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Effect of Na_2O Addition on the Properties and Structure of Germanate Glass

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Abstract: The Li_2O (Na_2O)–CaO–Al_2O_3–GeO_2 system, was prepared for infrared transmitting germanate glasses. The properties and structure of these glasses have been studied. The transition and crystallization temperatures are raised as Li_2O concentration is decreased and Na_2O concentration is increased. The refractive index and Abbe number are increased with increasing Na_2O content. The vibration modes observed in the high wave number regions of the FTIR spectra are from the symmetrical and antisymmetrical stretching and bending motions of GeO_4 tetrahedra.

1 INTRODUCTION

The vitreous solidification of GeO_2 melt was first reported by Dennis and Laubengayer.[1] In Imaoka's experiments, the visible immiscibility gaps were observed in the systems CaO–GeO_2 SrO–GeO_2 and BaO–GeO_2.[2] Relatively wide areas of glass formation were found in the R_2O–Al_2O_3–GeO_2,[3,4] R_2O–B_2O_3–GeO_2,[5,6] PbO–Sb_2O_3–GeO_2[7] and ZnO–BaO–CaO–Al_2O_3–GeO_2[8] systems.

There have been a large number of studies concerning the properties and structure of R_2O–Al_2 O_3–GeO_2 (or R_2O–Al_2O_3–SiO_2–GeO_2) glasses,[3,4,9–13] and the corresponding MO–Al_2O_3–GeO_2.[8,14]. However, an extensive literature search showed that details of the structure, thermal and optical properties related to the addition of Na_2O to the Li_2O–CaO–Al_2O_3–GeO_2 glass system have not been elaborated.

In the present paper, the thermal, optical properties and structure of Li_2O(–Na_2O)–CaO–Al_2O_3–GeO_2 glasses were studied. The refractive index of these glasses was measured as a function of Na_2O content in the visible region of the spectrum.

The purposes of this investigation are two-fold: (1) to evaluate the effect of composition on the thermal and optical properties of these germanate glasses, (ii) to determine the effect of Na_2O content on the structure of these glass samples.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

Specimens were prepared from materials of electronic grade GeO_2 and analytical grade Li_2CO_3, Na_2CO_3, Al_2O_3, and $CaCO_3$ in 20 g quantities by melting at 1420°C in a platinum crucible for 2 h. After homogenizing, the melt was quenched in water, dried, crushed, and remelted at 1420°C for another 2 h, cast onto a 400°C hot stainless steel plate and transferred to an annealing furnace held for 1 h. Finally, a clear, transparent and colourless glass was obtained. The glass compositions are listed in Table 1, which are formulated on the basis of weight percent of the constituents of the glasses. The Na_2O was introduced in 1·61 wt% stepwise substitutions for the Li_2O.

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Table 1. Chemical composition of glasses (wt%)

Samples	Oxides				
	Na_2O	Li_2O	CaO	Al_2O_3	GeO_2
C_1	0	6·44	12·97	21·51	59·18
C_2	1·61	4·83	12·97	21·51	59·18
C_3	3·22	3·22	12·97	21·51	59·18
C_4	4·83	1·61	12·97	21·51	59·18
C_5	6·44	0	12·97	21·51	59·18

2.2 Thermal property measurement

Differential thermal analysis (DTA) on a 200 mg powder sample (67, 48 μm) at 10°C/min in air was conducted by SETARAM TAG24 Simultaneous Symmetrical Thermoanalyzer with powdered Al_2O_3 as the reference material.

Typical thermal expansion specimens were 25 mm long, 2·5 mm thick, and 3·5 mm wide. Thermal expansion coefficients were measured in a horizontal vitreous silica dilatometer (SETARAM High Temperature Dilatometer). Specimen temperature was measured by an X-type thermocouple in contact with the specimen surface. Each specimen was heated to the softening temperature in a dilatometer at a heating rate of 3°C/min and thermal expansion coefficients are reported for the temperature range from 70 to 400°C. The glass transition and dilatometric softening temperatures were obtained from the thermal expansion curves by the usual techniques.[15]

2.3 Infrared and Fourier transform infrared spectra measurement

The glass samples (about 2·0 mm thick) for optical absorption measurement, were polished for parallel faces. The infrared spectra were recorded with a Hitachi Infrared Spectrometer Model 290-30.

Fourier transform infrared spectra were measured in the 400–1200 cm^{-1} region using a Nicolet 800 system, with a resolution of 2 cm^{-1}. KBr pelletized disks were fabricated containing 2 mg of the glass sample and 600 mg KBr.

2.4 Refractive index measurement

The refractive index of these glass samples which were polished for adjacent perpendicular faces was measured as a function of Na_2O content at wavelengths n_d = 587·56 nm, n_f = 486·13 nm and n_c = 656·27 nm.

3 RESULTS

The typical DTA curves obtained from the as-quenched glasses are shown in Fig. 1. The first endotherm, which corresponds to the glass transition point, varies from 525 to 635°C for samples with different compositions. These glass samples showed the two stage crystallization temperatures, and also two melting endotherm temperatures. In Fig. 1 the single glass transition temperature suggests the existence of compositionally homogeneous amorphous state in the as-quenched glass.

The glass transition temperature (T_g), dilatometric softening temperature (M_g) and the first

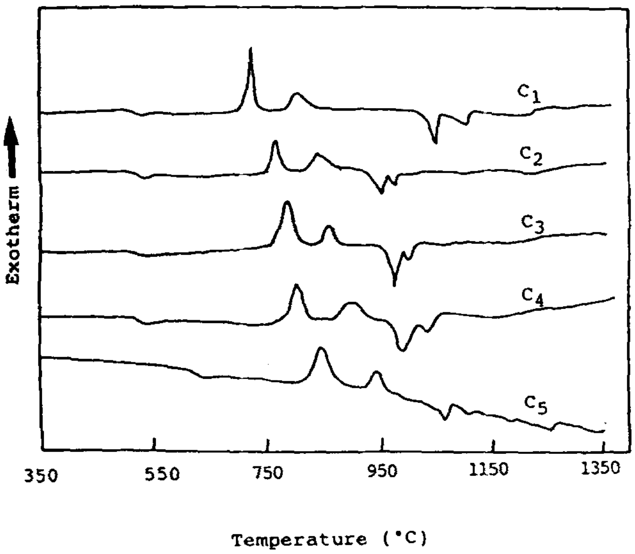

Fig. 1. DTA curves of the germanate glasses heating at a rate of 10°C/min.

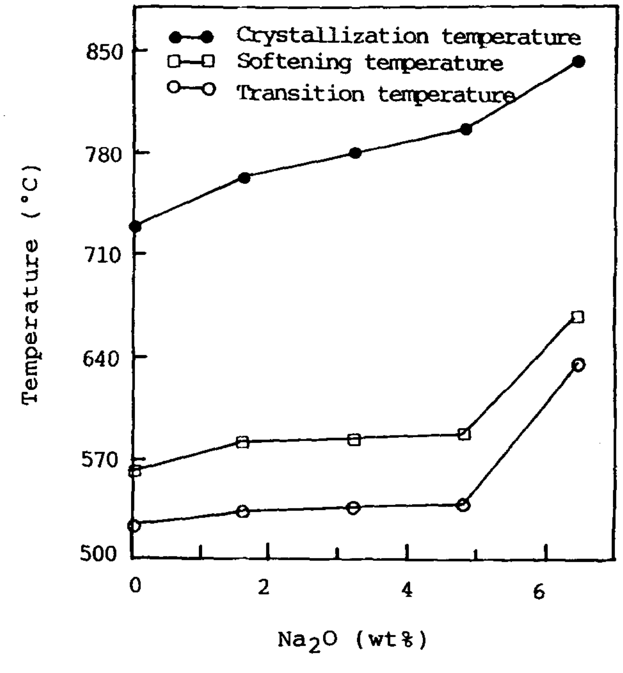

Fig. 2. Effect of Na_2O addition on the T_g, M_g and T_c for the germanate glass samples.

crystallization temperature (T_c) of these glass samples are shown in Fig. 2. It is seen that the T_g, M_g and T_c are raised as Li_2O decreased and Na_2O increased. The hypotheses suggested the consistence with the behaviour of T_g as a function of glass composition.[16] The T_g corresponding to the temperature at which the network acquires mobility, changes from a rigid to a plastic structure.[16] The T_g of these glasses is around 531 ± 6°C, which suggests that the tetrahedra are the same mobile components of glasses, except C_5 glass at 635°C.[17] Mazurin *et al.*[18,19] discussed the effect of dilatometric softening temperature on the morphology of phase-separated glasses and found that M_g is controlled by the higher-viscosity phase as long as that phase is continuous, with a rather abrupt change as the continuity of that phase disappears. On this basis, the M_g in Fig. 2 indicates that the glass sample containing 6·44% Na_2O has a considerable concentration of continuous high-viscosity phase which gradually loses the continuity between the composition of 6·44% and 1·61% Li_2O.[15]

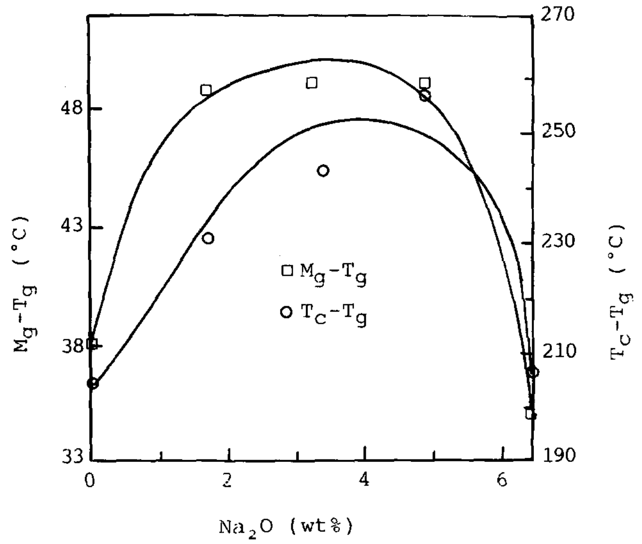

Fig. 3. Effect of Na_2O content on the difference between M_g and T_g, and T_c and T_g for the germanate glass samples.

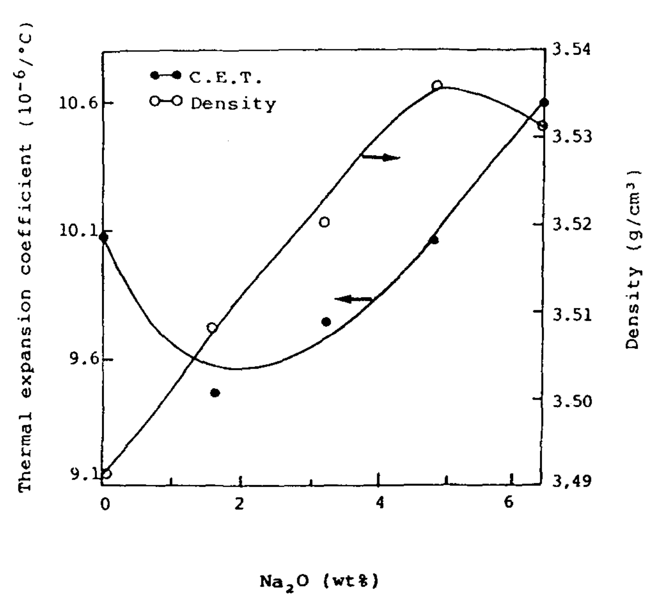

Fig. 4. The variation of thermal expansion coefficients and density for the glass samples.

The difference of the glass transition and dilatometric softening temperature ($M_g - T_g$) decreases sharply at about 4·83 wt% Na_2O addition as shown in Fig. 3. This type of behaviour found in other glass-forming systems is often indicative of phase separation.[15] It seems reasonable to suggest that this also occurs here and that the glasses containing >6·44% Na_2O lie in a region of immiscibility. The changes of the difference of the first crystallization temperature and transition temperature ($T_c - T_g$) of these glasses are also shown in Fig. 3. The maximum point in the T_c–T_g curve corresponds to the glass composition with the ratio $Li_2O/Na_2O = 1$.

The effect of Na_2O addition on the thermal expansion coefficients (α) and density of these glass samples is shown in Fig. 4. In general, the replacement of Li_2O by Na_2O in glasses with the same other contents, α values from 70 to 400°C are 9·2 × 10^{-6}/°C to 10·6 × 10^{-6}/°C as Na_2O content is increased from 1·61% to 6·44%. Mazurin *et al.*[20] pointed out that in the Na_2O–GeO_2 system, the expansion coefficient of the glass in this system increases almost linearly with increasing Na_2O content. The density of these germanate glasses is a function of composition and the maximum in

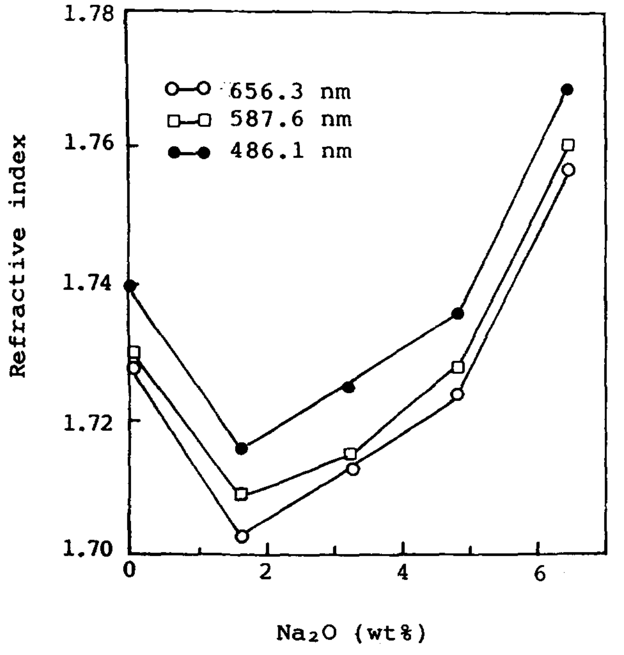

Fig. 5. Effect of Na_2O content and wavelength variation on the refractive index for the germanate glasses.

this curve is related to the change of coordination number of germanium from six to four.[21]

The refractive index of a glass, as of other materials, varies with wavelength. This variation can be considerable and it is necessary for the application of glass in optical system to have accurate information on the variation, not only in the visible part of the spectrum, but also for some applications, in the near infrared and ultraviolet regions. The measured index of refraction as a function of Na_2O content and wavelength for these germanate glasses is shown in Fig. 5. The Abbe number, V_d, which is a measure of optical dispersion, may be estimated from the refractive index by $V_d = (n_d - 1)/(n_f - n_c)$, where n_d, n_f and n_c are refractive indexes at wavelengths 587·56 nm, 486·13 nm and 656·27 nm, respectively. The variation of V_d with Na_2O content is shown in Fig. 6. For Figs 5 and 6, the refractive index and V_d of these germanate glasses are increasing as Na_2O content is increased.

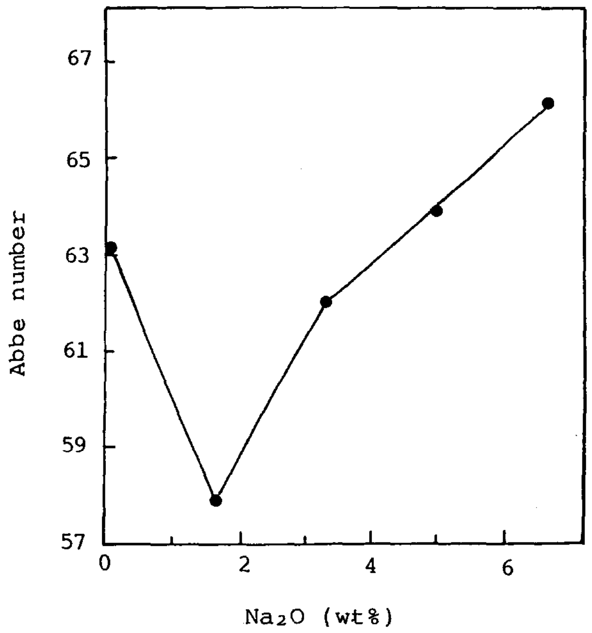

Fig. 6. Effect of Na_2O addition on the variation of Abbe number for the glass samples.

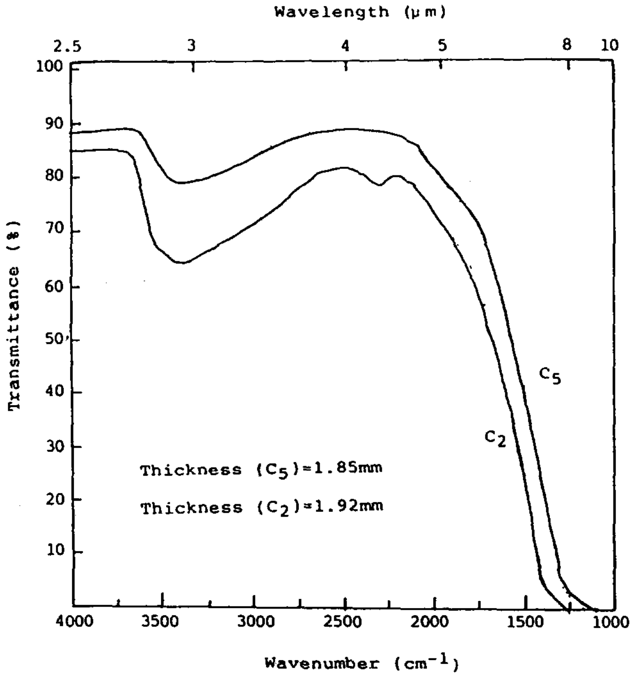

Fig. 7. The infrared transmittance of C_2 and C_5 glasses.

The infrared transmittance of C_2 and C_5 glasses is shown in Fig. 7. The glass begins with a relative broad absorption in the region of 2·9 μm, which may be suggested to be due to the O–H bond bending and stretching vibration, and transmission in the near infrared is thus restricted.[22] The infrared cut-off is at about 6·9 and 7·5 μm for C_2 and C_5 glass samples, respectively, which are longer than that of 5·0 μm for silicate glass. The ability

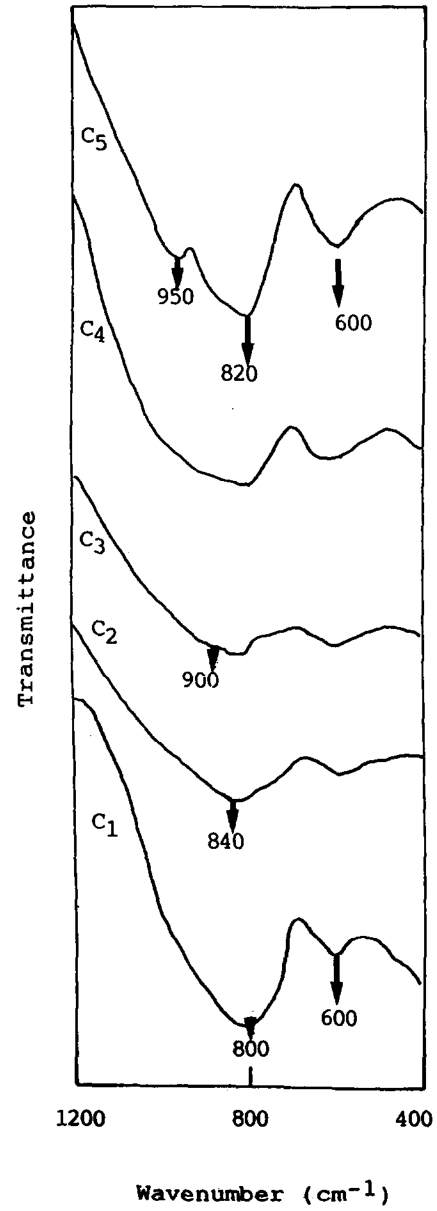

Fig. 8. FTIR spectra for glass samples.

of a material to exhibit a long wavelength transmittance is dependent not only on the material possessing a large band gap, but is also governed by the frequency of vibration of cation–anion bonds resulting in the infrared absorption cut-off.[8] Bond strengths and lengths tend to vary depending on the particular glass composition. In this study, the species of Li_2O, Na_2O and CaO, act as the glass network modifier cations of lower field strength. Larger cations and anions with lower field strength will move the infrared transmittance to longer wavelengths.[8]

FTIR spectra of these germanate glass samples have two regions of absorption as shown in Fig. 8. The most intense absorption band is in the 800–900 cm^{-1} region. The strongest infrared absorption bands of these germanate glasses lie in the 800–900 cm^{-1} region which may be assigned to antisymmetric stretching motions of GeO_4 tetrahedra containing bridging (i.e. Ge–O–Ge bond) and non-bridging (i.e. $Ge–O^-$ bonding) oxygens.[9,23–26] The second strong region of absorption lies between 500–600 cm^{-1}, and may be related to mixed stretching–bending motions.[9] It can be assumed that in germanate glass the O–Ge–O ($O–Ge–O^-$) bending vibrations and symmetric stretching motions across the Ge–O–Ge bridging oxygens are coupled because of the small difference in frequency of these vibrations.[9] The coupling between these two modes produces the single broad band which is observed with an apparent frequency weighted according to the bend–stretch vibration frequencies and corresponding intensities.[9,23–26]

4 DISCUSSION

In fused silica there is a continuous random network of SiO_4 tetrahedra and all the oxygens are doubly bonded, i.e. they are linked to two silicon atoms, the tetrahedra do not share corners, but are linked through the apices. Similarly, fused germania consists of a continuous random network of GeO_4 tetrahedra.[3] The bonds in spectra of germanate glasses are consistent with the similar assignment of corresponding bonds in the silicate glasses.[9] The high-frequency bands in the FTIR of these germanate glasses are narrower than their counterparts in silicate glasses, indicating that Ge–O–Ge bond angles have smaller fluctuations in the germanate glasses than do the Si–O–Si bond angles in the silicate glasses.[9,25,26] Vibrational spectra of the studied germanate glasses exhibit bands which are characteristic for the network-forming, i.e. germanate tetrahedra. The inability to form alkali–aluminogermanate glasses with a M/Al ratio less than unity can be attributed to the fact that in these glasses some of the Al^{3+} ions must exist in octahedral coordination but cannot do so because of the presence of octahedra which are already present in the structure.[3] There is no direct evidence in the present spectra that these glasses contain higher than four-fold coordination of Al cations.[9,26,27]

Murthy *et al.*[3] pointed out that when an M_2O oxide is added to fused germanate, however, two things can happen, the coordination number of the Ge^{4+} ions can remain the same (four), with the formation of singly bonded non-bridging oxygens as in the case of alkali–silicates, or the coordination of some of the Ge^{4+} ions can change from four to six without the formation of non-bridging oxygens with the alkali ions going into the interstitial position as usual. That the latter mechanism is the most probable one is indicated by the fact that pronounced maxima exist in the property–composition curves for the alkali–germanate glasses.[28] Ivanov and Yestropiev[29] indicated that each of the six oxygen apices of the GeO_6 octahedra is shared by neighbouring tetrahedra (GeO_4), i.e. a continuous network of tetrahedra and octahedra exists, and that no non-bridging oxygen is present. This is true, however, only for those alkali–germanate glasses in which the density and refractive index are increasing with the addition of alkali oxide.

The FTIR spectra of analysed glasses have shown that the glasses have a three-dimensional, random network structure consisting of GeO_4 tetrahedra as their most fundamental units.

5 CONCLUSIONS

By a progressive weight percent substitution of Na_2O for Li_2O at constant ratio of concentration of CaO, Al_2O_3, and GeO_2, the $Li_2O(–Na_2O)–CaO–Al_2O_3–GeO_2$ system was prepared for infrared transmitting germanate glasses. For these glass samples, the transition, dilatometric and first crystallization temperatures are raised as Li_2O content decreased and Na_2O content increased. The thermal expansion coefficients from 70 to 400°C are $9{\cdot}2 \times 10^{-6}/°C$ to $10{\cdot}6 \times 10^{-6}/°C$, respectively, as Na_2O content increased from 1·61% to 6·44%.

The infrared cut-off for C_2 and C_5 germanate glass samples are about 6·9 and 7·5 μm, respectively, which are longer than that of 5·0 μm for silicate glasses. For these glasses, the refractive indexes are from 1·703 to 1·769, as Na_2O content increased from 1·61% to 6·44%. The Abbe number for the glass samples is about 62·03 ± 4·07.

The observed results in the FTIR spectra of analysed glasses have shown that the glasses have a three-dimensional, random network structure consisting of GeO_4 tetrahedra as their most fundamental units.

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