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Thermochimica Acta 269/270 (1995) 453–456

thermochimica
acta

The effect of disorder on the thermodynamic parameters of silicate glasses[☆]

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Received 16 September 1994; accepted 2 May 1995

Abstract

The temperature dependences of the heat capacities of SiO_2 and $CaSiO_3$ before and after vitrification are studied experimentally in the range 300–1100 K in order to analyse the role of structural disorder. The results for SiO_2 are discussed in terms of a simple cluster approximation.

Keywords: Disorder; Glass; Silicate; Vitrification

1. Introduction

Thermal analysis and calorimetry are powerful experimental methods for studying the phase transitions and thermodynamic parameters of solids. However, in order to specify the solid local structure and the corresponding vibrational density of states (VDOS) one needs other methods to complete thermal analysis data [1, 2]. Combined with X-ray diffraction, Raman and infrared (IR) spectroscopy, thermal analysis can become important in analysing order–disorder transformations and the effect of disorder on the vibrational and thermodynamical parameters of solids. However, in contrast to X-ray diffraction and vibrational spectroscopy data [3, 4], it is difficult to model thermal parameters of disordered solids on the basis of microscopic concepts and very few studies have addressed such problems [5, 6]. The aim of the present communication is to report on the changes arising in the temperature dependence of

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[☆] Presented at the 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 11–16 September 1994.

SSDI 0040-6031(95)02520-0

the heat capacity of quartz and wollastonite ($CaSiO_3$) as a result of vitrification. The observed dependency for quartz is discussed in terms of a simple VDOS approximation.

2. Experimental

Four types of samples were studied throughout this work: quartz (two-component silicate) and wollastonite, $CaSiO_3$ (three-component silicate), both in crystalline and vitreous phases. As crystalline and vitreous samples of SiO_2, we used respectively synthetic quartz crystals of a very high quality factor for piezoelectric resonators (Interquartz Co, Bulgaria) and highly optically transparent silica glass (Suprasil I). The crystalline $CaSiO_3$ sample used in this study was natural wollastonite (space-group symmetry $P\bar{1}$), while the vitreous sample of $CaSiO_3$ was prepared by melting the crystalline phase at 1600°C with subsequent quenching. No impurities were detected in the samples by TEM and X-ray powder diffraction.

The temperature dependences of the heat capacities, $C(T)$, of the samples (milled to micrometer size), were measured by a DSC-1500 Stanton-Redcroft calorimeter with a computerized data acquisition system in the temperature range 300–1100 K with a heating rate of 10 K min^{-1}. Fig. 1 shows the temperature dependence of the ratio

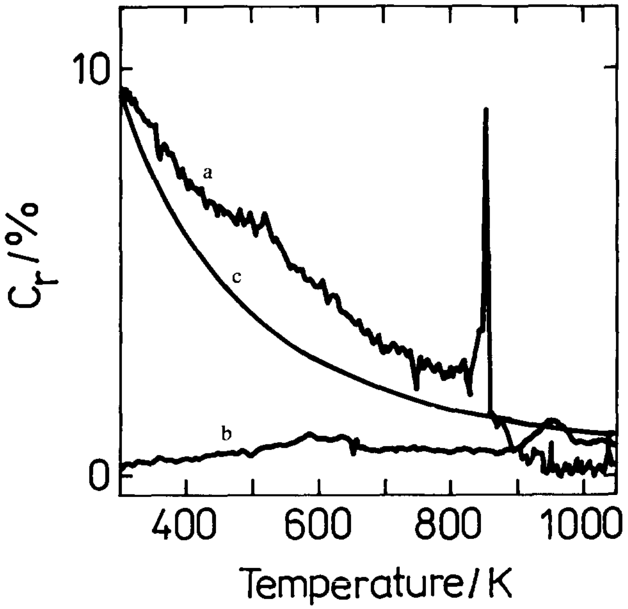

Fig. 1. Temperature dependence of the ratio $C_r = (C_{cr} - C_{vit})/C_{cr}$ for SiO_2 (curve a), $CaSiO_3$ (curve b) and the theoretical curve for SiO_2 (c), where C_{cr} and C_{vit} are the heat capacities of the crystalline and vitreous phases, respectively.

$C_r = (C_{cr} - C_{vit})/C_{cr}$ for SiO_2 (curve a) and for $CaSiO_3$ (curve b), where C_{cr} and C_{vit} are the heat capacities of the crystalline and the vitreous phases, respectively.

2.1. Modelling

The effect of structural disorder on the heat capacity of SiO_2 was modelled in a simple cluster approximation [7]. For this purpose, first the VDOS of Si_2O_7 dimers with structural disorder was calculated in the "corresponding system approximation" (for details see Ref. [17]), and then the result was integrated over the frequency range of interest. As an illustration, Fig. 2 presents VDOS of the dimer without (thin line) and with (bold line) disorder, the random disorder parameter in the latter case being equal to 230 cm^{-1}. The temperature dependence of the ratio C_r for SiO_2 calculated in this approximation is shown in Fig. 1 by curve c. The value of the random disorder parameter in the calculations was specified in such a way that the theoretical and experimental curves for SiO_2 coincide at 300 K. No other parameter adjustments were used in calculating the heat capacity.

3. Discussion

The main results reported in this work can be summarized as follows.

(i) The structural disorder influences differently the heat capacities of SiO_2 and $CaSiO_3$ in the temperature range 300–1100 K. This is evident from the behaviour of the characteristic ratio C_r for the two materials (Fig. 1). Whereas for SiO_2 this ratio drops, non-linearly with temperature from about 10% to zero, for $CaSiO_3$ it remains close to zero within experimental accuracy in the temperature range studied. The reason for

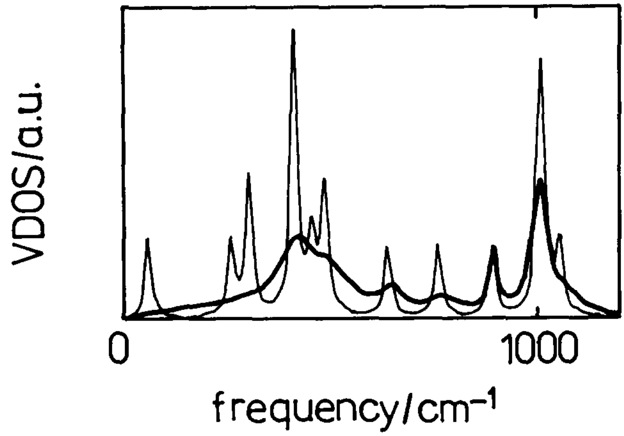

Fig. 2. Vibrational density of states (VDOS) of dimer without disorder (thin line) and dimer with disorder (bold line).

such behaviour in the latter case is the presence of a second type of cation in wollastonite, which "eliminates" to a great extent the effect of structural disorder in this material due to strong Ca–O–Si interactions.

(ii) The observed values and the general behaviour of the temperature dependence of the heat capacity of SiO_2, including the endothermal peak in the crystalline phase, which corresponds to the well-known $\alpha \rightarrow \beta$ phase transition in this material, are in good agreement with data reported in the literature [8]. According to these data, the ratio C_r, as defined by us, is positive below the temperature of the $\alpha \rightarrow \beta$ phase transition and decreases on increasing the temperature, just as observed experimentally (curve a, Fig. 1). However, at temperatures above the transition temperature one can hardly measure C_r since its value becomes of the order of the experimental accuracy.

(iii) The temperature dependence of the ratio C_r for SiO_2 can be successfully described in terms of simple cluster approximations to VDOS (Fig. 2). As such approximations do not take into account phase transitions in the cluster structure, the peak in curve a (Fig. 1) is not reproduced on the theoretical curve c. One may improve considerably the agreement with the experimental curve by using more precise approximations to calculate VDOS of vitreous SiO_2

Acknowledgement

Financial support of this work by the National Science Fund of the Bulgarian Ministry of Science and Technologies under contract SR F 213 is gratefully acknowledged.

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