Comment on "Atomic ordering in $x ZrO_2 \cdot (1-x)\ SiO_2$ xerogels ($x = 0.3, 0.5$) by X-ray diffraction and reverse Monte Carlo simulations"

G. MOUNTJOY, D. M. PICKUP, R. J. NEWPORT
School of Physical Sciences, University of Kent, Canterbury CT2 7NR, UK

M. E. SMITH
Department of Physics, University of Warwick, Coventry CV4 7AL, UK
E-mail: g.mountjoy@ukc.ac.uk

There is increasing interest in better understanding and quantifying the structure of amorphous solids. Over the last decade many advanced probe techniques have developed that provide specific information regarding parts of the structure, and it is important that any structural model proposed is consistent with all the information available. Reverse Monte Carlo (RMC) modeling can provide insight into amorphous structures that are consistent with the experimental (usually diffraction) data. Recently, Stachs *et al.* have reported an X-ray diffraction and RMC modeling study of $xZrO_2 \cdot (1-x)SiO_2$ xerogels [1, 2]. X-ray diffraction showed that a $0.5ZrO_2 \cdot 0.5SiO_2$ xerogel remained amorphous at heat treatments above 500 °C and RMC modeling was performed to elucidate the local atomic structure. The conclusion obtained from the RMC modeling was that the local atomic structure of $0.5ZrO_2 \cdot 0.5SiO_2$ xerogel heat treated at 500 °C is similar to that in zircon, $ZrSiO_4$ [3]. We note the following points about the use of RMC modeling. Firstly, RMC modeling usually involves the use of additional constraints other than the diffraction data, and the models produced are hence necessarily subject to these constraints. Stachs *et al.* [1, 2] used a crystalline zircon starting configuration, and constraints such that the zircon-like local structure was maintained in the model. Secondly, good agreement between an RMC model and diffraction data is a necessary, but not sufficient, condition that the model accurately represents a material.

One characteristic of the zircon structure [3] is that Si atoms are coordinated only to Zr atoms as next nearest neighbors. Thus zircon contains only Q^0 silicate units, where Q^n represents SiO_4 tetrahedra with n bridging oxygens, i.e. Si–O–Si. The distribution of Q^n units in a material can be measured using ^{29}Si NMR. We have performed ^{29}Si NMR measurements on zirconia-silica xerogels [4, 5] with compositions $x = 0.1, 0.2, 0.3$ and 0.4 and heat treatments up to 750 °C. The results show no evidence of Q^0 or Q^1 units in *any* of the samples. For convenience, Table I shows the results for the $x = 0.4$ sample as a function of heat treatment temperature [5]. Similar results have been reported for $0.5ZrO_2 \cdot 0.5SiO_2$ prepared by the sol-gel method [6], by hydrolysis of liquid aerosols [7], and by non-hydrolytic method [8] (in each case the samples were heat treated at 500 °C). Hence the results of ^{29}Si NMR studies show clearly that there is no zircon-like atomic structure in zirconia-silica xerogels. This point is further emphasized by using ^{17}O solid state NMR. Zircon contains only Zr–O–Si linkages whereas the ^{17}O spectrum from amorphous ZrO_2–SiO_2 samples that have been heated to 500 °C and above show distinct resonances from OZr_3, OZr_4, Zr–O–Si and Si–O–Si [5]. This illustrates the need to be cautious when basing conclusions about structure on a single technique, and conversely, the advantage in using information from as many different structural techniques as possible.

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TABLE I Q^n distribution for $0.4ZrO_2 \cdot 0.6SiO_2$ xerogels from ^{29}Si NMR [5]

Heat treatment (°C)	Q^2 (%) (±5)	Q^3 (%) (±5)	Q^4 (%) (±5)
None	42	43	15
100	42	38	20
250	39	35	26
500	27	24	49
750	24	26	50

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