SYNTHESIS AND PROPERTIES
OF INORGANIC COMPOUNDS

Thermodynamic Stability of Calcium Vanadium Garnet Ferrites upon Formation of Substitutional Solid Solutions

G. V. Denisov

Russian State Professional Pedagogical University, Yekaterinburg, Russia
Received June 30, 2010

Abstract—The thermodynamic stability of calcium vanadium garnet ferrites $Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12}$ upon isomorphic substitution of titanium ions for iron and vanadium ions was studied by the EMF method using $ZrO_2(Y_2O_3)$ ceramic solid electrolyte. Temperature-dependent ΔG^0 was determined. Isomorphic substitutions of titanium ions for iron and vanadium ions in the inequivalent sublattices of the garnet structure in a temperature range of 1100–1483 K cause changes in ΔG^0 due to the entropy and enthalpy components and has a minimal value when $x = 0.15$.

Polycrystalline ferrites with the garnet structure are indispensable materials for microwave engineering, for they successfully combine the required values of saturation magnetization with the optimal temperature dependence, high Curie temperatures, and low dielectric losses [1].

$Y_3Fe_5O_{12}$, which gives rise to a number of specialty ceramic materials, is the basic garnet ferrite for ferrimagnets [2, 3]. The possibility of existence of particular ion combinations within the garnet structure and their distribution over various positions are primarily determined by the absolute and relative size of cations and configuration of their electronic shells [3].

A high isomorphic capacity of the ferrogarnet structure opens broad possibilities for varying the chemical composition and changing the magnetic properties of materials based on them. All this allows one to obtain compounds with the garnet structure having diverse compositions.

A promising class of calcium vanadium ferrogarnets of rare-earth elements (REE) $R_{3-2x}Ca_{2x}Fe_{5-x}V_xO_{12}$ convincingly supports the foregoing [4]. Partial isomorphic substitution of diamagnetic vanadium ions for iron ions in tetrahedral positions with the compensating introduction of calcium to dodecahedra changes the coercive force and enhances the thermal stability of magnetic properties [5]. The possibility of complete isomorphic substitutions of REE ions in $Ca_3Fe_{3.5}V_{1.5}O_{12}$ makes production of these materials more profitable, and variations of chemical composition at tetrahedral and octahedral positions allows one to optimize the target properties of these materials. These compounds are exemplified by a continuous series of substitutional solid solutions $Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12}$, whose implementation into large-scale production can be limited by the absence of reliable data on their thermodynamic stability.

EXPERIMENTAL

Thermodynamic studies of garnet solid solutions $Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12}$, where $x = 0.00$, 0.05, 0.10, 0.15, or 0.20, were carried out by the EMF method using $ZrO_2(Y_2O_3)$ ceramic solid electrolyte with unipolar oxygen conductivity .

Figure 1 shows the scheme of a cell used to study the thermodynamic equilibria occurring in this system.

The structural feature of this cell consists of a controllable buffer gas space formed by the volume between the internal and external vials (*2*), which are made of ceramic solid electrolytes. The buffer space is required to reduce the oxygen concentration gradient between the gas volume under study and the reference electrode and to avoid oxygen leaking into the internal vial containing the sample under study (*3*). This is of particular importance when the electronic fraction of conductivity of the ceramic solid electrolyte increases at high temperatures.

The oxygen partial pressure (p_{O_2}) in the buffer space was controlled in an automatic mode using a regulating device. The oxygen partial pressure in the buffer space was maintained equal to the p_{O_2} value that was dictated by the potential-forming reaction in the internal electrolyte with the sample under study (*3*).

In automatic regulation of p_{O_2}, the external electrolyte acted as an electrochemical pump, while the internal electrolyte acted as a regulating sensor. The EMF of internal electrolyte with respect to the buffer space was always maintained equal to zero.

The operability of the electrochemical sensors was verified by measuring the spurious EMF that can emerge due to non-uniform firing and different gas permeability values of gas-diffusion platinum electrodes applied onto ceramics (1). The spurious EMF
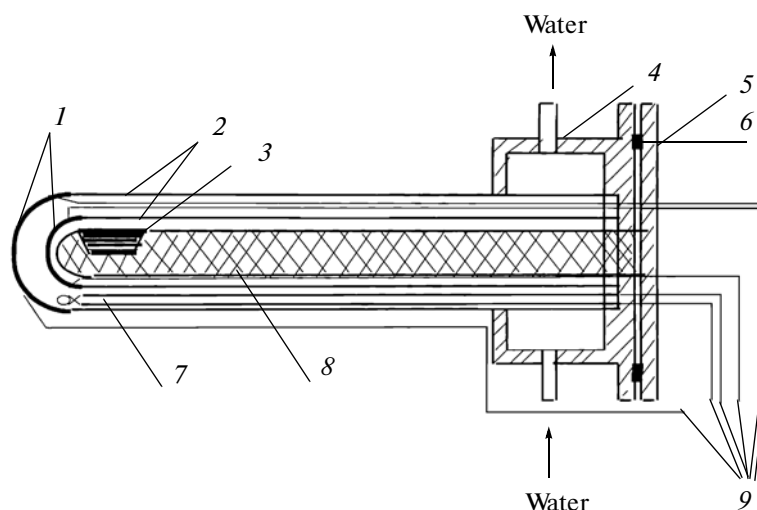
Fig. 1. Cell used to study the thermodynamic characteristics of complex oxides using the EMF method: (*1*) platinum electrodes, (*2*) sensors of partial oxygen pressure in $ZrO_2(Y_2O_3)$, (*3*) platinum container with a sample, (*4*) refrigerator, (*5*) stopper, (*6*) sealing gaskets, (*7*) thermocouple, (*8*) ceramic holder, and (*9*) platinum current leads.

value was determined by measuring the EMF of the element

$$(-)O_2(air)(Pt) \mid O^{2-} \mid (Pt)O_2(air)(+). \qquad (1)$$
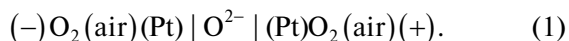
Element (1) with an EMF no higher than 0.3 mV was used in this study.

The relative operability of the internal and external sensors was verified within a broad range of temperatures and partial pressures by measuring p_{O_2} in the buffer space relative to air. In processing the results, the difference between the readings for the internal and external electrolytes in the cell was taken into account; this difference remained constant over the entire range of p_{O_2} and T and was 0.7 mV.

A powder sample was loaded into a platinum container (*3*) and placed into the internal electrolyte on a specialized ceramic holder (*8*), thus occupying more than 95% of the volume of the internal electrolyte, which was sealed using a stopper (*5*).

A PR-30/6 measuring thermocouple (*7*) was placed between the electrolytes in a direct proximity to the sample under study. The furnace temperature was maintained using a VRT-3 temperature controller with ±0.5-K accuracy. The EMFs of the cell and thermocouple were measured using an R-386 digital ampere meter/voltmeter.

The decomposition products of the sample under study, which determine the potential-forming reaction, were identified by X-ray powder diffraction and electron probe microanalysis (EPMA).

X-ray powder diffraction was used to determine the phase composition of powder samples kept at specified p_{O_2} and T for 20–30 h and then quenched without unsealing the gas space in a setup constructed specially for this purpose.

The phase composition of the potential-forming mixture was also monitored using samples cooled along with the electrochemical cell after the temperature-dependent EMF had been measured.

The phase composition of compact sintered samples kept at low p_{O_2} under isothermal conditions for 20 h followed by a ~100°C increase in temperature was determined by EPMA. The increase in temperature of the sample being in equilibrium with the gas phase under low p_{O_2} was accompanied by an abrupt ~40-fold rise in resistance due to the release of the $CaTiO_3$ phase upon the decomposition of the $Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12}$ samples.

The samples to be studied were prepared from the corresponding oxide using ceramic technology.

The single-phase sample of $Ca_3Fe_{3.5}V_{1.5}O_{12}$ composition to be used for thermodynamic studies was prepared via magnetic separation of a non-single-phase sample in alcohol. According to X-ray powder diffraction data, the sample of this composition contained no phases belonging to another crystal structure type after it had been magnetically separated.

RESULTS AND DISCUSSION

Based on the natures of phases formed upon decomposition of $Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12}$, the potential-forming reaction can be represented as

$$(1.5-x)/2Ca_4V_2O_9 + (3.5-x)/3Fe_3O_4$$
$$+ 2xCaTiO_3 + (3.5-x)/12O_2 \qquad (2)$$
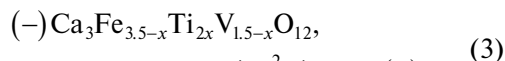$$\rightleftarrows Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12}$$
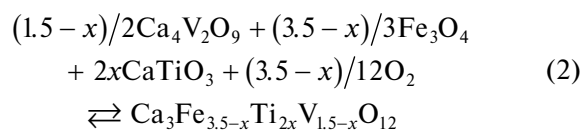
for the entire range of compositions investigated.
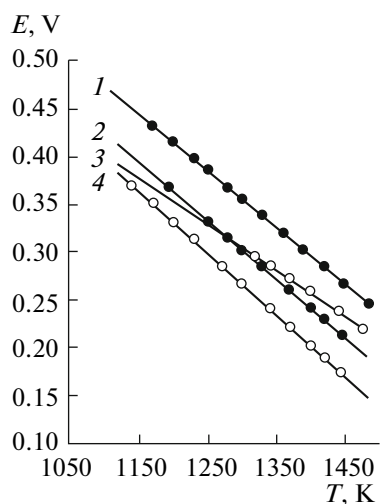
Fig. 2. Temperature-dependent EMF of a galvanic cell for the potential-forming reaction (2), where $x = (1)$ 0.15, (2) 0.00, (3) 0.20, and (4) 0.05.

Then, an electrochemical cell for the compositions with $x \neq 0$ can be written as follows:

$$(-)Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12},$$
$$Ca_4V_2O_9, Fe_3O_4, CaTiO_3(Pt) \mid O^{2-} \mid O_{2(air)}(+), \quad (3)$$

and for the composition $Ca_3Fe_{3.5}V_{1.5}O_{12}$, as

$$(-)Ca_3Fe_{3.5}V_{1.5}O_{12}, Ca_4V_2O_9,$$
$$Fe_3O_4, (Pt) \mid O^{2-} \mid O_{2\,(air)}(+). \quad (4)$$
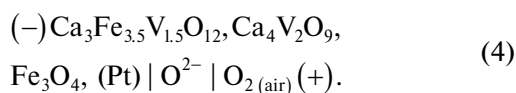
In studying the electrochemical circuit, the major attention was paid to the problems of equilibrium attainment and reversibility of electrode functioning. Hence, EMF was measured both in cooling and heating modes.

Figure 2 and Table 1 show the temperature-dependent EMF of the cells of type (3), (4) for most of the investigated compositions of calcium vanadium garnets. It is clear from Fig. 2 that these dependences can be fairly fitted with straight lines. therefore, they can be regarded as being equivalent to the expression

$$\Delta G^0 = \Delta H^0 - \Delta S^0 T. \quad (5)$$

Isobaric-isothermal potential changes ($\Delta G^0_{(2)}$) were determined using the equilibrium constant (K_{eq}) of reaction (2):

$$\Delta G^0_{(2)} = -RT\ln K_p = -RT\ln\left(p_{O_2}/p^0_{O_2}\right)^{-(3.5-x)/12}$$
$$= \left(RT(3.5-x)/12\right)\ln\left(p_{O_2}/p^0_{O_2}\right), \quad (6)$$

where $p^0_{O_2}$ is the standard oxygen pressure, 10^5 Pa; and R is the universal gas constant.

The relative oxygen partial pressure $p_{O_2}/p^0_{O_2}$ was derived from the EMF value of the concentration circuit (3), (4):

$$E = (RT/4F)\ln\left(p^1_{O_2}/p^0_{O_2}\right)/\left(p_{O_2}/p^0_{O_2}\right), \quad (7)$$

where F is the Faraday constant, 96487 C; and $p^1_{O_2}$ is the oxygen partial pressure for the reference electrode, air, 21 kPa.

The resulting temperature-dependent EMF can be fitted with a good accuracy using lines with appreciably small confidence intervals of the values being determined at 99% confidence level.

Based on this fact, the temperature dependence of the electrochemical cells (3), (4) under study was considered to be equivalent to expression (5).

ΔG values for reaction (2) were calculated from the temperature dependence (Table 1) using expression (6).

The parameters of the expression that describes Gibbs energy changes as a function of temperature at various titanium contents in the compound of the general formula $Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12}$ are given in Table 2.

As can be seen in Table 2, the enthalpy component of (5) contributes most significantly to the Gibbs free energy to be dermined; the contribution from the entropy component is considerably lower.

The entropy component determines the intensity of changes in the temperature-dependent Gibbs free energy and is directly connected to the degree of disorder in the garnet structure.

Table 1. Temperature-dependent EMF of electrochemical cell (3)

x	$E = a + bT$, V		r	Temperature range, ΔT
	$a \pm \Delta a$	$-(b \pm \Delta b) \times 10^4$		
0.00	1.108 ± 0.005	6.4 ± 0.2	0.9969	1192–1446
0.05	1.116 ± 0.004	6.54 ± 0.09	0.9984	1110–1444
0.10	0.966 ± 0.008	5.4 ± 0.3	0.9812	1212–1433
0.15	1.135 ± 0.004	6.0 ± 0.1	0.9982	1171–1483
0.20	0.942 ± 0.006	4.9 ± 0.4	0.9864	1279–1477

Table 2. Temperature dependent Gibbs free energy of reaction (2)

x	$\Delta G^0 = \Delta H^0 - \Delta S^0 T$		$-\Delta G^0_{1250\,K}$, kJ/mol	$-\Delta G^0_{1480\,K}$, kJ/mol
	$-\Delta H^0$, kJ/mol	$-\Delta S^0$, J/(mol K)		
0.00	124.8 ± 0.5	69 ± 1	39	23
0.05	123.6 ± 0.4	69 ± 2	38	22
0.10	105.6 ± 0.9	55.0 ± 0.1	37	24
0.15	122.3 ± 0.5	61 ± 2	46	32
0.20	100.0 ± 0.6	48.0 ± 0.3	40	29

It should be mentioned that the temperature dependences of the Gibbs free energy almost completely coincide for two compounds having similar compositions ($x = 0.00$ and 0.05). The free Gibbs energy has rather similar values for almost all compositions of the investigated substitutional solid solutions, as indicated by the values listed in Table 2 for two temperatures. It is only for the composition with $x = 0.15$ that this parameter is considerably lower than for the other compositions. While the enthalpy component is insignificantly varied for the compositions with $x = 0.00$, 0.05, and 0.15, the lower value of the Gibbs free energy is implemented for the composition 0.15 (this is due to a higher value of entropy change as a result of the reaction that occurs).

The entropy changes for the compositions with $x = 0.10$, 0.15, and 0.20 are -55.0, -61.0, and -48.0 J/(mol K), respectively.

An enthalpy change compensates for the increase in the entropy contribution for the compositions with $x = 0.10$ and 0.20 to virtually equalize the ΔG^0 of of formation of these compounds with the least disordered compositions ($x = 0.00$ and 0.05), for which the lower ΔS^0 values were determined.

Figure 3 shows the Gibbs free energy changes at two temperatures as a function of titanium content in the compound with the general formula $Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12}$.

It is clear from Fig. 3 that the lowest ΔG^0 value, corresponding to the composition with $x = 0.15$, is achieved due to a small enthalpy change (Table 2), which is comparable to that for the compositions with $x = 0.00$ and 0.05 (with a more significant contribution from the entropy change).

An appreciably high ΔS^0 value for this composition and low crystal lattice energy (ΔH^0) are responsible for the high relative stability of this compound and certain advantages of using solid-phase synthesis to prepare it.

Thus, introduction of titanium to the initial oxide mixture intensifies the synthesis process due to structure disordering. An increase in ΔS^0 for the compositions with $x = 0.10$, 0.15, and 0.20 can correspond to the degree of ordering of defects in the garnet structure and determine the kinetics of synthesis of these compound through the diffusion mobility of the compo-
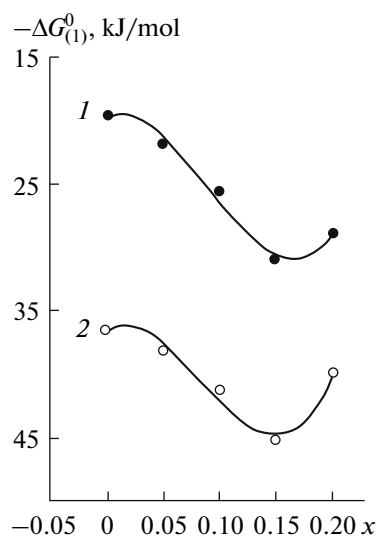

Fig. 3. Standard Gibbs free energy of reaction (2) as a function of titanium content in calcium vanadium garnet $Ca_3Fe_{3.5-x}Ti_{2x}V_{1.5-x}O_{12}$. T, K: (*1*) 1480, (*2*) 1250.

nents in the bulk of the phase. The latter fact can play a crucial role for the delivery of reagents to the reaction zone through extensive layers of the garnet phase, which takes place at the final synthesis stages.

REFERENCES

1. Levin, B.E., Tret'yakov, Yu.D., and Letyuk, L.M., *Physicochemical Rationale for Preparation, Properties, and Applications of Ferrites* (Metallurgiya, Moscow, 1979) [in Russian].
2. V. F. Shkar', E. I. Nikolaev, V. N. Sayapin, et al., Fiz. Tverd. Tela **47**, 1071 (2005).
3. V. F. Shkar', V. P. Denisenkov, A. M. Grishin, et al., Fiz. Tverd. Tela **45**, 2227 (2003).
4. S. Jeller, Kristallogr. **125**, 1 (1967).
5. Yu. R. Shil'nikov, B. V. Zaitsev, G. M. Galaktionova, and V. G. Kurilenko, USSR Inventor's Certificate 496 609, Byull. Izobret. No. 47 (1975).
6. M. P. Petrov, A. P. Paugart, and N. N. Parfenova, Fiz. Tv. Tela **11**, 1242 (1969).