

## MASS SPECTROMETRIC STUDY OF PEROVSKITE EVAPORATION FROM KNUDSEN CELL

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**Introduction:** Calcium titanate  $\text{CaTiO}_3$  (perovskite) is of particular interest for cosmochemical studies as a mineral that is part of the substance of refractory Ca–Al–inclusions (CAIs) and is the earliest object of the Solar system with unusual isotopic characteristics [1]. It is believed that perovskite is a polygenic material that combines a relict substance formed in the inner shells of supernova stars, and a condensation product from a high-temperature gas, and a crystallization product of a silicate melt [2, 3]. In this regard, experimental information on evaporation processes and thermodynamic properties of perovskite is of particular importance for understanding of their formation in CAIs.

**Results and discussion:** We studied evaporation of perovskite in the temperature range 1791–2241 K and the CaO–TiO<sub>2</sub> 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–TiO<sub>2</sub> melts shows to evaporation according to reactions typical for the evaporation of individual oxides. The  $(\text{CaTiO}_3)$  presence in minor amounts in the gas phase testified to the occurrence of the following heterogeneous reactions  $[\text{CaTiO}_3] = (\text{CaTiO}_3)$ . The values of partial pressures of vapor species ( $p_i$ ) over perovskite (Fig. 1) and over the CaO–TiO<sub>2</sub> melts were determined by the Hertz-Knudsen equation. The CaO, TiO<sub>2</sub> and CaTiO<sub>3</sub> activities ( $a_i$ ) were calculated from the partial pressures values (Fig. 2). They allowed to determine the values of mixing energy, as well as the enthalpy and entropy of perovskite formation equal to  $-39.88 \pm 0.54$  kJ/mol and  $3.15 \pm 0.28$  J/(mol·K), respectively, and the melting enthalpy of perovskite at  $2241 \pm 10$  K, equal to  $47.61 \pm 1.84$  kJ/mol (per 1 mol compound) [4].

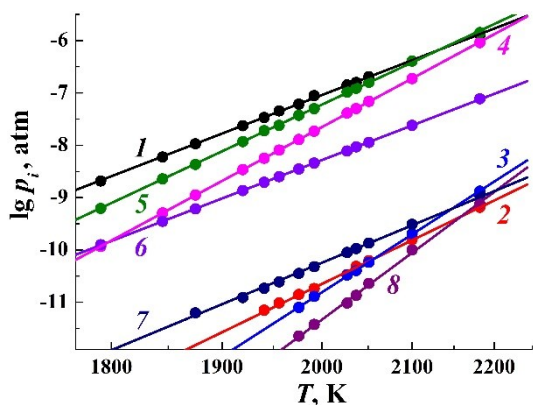


Fig. 1. The partial pressure values of vapor species over perovskite: Ca (1), CaO (2), Ti (3), TiO (4), TiO<sub>2</sub> (5), O (6), O<sub>2</sub> (7), CaTiO<sub>3</sub> (8).

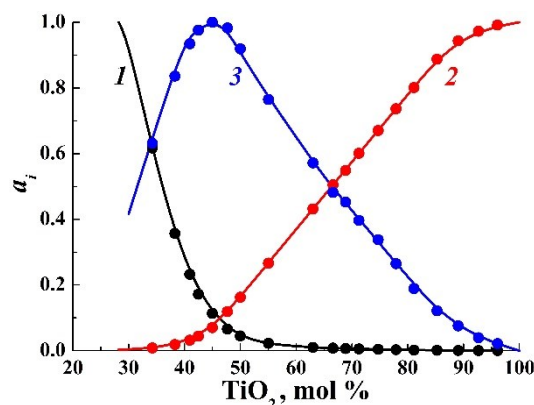


Fig. 2. The activities of CaO (1), TiO<sub>2</sub> (2) and CaTiO<sub>3</sub> (3) in the CaO–TiO<sub>2</sub> system, determined at the present study at 2250 K.

According to the rules established earlier in [5] the change in the composition of the gas phase over perovskite in the temperature region 1700–2400 K (Table 1), calculated from the values of the oxide activity, shows an increase in the  $(\text{CaTiO}_3)$  content in the vapor by  $10^4$  times. It should be taken into account when considering the perovskite fractionation during evaporation [1].

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Table 1. The composition of the gas phase over perovskite (mol %).

T, K	O	O <sub>2</sub>	Ca	CaO	Ti	TiO	TiO <sub>2</sub>	Ti <sub>2</sub> O <sub>3</sub>	Ti <sub>2</sub> O <sub>4</sub>	CaTiO <sub>3</sub>
1700	34	1.3	35	$8.0 \times 10^{-3}$	$3.4 \times 10^{-5}$	0.96	29	$4.7 \times 10^{-3}$	$2.5 \times 10^{-3}$	$3.9 \times 10^{-5}$
2241	16	1.2	10	$3.4 \times 10^{-2}$	$2.8 \times 10^{-3}$	8.2	64	0.13	0.11	$6.6 \times 10^{-2}$
2400	17	1.4	8.6	$5.1 \times 10^{-2}$	$6.0 \times 10^{-3}$	11	62	0.15	0.12	0.39

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