Journal of Non-Crystalline Solids 428 (2015) 121–131

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Analysis of soda-lime glasses using non-negative matrix factor deconvolution of Raman spectra

William Woelffel [a,*], Corinne Claireaux [a], Michael J. Toplis [b], Ekaterina Burov [a], Étienne Barthel [a,d,e], Abhay Shukla [c], Johan Biscaras [c], Marie-Hélène Chopinet [a], Emmanuelle Gouillart [a]

[a] Surface du Verre et Interfaces (UMR 125), CNRS/Saint-Gobain Recherche, 39 quai Lucien Lefranc, 93300 Aubervilliers, France
[b] Institut de Recherche en Astrophysique et Planétologie (UMR 5277), Observatoire Midi-Pyrénées, 14 avenue Belin, Toulouse 31400, France
[c] Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (UMR 7590), CNRS/UPMC, 4 place Jussieu, 75005 Paris, France
[d] Ecole Supérieure de Physique et de Chimie Industrielles de la Ville de Paris (ESPCI) ParisTech, PSL Research University, Sciences et Ingénierie de la Matière Molle, CNRS UMR 7615, 10 rue Vauquelin, F-75231 Paris Cedex 05, France
[e] Sorbonne-Universités, UPMC Univ. Paris 06, SIMM, 10, Rue Vauquelin, F-75231 Paris Cedex 05, France

ARTICLE INFO

Article history:
Received 15 April 2015
Received in revised form 6 August 2015
Accepted 11 August 2015
Available online 28 August 2015

Keywords:
Soda-lime glass;
Raman spectroscopy;
EPMA;
Diffusion;
Chemical analysis;
Deconvolution

ABSTRACT

Novel statistical analysis and machine learning algorithms are proposed for the deconvolution and interpretation of Raman spectra of silicate glasses in the Na_2O–CaO–SiO_2 system. Raman spectra are acquired along diffusion profiles of three pairs of glasses centered around an average composition of 69.9 wt.% SiO_2, 12.7 wt.% CaO, and 16.8 wt.% Na_2O. The shape changes of the Raman spectra across the compositional domain are analyzed using a combination of principal component analysis (PCA) and sparse non-negative matrix factorization (NMF). This procedure yields components accounting for the observed changes, as well as their mixing proportions, without any direct prior assumption as to their actual shape, number or position. These methods are applied separately to the Q band (wavenumbers in the range 850–1400 cm^{-1}), the main band (200–850 cm^{-1}), and to the whole spectra (200–1400 cm^{-1}). Compositional profiles obtained by Electron Probe Micro-Analysis (EPMA) are then used to relate spectral components to structural entities. Spectral components extracted from a Q band analysis and a complete spectral analysis show significant similarities both in terms of shape of the components and their mixing proportions. This result implies a link between Q^n species and the shift of the medium-range network features in the main band of the Raman spectra. To illustrate the possibilities of the method, a linear regression model is used to relate the proportions of spectral components derived from the Raman spectra to chemical composition. This model can be used to determine the composition of different glasses inside the investigated compositional domain with reasonable accuracy.

1. Introduction

Raman spectroscopy is a widely used technique for the study of the structure of silicate glasses and melts [1,2]. Various structural units of the silicate network have Raman-active vibrational modes, and rapid acquisition times enable in situ studies of melt structure at high temperature [3–10] or phase transformations [11]. Furthermore, Raman spectroscopy is appreciated for the fact that it is non-destructive and can be used in fields such as cultural heritage [12–14]. It also has the advantage that the volume excited by the laser is small (~1 μm^3) allowing the study of spatial heterogeneities of composition or structure, e.g. resulting from ionic exchange [15], laser-irradiation [16] or densification following micro-indentation [17,18].

Despite such successes, application of Raman spectroscopy to amorphous silicates is hampered by the fact that there is no simple a priori way to relate the shape of broad Raman bands to specific network vibrations and structures, and that the intensity of a Raman band is not a quantitative measure of species abundance, in contrast to other widely used techniques such as Nuclear Magnetic Resonance (NMR) [19]. A comparison with crystalline structures and the evolution of spectra with chemical composition has been used to interpret the positions of broad Raman bands in terms of structural entities. This approach has been particularly applied to the spectral range 850–1400 cm^{-1}, where silicate tetrahedra surrounded by a variable number of non-bridging oxygens (the Q^n species defined by the NMR community, where n is the number of bridging oxygens) are expected to resonate [20,21]. Indeed, a large body of the silicate literature is devoted to discussions of how to interpret Raman spectra in terms of Q^n species, for different kinds of network modifiers [4,20,21] or in the presence of other network formers [22–25]. At lower wavenumber, silicate glasses also show significant broad intensity in the range (200–850 cm^{-1}) typically referred

---

* Corresponding author at: Surface du Verre et Interfaces (UMR 125), CNRS/Saint-Gobain Recherche, 39 quai Lucien Lefranc, 93300 Aubervilliers, France.
E-mail addresses: william.woelffel@saint-gobain.com (W. Woelffel), corinne.claireaux@saint-gobain.com (C. Claireaux).

http://dx.doi.org/10.1016/j.jnoncrysol.2015.08.016
0022-3093/

to as the main band. These resonances are associated with T–O–T bending (where T is a tetrahedral network forming cation), although the exact relationship to the structural entities that resonate in the high wavenumber Q band (850–1300 cm^{-1}) is not generally considered [26]. Although theoretical models have been used to provide insight into the principal features of Raman spectra of amorphous silicates [27,28] and amorphous silica [29], this approach does not currently have the ability to quantitatively interpret signal shape and intensity of multicomponent glasses. Historically, a common proxy for band shapes consists in fitting Raman spectra with a given number of Gaussians of variable positions, widths, and intensities [13,14,30–32]. Inside the Q band, such Gaussians are attributed to specific Q^n units and environments. Using such an approach, a reasonable correlation has been found in lithium silicates [32] between the ratios of Gaussian bands fitted to Raman spectra, and the ratio of Q^n units determined from ^{29}Si NMR. However, broad and complex band shapes often require the use of a large number of Gaussian components [10,33,34] for a correct fit. Furthermore, Gaussian-fitting methods typically do not impose band positions, which may thus vary between spectra, limiting the interpretation in terms of well defined Q^n units. Finally, even in simple binary silicates the number of Gaussian components required to fit the Raman spectra is greater than the number of potential Q^n species, leading to ambiguity and controversy concerning spectral assignments [6,7,33]. In the light of these difficulties, application of statistical methods has emerged as an alternative approach for the decomposition of spectra into several components (using techniques inspired by those used for blind source separation). Such methods typically make fewer assumptions concerning the shape of partial spectral components, and hence require a smaller number of adjustable parameters than Gaussian-based methods. For example, principal component analysis [35] decomposes a signal into orthogonal components and is one of the most popular methods [36], followed by independent component analysis [37] for statistically-independent signals. Non-negative matrix factorization (NMF) [38] has recently gained attention since it enables a spectroscopic interpretation of the non-negative extracted features. NMF has been used and improved [39] for fluorescence spectroscopy [40], ^{1}H-NMR spectroscopy [41] or hyperspectral imaging [42]. Recent studies [43–46] have applied NMF-inspired techniques, coupled with chemical constraints, to shed light on the speciation of glasses and melts in binary alkali and alkali-earth silicates, an approach that leads to the isolation of spectral components in the Q band that can be assigned to the spectral signature of the different Q^n species.

In this paper, we extend previous work in binary systems [43–46] to the ternary system of sodium and calcium-bearing silicates. Inter-diffusion experiments of melts with different initial compositions are used to generate a range of compositions for which a large number of Raman spectra may be acquired. A novel deconvolution algorithm based on NMF is developed and applied to this comprehensive dataset. The shapes of the different components identified by the algorithm for our ternary system are presented and the correlations between the high-frequency envelope (Q band) and the main band are discussed. A chemical model that relates Raman spectra to chemical composition is proposed and tested against compositions lying outside the training dataset.

2. Experimental methods

2.1. Glasses preparation

Three initial glass compositions were prepared from industrial grade sand, limestone, and sodium carbonate. Reagent grade Na_2SO_4 was used as a fining agent. Small amounts of coloring agents CoO and $FeCr_2O_4$ were added to certain glasses to provide a quick means of identification after diffusion experiments. The different glass compositions are summarized in Table 1. Glasses used for diffusion experiments are centered around an average composition of 69.9 wt.% SiO_2, 12.7 wt.% CaO, and 16.8 wt.% Na_2O, close to common window glass. Trace amounts (0.1 wt.%) of Al_2O_3 and MgO are also present due to the use of industrial grade sand and limestone. Three other test glasses (compositions given in Table 1) were also prepared.

The raw materials were dried at 110 °C for over 24 h, then mixed with a Turbula shaker-mixer. 1-kg batches used to prepare glasses for diffusion experiments were melted in a Pt-Rh Joule-heated crucible at 1450 °C and stirred for 2 h with a Pt-Rh rod. The melts were poured onto an iron plate, air-quenched and annealed at 550 °C for 2 h. The compositions were also checked by electron microprobe (EPMA) on fragments of the resulting glasses, and were found to be homogeneous (standard deviation below 0.2 wt.%).

2.2. Diffusion profiles

20 × 20 × 5 mm slices were cut from previously prepared glasses and one surface (one side) for each glass slice was polished to 40 μm. Slices were stacked so that the lower-density one was on top of the other to limit convection. Densities at 1000 °C were predicted using the model of [47]. The space around glass slices was filled with silica sand to limit liquid movement (see Fig. 1). This setup accommodates thermal expansion while reducing mass transfer acceleration due to flow of the softening glass.

Samples were introduced in a preheated muffle furnace at 1000 °C for 1 h. This temperature-time range was selected such that compositional profiles generated by diffusion were on the order of a couple of millimeters. At the end of the experiment the samples were quenched in air to avoid crystallization. This quench typically fractured the glass. Samples were subsequently annealed for 1 h at 600 °C and cooled inside the furnace overnight. Slices of the glass stack were cut perpendicular to the initial interface, the presence of coloring agents helping to identify the region of variable composition and/or avoid areas where complex convection had taken place. Samples were polished to optical quality before further analysis. Each diffusion couple is named after its two endmember glasses, e.g. the diffusion sample extracted from S glass (silica-rich) over C glass (lime-rich) is referred to as SC, and allows for measurements over a continuous range of compositions from one endmember to the other.

Composition measurements along the diffusion profiles were made on a Cameca SX 100 EPMA with a 15 keV, 1 nA electron beam during 1 min for Si and Ca analysis and 3 × 20 s counting time for Na analysis.

2.3. Raman spectroscopy

Raman spectra along the diffusion profiles were collected with a confocal Jobin-Yvon Xplora system in back-scatter geometry, focusing a 532 nm laser on the sample through a × 100 microscope objective. Nominal power of the laser is about 15 mW. The spectra were collected with 3 acquisitions of 1 min each.

Raman spectra of the test glasses were collected with a confocal ThermoFischer DXR system in back-scatter geometry, using a 532 nm

Table 1
Glasses compositions from X-ray fluorescence analysis in wt.%. Standard deviations from repeated measurements on a standard glass are as follows: 0.02 wt.% CaO, 0.07 wt.% Na_2O, 0.01 wt.% Al_2O_3, 0.02 wt.% MgO, 0.002 wt.% Fe_2O_3, 0.0002 wt.% Cr_2O_3.

Name	SiO_2	CaO	Na_2O	Al_2O_3	MgO	Fe_2O_3	Cr_2O_3
S	75.4	10.1	14.2	0.1	0.1	0.0	0.0
C	67.6	17.9	14.0	0.1	0.1	0.0	0.0
N	66.7	10.1	22.3	0.2	0.2	0.1	0.1
TEST1	73.4	10.4	15.6	0.0	0.0	0.0	0.0
TEST2	66.1	16.3	17.2	0.0	0.0	0.0	0.0
TEST3	72.7	13.7	13.3	0.0	0.0	0.0	0.0