$
ASP-1	60	0.34	19	–
ASP-2	75	0.17	20	20
ASP-3	82	0.11	16	20
ASP-4	87	0.07	26	28
ASP-5	90	0.06	35	24

raw materials, water and alcohol were mixed at room temperature for about 2 h. With the molar ratio of P_2O_5 to Al_2O_3 set at 3, the SiO_2 concentration was changed from 60 to 90 mol% and the molar ratio of water to $Si(OC_2H_5)_4$ was changed from 4 to 32. After the solution mixtures were wrapped with thin plastic film to control the evaporation of alcohol, they were allowed to stand for about a month. Monolithic transparent gels were obtained within 35 days in the case of the molar ratio of water to $Si(OC_2H_5)_4$ above 16 (Table I).

2.2. Pyrolysis

After the bulky gels obtained were kept standing in an open system for about one month for drying, these were heat treated up to 800° C. Differential thermal analysis (DTA) was carried out at the heating rate of $10^\circ\,C\,min^{-1}$ to determine the heating program. All gels showed endothermic peaks corresponding to the desorption of water and alcohol which appeared in the temperature ranges from 110 to 150° C. The more the P_2O_5 concentration increased, the higher the temperatures at which the endothermic peaks appeared. The obtained gels were heated at the rate of $30^\circ\,C\,h^{-1}$ and were kept at 150, 300, 500, 700 and 800° C for a day, respectively. A photograph of a glassy solid heated up to 800° C is shown in Fig. 1. With the SiO_2 concentration above 75 mol% in bath compositions, glassy solids were obtained, but in the 60 mol% concentration of SiO_2, no transparent solids were obtained. Above 800° C, samples tended to devitrify because of the precipitation of tridymite. Accordingly, samples with the concentration of SiO_2 above 75 mol% were studied.

2.3. Measurements of properties

Infrared spectra, thermal expansion coefficients, specific surface area and microVickers hardness were measured for heat treated gels and glassy solids. Infrared spectra were observed with the Shimadz IR-450 infrared spectrophotometer by the KBr pellet method. Thermal expansion coefficient of glassy solid and thermal shrinkage of gels were measured with a dilatometer with a load of 2 g, at a heating rate of $5^\circ\,C\,min^{-1}$ and the sample thickness ranged from 5 to 10 mm. The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method using nitrogen as desorption gas. The changes in Vickers hardness of the gels were observed up to 900° C under a load of 50 g for 15 sec.

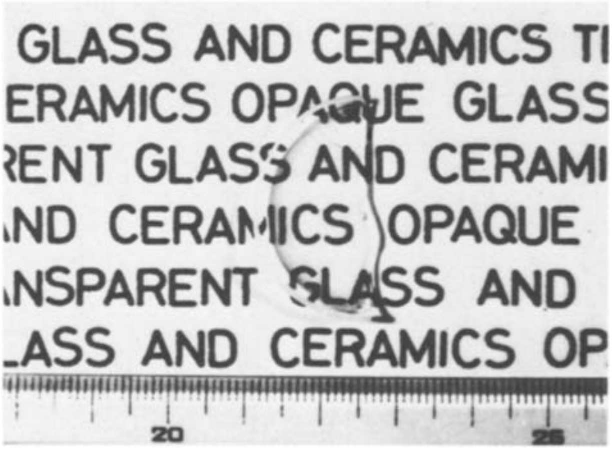

Figure 1 Glassy solid containing SiO_2 82 mol%, heated up to 800° C, $H_2O/Si(OC_2H_5)_4 = 32$ (mol/mol alkoxide).

3. Results and discussion

3.1. Hydrolysis and gelation

In the gel method, metal alkoxides have generally been utilized, but $AlCl_3 \cdot 6H_2O$, H_3PO_4 and $Si(OC_2H_5)_4$ were used as raw materials in this work because it was thought possible that solution mixtures and gels could be easily obtained. Yamane and Kojima [9] prepared non-crystalline solids with a composition which was in the immiscible region of the system SiO_2–SrO, using strontium nitrate as raw materials of SrO. But in this case, the preparation of gels was accompanied by crystal growth of $Sr(NO_3)_2$ because of the non-participation of Sr^{2+} ions in either the hydrolysis of $Si(OCH_3)_4$ or the subsequent dehydration condensation. In this work, however, the participation of $AlCl_3$ and H_3PO_4 in the reaction to form non-crystalline solids was expected.

Hydrolysis and dehydration condensation may progress according to the following equations:

$$Si(OC_2H_5)_4 + 4H_2O \rightarrow Si(OH)_4 + 4C_2H_5OH \quad (2)$$

$$Si(OH)_4 \rightarrow SiO_2 + 2H_2O \quad (3)$$

$$AlCl_3 + 3H_3PO_4 \rightarrow Al(H_2PO_4)_3 + 3HCl \quad (4)$$

$$Al(H_2PO_4)_3 \rightarrow Al(PO_3)_3 + 3H_2O \quad (5)$$

Gelation times are shown in Table I in the case of the molar ratio of water to alcoholate above 16. In the case of the lower molar ratio of water to alcoholate ($H_2O/Si(OC_2H_5)_4 \leq 8$), gelation was so slow that no solution mixtures solidified in 2 months. In the SiO_2 concentrations below 82 mol%, solidification occurred in 20 days and dense gels (bulk density was about 1.7 g cm^{-3}, as indicated in Fig. 2) were obtained, whereas above 87 mol%, gelation times were considerably longer and relatively bulky gels (about 1.3 g cm^{-3}) were obtained. This may be due to the difference of the amount of HCl (i.e. pH of the solution) liberated from $AlCl_3 \cdot 6H_2O$ (Equation 3), which is effective as a catalyst for hydrolysis and dehydration condensation of $Si(OC_2H_5)_4$. The difference of the microstructure of the gels had important effects upon the conversion of the gels to glasses.

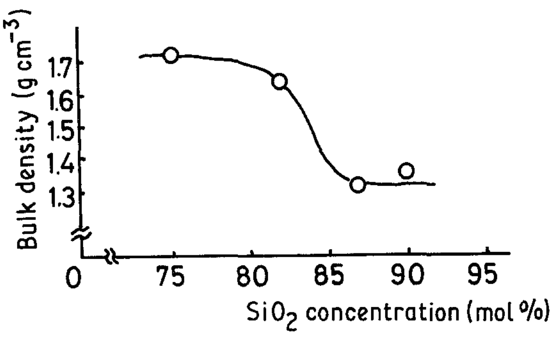

Figure 2 Bulk density of the gels.

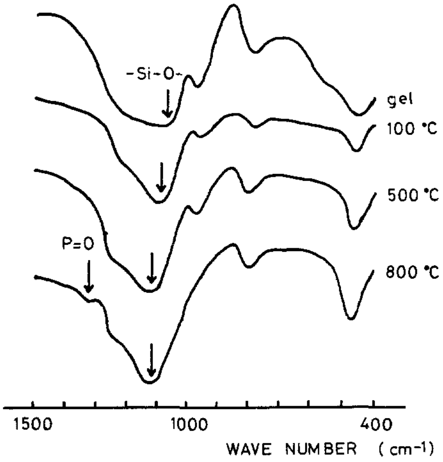

Figure 3 Change in infrared spectra peaks with heating.

3.2. Conversion of gel to glass

The changes in infrared spectra peaks of heating gels and the glassy solids heated up to 800° C are shown in Figs. 3 and 4, respectively. In addition to the characteristic bands of vitreous silica (470, 800 and 1100 cm^{-1}), there were bands corresponding to P=O stretching vibrations around 1300 cm^{-1}

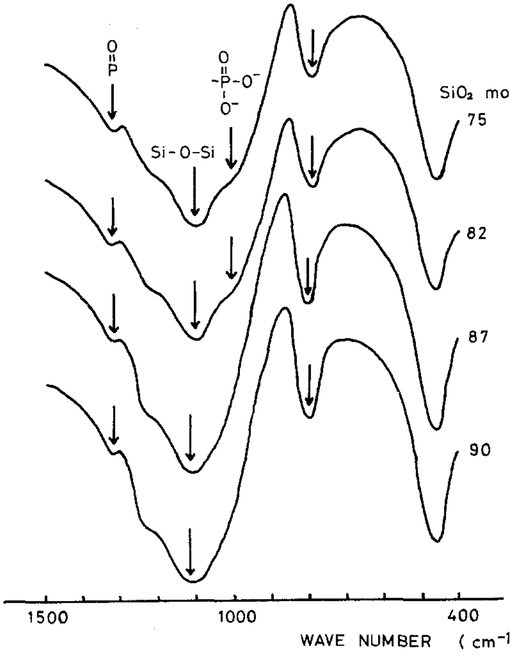

Figure 4 Infrared spectra of samples heated up to 800° C.

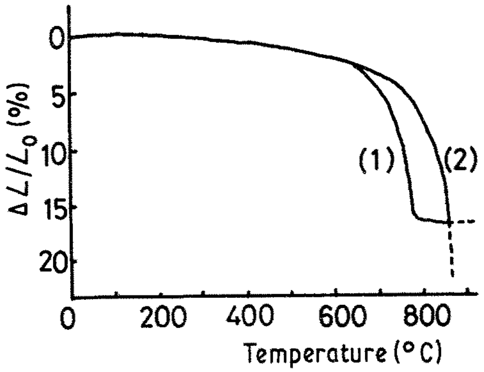

Figure 5 Change in linear shrinkage of the gels. (1) SiO_2 = 82 mol %, (2) SiO_2 = 87 mol %.

and the characteristic bands of vitreous silica shifted towards high wave number with heating (Fig. 3). In SiO_2 concentrations below 82 mol %, the additional bands around 1000 cm^{-1} corresponding to $(PO_3)^{2-}$ appeared (Fig. 4). The bands around 950 cm^{-1} corresponding to Si–O– or P–O– disappeared at 700° C in all gels, indicating the adsorption of OH groups.

The conversion of gels to glasses was investigated by measuring the change in the linear shrinkage of gels (Fig. 5), the specific surface areas of gels and glassy solids (Fig. 6), and the change in Vickers hardness with heating (Fig. 7). The gels suddenly began to shrink about 600° C, and in the SiO_2 concentrations below 82 mol %, shrinkage scarcely occurred above 800° C but it continued in the SiO_2 concentrations above 87 mol % (Fig. 5). The specific surface areas of the gels and glassy solids heated up to 800° C with compositions of 75 and 87 mol % of SiO_2, respectively, were measured (Fig. 6). It was confirmed that in the SiO_2 concentrations below 82 mol %, the specific surface areas of glassy solids were very small. From Fig. 7 it can be seen that gels increased their hardness with heating and at 800° C, sufficiently hard transparent solids (i.e. glasses) were obtained in the SiO_2 concentrations below 82 mol %. These results indicate that heat treatment up to 800° C was enough for gels containing less than 82 mol % of SiO_2 to become sufficiently hard and non-porous solids.

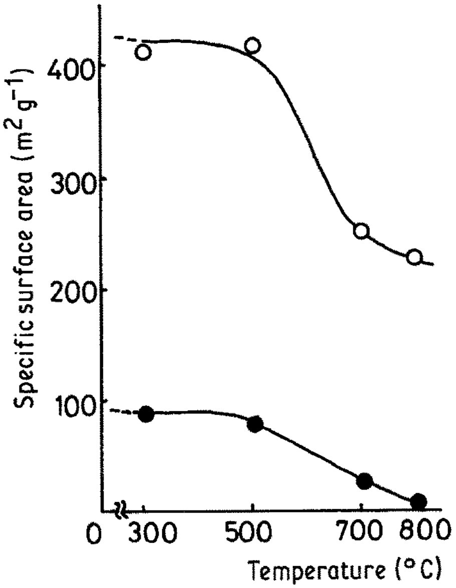

Figure 6 Specific surface area of the gels. ●, SiO_2 = 75 mol %; ○, SiO_2 = 87 mol %.

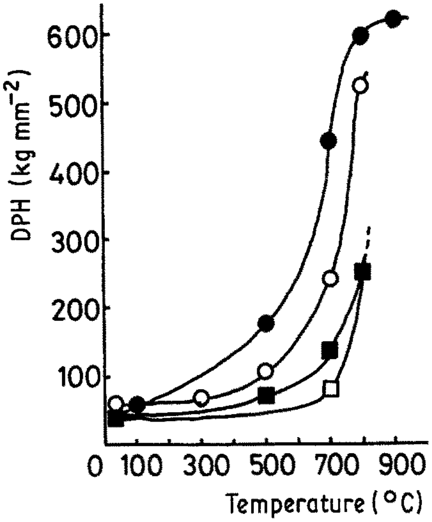

Figure 7 Change in Vickers hardness of the gels with heating. ○, SiO_2 = 75 mol %; ●, SiO_2 = 82 mol %; □, SiO_2 = 87 mol %; ■, SiO_2 = 90 mol %.

These samples heated up to 800° C were observed with a transmission electron microscope (TEM). It was found that in the compositions where the SiO_2 concentration was above 87 mol %, samples heated up to 800° C were transparent but had uniformly distributed micropores ranging from 10 to 20 nm in diameter and crystallites were observed (Fig. 8a). On the other hand in the SiO_2 concentrations below 82 mol %, no pore was observed with TEM (Fig. 8b).

3.3. Properties of glassy solids

It was possible to obtain transparent non-crystalline and non-porous solids (i.e. glasses) with the concentration of SiO_2 from 75 to 87 mol % by heat treatment up to 800° C. But with SiO_2 concentrations above 87 mol %, glassy solids

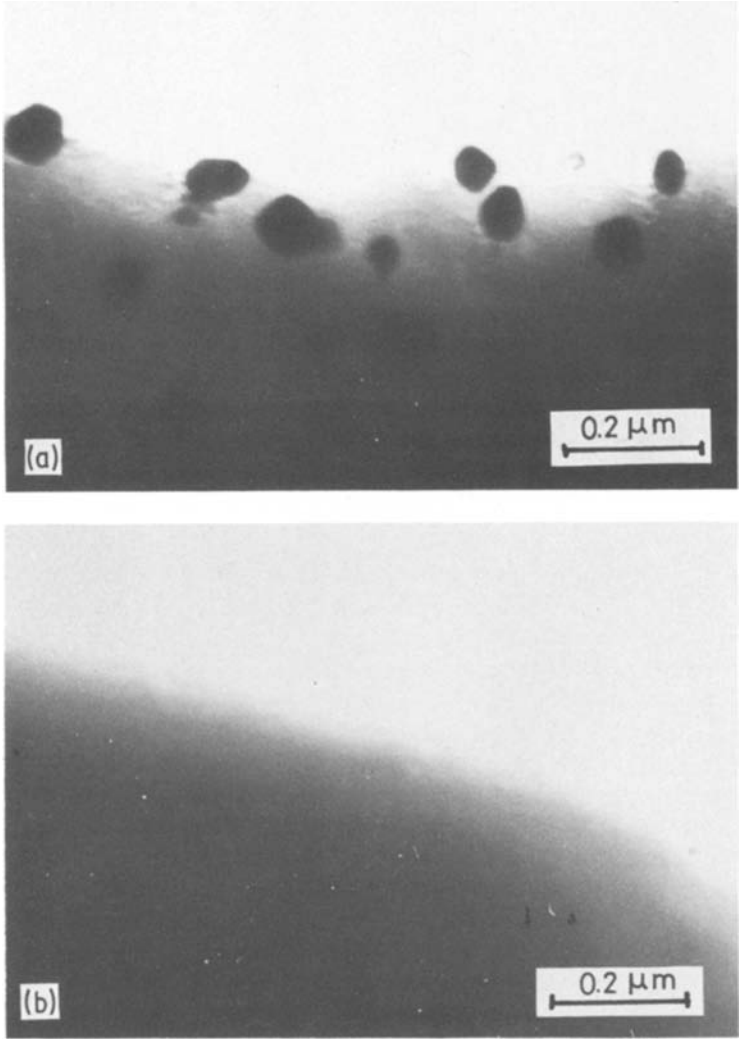

Figure 8 Electron micrographs of samples heated up to 800° C. (a) Sample containing SiO_2 87 mol %, and (b) sample containing SiO_2 75 mol % (× 90 000).

were still porous. Nevertheless, they were transparent because the pores were smaller than the wavelengths of visible light.

The density and refractive index of glassy solids heated up to 800° C are shown in Fig. 9. Density changed from 2.15 to 2.54 ($g\,cm^{-3}$) and the refractive index changed from 1.49 to 1.53 with an increase in the SiO_2 concentration. In SiO_2 concentrations above 87 mol %, the true density of the solids was considerably lower than that of SiO_2 glass (2.21 $g\,cm^{-3}$), because the solids heated up to 800° C still retained the gel structure.

The compositions of the glassy solids were determined by using an electron probe X-ray microanalyser (EPMA) (Table II). The degree of fluctuation of a composition became larger as the SiO_2 concentration increased. The fluctuation of the compositions may be due to the volatility of P_2O_5 at high temperature and the devitrification in the SiO_2 concentration above 87 mol %.

TABLE II Chemical composition of samples heated up to 800° C by EPMA

Sample	Calculated composition (molar ratio)	Analysed composition (molar ratio)
ASP-2	6.3 Al_2O_3–18.7 P_2O_5–75.0 SiO_2	6.0 Al_2O_3–15.8 P_2O_5–78.2 SiO_2
ASP-3	4.6 Al_2O_3–13.6 P_2O_5–81.8 SiO_2	4.2 Al_2O_3–9.7 P_2O_5–86.1 SiO_2
ASP-4	3.2 Al_2O_3–9.7 P_2O_5–87.1 SiO_2	2.6 Al_2O_3–4.6 P_2O_5–92.8 SiO_2

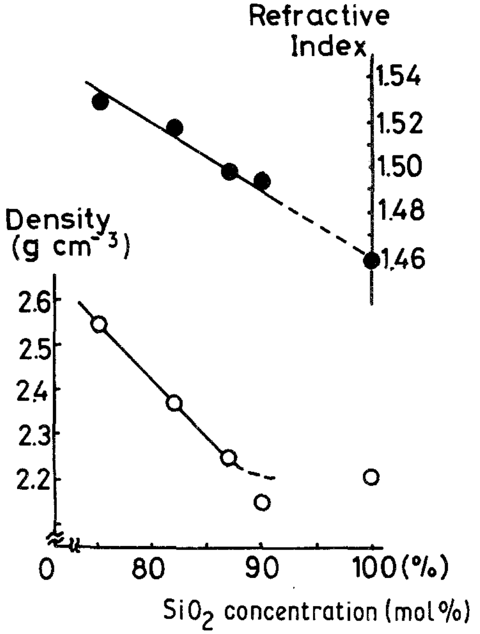

Figure 9 The density and refractive index of samples heated up to 800° C. ○, density; ●, refractive index.

The thermal expansion coefficients are shown in Fig. 10. The values of the expansion coefficients were approximately the same as those calculated from Dauvalter's expansion coefficients measured from glaze. This indicates that in this system, the structure was weakened by the introduction of P–O bonds into glass former. And it was found that the values of the thermal expansion coefficients of the glassy solids were considerably larger and were greatly dependent upon the P_2O_5 concentrations. This is advantageous for making glass-coatings from this system because it was possible to choose the composition in which the thermal expansion coefficient of glass-coating is close to that of the substrate.

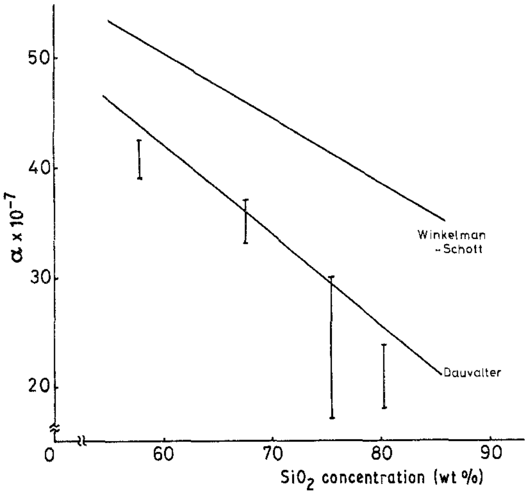

Figure 10 Thermal expansion coefficients of samples heated up to 800° C.

4. Conclusion

Glassy solids of the system Al_2O_3–P_2O_5–SiO_2 were obtained by the hydrolysis of silicon tetraethoxide solutions with an aqueous solution of aluminium chloride and phosphoric acid. Samples which contained SiO_2 above 87 mol% in batch compositions were transparent but still porous after heat treatment up to 800° C, while transparent non-porous glassy solids were obtained in the compositions from 75 to 82 mol% of SiO_2. It depended upon the microstructure of the gels whether the glasses were obtainable or not. Thermal expansion coefficients of glassy solids were greatly dependent upon the P_2O_5 concentrations. From the observation of TEM and EPMA, it was concluded that homogeneous glassy solids containing SiO_2 from 75 to 82 mol% were obtained.

Acknowledgement

This work was carried out at Nagoya University. We wish to thank Mr Y. Imada for his cooperation in performing EPMA.

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Received 31 January
and accepted 18 May 1983