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Neutron diffraction of calcium aluminosilicate glasses and melts

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ABSTRACT

The combination of neutron diffraction with aerodynamic levitation and laser heating, pioneered by Neville Greaves and co-workers about 15 years ago, is an important tool for studying the structure of liquid melts. Since the first work on liquid Al_2O_3 published in 2001, the technique has been largely improved and experiments are now routinely performed at neutron sources, providing interesting structural information on various materials.

In this paper, the structure of glass-forming compounds in the system CaO-Al_2O_3-SiO_2 was measured by applying neutron diffraction with aerodynamic levitation. Results obtained in the liquid state above the melting point and from the glass at room temperatures are presented. Various compositions were studied by increasing the silica content and by changing the ratio CaO/Al_2O_3. As observed using other methods, the main structural changes relate to modification of the Al-O short range order.

1. Introduction

Calcium aluminosilicate, CaO-Al_2O_3-SiO_2 (CAS), glasses and melts are of both technological and scientific interest. In particular their good optical and mechanical properties [1,2] and their refractory nature make them attractive for a wide range of industrial applications, including the production of concrete [3,4]. CAS melts are also the main components of slags produced in furnaces in coal and steel industries. In geosciences, they are of fundamental importance as they form a significant fraction of the composition of geological magmas [5,6,7].

The thermodynamic and dynamic properties of CAS show a strong dependence with the microscopic structure [8]. It is, therefore, important to study in detail the high temperature properties of the melts. In order to study the liquid state, we used neutron diffraction combined with aerodynamic levitation with CO_2 laser heating. This technique was pioneered about 15 years ago by Neville Greaves with teams from the University of Aberystwyth (UK) and the CNRS-CEMHTI in Orléans (France) [9,10].

In this paper, we present results obtained from various CAS glass compositions at both room temperature and in the liquid state. Some of these glass compositions have already been studied by x-ray diffraction at room temperature [11,12] but only a few have been analyzed by neutron diffraction, in particular along the join $R = 1.57$ [11,13]. Here and in the following, the R value is defined as the ratio CaO/Al_2O_3. In the liquid state only the compositions without silica have been studied extensively [14,15]. Our first results obtained for CAS liquids with low silica content have been reported recently in combination with Molecular Dynamics (MD) simulations. [16]. A recent work is also devoted to the study of CAS slags with other compositions [17]. The objective of the present investigation is to complete these previous works by extending the range of CAS compositions studied by neutron diffraction in order to better understand the structure of the glasses and melts, in relation to the observed properties.

2. Technical details

2.1. Sample preparation

The samples were prepared from high purity crystalline $CaCO_3$, Al_2O_3 and SiO_2 powders. The appropriate quantities of powders were melted at 1600 °C for 4 h in a platinum crucible and then quenched to room temperature. The resulting materials were ground and remelted several times in order to ensure a good homogeneity of the glasses. A full description of the sample preparation is described in Neuville *et al.* [18]. The required quantity of material for each sample was then levitated in air using an argon-oxygen (~3%) gas flow and melted by laser heating. Rapid quenching, achieved by switching off

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Table 1
Summary of the structural parameters for all samples. The join composition is indicated as well as the proportion of AlO_5 units in the glasses determined by NMR [19] and for the melts by MD simulations.

	R	T (°C)	ρ_0 ($Å^{-3}$)	$r^{Si\text{-}O}$ ±0.02 Å	$r^{Al\text{-}O}$ ±0.02 Å	$r^{Ca\text{-}O}$ ±0.05 Å	$CN^{Si\text{-}O}$ ±0.5	$CN^{Al\text{-}O}$ ±0.5	AlO_5 units
Ca10.50	0.8	RT	0.0783	1.62	1.75	2.32	4.04	4.09	4.2%
		1800	0.0745	1.65	1.76	2.34	4.05	4.26	/
Ca0.50	1	RT	0.0773	/	1.75	2.35	/	4.05	3.5%
		1700	0.0734	/	1.78	2.32	/	4.20	15%,18% [14,25]
Ca12.44	1	RT	0.0772	1.62	1.76	2.34	4.02	4.07	4.5%
		1650	0.0737	1.65	1.77	2.32	4.05	4.18	10% [33]
Ca19.40	1	RT	0.0773	1.62	1.76	2.34	4.08	4.05	5.8%
		1650	0.0737	1.65	1.77	2.34	4.05	4.10	8% [33]
Ca33.33	1	RT	0.0770	1.62	1.75	2.34	4.05	4.06	8%
		1550	0.0735	1.65	1.77	2.36	4.05	4.23	/
Ca10.35	1.57	RT	0.0758	1.62	1.76	2.35	4.04	4.11	2.6%
		1700	0.0716	1.65	1.77	2.32	4.05	4.15	1.2 [27]
Ca0.25	3	RT	0.0723	/	1.74	2.34	/	4.20	0%
		1900	0.0632	/	1.77	2.32	/	4.20	5%;10% [14,34]
Ca10.23	3	RT	0.0736	1.62	1.75	2.34	4.02	4.05	0%
		1600	0.0684	1.65	1.77	2.30	4.05	4.18	/
Ca16.21	3	RT	0.0744	1.62	1.75	2.34	4.08	4.09	0%
		1600	0.0691	1.65	1.76	2.30	4.04	4.20	/
Ca33.18	3	RT	0.0759	1.62	1.74	2.34	4.05	4.12	7%
		1620	0.0703	1.65	1.76	2.32	4.05	4.19	/

the laser power, resulted in the formation, on cooling, of solid spherical samples with diameters of 4 mm (for the glass measurements) and 2.7 mm (to investigate the liquid state under levitation). The samples studied are listed in Table 1. As in previous works, we employ the notation Ca*x*.*y*, where *x* and *y* refer to the molar concentration of SiO_2 and Al_2O_3, respectively, and 1-*x*-*y* is the CaO molar content. The precise molar compositions of the glasses are reported in Neuville *et al.* [7,19].

2.2. Neutron diffraction

The neutron diffraction (ND) measurements were made using the aerodynamic levitation and laser heating device installed on the D4C diffractometer [20] at the Institut Laue–Langevin (Grenoble, France), as described in ref. [21]. Diffraction measurements were taken for the liquid samples at temperatures above the melting point for all studied compositions, for the empty levitation device inside the diffraction chamber, and for vanadium samples with the aim of making an absolute normalization of the scattering intensity to barns·st^{-1}·$atom^{-1}$. The neutron wavelength and zero-angle shift were determined by fitting the positions of the Bragg peaks obtained from a reference nickel sample. The neutron wavelength used during the experiment was 0.4969 Å, giving a scattering vector Q-range of 0.3–23.6 $Å^{-1}$. The data processing was performed using the program CORRECT [22] which corrects the data for attenuation, background, multiple scattering and inelasticity (Placzek) effects. Since, for various technical reasons, there can be appreciable uncertainties with respect to the relative beam-illuminated volumes of the vanadium samples compared to the CAS samples using the levitation technique, we found it more accurate and reliable to perform an auto-normalization of the scattered intensity from the CAS samples. Specifically, the high-*Q* asymptote of the sample's intensity (after accounting for the Placzek inelasticity effect) was scaled so as to be equal to the theoretical self-scattering that depends only on the known composition of the sample. We then also confirmed that the atomic number density required for accurate

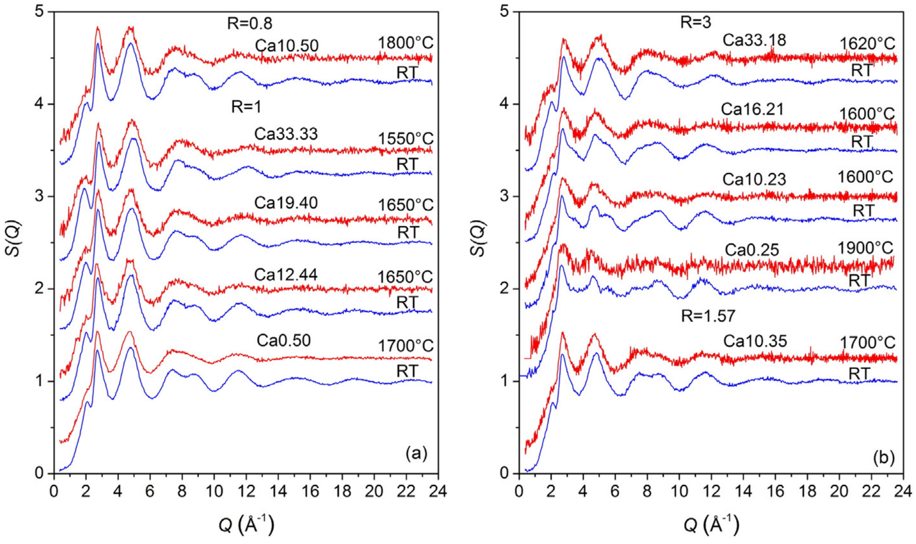

Fig. 1. Total structure factors *S*(Q) of the CAS glasses and liquids for R = 0.8 and 1 (a) and R = 1.57 and 3 (b). The liquid temperatures are reported in the figure.

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