Glass formation in the system $SnO{-}GeO_2$

Although many mixed metal oxide systems containing PbO have been studied [1], there are very few reports of similar studies with SnO, mainly because tin (II) oxide disproportionates to give a mixture of Sn and SnO_2. Decomposition of SnO is complete at 385° C at atmospheric pressure [2]. Amongst the PbO systems studied is $PbO{-}GeO_2$ [3–9]. The results for this system are contradictory but two features of interest have been reported, namely, (1) the preparation of a phase of composition $Pb_5Ge_3O_{11}$ [10, 11] which is an important new ferroelectric material, and (2) the formation of $PbO{-}GeO_2$ glasses with extremely high refractive indices [3]. We now report on a study of the $SnO{-}GeO_2$ systems and on three types of glass obtained from it.

Glass of composition (a) $Sn_5Ge_3O_{11}$, (b) approximately $SnGeO_3$, and (c) Sn_xGeO_{2+x} ($x \geqslant 2$), were prepared as follows.

(a) $Sn_5Ge_3O_{11}$. This opaque yellow glass was prepared from stoichiometric proportions 5SnO: $3GeO_2$ of the powdered starting materials in an open carbon crucible heated to 800° C. Some metallic Sn and SnO_2 from SnO disproportion were found in the glass and on its surface respectively.

(b) $SnGeO_3$. Glass compositions close to 1:1 $SnO{:}GeO_2$ were prepared from powdered starting materials in silica ampoules, which were vacuum out-gassed at room temperature and sealed. The ampoules which were pointed at the lower end to encourage crystal growth, were lowered through a two-zone vertical furnace at a rate of $5\,mm\,h^{-1}$. The temperature gradient between the zones is approximately $20°\,C\,cm^{-1}$ and the furnace temperatures were between 700 and 800° C. The glasses obtained varied in colour between yellow-green and orange-yellow. In most cases a little unreacted material (identified as SnO_2 by its X-ray powder pattern) was formed on top of the glass.

(c) Sn_xGeO_{2+x} ($x \geqslant 2$). Compositions of 2:1 $SnO{:}GeO_2$ or greater yield Sn_5GeO_{11} with mixtures of the green-yellow and orange-yellow glasses of compositions close to $SnGeO_3$.

All three types of material were analysed by electron probe analysis and the results appear in Table I. The X-ray diffraction powder data were recorded on Debye Scherrer 116.4 mm cameras using Ni-filtered $CuK\alpha$ radiation and the data for crystalline phases in $SnGeO_3$ and $Sn_5Ge_3O_{11}$ are given in Table II. The refractive indices for the yellow-green, and yellow-orange glasses are listed in Table III, under the colour of the filters used.

TABLE I Electron probe analyses for the $SnO{-}GeO_2$ system

Sample	Ge (%)	GeO_2 (%)	Sn (%)	SnO (%)
Opaque yellow $Sn_5Ge_3O_{11}$	22.2 (22.1)	32.0 (31.8)	59.9 (60.1)	68.0 (68.2)
Yellow-green $SnGeO_3$	30.7 (30.3)	44.2 (43.7)	49.2 (49.6)	55.8 (56.3)
Yellow-orange $Sn_6Ge_7O_{20}$	32.7 (33.0)	47.1 (47.5)	46.2 (46.2)	52.9 (52.5)

Values in parentheses are calculated assuming given formulae.

TABLE II X-ray powder diffraction data

$Sn_5Ge_3O_{11}$		$SnGeO_3$	
Relative intensity	d (Å)	Relative intensity	d (Å)
m	6.1		
mw	5.3		
w	4.2		
mw	3.75	s	3.70
w	3.19	m	3.20
vvs	3.06	vvs	3.06
s	2.65	m	2.50
vw	2.40	w	1.35
mw	2.37	s	2.25
mw	2.16	m	2.10
m	2.03	m	1.94
vs	1.86	w	1.29
w	1.79	ms	1.87
w	1.76		
vw	1.67		
vs	1.595	ms	1.6000
m	1.525	m	1.52
mw	1.480	m	1.44
vvw	1.410		
m	1.375		
m	1.320		
vvw	1.255		
ms	1.215		
ms	1.180	w	1.177
w	1.160	vw	1.155
m	1.078	m	1.080
w	1.023	vw	1.049
m	1.019	vvw	1.018

TABLE III Refractive indices of glasses in the $SnO-GeO_2$ system

	White light	Filters		
		blue	green	red
Yellow-green ($SnGeO_3$)	2.13	*	2.03	2.14
Yellow-orange ($Sn_6Ge_7O_{20}$)	1.98	1.92	1.95	2.03

* Not measurable using blue filter.

^{119}Sn Mössbauer data for the glasses (Table IV) were obtained at 80 K with the ground glasses as absorbers in perspex holders. The source motion for the Mössbauer effect was provided by a vertically mounted moving coil drive which was built to a design by Cranshaw [12]. The solid state waveform generator, 256 channel (N.M. 710), store A.D.C. (N.M. 730), power supply (N.M. 231), display unit (N.M. 720) and print-out controller (N.M. 195) supplied by J. and P. Engineering, Reading, give some improved stability over the original design [13]. The gamma detector was a 1 cm x 0.1 cm NaI (Tl) scintillator and a palladium foil (0.3 mg cm^{-2}) was used to reduce the tin X-ray contribution to the counting rate. The source used was a 2.0 m Ci $BaSnO_3$ source supplied by UKAEA Radiochemical Centre, Amersham. The spectrometer was calibrated by means of the natural ion spectrum using a Co-stainless steel source.

All samples were seen to have a conchoidal fracture suggesting glass rather than crystal formation.

$Sn_5Ge_3O_{11}$. Microscope examination of the opaque yellow material shows scattered metallic particles, and an apparently two-phase matrix of fine feathery opaque yellow particles in a yellow fairly transparent matrix. The metallic particles were analysed on the probe and are almost pure tin. The probe examination showed that this opaque yellow material surface is rather porous and this made it difficult to see atomic number effect in the resultant topography. Traces across the sample for Sn and Ge are rather erratic, the two phase structure apparently being too fine to be resolved properly. The average composition of the sample was taken by counting while area scanning. This material was analysed as $Sn_5Ge_3O_{11}$. The X-ray powder data (Table II) shows that the fine feathery material is crystalline.

TABLE IV Room temperature Mössbauer data for the $SnO:GeO_2$ materials (all ± 0.03)

$Sn_5Ge_3O_{11}$	3.49	2.08
$SnGeO_3$	3.49	2.00
$Sn_6Ge_7O_{20}$	3.44	1.85
SnO	2.72	1.50

$SnGeO_3$. Microscopic examinations of the green-yellow and orange-yellow glasses showed them to be homogeneous and transparent. Analysis of the green-yellow glass gives a composition close to $SnGeO_3$ (Table I), and that of the orange-yellow glass, which contains less tin, gives a composition of $Sn_6Ge_7O_{20}$. A very long X-ray powder diffraction exposure (3 days) gave a weak pattern for $SnGeO_3$ (Table II), this probably indicates that a second phase in this glass is crystalline, although because of the very weak pattern and from the appearance of the glass under the microscope, it is probably only present in very small quantities. No X-ray diffraction data were obtained for the orange-yellow glass confirming its homogeneous nature.

The refractive indices for $SnGeO_3$ and $Sn_6Ge_7O_{20}$ glasses are given in Table III; they are very high for glasses and are of the order of those found for the $PbO:GeO_2$ system [3].

The X-ray data of the crystalline phases found in the glass matrices are compared in Table II and some similarity in the *d* spacing indicates that these crystalline materials are similar in structure.

The Mössbauer data for the three materials are given in Table IV. Only tin (II) peaks are observed in the spectra, indicating that the specimens are free from tin (IV), and showing that calculations of the Sn(II) formulae from the microprobe data are valid. No attempt was made to fit the Mössbauer data of the opaque yellow $Sn_5Ge_3O_{11}$ to more than one site, as no basis for the environments present was known either for the predominant glass or the minority crystalline material.

The chemical shifts δ and the quadrupole splittings Δ are higher than those of SnO. This indicates that there is more electron density at the tin(II) nuclei in the glasses than in SnO, and that the electronic environment around the tin atoms is more distorted in the glasses. If the glasses are considered to contain tin(II) environments essentially similar to that of SnO, then the higher chemical shifts and quadrupole splittings observed would be consistent with the freezing-in of a metastable high temperature environment as the glass solidifies. Similar results are observed with tin II borate glasses [14].

Although several different starting ratios are investigated in the $SnO-GeO_2$ system, only three products were produced. The major phases in these products all display the properties of glasses. They all contain distorted Sn (II) electronic environments. The transparent glasses have large refractive indices similar to those found in the $PbO-GeO_2$ system and higher than those found for all other two-component oxide glasses [3].

Although the SnO must disproportionate during the formation of these materials, the results of this investigation infer that as it is intimately mixed with the GeO_2, it reacts as it disproportionates. Only in the case of $Sn_5Ge_3O_{11}$ was metallic tin apparent. SnO_2 appears to be rejected from the system and was always found on top of the glasses.

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J. SILVER
E. A. D. WHITE
Department of Electrical Engineering,
Imperial College,
London, UK
J. D. DONALDSON
Department of Chemistry,
Chelsea College,
London, UK

Recoil implantation of materials

In many applications of ion implantation, a shallow (few atomic layers) implant is needed in order to modify the physical and/or chemical properties of the surfaces of materials. An alternative process to conventional ion implantation is recoil implantation which requires less expensive equipment and is possibly more readily adaptable to different material combinations.

In early work of Stroud and co-workers [1–3] a thin film of dopant material was bombarded by energetic argon ions. A fraction of the dopant atoms was recoil implanted into the substrate surface (forward sputtered) and the remainder was sputtered away. Obviously, the forward sputtering yield depends upon the film thickness for given bombarding ion energies and dopant, bombarding and substrate material combinations.

The method proposed is based on maintaining a constant optimal film thickness during the process. A layer which is too thick would effectively shield the interface region, whereas, for a very thin film, the probability of collision between a bombarding ion and a dopant atom would decrease. A continuous deposition of dopant material occurs during the bombardment which just compensates for the loss by resputtering.

The apparatus comprises two adjacent, separately pumped, vacuum chambers, connected by a small aperture. In the higher pressure chamber ($\sim 10^{-3}$ Torr) there is a magnetically confined thermionic argon discharge and a target plate, made of the dopant material and biased to approxi-