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Neutron diffraction study on the structure of pure TeO_2 glass

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고순도 TeO_2 유리 구조의 중성자 회절 연구

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Abstract The short range structure of pure TeO_2 glass was studied by neutron diffraction. In order to decide the values of Te-O bond length (d_{Te-O}) and the coordination number (N_{Te-O}) of oxygen atoms surrounding a Te atom, the first peak of the $Q_{max} = 20$, 23, 25, 28 and 30 in the highly resolved RDF curves was deconvoluted by the least-squares method under the assumption that both of the pair distribution functions have a Gaussian form. On the basis of these results, it is found that pure TeO_2 glass consists of TeO_4 structural units, in which Te atoms are coordinated by four oxygens and each two oxygen atoms are bonded to a Te atom with the average bond length of 1.916 Å and 2.123 Å, respectively.

요　약 중성자 회절에 의해 고순도 TeO_2 유리의 단범위 구조를 조사하였다. Te-O의 결합길이(d_{Te-O})와 산소원자를 둘러싼 Te 원자의 배위수(N_{Te-O})를 결정하기 위해 고해상도 RDF 곡선의 $Q_{max} = 20$, 23, 25, 28, 30의 첫번째 peak를, pair distribution 함수 모두 Gaussian 형식을 따른다는 가정하에 least-square법으로 peak 분리를 했다. 이 결과를 토대로, 고순도 TeO_2 유리는 하나의 Te 원자에 4개의 산소가 배위되어 있는 TeO_4의 단위구조로 이루어져 있으며, 각 2개의 산소원자는 평균 결합길이가 각각 1.916 Å과 2.123 Å으로 Te 원자에 결합하고 있는 것으로 밝혀졌다.

1. Introduction

TeO_2-based glasses are characterized by high refractive index and dielectric constant compared to conventional glasses. Therefore, tellurite glasses are promising materials applicable to acousto-optic device [1] and nonlinear optical devices [2]. These outstanding properties probably stem from their unique structure. Accordingly, detalied structural information is very important. Crystalline tellurium dioxide, TeO_2 has a unique structural unit, that is, an asymmetrical TeO_4 trigonal bipyramid with a lone pair of electron, in which there are two different kinds of sites, two axial and three equatorial positions as shown in Fig. 1 and 2. Compare with the conventional glasses, such as silicate and borate glasses, the structure of the tellurite glasses is somewhat extraordinary in the sense that the basic structural unit of glasses is an asymmetrical TeO_4 trigonal bipyramid with a lone pair of electrons in an equatorial position and the coordination number of tellurium ion with respect to oxygen ions changes with the network modifying oxide content, eventually leading to a TeO_3 trigonal pyramid which is considered to restrict the glass formation by spectroscopic approach [3-5]. Since the first contribution of pure vitreous TeO_2 by Sarjeant and Roy in 1967 [6], the atomic scale structure of single component TeO_2 glass has been considered as an important key to analysis the multicomponent tellurite glasses. Furthermore, the network structure

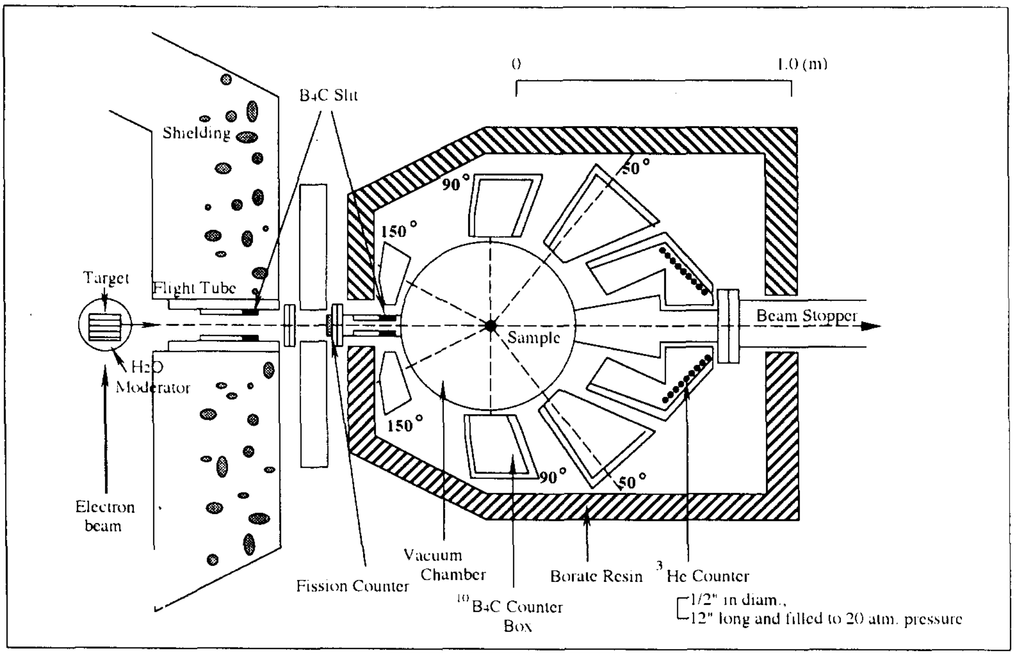

Fig. 1. Schematic diagram of TOF pulsed neutron total scattering spectrometer.

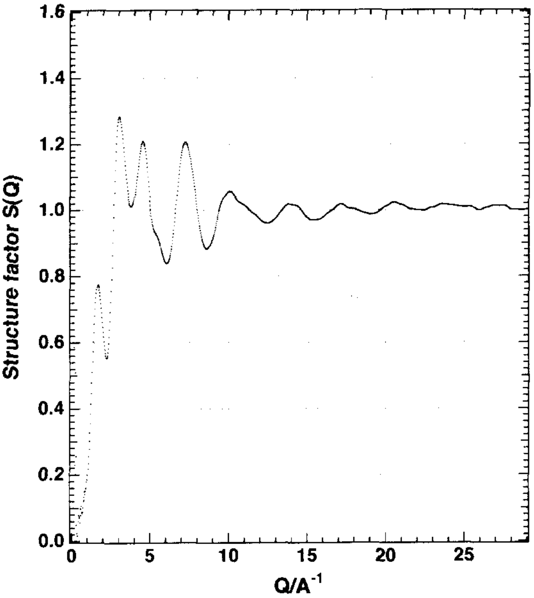

Fig. 2. Experimental structure factor S(Q) of TeO_2 glass.

of the single component TeO_2 glass is left open in view of the probelm which crystalline structure, α-TeO_2 or β-TeO_2, is more suitable for describing it as shown in Table 1. This may have been caused by impurities contained in the glass. No pure TeO_2 glass has been obtained so far.

In the present study, the short-range order in atomic scale of pure TeO_2 glass is investigated by T-O-F pulsed neutron diffraction.

2. Experimental

2.1. Sample preparation

Pure crystalline β-TeO_2 as the starting material was melted in a Pt-5% Au crucible at 800℃ for 20 min. TeO_2 glass was obtained by rapidly quenching the bottom of crucible containing 0.1 ~ 0.15 g of glass melt using a freezing mixture consisting of ice, ethanol and NaCl kept at -11℃. The TeO_2 glass of $5.0 \times 4.0 \times 0.25$ mm^3 in size was successfully obtained [7].

2.2. Neutron diffraction

Neutron diffraction measurements were carried out by use of a high intensity total scattering spectrometer (HIT) with a pulsed neutron source at the National Laboratory for High Energy Physics (KEK, Tsukuba, Japan). A layout of the spectrometer as installed at the beam hole of the KENS facility is shown in Fig. 3. Since the details of the HIT have been reported by Watanabe and Fukunaga [8] elsewhere, only a brief description is given below. A pulsed neutron beam from the KEK booster synchrotron and a uranium target cooled by pure water were used to generate the pulsed neutron beam, and the diffracted neutron was detected by the Time-of-Flight method. The height of incident beam was 40 mm. The spectrometer was constructed with a 4.5 m long incident flight path and had 50 ^{3}He counters. In this experiment, seven counterbanks at angles of 150°, 90°, 50°, 30°, 23°, 13° and 8° were used. The powder sample was loaded in a vanadium metal cylinder with a wall thickness of 0.025 mm an inner diameter of 8 mm, a length of 40 mm, and set in a vacuum chamber to avoid moisture uptake and eliminate the background due to air scattering during the measure-

Table 1
Previous works on the structure of tellurite glasses

Method	Workers	System	Year	Basic structure
X-ray diffraction	Brady	LiO_2-TeO_2	1957	TeO_{4+2} : 4(1.95 Å)/2(2.75 Å) $\Rightarrow \beta$-TeO_2
	Dimitriev et al.	V_2O_5-TeO_2	1978	α-TeO_2
	Imaoka et al.	Li_2O-TeO_2	1980	α-TeO_2
	Yoko et al.	TeO_2	1987	α-TeO_2
Neutron diffraction	Neov et al.	Fe_2O_3-TeO_2	1978	α-TeO_2
	Neov et al.	Li_2O-TeO_2	1979	TeO_4(tbp.) + TeO_4(tp.) $\Rightarrow \alpha$-TeO_2
	Neov et al.	P_2O_5-TeO_2	1980	α-TeO_2
	Ueno et al.	TeO_2	1981	α-TeO_2
	Johnson et al.	V_2O_5-TeO_2	1986	α-TeO_2(?)
	Kozhukharov et al.	WO_3-TeO_2	1986	α-TeO_2
I.R. Spectra	Mochida et al.	M_2O(MO)-TeO_2	1978	α-TeO_2
	Dimitriev et al.	TeO_2	1983	α-TeO_2
	Yoko et al.	LiCl-Li_2O-TeO_2	1987	α-TeO_2

ments.

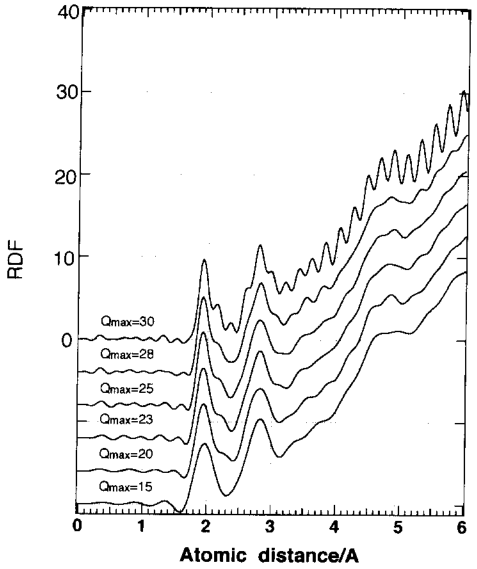

Fig. 3. Radial distribution function of TeO_2 glass. Fourier transformation of S(Q) to RDF is truncated at various scattering vector Q_{max}.

3. Results

The structure factor S(Q) of present glass was experimentally obtained over the range of the scattering vector,

$$Q = 4\pi \cdot \sin\theta/\lambda \qquad (1)$$

where θ is the scattering angle and λ is the neutron wavelength, from 0 to 30 $Å^{-1}$. The cross sections of Te and O used to obtain the scattering factor S(Q) are 0.543, 0.5805×10^{-12} cm, respectively [9]. The result is shown in Fig. 2. Figure 3 shows the radial distribution function (RDF) of TeO_2 glass, which was obtained by the Fourier transformation of S(Q) truncated at various values the scattering vector Q_{max} indicated in the figures. The first peak around $d \approx 2$ Å in the RDF curves is ascribed to the Te-O nearest neighbor pair correlation. With increasing Q_{max}, the first peak becomes drastically narrower and more steep to lead to a characteristic splitting as well as the second peak does as shown in Fig. 3. In order to decide the values of Te-O bond length (d_{Te-O}) and the coordination number (N_{Te-O}) of oxygen atoms surrounding a Te atom, the first peak of the $Q_{max} = 20$, 23, 25, 28 and 30 in the RDF curves was deconvoluted by the least-squares method under the assumption that both of the pair distribution functions have a Gaussian form. Gaussian parameters (position and broadness) were allowed to float until a best fit was obtained. The

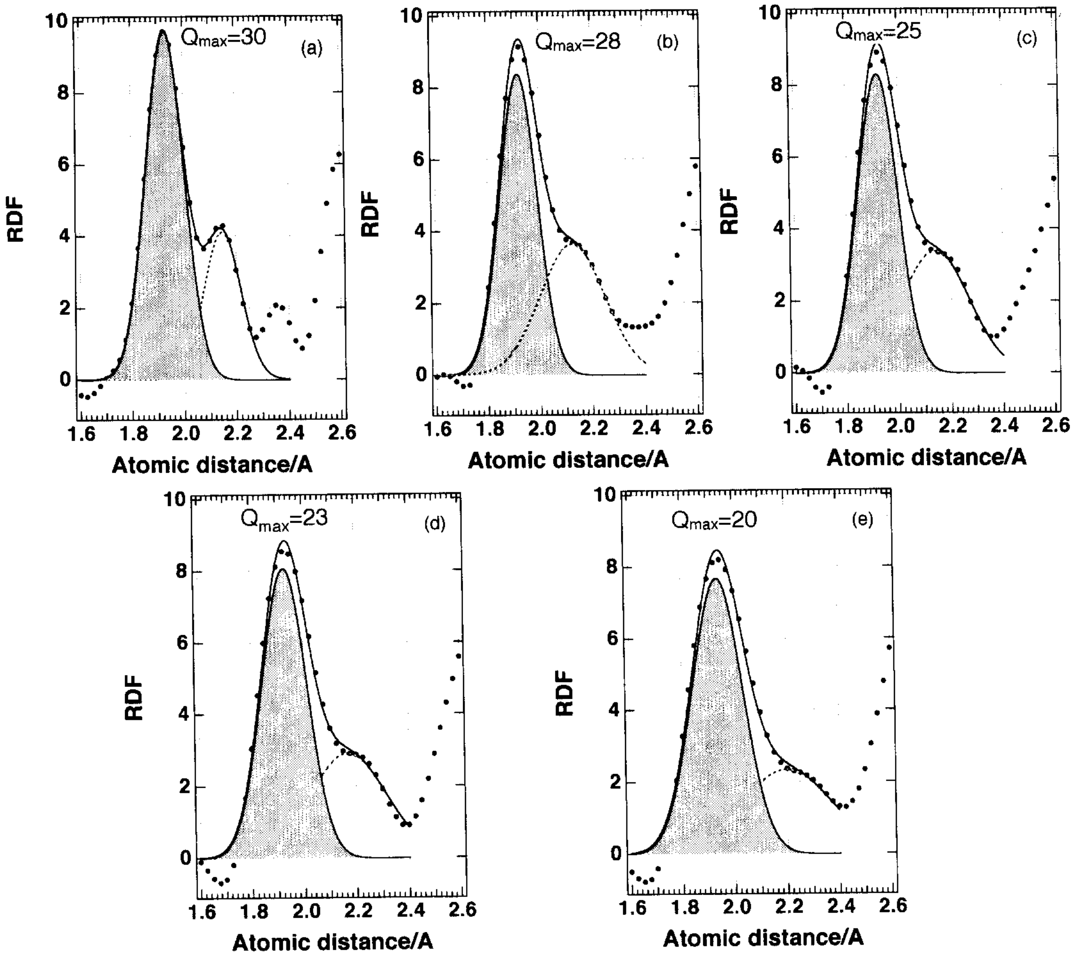

Fig. 4. Radial distribution function of TeO_2 glass. Dotted and dashedcurves indicated the Gaussian approximations for Te-O pair distribution functions for (a) $Q_{max} = 30$, (b) $Q_{max} = 28$, (c) $Q_{max} = 25$, (d) $Q_{max} = 23$ and (e) $Q_{max} = 20$.

results of deconvolution for $Q_{max} = 20$, 23, 25, 28 and 30 in the RDF curves are shown in Fig. 4 (a), (b), (c), (d) and (e), respectively. The least-squares calculation was made several times with small variations of the initial values of bond length and intensity.

4. Discussion

Crystalline tellurium dioxide, TeO_2 has two types of orthorhombic form (β-TeO_2) and tetragonal form (α-TeO_2 : paratellurite) as shown in Fig. 5 and 6. There is 4-coordination of Te in both forms, the neighbours being arranged at four of the vertices of a trigonal bipyramid, suggesting considerable covalnt character of the Te-O bonds. β-TeO_2 has a layer structure in which TeO_4 groups form edge-sharing pairs which form a layer by sharing the remaining vertices. The distance of Te-Te is shorter (3.17 Å) than that of α-TeO_2 crystal (3.74 Å). In paratellurite very similar TeO_4 groups share all vertices to form a three-dimension structure of 4 : 2 coordination in which the oxygen bond angle is 140°. These similarity of structure of two crystalline tellurium dioxide make it possible to judge which crystalline structure, α-TeO_2 or β-TeO_2, is more suitable for describing the structure of TeO_2 glass.

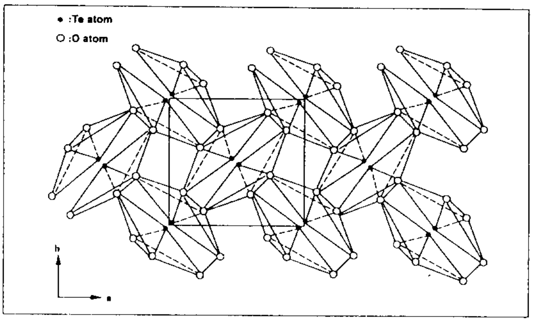

Fig. 5. Structure of α-TeO_2 crystal.

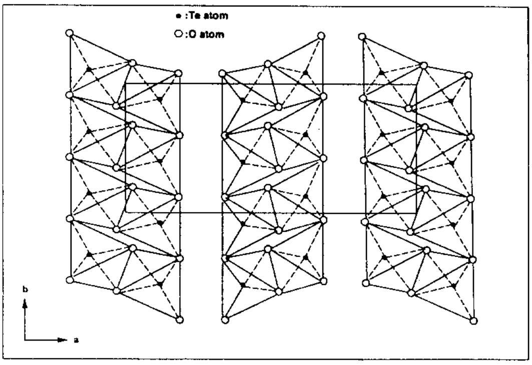

Fig. 6. Structure of β-TeO_2 crystal.

In this study, the numbers of oxygen atoms bound to a Te atom ($N_{Te-O^{P1}}$ and $N_{Te-O^{P2}}$) are calculated from the first peak areas using the following equations :

$$N_{Te-O}^{P1} = A_{Te-O}^{P1} \cdot \frac{(b)^2}{b_{Te} \times b_O} \cdot \frac{1}{2X_{Te}} \qquad (2)$$

$$N_{Te-O}^{P2} = A_{Te-O}^{P2} \cdot \frac{(b)^2}{b_{Te} \times b_O} \cdot \frac{1}{2X_{Te}} \qquad (3)$$

where A_{i-j} is the peak area of the $i-j$ pair, b_i the neutron scattering amplitude and X_i atomic fraction of element i, respectively, and

$$(b) = \Sigma\ X_i b_i \qquad (4)$$

The number of oxygens surrounding a Te atom and the value of the Te-O bond length can be decide from the area and position of the first peak in the RDF as a function of

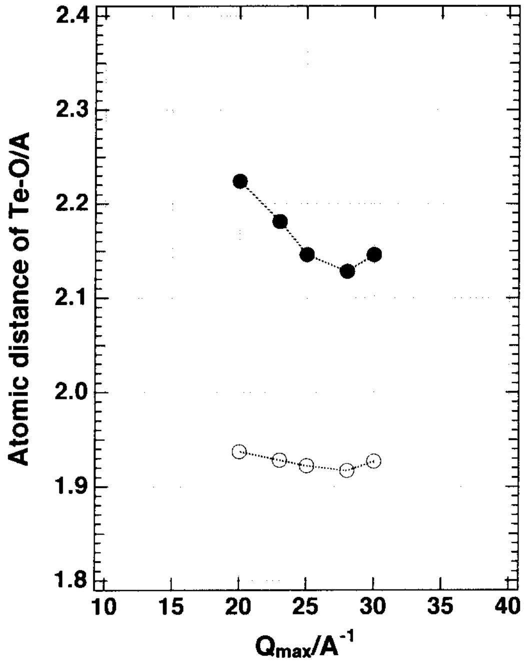

Fig. 7. Q_{max} dependences on Te-O bond length.

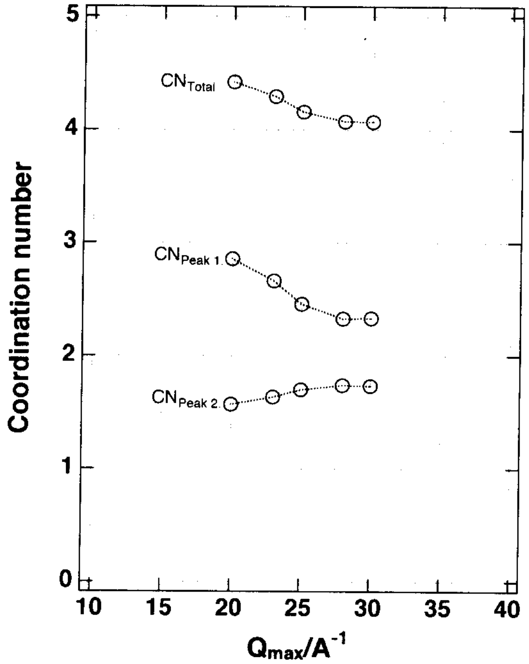

Fig. 8. Q_{max} dependences on coordination number of O atoms surrounding a Te atom.

Q_{max}. The results are shown in Fig. 7 and 8.

In the high resolution short-range order in single component vitreous TeO_2, the first peak in the RDF curves is divided into two subpeaks as shown in Fig. 4. On the basis of the results of deconvolution for $Q_{max} = 28$ in the RDF curves as shown in Table 2, it is found that the large subpeak and the small subpeak are located at the position of 1.916 Å and 2.123 Å, respectively. This results indicates that two oxygen atoms are coordinated to a Te atom with the average bond length of 1.916 Å, while the other oxygen atoms is located at the position of 2.123 Å apart from a Te atom. Comparing with crystalline structure, α-TeO_2 and β-TeO_2 as shown in Fig. 9, the short-range structure for Te-O pairs is similer to that of α-TeO_2 which has oxygen atoms (2.3 + 1.7) around a Te atom. The results obtained in this study is tabulated in Table 2.

Table 2
Atomic distance (d) and coordination number (N) for Te-O pair in pure TeO_2 glass

Parameters	Te-O^{P1}	Te-O^{P2}
d_{Te-O}(Å)	1.916	2.123
N_{Te-O}	2.3	1.7

5. Conclusion

The high resolution short-range order in single component pure TeO_2 glass has been

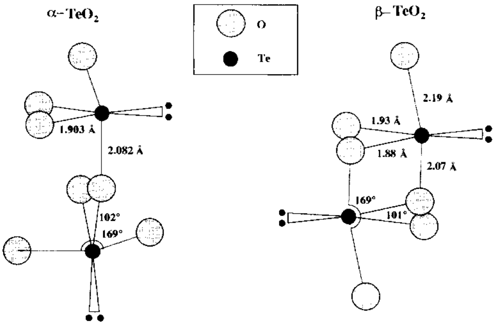

Fig. 9. Schematic diagram of TeO_2 crystal.

investigated by the Time-of-Flight pulsed neutron scattering. The following conclusions have been obtained.

(1) Pure TeO_2 glass consists of TeO_4 structural units, in which Te atoms are coordinated by four oxygens.

(2) In the short-range TeO_4 structural unit, it is found that each two oxygen atoms are bonded to a Te atom with the average bond length of 1.916 Å and 2.123 Å, respectively.

(3) The number of O atoms surrounding a Te atom (N_{Te-O}) in pure TeO_2 glass can be decided with the ration of 2.3 : 1.7. The single component of TeO_2 glass resembles α-TeO_2 crystal in appearance.

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References

[1] T. Yano, A. Fukumoto and A. Watanabe, J. Appl. Phy. 4 (1971) 3674.

[2] E.M. Vogel, M.J. Weber and D.M. Krol, Phys. Chem. Glasses 32 (1991) 231.

[3] Y. Dimitriev, V. Dimitrov and M. Arnaudov, J. Mater. Sci. 18 (1983) 1353.

[4] S. Neov, V. Kozhukharov, I. Gerasimova, K. Krezhov and B. Sidzhimov, J. Phys. C : Solid State Phys. 12 (1979) 2475.

86 (1978) 316.

[6] P.T. Sarjeant and R. Roy, J. Am. Ceram. Soc. 50 (1967) 500.

[7] S.H. Kim, T. Yoko and S. Sakka, J. Am. Ceram. Soc. 76 (1993) 2486.

[8] N. Watanabe, T. Fukunaga, T. Shiohe, K. Yamada and T. Mizoguchi, KENS Rep. 2 (1971) 539.

[9] V.F. Sears, "Atomic Energy of Canada Limited, Thermal-Neutron Scattering Lengths and Cross Sections for condensed-Matter Research", AECL-8490, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada KOJLJO, June (1984).