Experimental Study of Perovskite Evaporation from Knudsen Cell

Sergey I Shornikov[1], **Oleg I Yakovlev**[1], **Marina A Ivanova**[1,2], **Mariya S Minaeva**[3]

[1]Vernadsky Institute of Geochemistry & Analytical Chemistry of RAS, Kosygin st., 19, Moscow, 119991, e-mail: sergey.shornikov@gmail.com, yakovlev@geokhi.ru;

[2]National Museum of Natural History, Smithsonian Institution, Washington, DC 20560, e-mail: ivanovama@si.edu;

[3]NVIDIA Ltd, Dvintsev st., 12, Moscow, 127018, e-mail: mshornikova@nvidia.com.
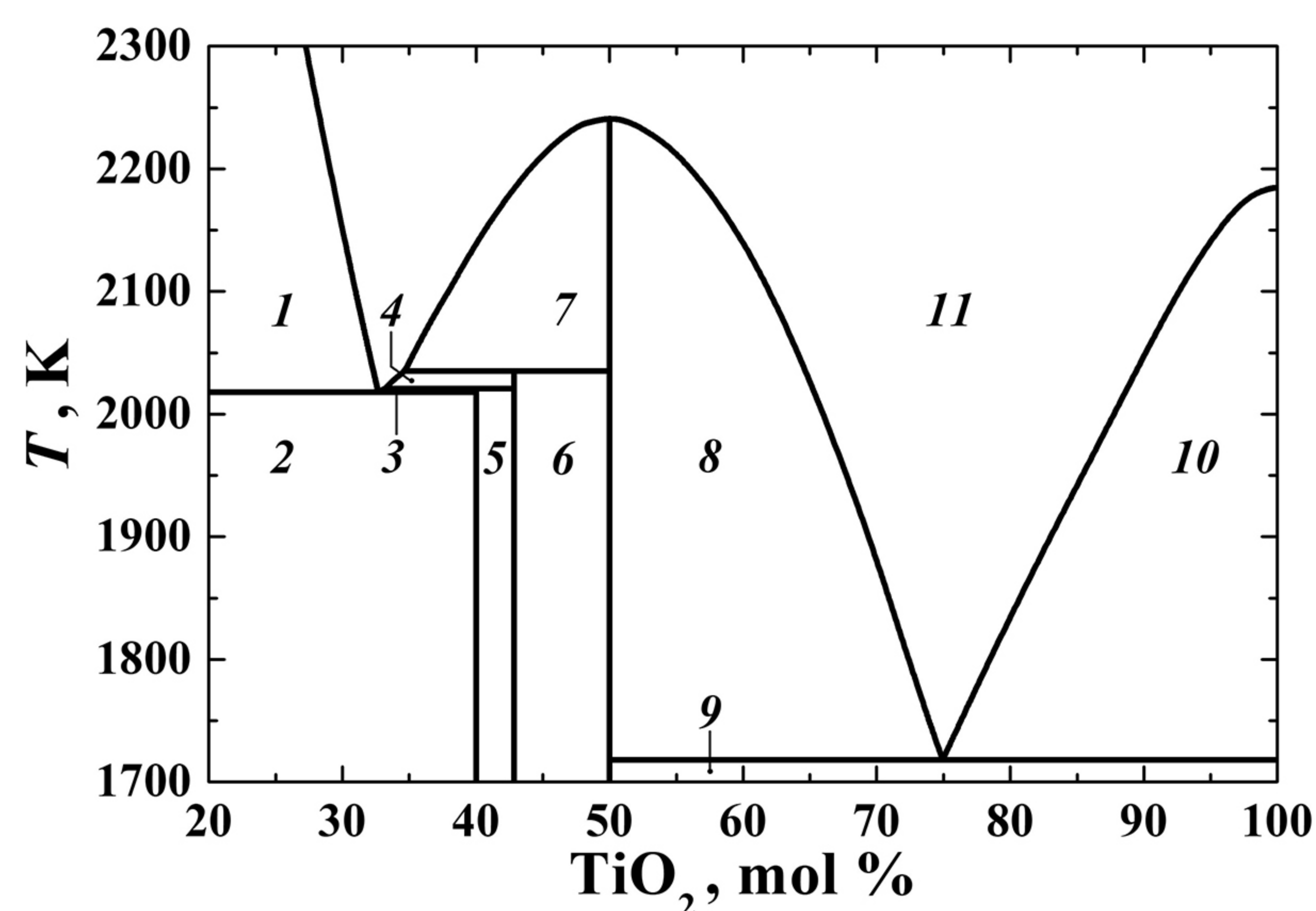
Fig. 1. The phase diagram of the CaO–TiO₂ system [2]: *1* – CaO + liquid; *2* – CaO + Ca₃Ti₂O₇; *3* – Ca₃Ti₂O₇ + liquid; *4* – Ca₄Ti₃O₁₀ + liquid; *5* – Ca₃Ti₂O₇ + Ca₄Ti₃O₁₀; *6* – Ca₄Ti₃O₁₀ + CaTiO₃; *7, 8* – CaTiO₃ + liquid; *9* – CaTiO₃ + TiO₂; *10* – TiO₂ + liquid; *11* – liquid.

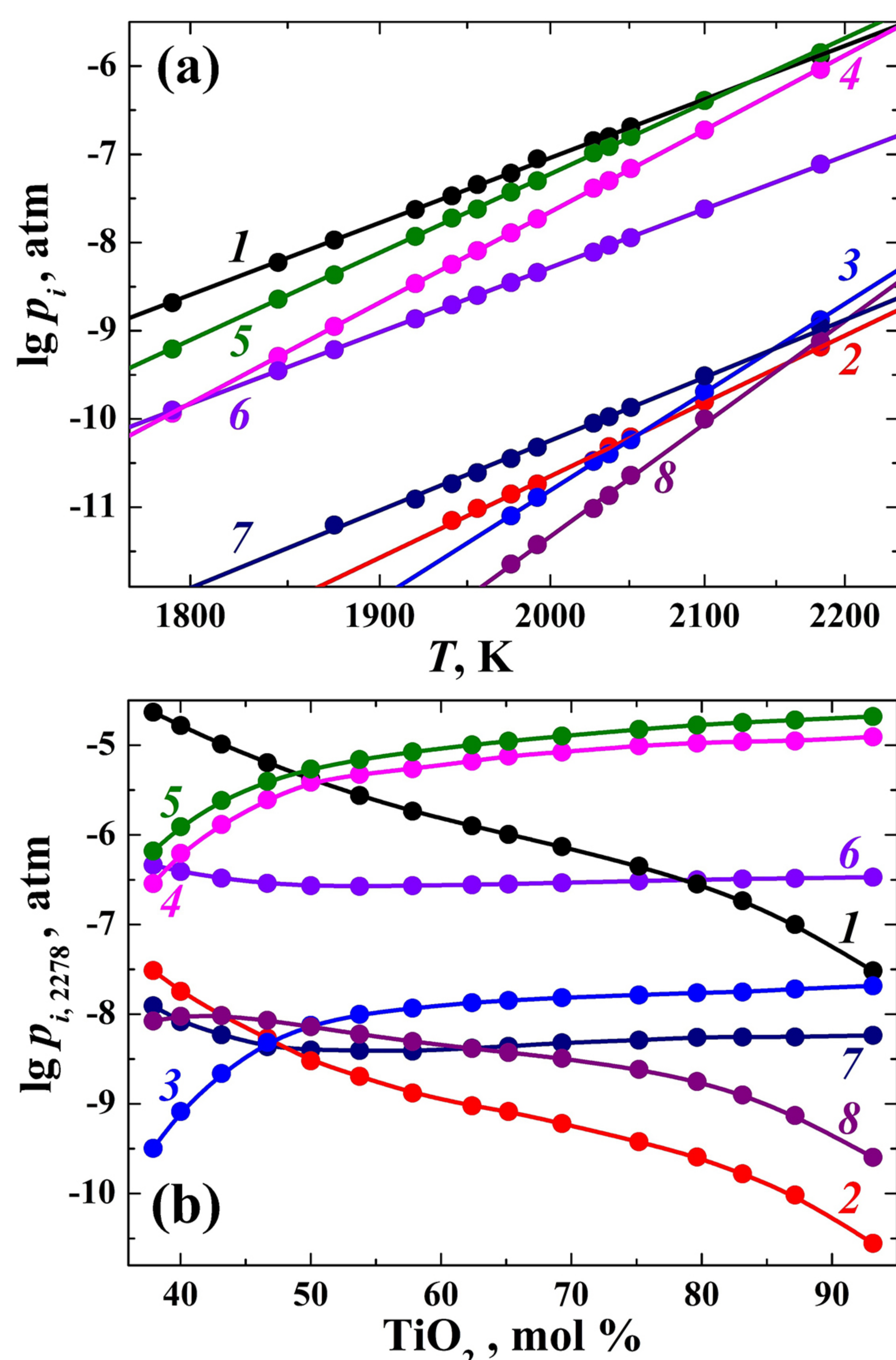
Fig. 2. The partial pressure values of vapor species over perovskite (a) and over the CaO–TiO₂ melts at 2278 K (b): *1* – Ca, *2* – CaO, *3* – Ti, *4* – TiO, *5* – TiO₂, *6* – O, *7* – O₂, *8* – CaTiO₃.

Introduction: Calcium titanate $CaTiO_3$ (perovskite) – a relatively rare mineral, is of particular interest for cosmochemical studies as a mineral of refractory Ca–Al–inclusions (CAIs) found in carbonaceous chondrites. Perovskite is one of the first condensates of the Solar System and the earliest mineral with unusual isotopic chatacteristics [1]. In addition to the perovskite, the existence of two titanates of calcium – $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$, which are melted incongruently (Fig. 1), were established in the CaO–TiO₂ system.

It is believed that perovskite is a polygenic material that combines a relict substance formed in a shell in the inner part of supernova stars, a condensation product from a high-tenperature gas, and a crystallization product of a silicate melt [3, 4]. Therefore, experimental information on evaporation processes and thermodynamic properties of perovskite is very important for understanding of their formation in CAIs.

Results and discussion: We studied evaporation of perovskite in the temperature range 1791–2182 K and the CaO–TiO₂ melts in the temperature range 2241–2441 K from the Knudsen molybdenum effusion cell by the mass spectrometric method.

The established molecular composition of the gas phase over perovskite and over the CaO–TiO₂ melts according to reactions, typical for the evaporation of individual oxides is shown below:

$$[CaO] = (CaO) \tag{1}$$
$$(CaO) = (Ca) + (O) \tag{2}$$
$$[TiO_2] = (TiO_2) \tag{3}$$
$$(TiO_2) = (TiO) + (O) \tag{4}$$
$$(TiO) = (Ti) + (O) \tag{5}$$
$$2(O) = (O_2) \tag{6}$$

(here and further square brackets denote the condensed phase, round brackets denote the gas phase).

The (CaTiO₃) presence in the gas phase in minor amounts was testified by the occurrence of the following heterogeneous reaction:

$$[CaTiO_3] = (CaTiO_3). \tag{7}$$

Values of partial pressures of vapor species (p_i) over perovskite and over the CaO–TiO₂ melts were determined by the Hertz-Knudsen equation (Fig. 2).

The oxide activities (a_i) were calculated from the partial pressures. They allowed to determine the mixing energy (ΔG^m), as well as the enthalpy and entropy of perovskite formation equal to –39.88±0.54 kJ/mol and 3.15±0.28 J/(mol×K), respectively, and the melting enthalpy of perovskite at 2241±10 K, equal to 47.61±1.84 kJ/mol (per 1 mol compound). The determined values of CaO, TiO₂ and CaTiO₃ activities in the CaO–TiO₂ melts at 2250 K are consistent with those obtained by Banon et al. [5] at slightly lower temperature – 2150 K (Fig. 3). Some difference in the TiO₂ activity is probably due to the extrapolation procedures of data obtained by Banon et al. [5] for the compositions of the CaTiO₃–Ti₂O₃–TiO₂ ternary system, which could reduce their accuracy. The behavior of the TiO₂ activity in the melts closed to rutile, observed by Banon et al. (Fig. 3), as well as the constancy of partial pressure of vapor species obtained in the present study (Fig. 2, lines *3–7*), indicate some immiscibility of the melt. The maximum of CaTiO₃ activity corresponds to the region of compositions closed to perovskite (Fig. 3, lines *4* and *5*).

A comparison of the mixing energies in the CaO–TiO₂ melt at 2300 K with the mixing energies of melts containing calcium oxide (CaO–Al₂O₃ [6], CaO–SiO₂ [7] and CaO–FeO [8]) and titanate melts (FeO–TiO₂ [9], Al₂O₃–TiO₂ [10] and MgO–TiO₂ [11]) shown in Fig. 4. The melts containing CaO are in the series according to the degree of chemical interaction: FeO → Al₂O₃ → TiO₂ → SiO₂ (Fig. 4a), which is manifested in more negative values of the mixing energy of the melt. The titanate melts are in the following series: FeO → Al₂O₃ → MgO → CaO according to the rising of melt basicity (Fig. 4b).

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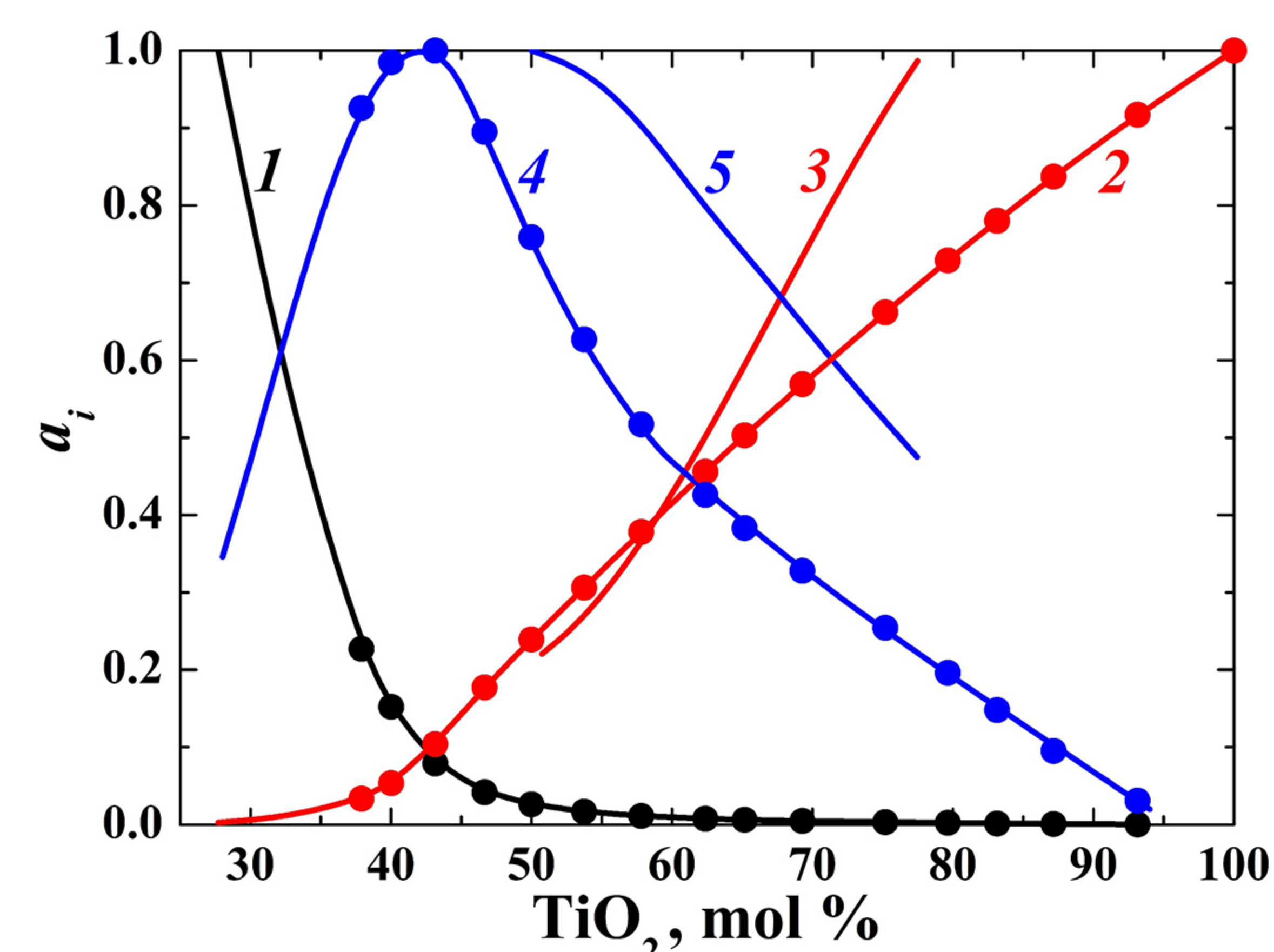
Fig. 3. The activities of CaO (*1*), TiO₂ (*2, 3*) and CaTiO₃ (*4, 5*) in the CaO–TiO₂ system, determined at the present study at 2250 K (*1, 2, 4*) and in [5] at 2150 K (*3, 5*).
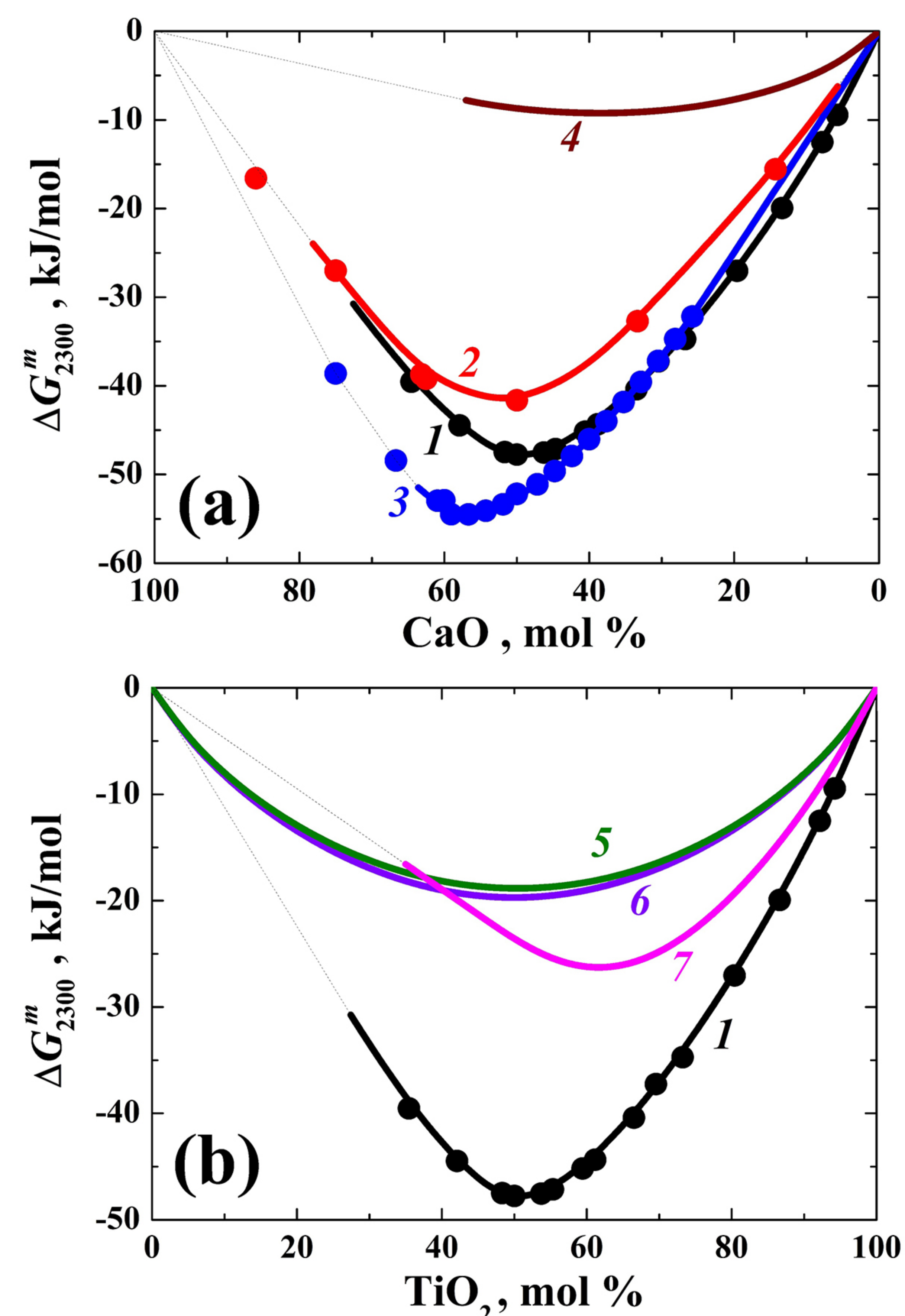

Fig. 4. The mixing energies in the CaO–TiO₂ (*1*), CaO–Al₂O₃ (*2*), CaO–SiO₂ (*3*), CaO–FeO (*4*), FeO–TiO₂ (*5*), Al₂O₃–TiO₂ (*6*) and MgO–TiO₂ (*7*) melts at 2300 K, determined by the Knudsen mass spectrometric effusion method (*1–3*) and calculated (*4–7*) at 2300 K, obtained at the present study and in [6–11], respectively. Dotted lines correspond to heterogeneous areas.