Vaporization and physicochemical properties of glasses and melts of the CaO-TiO_2-SiO_2 system

Valentina Stolyarova, Kirill Zapko, Dmitrii Zhegalin, Sergei Stolyar
Institute of Silicate Chemistry of the Russian Academy of Sciences, ul. Odoevskogo 24 korp. 2, 199155 Sankt Petersburg, Russia

The Knudsen effusion mass spectrometric method was used to study the vaporization processes and thermodynamic properties of the glasses and melts in the CaO- SiO_2-TiO_2 system at the temperature 1960 K. Activities of SiO_2 system in this system were obtained. The CaO and TiO_2 activitites were calculated using the McKay method. Isoactivities lines of components in the melts were presented. The Gibbs energy of formation of glasses and melts of the CaO- SiO_2-TiO_2 system is calculated. Thermal expansion of the glasses in the system was studied in the glasses of the CaO- SiO_2-TiO_2 system in the temperature range 900- 1100 K using the silica delatometer-viscosimeter. Correlation between thermal expansion data and thermodynamic properties of glasses and melts in the CaO- SiO_2-TiO_2 system was discussed.

Introduction

The CaO- SiO_2-TiO_2 system is one of the main systems of glass forming industry for the production titanium glasses. Thermodynamic and thermal expension data of this system are the most important for the consideration of various technological processes. Phase diagram of the CaO-TiO_2-SiO_2 system have been considered in detail in [1] using microprobe analysis (beam size 200 μm). Sphene ($CaTiSiO_5$) with the melting point of 1655 K was the only ternary compound identified in the condensed phase of this system. Glass-forming region of the CaO-TiO_2-SiO_2 system is situated in the concentration range (mole %): CaO-25-55, SiO_2-45-75, TiO_2-5-35 [2]. Physicochemical properties of glasses in the CaO-TiO_2-SiO_2 system are summarized also in [2]. The main vaporization processes for the individual oxides formed the CaO-TiO_2-SiO_2 system at the temperatures higher than 1700 K are the following [3] :

$$[SiO_2] = (SiO) + \tfrac{1}{2} (O_2), \quad (1)$$

$$[SiO_2] = (SiO_2), \quad (2)$$

$$[CaO] = (Ca) + \tfrac{1}{2} (O_2), \quad (3)$$

$$2(CaO) = 2(Ca) + (O_2), \quad (4)$$

$$[TiO_2] = (TiO_2), \quad (5)$$

$$[TiO_2] = (TiO) + \tfrac{1}{2} (O_2). \quad (6)$$

(Square brackets [ ] correspond to condensed phase and parentheses ( ) to the gaseous phase). Formation of the gaseous molecule $CaTiO_3$ was found over calcium titanate at high temperatures also by the Knudsen effusion mass spectrometric method [4]. High temperature mass spectrometric study of some samples the CaO-TiO_2-SiO_2 system was carried out in [5]. Various types of deviations from the ideality of the SiO_2 activities were observed in this system in the concentration range with the content of CaO:SiO_2= 0.6 and 16 mole % TiO_2.

In the present study the Knudsen effusion mass spectrometric method was used to continue of the investigation of the vaporization processes and activities of components in the CaO-TiO_2-SiO_2 system.

Experimental

This study was carried out on a magnetic mass spectrometer MS 1301, developed and produced by the Institute of Analytical Instrument Manufactures (USSR) for high temperature studies [3] according to the traditional approach.

The purpose of the experimental apparatus of this type is to produce a molecular beam characteristic of the vapour under investigation, to produce ions which reflect the true composition of the molecular beam, and finally to resolve these ions into their various mass components to enable a quantitative study of each species in the vapour from the sample. The three distinct parts of the experimental set-up are: (1) the molecular beam source, (2) the ion source, and (3) mass spectrometer. The general idea of the technique is based on the combination of : (1) a source of neutral vapour species, to be identified, which can be heated to the appropriate temperature and from which a representative vapour sample can be withdrawn continuously; (2) a method of identification of the neutral molecules through ionization by electron impact and mass analysis of the positive ions formed. This procedure allows the following main advantages of the Knudsen effusion mass spectrometric method such as the identification of the composition and the determination of the partial pressures of species of vapour phase over the sample studied as a function of the vaporization temperature and time. The main features of the mass spectrometer used are the following: the mass range was 1000 u (m/z) and resolution was 600. Magnetic statistic mass analyzer with the radius of the central trajectory 300 mm and the deflection angle in the homogeneous magnetic field equal $90\ ^{o}$ was used in mass spectrometer MS 1301. Mass analyzer provided with the resolution ability 600 on the level 10 % intensity of the lines in mass spectra in the mass range 2-500 mass units at the accelerated voltage 3 kV at the width of the exit slit equal 1 mm and at the term that the scattered energy of ions which leave the ion source did not exceed ± (0,5-1,0) electron volt. The high temperature Knudsen effusion assembly was situated in such a way that it allowed a perpendicular molecular beam from the Knudsen effusion cell to cross the electron beam in the ion source. The mass spectrometer was separated by a moving shutter from the Knudsen effusion cell. By closing the shutter, the background peaks in the mass spectrometer could be followed, which in turn, enabled the correction of the experimental data. Two molybdenum effusion cells were put into molybdenum block and heated by electron bombardment. The temperature was measured by one optical pyrometer. Vaporization of the samples (about 15-20 mg) was carried out in vacuum from the effusion cells with the ratio of the effusion orifice to the vaporization surface of 1:100. The vaporizer had a special transmission mechanism, which allowed the same block to be used in two effusion cells simultaneously and to study two different samples in two different cells during the same experiment. Molecular beam of vapour effused from the Knudsen cell as a result of vaporization was ionized in the ion-source region of mass spectrometer by electron bombardment. The ions were then accelerated and their masses analyzed. For the identification of the ions and their correlation with the corresponding molecular precursors, their mass-to-charge ratio, isotopic abundance distribution and intensity profile in the molecular beam were measured. Experiments were carried out at the ionization energy 70 eV and current of ionizing electrons 1 mA. Vacuum in the ionization region was about 10^{-7} mm Hg.

Results and discussion

The samples of the system studied were prepared as have been described in [5]. Thermodynamic data of the glasses and melts of the CaO-TiO_2-SiO_2 system in the present study were obtained by the same experimental approach as in [5]. These values are given in Table 1. Thermal expansion coefficients in the glasses of the CaO- SiO_2-TiO_2 system in the temperature range 900-1100 K were studied using the silica delatometer-viscosimeter according to the procedure described in [6]. The data obtained are presented in Table 2. Comparison of the values of Gibbs energy, Table 1, with the data of thermal expansion coefficient, Table 2, in glass-forming region of the CaO-TiO_2-SiO_2 system studied allows to conclude that in the frame of experimental accuracy the correlation between constant values is observed. This phenomena reflects the features of glass structure of the CaO-TiO_2-SiO_2 system in the concentration range studied.

Table 1. The component activities and Gibbs energy in the melts of the CaO-TiO_2-SiO_2 at the temperature (1981±22) K.

Composition of melt, mole %			Activities of component			Gibbs energy, kcal/mole
CaO	TiO_2	SiO_2	CaO	TiO_2	SiO_2	
34	22	44	0.31	0.11	0.85	- 3.8
42	29	29	0.36	0.23	0.75	- 4.4
47	32	21	0.39	0.28	0.60	-3.8
51	34	15	0.44	0.33	0.50	-4.5
44	19	37	0.31	0.15	0.65	-4.1
54	23	23	0.36	0.21	0.45	-4.3
58	25	17	0.39	0.24	0.35	-4.3
62	27	11	0.44	0.26	0.25	-4.0
Average value:						-4.2±0.2

The existence of the immiscibility region in the CaO-TiO_2-SiO_2 system [2] may be one of the reasons of the positive deviations from the ideality of the SiO_2 activities. Results of the present study illustrated the fact that the addition of CaO to the samples of the CaO-TiO_2-SiO_2 system decreased the SiO_2 activities and the addition of TiO_2 increased these values.

Table 2. Thermal expansion coefficients and glass transition temperature (T_g) of glasses in the CaO-TiO_2-SiO_2 system.

Composition of glass, mole %			Thermal expansion coefficient, (1/K)•10^6	T_g (° C)
CaO	TiO_2	SiO_2		
40	42	18	10.0	770
40	36	24	8.2	620
50	35	15	11.0	780
50	30	20	9.0	760

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