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Development and Application of a Rapid Scan Technique for Emissivity Measurements of Cooled-Down Molten Materials †

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Abstract: The real-time observation of molten materials and their cooling to solid state is of importance for many industrial processes. In this work, we describe additional possibilities obtained by the implementation of a Rapid Scan technique on an FT-IR emissometer designed to allow the observation of materials under extreme temperature conditions. The possibility of following liquid-to-solid state phase transition mechanisms through time-resolved emissivity will be illustrated. This new methodology presents interesting possibilities for the study of structural transformations through the real-time monitoring of the dielectric function and true sample temperature of the experimental emissivity spectra acquired every 50 ms under free cooling conditions.

Keywords: real-time FT-IR; solidification process; high temperature

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1. Introduction

The observation of fast-occurring phenomena is of utter importance and interest for high-temperature processes. Transient or metastable phase formation can occur during cooling from the molten state, which is a big concern for large-scale industrial production [1]. In order to allow exploration of the liquid region and the mechanisms driving phase change or formation, an out-of-equilibrium study is mandatory.

Various techniques have implemented new methods for in situ probing of the structural modifications occurring during cooling from liquid states [2–4]. In this paper, we describe the potentialities of the implementation of a Rapid Scan feature on an FT-IR emissometer built to perform measurements of oxides at extreme temperatures.

The originality and versatility of the described setup will be shown through example measurements performed consecutively at different cooling rates. Materials with the $SrAl_2Si_2O_8$ composition have been chosen to illustrate the possibility of controlling the cooling rate, as it has a high impact on the final structure created in the solid form, and to determine the cooling speed range in which the same polymorph is found. Indeed, this compound has already been reported for its ability to form different crystalline phases or even glass depending on the cooling rate [5]. Thus, a more precise characterization by monitoring the impact of this parameter on the final structure is of great interest.

2. Materials and Methods

A circular pellet was used as a sample for this study. Its production was realized in the laboratory using the method illustrated in [5] to obtain a glass, which was then crushed and compressed with a hydraulic press operating at 8 tons.

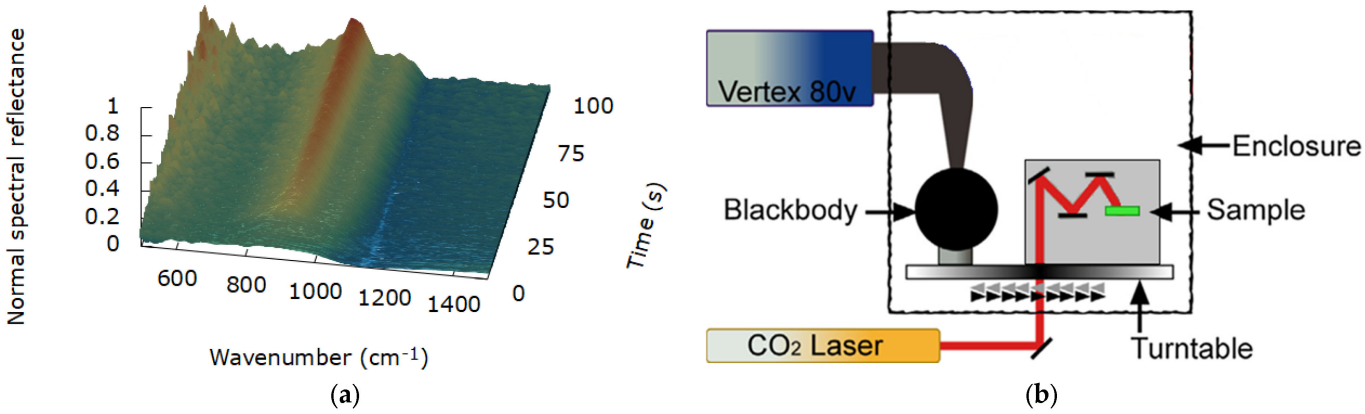
The experimental setup as well as the method of data acquisition and analysis has already been described in detail [6], so only a brief description will be provided. Data are acquired through heat flux measurements coming from the sample and a blackbody furnace. Infrared emittance spectra are computed from that data, after proper background correction, and the real-time temperature of the sample is obtained through the use of the Christiansen point method [7]. Then, spectra are converted from emittance to reflectance. The advantages of this technique are as follows:

- Laser heating allows the control of the starting temperature and the cooling rate;
- Chemical contamination is avoided as the liquid sample is self-contained;
- The probed volume is very limited such that the temperature gradient is minimal.

The data acquisition procedure is either free cooling by the complete shutdown of the heating laser after reaching the molten state, or the progressive lowering of the laser power to produce slower cooling rates.

3. Results

The reflectance spectra obtained from the free cooling of $SrAl_2Si_2O_8$ are illustrated in Figure 1a. Figure 1b presents a scheme of the experimental setup used.



(**a**) (**b**)

Figure 1. (**a**) Normal spectral emittance of $SrAl_2Si_2O_8$ recorded during free cooling from molten state (2500 K). (**b**) Scheme of the experimental setup. A CO_2 laser is used for heating. The turntable allows the acquisition of thermal fluxes from the blackbody, the background and the sample.

The free cooling curve obtained is illustrated in Figure 2a, together with other slower curves, corresponding to additional iterations of the method with the same starting conditions. For those experiments, we used a constant decrease in laser power measured in laser knob steps per minute (60 BPM = 1 step/s). Under these conditions, the maximum cooling speed obtained in free cooling conditions was 835 K/s and almost 87 K/s at 30 BPM (slowest cooling rate sampled).

Figure 2a shows that the process of crystallization takes place independent of the cooling speed at a temperature near 1857 K (blue dashed line), observed as a recoalescence plateau in the free cooling case. As expected, one can see that the undercooling region heavily depends on the cooling speed. It is also observed that the plateau temperature increases as the cooling rate decreases. This could be related to the formation of metastable phases during solidification at faster cooling speeds, as previously reported for polypropylene [8].

The goal of this infrared technique was to analyze the vibrational modes of the material as a function of its temperature and cooling rate. Information on these modes was obtained from fitting the reflectance data to a phenomenological model of the dielectric function, related to the optical response with Fresnel's equations [6]. In particular, it was interesting to perform this data fitting at the same temperature in different cooling conditions. As an example, two spectra measured at 1000 K in free cooling and 30 BPM speed conditions have been selected and fitted.

Figure 2a also illustrates the position of the spectra in the cooling curves (black dashed line). They clearly belong to the solid state. Figure 2b presents the two reflectance spectra, obtained by merging mid- and far-infrared spectra. Figure 2c,d show the imaginary dielectric functions obtained from fitting the free cooling spectrum and the 30 BPM one, respectively.

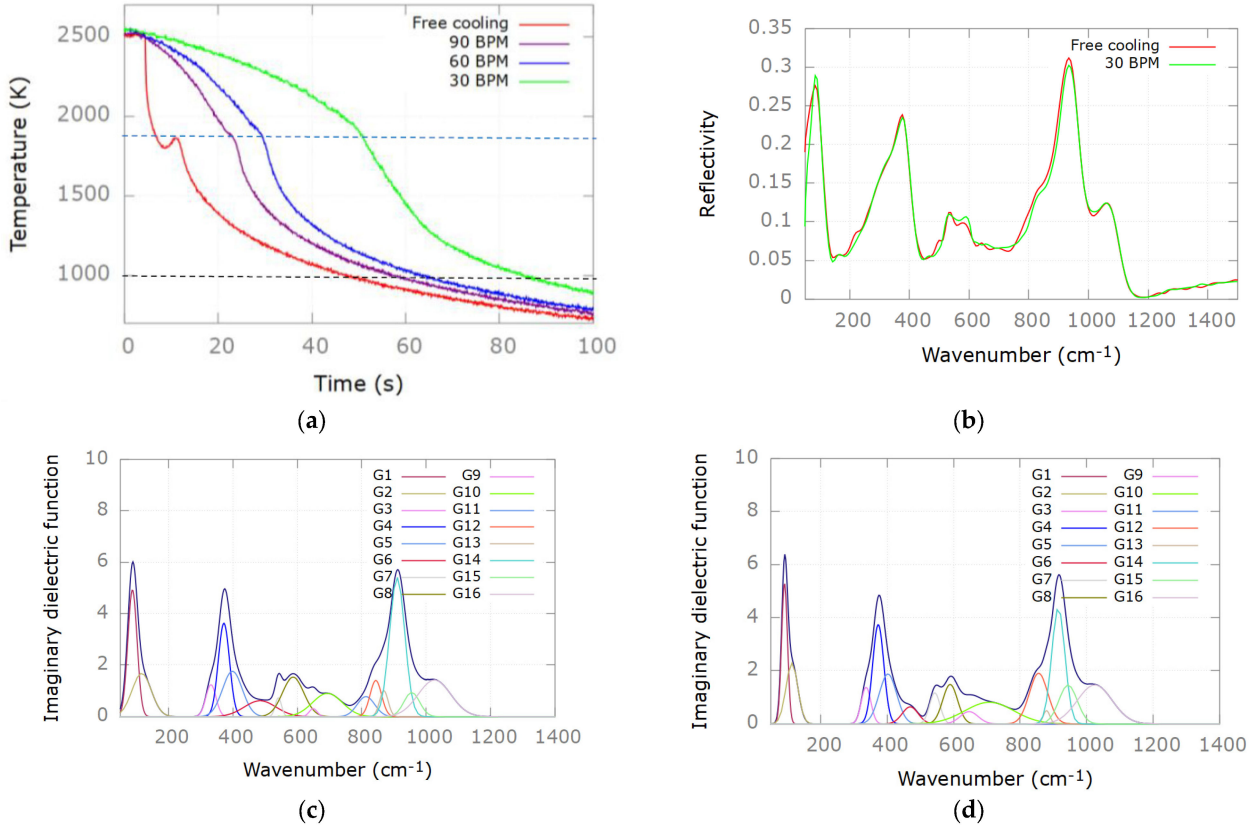


Figure 2. (**a**) Cooling curves corresponding to different experiments performed on the same sample. The crystallization temperature of 1857 K is represented by a blue line. The temperature of the extracted spectra (black line); (**b**) Reflectivity spectrum extracted from free cooling conditions and 30 BPM; (**c**) Imaginary dielectric function obtained from the fitting of the free cooling spectrum at 1000 K; (**d**) Imaginary dielectric function obtained from the fitting of the 30 BPM cooling spectrum at 1000 K.

Despite their overall similarity, the spectra present some clear changes in their imaginary dielectric functions. These changes and the structural information they provide will be discussed in the next section.

4. Discussion

The fitted dielectric functions show differences at the same temperatures, indicating that the cooling speed has an impact on the final structure of the solid. However, XRD analysis of the samples at all cooling rates reveal that they all crystallized in the monoclinic form. Thus, differences in the vibrational response are related to subtle variations in the intermediate range ordering in the structure. Indeed, it is well known that the Al/Si ordering in the tetrahedral site of aluminosilicate network depends on thermal history [9,10].

The spectra were fitted with a dielectric function model and with 16 Gaussian components Gx; additional details can be found in [6,11]. A full assignment of the components will not be discussed here, as the focus of this preliminary work is on the importance of the structural changes, mainly observed in G10, G12 and G14. These bands are indeed assigned, respectively, to the Si-O-Al band and to the tetrahedral stretching modes of Q^4_{4Al} and Q^4_{2Al} SiO_4 units involving different numbers of Si-O-Al and Si-O-Si bonds.

The increase in area of G10 and G12 and consequent decrease in G14 in Figure 2d show a process of replacement of Si-O-Si by Si-O-Al (and therefore, Al-O-Al, corresponding to G11) in the network at slower cooling rates. This process reflects the ordering of the network and the replacement observed is energetically more favorable, in agreement with the Lowenstein rule reported for aluminosilicates [12].

5. Conclusions

Time-resolved high-temperature infrared measurements allowed us to study the Al/Si ordering process in a fixed network as a function of cooling rate. This is a clear illustration of the potentialities of the method and its sensitivity to reveal small structural changes.

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References

1. Ulrich, J.; Frohberg, P. Problems, potentials and future of industrial crystallization. *Front. Chem. Sci. Eng.* **2013**, *7*, 1–8. [CrossRef]
2. Hennet, L.; Pozdnyakova, I.; Bytchkov, A.; Drewitt, J.W.E.; Kozaily, J.; Leydier, M.; Brassamin, S.; Zanghi, D.; Fischer, H.E.; Greaves, G.N.; et al. Application of time resolved x-ray diffraction to study the solidification of glass-forming melts. *High Temp.-High Press.* **2011**, *40*, 263–270.
3. Florian, P.; Massiot, D.; Poe, B.; Farnan, I.; Coutures, J.P. A time resolved ^{27}Al NMR study of the cooling process of liquid alumina from 2450 °C to crystallization. *Solid State Nucl. Magn. Reson.* **1995**, *5*, 233–238. [CrossRef] [PubMed]
4. Kühnel, M.; Fernández, J.M.; Tejeda, G.; Kalinin, A.; Montero, S.; Grisenti, R.E. Time-resolved study of crystallization in deeply cooled liquid parahydrogen. *Phys. Rev. Lett.* **2011**, *106*, 245301. [CrossRef] [PubMed]
5. Saghir, K.A.; Chenu, S.; Veron, E.; Fayon, F.; Suchomel, M.; Genevois, C.; Porcher, F.; Matzen, G.; Massiot, D.; Allix, M. Transparency through Structural Disorder: A New Concept for Innovative Transparent Ceramics. *Chem. Mat.* **2015**, *27*, 508–514. [CrossRef]
6. Ermini, I.M.; Cosson, L.; Fayon, F.; Zanghi, D.; Tardivat, C.; Meneses, D.D.S. Real time FT-IR observation of materials during their cooling from molten state. *Infrared Phys. Technol.* **2022**, *127*, 104424. [CrossRef]
7. Rousseau, B.; Brun, J.F.; Meneses, D.D.S.; Echegut, P. Temperature measurement: Christiansen wavelength and blackbody reference. *Int. J. Thermophys.* **2005**, *26*, 1277–1286. [CrossRef]
8. Gradys, A.; Sajkiewicz, P.; Minakov, A.A.; Adamovsky, S.; Schick, C.; Hashimoto, T.; Saijo, K. Crystallization of polypropylene at various cooling rates. *Mater. Sci. Eng. A* **2005**, *413*, 442–446. [CrossRef]
9. Carpenter, M.A. Equillibrium thermodynamics of Al/Si ordering in anorthite. *Phys. Chem. Miner.* **1992**, *19*, 1–24. [CrossRef]
10. Benna, P.; Tribaudino, M.; Bruno, E. Al-Si ordering in Sr-feldspar $SrAl_2Si_2O_8$–IR, TEM and single-crystal XRD evidences. *Phys. Chem. Miner.* **1995**, *22*, 343–350. [CrossRef]
11. Mabrouk, A.; Meneses, D.D.S.; Pellerin, N.; Véron, E.; Genevois, C.; Ory, S.; Vaills, Y. Effects of boron on structure of lanthanum and sodium aluminoborosilicate glasses studied by X-ray diffraction, transmission electron microscopy and infrared spectrometry. *J. Non-Cryst. Solids* **2019**, *503–504*, 69–77. [CrossRef]
12. Lowenstein, W. The distribution of aluminum in the tetrahedra of silicates and aluminates. *Am. Mineral.* **1954**, *39*, 92.