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# A neutron diffraction and $^{205}$Tl NMR study of the thallium germanate glass system

Emma R. Barney [a,*], Alex C. Hannon [a], Nattapol Laorodphan [b], Ray Dupree [b], Diane Holland [b]

[a] ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK
[b] Physics Department, University of Warwick, Coventry, CV4 7AL, UK

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ABSTRACT

Neutron diffraction data, measured for two thallium germanate glass compositions, are presented and compared with previously published data for caesium germanate glasses. The measured coordination number, $n_{Ge-O}$, for the 10 mol% $Tl_2O$ thallium germanate glass is in good agreement with the average coordination number measured for the equivalent caesium germanate. However, while $n_{Ge-O}$ declines for caesium germanate glasses as the amount of modifier increases above 18 mol% $Cs_2O$, $n_{Ge-O}$ for the 30 mol% $Tl_2O$ thallium germanate glass remains high with, on average, $4.40 \pm 0.03$ oxygen neighbours per germanium. The difference in behaviour of the germanium coordination, compared to caesium germanate glasses, arises from a change in the average thallium environment, as the role of the thallium changes from that of a modifier (similar to an alkali), to a role where some of the thallium atoms act as network formers. This is supported by $^{205}$Tl NMR measurements which indicate the presence of two thallium environments.



## 1. Introduction

Glasses which exhibit non-linear optical (NLO) properties are industrially important and have been utilised for a wide range of optical devices [1,2]. There is extensive ongoing research to further the understanding of this phenomenon and relate it to the physical properties of the glass, so that new materials can be predicted and better devices can be developed. The strength of the NLO effect has been measured for a wide range of glasses and it has been demonstrated unambiguously that the highest NLO responses are due to the presence of lone pair ions in glass and the steric effects which they exert [3,4]. Several optical studies have shown that glasses containing $Tl_2O$ give some of the highest non-linear optical responses measured in heavy-metal oxide glasses [4,5]. However, although many diffraction studies of glasses containing lone pair ions have been carried out, predominantly for tellurite and lead containing systems [6–21], almost none have been published on binary glasses containing thallium.

The structural role of the lone pair ions has strong implications for the NLO properties of the glass, as these are thought to arise from the structural distribution of the electrons in space. It has been proposed [22], on the basis of limited crystallographic information for the crystal phases in the $Tl_2O$–$GeO_2$ system, that thallium atoms undergo a coordination change from symmetric sites with long Tl–O bonds, to asymmetric sites with much shorter bond lengths as the concentration of $Tl_2O$ is increased. This supports a $^{205}$Tl NMR study [23] which demonstrated that similar structural changes occur in the glass system, and such behaviour is consistent with the traditional view of the structural role of lone pair ions in glasses [24,25], whereby they act as network modifiers in low concentrations, but behave as network formers when present in high concentrations. A detailed study of a thallium-containing glass system to investigate the change in thallium environment with composition is required to allow a better understanding of how the structure of glass affects NLO properties, and to enable the NLO measurements for related glass systems to be interpreted. Due to the large compositional range over which thallium germanate glasses can be formed, they are an ideal system for studying the changing role of thallium with composition. Also, as will be shown, the difference between the various bond lengths involved means that the thallium germanate system is well suited to the study of this problem by diffraction methods.

In addition to performing a detailed study of the thallium environment, the effect of thallium on the $GeO_2$ glass network is also of interest. Many structural studies have been carried out on germanate glasses in an attempt to understand the 'germanate anomaly'. This anomaly involves the non-linear variation in the thermophysical properties of (alkali) germanate glasses with composition. For example, Fig. 1 shows densities for five alkali glass systems, all of which exhibit a maximum at approximately 15–20 mol% $M_2O$ (M = Li, Na, K, Rb or Cs). It has been proposed that this behaviour is due to an increase, and then a decrease in the number of higher coordination germanium polyhedra ($[GeO_n]$ where $n = 5$ or 6) present in the glass as alkali modifier is added. This is analogous to the model used to explain the borate anomaly, where there is a change from a structure which is comprised entirely of $[BO_3]$ units in a pure $B_2O_3$ glass, to one which contains a growing, and then a declining, number of $[BO_4]$ units, as modifier is added to the

* Corresponding author.
*E-mail address:* Emma.Barney@stfc.ac.uk (E.R. Barney).

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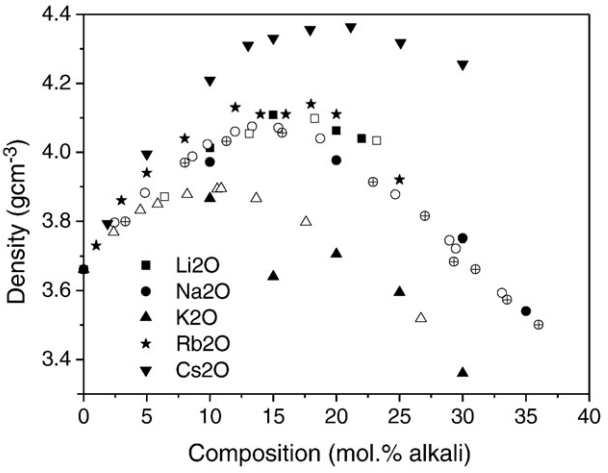


**Fig. 1.** A summary of density measurements made for a range of lithium (■ [56], □ [57]), sodium, (● [56],○ [58], ⊕ [59]), potassium (▲ [56], △ [58]), rubidium (★ [60]), and caesium germanates (▼ [29]).

system. However, while the ratio of $[BO_3]$ to $[BO_4]$ units can be measured directly and accurately using the NMR technique, germanium NMR is extremely difficult [26]. Therefore, the average germanium coordination number can only be quantified directly using diffraction techniques.

It has been demonstrated in several diffraction studies of germanate glasses [27–29] that there is a measurable change in germanium coordination with composition, but whether this is due to the formation of $[GeO_5]$ or $[GeO_6]$ polyhedra cannot be readily confirmed; distinct peaks in the neutron correlation function, $T(r)$, arising from the different bond lengths in $[GeO_4]$ and $[GeO_n]$ polyhedra cannot be resolved [28]. However, by adapting a model used to explain the change in coordination which occurs in borate glasses, a recent study of caesium germanate glasses has demonstrated that the variation in the Ge–O coordination number, $n_{Ge-O}$, is more consistent with the formation of $[GeO_5]$ structural units, rather than $[GeO_6]$ units [30]. Almost all diffraction studies of germanates have been carried out on alkali germanates, and no detailed studies of the effect of the addition of a lone pair cation (which itself may change coordination with composition) on the network structure of $GeO_2$ have been performed. A neutron diffraction, $^{119}$Sn NMR and Mössbauer study of the SnO–$GeO_2$ glass system [27] has been interpreted to show that, unlike the corresponding tin silicate system, there are two Sn–O distances, which correspond to coordination numbers of 3 and 5–6, arising from $[SnO_3]$ network units, and $[SnO_5]$ or $[SnO_6]$ modifier units, respectively.

## 2. Theory

### 2.1. Neutron diffraction

A neutron diffraction experiment measures the differential cross-section, $\frac{d\sigma}{d\Omega}$, which is equivalent to the total scattering from the sample, $I(Q)$, where $Q$ is the magnitude for the scattering vector for elastic scattering [31]. The total scattering is the sum of the self-scattering, $I^s(Q)$ (the interference between waves scattered from the same nucleus), and the distinct scattering, $i(Q)$ (the interference between waves scattered from different nuclei);

$$\frac{d\sigma}{d\Omega} = I(Q) = I^s(Q) + i(Q). \tag{1}$$

The self-scattering can be calculated within an approximation for a glass of known composition, and is subtracted from the data to give the distinct scattering in reciprocal-space, which can then be Fourier transformed to give a real-space correlation function,

$$T(r) = T^0(r) + \frac{2}{\pi}\int_0^\infty Qi(Q)M(Q)\sin(rQ)dQ \tag{2}$$

where $T^0(r)$ is the average density contribution to the correlation function, and $M(Q)$ is a modification function which is used to reduce termination ripples in the Fourier transform.

The result from a diffraction experiment is not element specific, and $T(r)$ is a weighted sum of all possible partial correlation functions, $t_{ll'}(r)$

$$T(r) = \sum_{ll'} c_l\ \overline{b}_l\ \overline{b}_{l'} t_{ll'}(r) \tag{3}$$

where $\overline{b}_l$ and $\overline{b}_{l'}$ are the coherent scattering lengths for elements $l$ and $l'$ respectively, and $c_l$ is the atomic fraction of element $l$. The summation is over all the pairwise combinations of elements in the sample. For a peak in $T(r)$ due to a particular correlation between atoms of element $l$ and $l'$, the coordination number, $n_{ll'}$, can be calculated from the area, $A_{ll'}$, and position, $r_{ll'}$, of the peak and the coefficient for $t_{ll'}(r)$ according to

$$n_{ll'} = \frac{r_{ll'}A_{ll'}}{(2-\delta_{ll'})c_l\ \overline{b}_l\ \overline{b}_{l'}}. \tag{4}$$

where $\delta_{ll'}$ is the Kronecker delta.

### 2.2. Thallium NMR

Thallium has two NMR active nuclei, $^{203}$Tl and $^{205}$Tl, both with spin $I = 1/2$ and relative abundances of 29.5 and 70.5%. These two nuclei are very close in frequency: 114.2 MHz for $^{203}$Tl and 115.6 MHz for $^{205}$Tl at the 4.7 T field used in this study. $^{205}$Tl is the preferred nucleus of study in natural abundance thallium samples because there is a smaller contribution to line broadening from the $^{205}$Tl–$^{203}$Tl exchange interaction [32]. Since this is a through-bond coupling, its presence requires Tl–O–Tl bonds and can be used to infer the presence of cation clustering [33]. Linewidths can be reduced by using isotopically pure materials — as demonstrated by Panek and Bray [33] in their study of thallium silicate, germanate and borate glasses. They concluded that thallium forms isolated ions at $Tl_2O$ concentrations up to about 15 mol%, beyond which increased covalency and pairing occur. They describe the $^{205}$Tl spectra of enriched glasses as consisting of broad, featureless, but slightly asymmetric peaks whose linewidth goes through a maximum. We report the use of static, pulsed NMR on natural abundance $^{205}$Tl in thallium germanate glasses.

## 3. Experimental detail

Two glass samples were prepared with nominal compositions of 10 and 30 mol% $Tl_2O$, using $Tl_2CO_3$ (Alfa Aesar, 99.99%) and $GeO_2$ (Alfa Aesar, 99.98%) as the starting ingredients. Batches with a weight to yield 25 g of glass were heated in Pt/Rh crucibles at 10°/min, and held at a maximum temperature for 15 min before being plate-quenched between copper sheets. The maximum temperature was chosen to be 100° above the melting temperature given in the thallium germanate phase diagram [22]. Density measurements for the two samples were made using a Micromeritics Accupyc 1330 pycnometer, with helium as a working fluid.

The neutron diffraction data were measured using the GEM diffractometer [34] at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, UK. 8.3 mm diameter cylindrical vanadium cans with walls of 25 μm thickness were used to contain the samples, in the form of glass fragments. The data were reduced and corrected for attenuation and multiple scattering, using the standard gudrun [35] and ATLAS [36] software. The corrected data, in both reciprocal- and