Atomic Structure of Rare Earth Si-Al-O-N Glasses

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In this paper the results of X-ray diffraction experiments of Ln-Si-Al-O-N (Ln = La, Gd, Yb) glasses are presented. Total structure factors and pair correlation functions allow the determination of the first coordination sphere of Ln atoms. The bond lengths observed correspond to the ionic radii of the Ln-ions surrounded by oxygen and nitrogen atoms. The presence of non-bridging nitrogen is discussed together with results of neutron diffraction, NMR-experiments and XPS-studies of other authors.

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1. Introduction

Silicon nitride ceramics are some of the most interesting structural materials for high- temperature applications. Because of the highly covalent bonding, Si_3N_4 has to be denisified with sintering additives. Today, it is a common practice to densify Si_3N_4 by pressureless sintering or pressure assisted densification methods. The sintering aids are usually metal oxides such as MgO, Al_2O_3 and most of the rare earth oxides [1, 2]. At higher temperatures, SiO_2, which is always present at the surface of the Si_3N_4 particles, reacts with the oxide additives to form an oxide melt and, with increasing temperature, an oxynitride melt by dissolving Si_3N_4. Depending upon the composition of the sintering aids, the liquid phase can form an amorphous or a crystalline grain boundary phase during cooling. Detailed high resolution and analytical TEM experiments indicate a complete covering of the silicon nitride grains with a thin amorphous intergranular film. The film thickness varies between 1 and 2 nm but it is constant for a given additive system [3].

Previous investigations of silicon nitride ceramics, densified with different Ln-Si-Al-O-N glasses reveal a strong influence of the type of the rare earth oxides on grain growth behaviour and grain morphology development of silicon nitride as well as on the resulting mechanical properties [4]. Furthermore, it has been found that the nitrogen solubility is also strongly dependent on the rare earth oxide [5]. The present work presents an analysis of the local order of the same Ln-Si-Al-O-N-glass compositions by use of X-ray diffraction, in order to understand the previous experimental observations. Due to the high absorption cross section for neutrons, these glasses are not expected to be good candidates for neutron diffraction experiments. But anyway, good contrast for X-ray diffraction between heavy and light elements could be successfully achieved due to the large cross section of heavy rare earth elements and to the small cross section of light atoms such as Si, Al, O, and N. Therefore, X-ray diffraction mainly probes pair correlations with rare earth ions.

2. Theoretical Background

From the coherently scattered intensity $I_{\mathrm{coh}}^{\mathrm{atom}}(Q)$, the total structure factor according to Faber and Ziman is obtained [6]:

$$S(Q)^{\mathrm{FZ}} = \frac{I_{\mathrm{coh}}^{\mathrm{atom}}(Q) - \left[\langle f(Q)^2\rangle - \langle f(Q)\rangle^2\right]}{\langle f(Q)\rangle^2} \quad (1)$$

where $I_{\mathrm{coh}}^{\mathrm{atom}}(Q)$ = coherently scattered intensity per atom, $\langle f(Q)^2\rangle = \sum_{i=1}^{n} c_i \cdot f_i(Q)^2$, $\langle f(Q)\rangle = \sum_{i=1}^{n} c_i \cdot f_i(Q)$, c_i = atomic concentration of atomic species i,

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$f_i(Q)$ = scattering length of atomic species i, n = number of atomic species in the sample, $Q = 4\pi \sin(\theta)/\lambda$. The Fourier transform of the total structure factor $S(Q)$ leads to the total reduced pair distribution function $G(R)$:

$$G(R) = \frac{2}{\pi} R \int_0^\infty Q^2 \left[S(Q) - 1\right] \frac{\sin QR}{QR} \, \mathrm{d}Q. \qquad (2)$$

The total structure factor is the weighted sum of the partial structure factors $S_{ij}(Q)$, which describe the contribution of ij pairs to the total structure factor:

$$S(Q) = \frac{1}{\langle f \rangle^2} \sum_{i=1}^{n} \sum_{j=1}^{n} c_i c_j \cdot f_i f_j \cdot S_{ij}(Q). \qquad (3)$$

The partial structure factors $S_{ij}(Q)$ will lead to partial pair distribution functions $G_{ij}(R)$ by Fourier transformation. Since $S_{ij}(Q)$ are the unknown functions, normally a simultaneous system of equations of the kind of (3) has to be handled. The amorphous phase studied in the present work consists of five components, which means 16 partial structure factors S_{ij}. It is not possible to resolve (3) containing 16 unknown parameters. But fortunately, pairs giving low contributions to the scattered intensity can be neglected in the evaluation and interpretation of the data.

3. Experiment

3.1. Samples

The aim of this study was the investigation of glasses with a high nitrogen content, but an identical concentration of rare earth oxides and a constant Ln : Si : Al ratio. All compositions form transparent glasses and had the composition $Ln_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$ (Ln = La, Gd, Yb). The glass forming regions of the systems are given in [5]. The samples were prepared by a conventional powder processing routine using Al_2O_3 (Aluminalux 49 SG, Alcoa), SiO_2 (Schott, Sipur A), a-Si_3N_4 (UBE, E-10), La_2O_3 (Merck 99.9%), Gd_2O_3 (Ventron 99.9%), and Yb_2O_3 (Johnson Matthey 99.9%). The raw materials of each batch were homogenized in isopropanol by using ultra sonic. Afterwards, the powder mixtures were dried at 50^{o}C, sieved and finally consolidated by cold isostatic pressing at 630 MPa pressure in rubber moulds. The heat treatment for the glass formation was performed in a gas pressure sintering furnace (Thermal Technology, Santa Rosa, CA) under 1 MPa nitrogen. The temperature was controlled with a boron-graphite thermocouple. Each sample was positioned in a covered boron nitride crucible, within a graphite crucible which contained a powder bed of SiO_2 and Si_3N_4 (1:2 ratio). The heating rate to the maximum temperature of 1710^{o}C was 50^{o}C/min. After 30 min at maximum temperature the furnace was switched off to achieve cooling rates $>$ 100^{o}C/min. The described crucible arrangement was necessary to avoid Si_3N_4 decomposition and significant weight losses [7].

3.2. Diffraction Experiments

X-ray diffraction experiments with all samples were done in transmission mode using Mo K_α radiation with a monochromator in the scattered beam in order to suppress the detection of flourescent radiation.

To avoid air scattering, a vacuum attachment around the sample holder was used. A standard scintillation-detector system with a single channel window was used for counting the pulses. These devices were mounted on a Seifert MZ IV goniometer. The samples were cut into small pieces, 1cm in diameter, and grinded to 60 µm in thickness. As Si, O and N are weak scatterers for X-rays, the 2Θ angle range from 70 up to 115° was covered three times with 200 sec/step and a step width of 0.05°.

4. Results

During the evaluation of the structure factors all necessary corrections including those for absorption and incoherent scattering [8] were applied. Finally the coherently scattered intensity was normalized according to [9]. In Fig. 1 we present the total structure factors of the $Ln_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$ glasses. All curves indicate a sharp maximum, similar shape and size, at about Q = 2.1 Å^{-1}. This maximum is followed by a second broad maximum at 3.1 Å^{-1} for the La-glass, at 3.5 Å^{-1} for the Gd-glass, and at 3.8 Å^{-1} for the Yb-glass. Also, in this sequence the shape alters from right asymmetric via symmetric to left asymmetric, and a remarkable shift towards larger Q-values is observed for the third maximum. A detailed list is given in Table 1.

For all these curves the noise level is acceptable. The Fourier transform was calculated with $Q_{\max}$ =

Table 1. Ln-Si-Al-O-N glasses. Characteristic data of the total structure factors obtained by X-ray diffraction.

Glass	1st max. Pos. [Å^{-1}]	1st max. FWHM [Å^{-1}]	2nd max. Pos. [Å^{-1}]	2nd max. FWHM [Å^{-1}]	3rd max. Pos. [Å^{-1}]
La-glass	2.04	0.51	3.15	0.98	5.1
Gd-glass	2.10	0.62	3.47	1.24	5.5
Yb-glass	2.16	0.59	3.87	1.36	5.8

Table 2. Ln-Si-Al-O-N glasses. Characteristic data of the total pair correlation functions obtained by X-ray diffraction.

Glass	1st max. Pos. [Å^{-1}]	1st max. FWHM [Å^{-1}]	2nd max. Pos. [Å^{-1}]	2nd max. FWHM [Å^{-1}]	3rd max. Pos. [Å^{-1}]	4rd max. Pos. [Å^{-1}]
La-glass	1.63	0.35	2.50	0.57	3.96	6.65
Gd-glass	1.72	0.22	2.40	0.51	3.75	6.39
Yb-glass	1.60	0.21	2.23	0.52	3.59	6.30

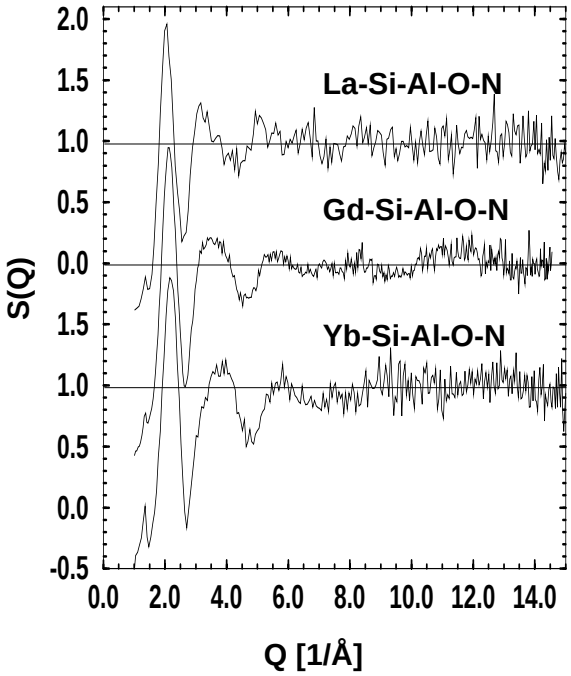

Fig. 1. $Ln_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$-glasses; Total structure factors obtained by X-ray diffraction.

13.9 Å^{-1}. The total pair correlation functions are presented in Figure 2. The first peak of the solid line around 1.65 Å is expected to be the result of mixed Si-O/N and possibly Al-O/N bonds. As this region suffers from the truncation effect, the error is about ±0.1 Å. The second peak is related to the Ln-O/N

Table 3. Ln-Si-Al-O-N glasses. Weighting factors w_{ij} for X-ray diffraction experiments.

Glass	— w_{ij} —							
	Ln-Ln	Ln-Si	Ln-Al	Ln-O	Ln-N	Si-O	Al-O	O-O
La-glass	0.2058	0.1153	0.0939	0.2601	0.0265	0.0729	0.0593	0.0821
Gd-glass	0.2326	0.1164	0.0946	0.2619	0.0289	0.0656	0.0532	0.0737
Yb-glass	0.2552	0.1166	0.0946	0.2619	0.0269	0.0598	0.0486	0.0672

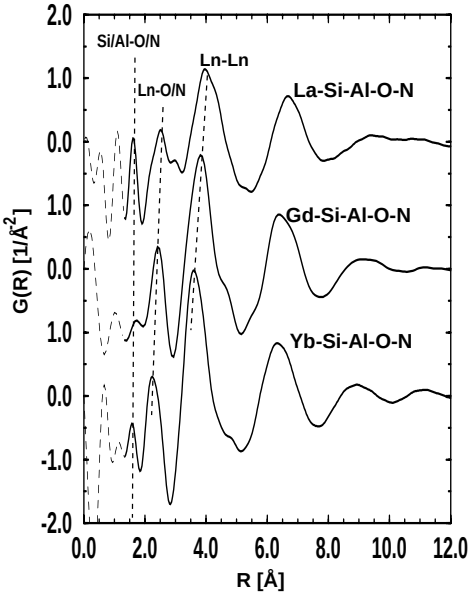

Fig. 2. $Ln_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$-glasses; Total pair correlation functions obtained by X-ray diffraction.

distances. It shifts from 2.50 Å (La-glass) via 2.40 Å (Gd-glass) to 2.23 Å (Yb-glass). The third peak in all curves is predominantly caused by the Ln-Ln distribution. Of course, some contribution of higher correlations of other elements falls within this region. Also a slight shift towards lower R-values is observed in the sequence (La,Gd, and Yb-glass). This behaviour reflects the ionic size of the rare earth elements. A list of the specific values is given in Table 2.

In order to justify these reflections, in Table 3 the weighting factors according to [6] for these glasses are presented. All contributions with weighting factors smaller than 0.02 are neglected in this table. The values of the weighting factors w_{ij} represent the visibility of each pair i-j in the total structure factor.

From Table 3, it is obvious that the Ln-X (X = Ln, Si, Al, O, N) correlations predominate in the total structure factors measured by X-ray scattering. Correlations which are not listed in Table 3 are neglected

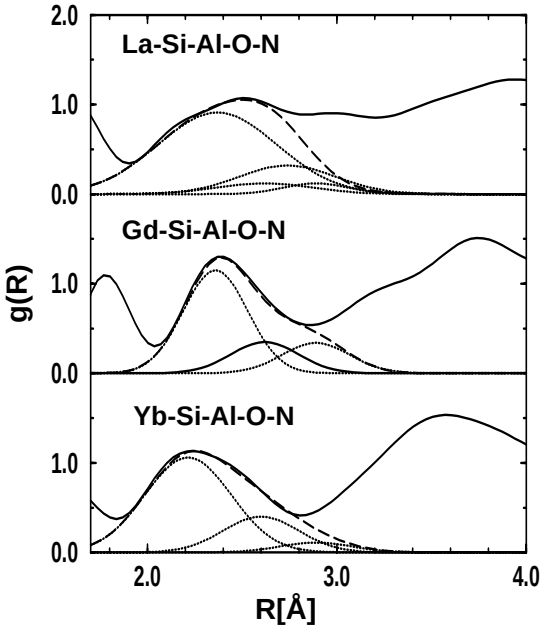

Fig. 3. $Ln_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$-glasses; Application of Gaussian-curve fitting.

in the further discussion, since they give rather low contributions to the total coherent scattered intensity.

The average coordination numbers were derived by fitting Gaussian curves to the peaks of the correlation function

$$g(R) = \frac{G(R)}{4\pi\rho_o R} + 1. \tag{4}$$

The area of a subpeak is connected with the coordination number Z_{ij}:

$$Z_{ij} = N_{ij} \cdot \frac{\langle f \rangle^2}{c_i c_j f_i f_j} \cdot c_j. \tag{5}$$

Assuming that the bond-lengths in amorphous solids are similar to those in related crystalline compounds, it is possible to deconvolute the main peaks in the total pair correlation functions into subpeaks of partial nature. This can be achieved empirically by the application of Gaussian fit-functions.

In Fig. 3 the application of these peak fits is presented. The fit parameters such as positions and half-widths are determined empirically. In Table 4, the results of the peak fitting procedures are presented.

The average coordination numbers as well as the subpeak-positions of the first coordination sphere of the Ln-element are listed in this table. Because of the asymmetric shape of the peaks, an overlay of three or four subpeaks is assumed. The left (and main) subpeak is considered to be of mixed type Ln-(O/N). This can be justified by the sum of coresponding values of the ionic radii [10]. Only for the La-Si-Al-O-N glass, the peak could be deconvoluted into La-O and La-N.

Table 4. $Ln_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$-glasses. Parameters of Gaussian curve fitting. Z_{O-O}(Si,Al): Pair correlations of oxygen atoms with Si, Al centered. —: Numbers not specified due to large experimental uncertainties.

Sub Peak Position [Å]	Half Width [Å]	Height	Coordination Number
$La_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$:			
2.37	0.74	0.91	$Z_{La-O} = 8.8 \pm 0.6$
2.62	0.40	0.22	Z_{O-O}(Si) = —
2.77	0.40	0.165	$Z_{La-N} = 1.6 \pm 0.6$
2.89	0.40	0.12	Z_{O-O}(Al) = —
$Gd_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$:			
2.36	0.40	1.15	$Z_{Gd-(O/N)} = 6.0 \pm 0.6$
2.62	0.42	0.35	Z_{O-O}(Si) = —
2.89	0.42	0.34	Z_{O-O}(Al) = —
$Yb_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$:			
2.215	0.536	1.06	$Z_{Yb-(O/N)} = 6.6 \pm 0.6$
2.60	0.40	0.47	Z_{O-O}(Si) = —
2.89	0.45	0.11	Z_{O-O}(Al) = —

For the O-O correlations, two different types have to be discussed. Oxygen atoms surrounding Si atoms give an O-O pair correlation with a maximum at 2.62 Å, and oxygen atoms surrounding Al atoms give an O-O pair correlation with a maximum at 2.89 Å. These distances are not affected by the type of the rare earth element.

In the case of the other glasses Gd-Si-Al-O-N and Yb-Si-Al-O-N, the Ln-N bonds could not be separated from the Ln-O bonds. These bonds are considered to have mixed type character. In Table 5, the Ln-O/N bond lengths are listed in particular.

For La-Si-Al-O-N glasses, the bond lengths are the same as in crystalline compounds. For Gd-Si-Al-O-N glasses and Yb-Si-Al-O-N glasses, the Ln-O bonds are not separable from the Ln-N bonds. However, the values of Table 5 indicate an average of mixed type.

5. Discussion

In general, the macroscopic properties, such as increased viscosity and increased glass transition temperatures confirm the model of the atomic structure of the oxynitride glasses [11, 12]. The replacement

Table 5. $Ln_{12.3}Si_{14.0}Al_{12.2}O_{55.1}N_{6.5}$-glasses. Peak positions from corresponding crystalline compounds and from this paper.

$Pair_{ij}$	Corr. Crystalline Compound R [Å]	this paper R[Å]
La-O	2.38	2.37
La-N	2.77	2.77
Gd-O	2.258	
Gd-N	2.648	
Gd-O/N		2.36
Yb-O	2.175	
Yb-N	2.565	
Yb-O/N		2.22

of some oxygen atoms by nitrogen atoms strengthens the amorphous network. The reason for these effects lies in the threefold coordination of nitrogen in the network. The first structural model was given by Mulfinger [13]. In this model, nitrogen is connected to three $Si(O,N)_4$ units. The logical consequence of this view is that all nitrogen atoms are considered to be brigding atoms, i.e. only connected to Si atoms. Indeed, this is a reasonable explanation for the strengthening of the amorphous network. Detailed results concerning Si-(O/N) bonds are provided by the neutron diffraction investigations on $20{\cdot}(Na_2O){\cdot}80(SiO_2)$ containing 0 and 4.4 at% bonded N [14] and $17{\cdot}(Y_2O_3){\cdot}25{\cdot}(Al_2O_3){\cdot}58{\cdot}(SiO_2)$ [15] containing 5at% N. In both cases, a slight shift of the 1.62 Å peak towards higher R-values was reported. A convolution of two subpeaks (Si-O and Si-N) was applied in both papers for the nitrogen containing glasses. The coordination number Z_{NSi} is 2.42 for the Na-Si-O-N glass [14] and 2.86 for the Y-Si-Al-O-N glass. In both cases, the ideal value of 3.0 is not achieved. This means that a certain amount of N atoms is not connected to three Si atoms. Uncertainties in their work, such as a result of the truncation effect can be excluded, due to the value of the maximum scattering vector Q_{max} = 30 Å^{-1}.

Whereas neutron diffraction experiments give good contrast for light elements, X-ray diffraction experiments are imaging the surrounding of heavy elements in Si-Al-O-N glasses. Therefore, X-ray diffraction provides information complementary to that obtained by neutron diffraction. Those bonds of nitrogen which are not connected to Si-atoms can now be explained as non bridging nitrogen atoms. On the one hand, as indicated in section 3 of this paper, they are connected to the network modifier ions, and on the other hand possibly a low amount is kept free, maybe as dangling bonds. The saturation of all nitrogen bonds is a very restrictive criterion which can not be fulfilled easily as in the case of oxygen in the amorphous Si-O network.

Al-N bonds are not detected in ^{27}Al NMR spectroscopy [16 - 18] where glasses of similar composition (Y-Si-Al-O-N, Mg-Si-Al-O-N) have been investigated. Schneider et al. [19], who performed XPS-studies on the system Ca-Si-Al-O-N, confirm the assumption of non bridging nitrogen. Furthermore, they report also that N-atoms avoid connections to Al in aluminosilicate glasses. Their work supports us with valuable information, keeping in mind that it is not possible to establish complete structural information with the analysis of the results of X-ray diffraction experiments.

6. Conclusion

In this paper, the structure of Ln-Si-Al-O-N glasses is treated. Total structure factors and pair correlation functions of certain glasses (Ln = La, Gd, Yb) obtained by X-ray diffraction are presented. These data allow statements concerning the first coordination sphere around the network modifier ions (Ln). A certain amount of nitrogen atoms is considered to be connected to the modifier ions. The aggravating circumstances of the low weighting factors for pairs of light elements did not allow to investigate the coordination spheres of Al or Si atoms.

[1] G. C. Deeley, J. M. Herbert, and N. C. Moore, Powd. Met. **8**, 141 (1961).

[2] J. Weiss and W. A. Kaysser, in: Progress in Nitrogen Ceramics, F. L. Riley (ed.), Martinus Nijhoff Publ., Boston 1983.

[3] H. -J. Kleebe, M. J. Hoffmann, and M. Ruehle, Z. Metallkunde **83**, 610 (1992).

[4] M. J. Hoffmann, Analysis of Microstructural Development and Mechanical Properties orf Si_3N_4-Ceramics, in: Tailoring of Mechanical Properties of Si_3N_4-Ceramics, M. Hoffmann and G. Petzow (eds.), NATO ASI, Series E, Kluwer Academic Press, Dordrecht 1994.

[5] M. Kanamaru, Doctoral Thesis, University of Stuttgart, Germany 1994.

[6] T. E. Faber and J. M. Ziman, Phil. Mag. **11**, 153, (1965).
[7] M. Krämer, M. J. Hoffmann, and G. Petzow, J. Amer. Cer. Soc. **76**, 2778 (1993).
[8] C. N. J. Wagner, J. Non-Cryst. Solids. **31**, 1 (1978).
[9] J. Krogh-Moe, Acta Cryst. **9**, 951 (1956).
[10] D'Ans-Lax, Taschenbuch für Physiker und Chemiker, M. D. Lechner (ed.), Springer Verlag, Berlin 1992.
[11] R. E. Loehman, Tractate on Mat. Sci. and Techn. **28**, 119 (1985).
[12] S. Sakka, Ann. Rev. Mat. Sci **16**, 29 (1986).
[13] H. O. Mulfinger, J. Amer. Cer. Society **49**, 46 (1965).
[14] S. J. Jin, T. Yoko, F. Miyaji, S. Sakka, T. Fukunaga, and M. Misawa, J. Amer. Cer. Soc. **76**, 630 (1993).
[15] S. J. Jin, T. Yoko, F. Miyaji, S. Sakka, T. Fukunaga, and M. Misawa, Philosoph. Mag. B **70**, 191 (1994).
[16] S. Sakka, J. Non-Cryst. Solids. **181**, 215 (1995).
[17] B. S. Aujila, G. Leng-Ward, M. H. Lewis and E. F. W Seymour, Phil. Mag. B **54**, L51 (1986).
[18] W. Hater, W. Müller-Warmuth, B. Steffestun and G. H. Frischat, Glastechn. Ber. **63**, 32 (1990).
[19] M. Schneider, V. A. Gasparov, W. Richter, Deckwerth and C. Rüssel, J. Non-Cryst. Sol. **215**, 201 (1997).