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Thermodynamic Characteristics of Zinc Niobates $Zn_3Nb_2O_8$, $ZnNb_2O_6$, and $Zn_2Nb_{34}O_{87}$. *p*–*x* Diagram of the $ZnO–Nb_2O_5$ System

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Abstract—Vapor formation in the $ZnO–Nb_2O_5$ system in the range 1223–1465 K was studied by Knudsen effusion mass spectrometry. Over the entire range of condensed phase compositions, the saturated vapor above the system consists of zinc atoms, oxygen molecules, and a small amount of ZnO molecules. The absolute component partial vapor pressures and activities were calculated. The *p*–*x* section of the global *p*–*T*–*x* phase diagram at 1353 and 1443 K was plotted. The second-law and third-law values were determined of the standard enthalpies of selected heterophase reactions and the standard enthalpies of formation zinc niobates: $\Delta_f H^\circ_{298}(Zn_3Nb_2O_8) = -2992.0 \pm 30.2$ kJ/mol, $\Delta_f H^\circ_{298}(ZnNb_2O_6) = -2292.4 \pm 19.9$ kJ/mol, and $\Delta_f H^\circ_{298}(Zn_2Nb_{34}O_{87}) = -33056.1 \pm 15.0$ kJ/mol, and their enthalpies of formation from simple oxides: $(Zn_3Nb_2O_8) = -50.0 \pm 20.0$ kJ/mol, $(ZnNb_2O_6) = -40.5 \pm 15.0$ kJ/mol, and $(Zn_2Nb_{34}O_{87}) = -90.9 \pm 15.0$ kJ/mol.

Keywords: mass spectrometry, vaporization processes, phase diagram, standard enthalpies of formation, heterophase reactions

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INTRODUCTION

Systems comprising wide-gap oxide semiconductors SnO_2 (3.54 eV) and ZnO (3.37 eV) are in the focus due to their optical, electrophysical, catalytic, and sensing properties. These compounds belong to the family of transparent conducting oxides (TCOs). TCO films are used as transparent contact layers for LEDs and solar cells and as displays. ZnO- and SnO_2-based nanomaterials have unique sensing and catalytic activities and high photosensitivity to UV radiation; they are used as field-effect transistors, emission displays, and luminescent materials. However, pure ZnO and SnO_2 have rather limited applications due to their high electrical resistance; therefore, they are almost always doped with donor impurities (Al, Ga, Nb, Ta, and other). In addition to the increased interest in physical properties of ZnO-based films and diverse nanomaterials doped with tantalum and niobium [1–9], the $ZnO–Ta_2O_5$ and $ZnO–Nb_2O_5$ systems have recently gained increased attention due to the mixed oxides $ZnTa_2O_6$, $Zn_3Ta_2O_8$, $ZnNb_2O_6$, and $Zn_3Nb_2O_8$ existing therein. Ceramics based on those compounds are promising materials in microwave electronics. The combination of a high dielectric constant, a high electrical Q-factor, and a low temperature coefficient of dielectric constant makes Zn–Nb–Ta–O ceramics useful for substrates of microwave microcircuits, dielectric resonators or filters in the microwave range [10–13]. $Zn_3Ta_2O_8$, $Zn_3Nb_2O_8$, and their combinations can be used as low-voltage cathodoluminescent phosphors in field-emission displays or vacuum luminescent displays [14–16]. Various compositions of $ZnO–Ta_2O_5$ and $ZnO–Nb_2O_5$ systems are used in heterogeneous organic catalysis and photocatalysis to degrade toxic organics in the environment [17, 18].

The physical and physicochemical properties of any oxide material strongly depend on the preparation method used and its parameters. There are two main approaches to the preparation of oxide materials. One involves gas-phase processes, while the second uses solutions. The solution methods, as the gas-phase methods, too, often employ high temperatures (up to 1400°C), as the material prepared from solution is subjected to long-term high-temperature annealing in order to obtain the required properties. Therefore, for the controlled synthesis of polyfunctional oxide materials with tailored cationic and anionic compositions, it is extremely important that their thermodynamic characteristics be known and vaporization thermodynamics be studied. We should emphasize that the key matters must be the determination of the vapor composition, absolute values of partial vapor pressures, mainly oxygen partial pressures, the standard enthalpies of formation of complex oxides and the Gibbs energies of formation of solid solutions; and the construction of the *p*–*x* and *p*–*T* sections of global *p*–*T*–*x* phase diagrams of oxide systems. The *T*–*x* diagrams of the $ZnO–Ta_2O_5$ and $ZnO–Nb_2O_5$ systems have been studied in sufficient detail.

EXPERIMENTAL

Our high-temperature studies of the vaporization and thermodynamic properties of the $ZnO–Nb_2O_5$ system over the entire range of compositions were performed by Knudsen effusion mass spectrometry on an MS 1301 instrument. Quartz effusion cells with the vaporization-to-effusion surface area ratio of ~100 were used. The Knudsen cell was heated by a resistance furnace; temperature was measured by a Pt/Pt(Rh) thermocouple and maintained accurate to ±1°C.

According to Dayal [19], the $ZnO–Nb_2O_5$ quasi-binary system forms three complex oxides, namely, $Zn_3Nb_2O_8$ (3 : 1), $ZnNb_2O_6$ (1 : 1), and $Zn_2Nb_{34}O_{87}$ (2 : 17). Up to 1085°C, these oxides are in equilibrium with four heterogeneous fields: [$ZnO + Zn_3Nb_2O_8$] (**I**), [$Zn_3Nb_2O_8 + ZnNb_2O_6$] (**II**), [$ZnNb_2O_6 + Zn_2Nb_{34}O_{87}$] (**III**), and [$Zn_2Nb_{34}O_{87} + Nb_2O_5$] (**IV**). Below 1085°C, the (2 : 17) compound is unstable; the other two are separated by three heterogeneous fields: [$ZnO + Zn_3Nb_2O_8$] (**I**), [$Zn_3Nb_2O_8 + ZnNb_2O_6$] (**II**), and [$ZnNb_2O_6 + Nb_2O_5$] (**V**). The (1 : 1) and (3 : 1) compounds melt congruently at 1312 and 1405°C, respectively, and the (2 : 17) compound melts incongruently with the peritectic temperature 1415°C. At 1350°C zinc niobate (1 : 1) undergoes polymorphic transition from the low-temperature phase α-$ZnNb_2O_6$ to the high-temperature phase β-$ZnNb_2O_6$.

The vaporization thermodynamics of the $ZnO–Nb_2O_5$ system has not been studied up to now, while the vaporization of its constituent individual oxides is described in detail in numerous documents [20–23]. According to those works, zinc oxide vaporization is congruent; the saturated vapor consists mostly of Zn atoms and dioxygen molecules O_2. This nature of the saturated vapor, despite its simplicity, makes it problematic to use platinum Knudsen cells in mass-spectrometric studies because they dissolve zinc [24–26]. It is for this reason that the vaporization of oxides and oxide systems where the vapor contains metal atoms is always accompanied by an uncontrolled monotonic decrease in metal partial pressure and an increase in oxygen pressure [25, 26]. However, the review of literature on the $ZnO–SiO_2$, $Nb_2O_5–SiO_2$, and $ZnO–Nb_2O_5–SiO_2$ phase diagrams [27, 28] showed that quartz Knudsen cells can be used to study the $ZnO–Nb_2O_5$ system in the range 1200–1400 K. The constancy of the measured ion currents during vaporization in the heterogeneous phase regions of the system, as well as the absence of zinc silicate in nonvolatile residues after evaporation according to X-ray powder diffraction data, proves that silicon oxide can be used as an inert material relative to the system under study in this temperature range.

The sublimation of niobium oxide Nb_2O_5 in the range 1100–1400°C is incongruent, with oxygen molecules transferred to the vapor phase and various condensed oxides formed, whose compositions lie in the range $Nb_{12}O_{29}–Nb_{53}O_{132}$ [29–34]. The lower volatility of niobium oxide compared to that of zinc oxide allows us to consider the system during vaporization in the range 1200–1500 K in the frame of a two-component system as

$$N_{ZnO} + N_{Nb_2O_5} = 1, \tag{1}$$

where N_{ZnO} ($N_{Nb_2O_5}$) is zinc oxide (niobium oxide) mole fraction.

$ZnO–Nb_2O_5$ samples containing 90, 75, 60, 50, 40, and 11 mol % ZnO were used in vaporization experiments. The first four of these samples were prepared by annealing homogenized mixtures of pure niobium oxide and zinc oxide in platinum crucibles under air at $T = 1173$ K for 30 h; the purity and phase composition of the samples were monitored by X-ray powder diffraction and X-ray fluorescence analysis. The 11 mol % ZnO sample was prepared immediately in the course of a mass-spectrometric experiment by annealing a thoroughly homogenized $ZnNb_2O_6 + Nb_2O_5$ sample containing 88.9 mol % Nb_2O_5 in the effusion cell at $T > 1360$ K.

RESULTS AND DISCUSSION

The requirements imposed on the experimental work where quartz effusion chambers are used did not allow us to determine the component partial vapor pressures over all phase areas of the $ZnO–Nb_2O_5$ system in one isothermal evaporation experiment [35]. We performed three isothermal partial sublimation experiments on **I**, **II**, and **V** phase systems at $T = 1353$ K and four similar experiments on **I**–**IV** phase systems at $T = 1443$ K. The thus-performed sublimation study and the known thermodynamic characteristics of zinc oxide [20–23] indicate that the saturated vapor of the system consists mostly of zinc atoms and oxygen molecules. However, Grade et al. [36] detected ZnO molecules in the vapor phase, with the partial pressure almost three orders of magnitude lower than the pressure of the major components. The partial pressures of zinc atoms and oxygen molecules were calculated by the Hertz–Knudsen equation subject to the congruent sublimation of zinc oxide in the settings of an effusion experiment:

$$(p_{Zn}/\sqrt{M_{Zn}})/(p_{O_2}/\sqrt{M_{O_2}}) = 2. \tag{2}$$

The results of these calculations appear in Tables 1 and 2. Table 1 also lists the partial vapor pressures upon zinc oxide sublimation in a closed space, where

Table 1. Component partial vapor pressures over the $ZnO–Nb_2O_5$ system, $T = 1353$ K

Condensed phase	Sublimation conditions	Component vapor pressures, atm			Total pressure, atm	Component activities	
		p_{Zn}	p_{O_2}	p_{ZnO}		a_{ZnO}	$a_{Nb_2O_5}$
ZnO	Knudsen	1.22×10^{-5}	0.43×10^{-5}	7.57×10^{-10}	1.65×10^{-5}	1	0
	Closed space	1.08×10^{-5}	0.54×10^{-5}	7.51×10^{-10}	1.62×10^{-5}		
$ZnO + Zn_3Nb_2O_8$	Knudsen	1.22×10^{-5}	0.43×10^{-5}	7.57×10^{-10}	1.65×10^{-5}	1	0.016
	Closed space	1.08×10^{-5}	0.54×10^{-5}	7.51×10^{-10}	1.62×10^{-5}		
$Zn_3Nb_2O_8 + ZnNb_2O_6$	Knudsen	7.63×10^{-6}	2.68×10^{-6}	3.73×10^{-10}	1.03×10^{-5}	0.51	0.12
	Closed space	6.72×10^{-6}	3.36×10^{-6}	3.71×10^{-10}	1.01×10^{-5}		
$ZnNb_2O_6 + Nb_2O_5$	Knudsen	1.91×10^{-6}	0.67×10^{-6}	4.48×10^{-11}	2.58×10^{-6}	0.062	1
	Closed space	1.63×10^{-6}	0.82×10^{-6}	4.43×10^{-11}	2.45×10^{-6}		

the vaporization process fulfills the equality of gas and condensed phase compositions:

$$p_{Zn}/p_{O_2} = 2. \qquad (3)$$

In so doing, we used the equilibrium constants of the reaction

$$ZnO(g) = Zn(g) + 0.5O_2 \qquad (4)$$

that we calculated using experimental data borrowed from [36]. The thus-determined partial pressures were used to plot the $p–x$ section of the global $p–T–x$ phase diagram (Figs. 1 and 2) at 1353 and 1443 K.

In order to determine the standard enthalpies of formation of zinc niobates, we calculated the enthalpies of the following heterophase reactions:

$$ZnO(cr) = Zn(g) + 0.5O_2, \qquad (5)$$

$$Zn_3Nb_2O_8(cr) = ZnNb_2O_6(cr) + 2Zn(g) + O_2, \qquad (6)$$

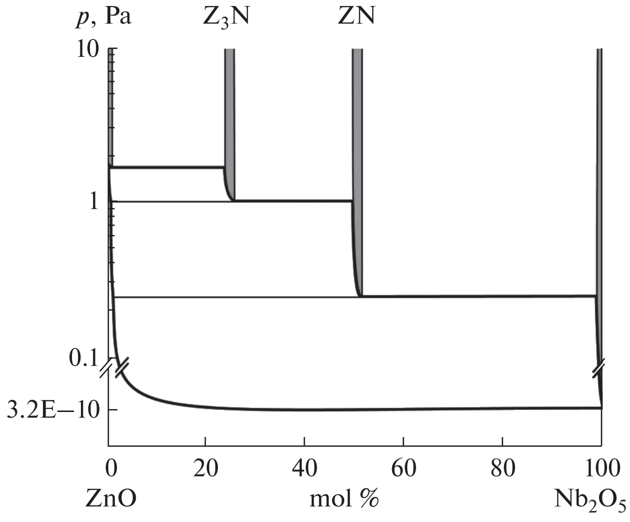

Fig. 1. $p–x$ diagram of the $ZnO–Nb_2O_5$ system at $T = 1353$ K.

$$ZnNb_2O_6(cr) = Nb_2O_5(cr) + Zn(g) + 0.5O_2, \qquad (7)$$

$$\begin{aligned} ZnNb_2O_6(cr) &= 1/17Zn_2Nb_{34}O_{87}(cr) \\ &+ 15/17Zn(g) + 15/34O_2, \end{aligned} \qquad (8)$$

$$\begin{aligned} &Zn_2Nb_{34}O_{87}(cr) \\ &= 17Nb_2O_5(cr) + 2Zn(g) + O_2. \end{aligned} \qquad (9)$$

The second-law and third-law enthalpies of reactions (5)–(9) were determined. To determine the second-law value, we studied temperature-dependent values proportional to the equilibrium constants of reactions (5)–(9), which were written as $k^*(5, 7) = (I_{Zn}T)^{1.5}$, $k^*(6, 9) = (I_{Zn}T)^3$, and $k^*(8) = (I_{Zn}T)^{45/34}$ by virtue of the congruent sublimation of zinc oxide.

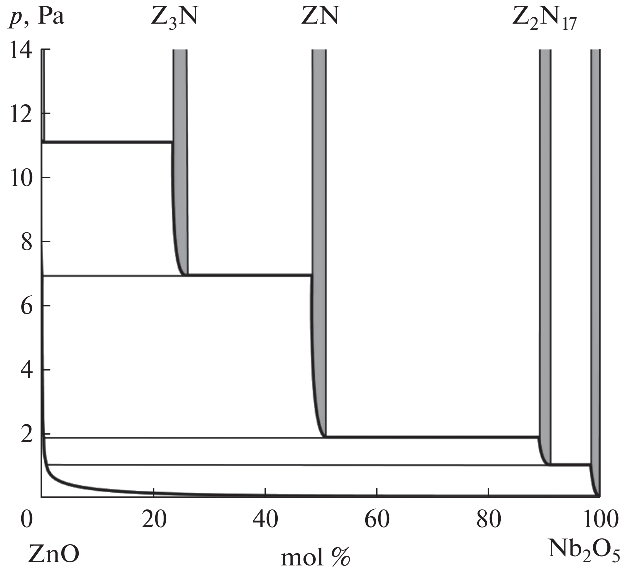

Fig. 2. $p–x$ diagram of the $ZnO–Nb_2O_5$ system at $T = 1443$ K.

Table 2. Component partial vapor pressures over the $ZnO–Nb_2O_5$ system, $T = 1443$ K

Condensed phase	Sublimation conditions	Component vapor pressures, atm			Total pressure, atm	Component activities	
		p_{Zn}	p_{O_2}	p_{ZnO}		a_{ZnO}	$a_{Nb_2O_5}$
ZnO	Knudsen	8.05×10^{-5}	2.83×10^{-5}	9.75×10^{-9}	10.90×10^{-5}	1	0
	Closed space	7.14×10^{-5}	3.57×10^{-5}	9.70×10^{-9}	10.70×10^{-5}		
$ZnO + Zn_3Nb_2O_8$	Knudsen	8.05×10^{-5}	2.83×10^{-5}	9.75×10^{-9}	10.90×10^{-5}	1	0.016
	Closed space	7.14×10^{-5}	3.57×10^{-5}	9.70×10^{-9}	10.70×10^{-5}		
$Zn_3Nb_2O_8 + ZnNb_2O_6$	Knudsen	5.05×10^{-5}	1.77×10^{-5}	4.84×10^{-9}	6.82×10^{-5}	0.50	0.13
	Closed space	4.46×10^{-5}	2.23×10^{-5}	4.81×10^{-9}	6.69×10^{-5}		
$ZnNb_2O_6 + Zn_2Nb_{34}O_{87}$	Knudsen	1.38×10^{-5}	0.49×10^{-5}	0.69×10^{-9}	1.87×10^{-5}	0.071	0.90
	Closed space	1.22×10^{-5}	0.61×10^{-5}	0.69×10^{-9}	1.83×10^{-5}		
$Zn_2Nb_{34}O_{87} + Nb_2O_5$	Knudsen	7.69×10^{-6}	2.71×10^{-6}	0.29×10^{-9}	1.04×10^{-5}	0.03	1
	Closed space	6.87×10^{-6}	3.44×10^{-6}	0.29×10^{-9}	1.03×10^{-5}		

Table 3. Standard enthalpies of heterophase reactions (kJ/mol)

Temperature range, K				
1223–1398	1230–1363	1240–1340	1353–1443	1353–1465
Enthalpies of reactions, kJ/mol				
ΔH_T° (5)	$\Delta H_T^\circ(6)$	$\Delta H_T^\circ(7)$	$\Delta H_T^\circ(8)$	$\Delta H_T^\circ(9)$
477.0 ± 14.7	958.7 ± 33.1	506.6 ± 12.5	473.1 ± 26.2	1060.6 ± 18.4
474.8 ± 11.5	911.1 ± 18.1	505.1 ± 12.0	478.9 ± 21.6	1069.3 ± 12.2
480.2 ± 20.0	925.7 ± 36.1	501.6 ± 12.0	482.0 ± 17.0	1039.6 ± 14.9
481.6 ± 14.9	931.2 ± 30.2	–	476.0 ± 25.3	–
476.4 ± 13.6	–	–	–	–
481.9 ± 10.8	–	–	–	–
Average				
478.7 ± 14.3	931.7 ± 32.6	504.4 ± 12.3	477.5 ± 22.6	1056.5 ± 18.6

The standard enthalpies of reactions (5)–(9) were calculated by the reaction isobar equation by the least-squares method (Table 3).

Here, we should emphasize that those enthalpies can have a certain systematic error associated with the enrichment of the surface layer of the system under study with non-volatile niobium oxide Nb_2O_5 in the process of vaporization and possible attendant hampering of zinc oxide sublimation. It is possible that niobium pentoxide would retain its original stoichiometric composition in these experiments, as vaporization in the system takes place at a relatively high oxygen pressure (Tables 1, 2). The enthalpies of reactions (5)–(9) were referred to 298.15 K using the known heat capacity values: $c_p^\circ(Zn_g) = 20.79$ J/(mol K), $c_p^\circ(O_{2g}) = 29.35$ J/(mol K), $c_p^\circ(ZnO_{cr}) = 40.25$ J/(mol K) [38, 39], and $c_p^\circ(Nb_2O_{5cr}) = 131.95$ J/(mol K) [37, 38]; and the heat capacities of mixed oxides calculated according to the Neumann–Kopp rule: $c_p^\circ(Zn_3NbO_{8cr}) = 252.7$ J/(mol K), $c_p^\circ(ZnNbO_{6cr}) = 172.2$ J/(mol K), and $c_p^\circ(Zn_2Nb_{34}O_{87cr}) = 2323.65$ J/(mol K) on the assumption of their temperature independence. The standard enthalpies of these reactions referred to 298.15 K appear in Table 4.

The standard enthalpies of heterophase reactions (5)–(9) were also calculated by the third law of thermodynamics. In the calculations, used were the experimentally determined absolute partial vapor pressures of zinc atoms and oxygen molecules at $T = 1353$ and 1443 K (Table 1); known entropies of components of these reactions at $T = 298.15$ K: $S^\circ(Zn_g) = 160.88$ J/(mol K) [37, 38], $S^\circ(ZnO_g) = 37.89$ J/(mol K) [38, 39], $S^\circ(O_{2g}) = 205.03$ J/(mol K) [37, 38], and $S^\circ(Nb_2O_{5cr}) = 137.10$ J/(mol K) [37, 38]; and the entropies of mixed oxides calculated as means of the Kelley and Latimer increments [39–42]: $S°(Zn_3Nb_2O_{8cr})$ = 274.0 J/(mol K), $S°(ZnNb_2O_{6cr})$ = 181.7 J/(mol K), and $S°(Zn_2Nb_{34}O_{87cr})$ = 2422.5 J/(mol K). The thus-determined standard enthalpies of reactions (5)–(9) are as follows:

$\Delta_r H^\circ_{1353\ K}(5) = 494.2 \pm 20.0$ kJ/mol, $\Delta_r H^\circ_{1353\ K}(6) = 981.5 \pm 25.0$ kJ/mol, $\Delta_r H^\circ_{1353\ K}(7) = 524.1 \pm 20.0$ kJ/mol, $\Delta_r H^\circ_{1443\ K}(8) = 463.1 \pm 20.1$ kJ/mol, and $\Delta_r H^\circ_{1443\ K}(9) = 1067.1 \pm 25.0$ kJ/mol. Table 4 lists the enthalpies referred to 298.15 K. The uncertainty in the third-law enthalpies is due mainly to the accuracies of determination of equilibrium constants and estimation of entropy changes of heterophase reactions. Thermodynamic analysis showed that these factors have roughly equivalent contributions. The recommended values of the enthalpies of reactions (5)–(9) obtained as arithmetic means of the second-law and third-law values also appear in Table 3. This is because, in this experimental work, it is difficult to give preference to any method for determining the values of enthalpies. The total uncertainty for the recommended values was calculated according to the law of addition of random variables.

We used the recommended values of the enthalpies of reactions (5)–(9) and borrowed the standard enthalpies of formation $\Delta_f H^\circ_{298}(Nb_2O_{5cr}) = -1897.0$ kJ/mol [37, 38] and $\Delta_f H^\circ_{298}(Zn_g) = 130.7$ kJ/mol [37, 38] to calculate, by the Hess law, the standard enthalpies of formation of zinc niobates from constituent elements and from simple oxides (Tables 4, 5). Our value of the standard enthalpy of formation of crystalline zinc oxide correlates with the published values, and this may serve to validate the correctness of our study. We should mention here a rather low relative accuracy of the calculations of standard enthalpies of formation of zinc niobates from simple oxides using the thermodynamic cycle. This is due to the calculation method used, in which the determined small value (the enthalpy of formation of a mixed oxide from simple oxides) is calculated as the algebraic sum of several large values (the standard enthalpies of formation from elements). For this reason, the standard enthalpies of formation of zinc niobates from simple oxides were also calculated from the Gibbs energies of formation of zinc niobates from simple oxides [43] and the absolute entropies of components of reaction (10):

$$n\mathrm{ZnO_{cr}} + m\mathrm{Nb_2O_{5cr}} = n\mathrm{ZnO}m\mathrm{Nb_2O_{5cr}}, \quad (10)$$

$$\Delta_f G^\circ_T(n\mathrm{ZnO}m\mathrm{Nb_2O_{5cr}}) = RT\ln(a^n_{\mathrm{ZnO}}a^m_{\mathrm{Nb_2O_5}}). \quad (11)$$

Table 4. Second-law and third-law standard enthalpies $\Delta_r H^\circ_{298}$ of heterophase reactions (kJ/mol)

Reaction	Second law	Third law	Recommended value
(5)	483.7 ± 15.5	484.7 ± 7.0	484.7 ± 7.0
(6)	941.3 ± 35.7	991.5 ± 16.0	966.4 ± 25.9
(7)	509.4 ± 13.0	529.1 ± 7.5	516.9 ± 10.0
(8)	481.6 ± 24.6	467.2 ± 7.5	474.2 ± 16.1
(9)	1061.5 ± 5.3	1077.1 ± 16.0	1068.5 ± 8.5

Table 5. Standard enthalpies of formation of zinc niobates (kJ/mol)

Compound	$-\Delta_f H^\circ_{298}$	$-\Delta_f H^\circ_{298}$ (from oxides)
$Zn_3Nb_2O_8$(cr)	2992.0 ± 30.2	50.1 ± 32.1
$ZnNb_2O_6$(cr)	2292.4 ± 19.9	48.3 ± 21.3
$Zn_2Nb_{34}O_{87}$(cr)	33056.1 ± 15.0	89.7 ± 19.4

The niobium oxide activities necessary for the calculations were found from Eq. (11), according to which relationships can be written to calculate niobium oxide activities in all heterogeneous areas of the $ZnO–Nb_2O_5$ system at T = 1353 K:

$$(a_{\mathrm{ZnO}}a_{\mathrm{Nb_2O_5}})_{\mathrm{V}} = (a_{\mathrm{ZnO}})_{\mathrm{V}} = (a_{\mathrm{ZnO}}a_{\mathrm{Nb_2O_5}})_{\mathrm{II}}, \quad (12)$$

$$(a_{\mathrm{Nb_2O_5}})_{\mathrm{II}} = (a_{\mathrm{ZnO}})_{\mathrm{V}}/(a_{\mathrm{ZnO}})_{\mathrm{II}}, \quad (13)$$

$$(a^3_{\mathrm{ZnO}}a_{\mathrm{Nb_2O_5}})_{\mathrm{I}} = (a_{\mathrm{Nb_2O_5}})_{\mathrm{I}} = (a^3_{\mathrm{ZnO}}a_{\mathrm{Nb_2O_5}})_{\mathrm{II}}, \quad (14)$$

$$(a_{\mathrm{Nb_2O_5}})_{\mathrm{I}} = (a^3_{\mathrm{ZnO}}a_{\mathrm{Nb_2O_5}})_{\mathrm{II}}, \quad (15)$$

and at T = 1443 K:

$$(a^2_{\mathrm{ZnO}}a^{17}_{\mathrm{Nb_2O_5}})_{\mathrm{IV}} = (a^2_{\mathrm{ZnO}})_{\mathrm{IV}} = (a^2_{\mathrm{ZnO}}a^{17}_{\mathrm{Nb_2O_5}})_{\mathrm{III}}, \quad (16)$$

$$(a^{17}_{\mathrm{Nb_2O_5}})_{\mathrm{III}} = (a^2_{\mathrm{ZnO}})_{\mathrm{IV}}/(a^2_{\mathrm{ZnO}})_{\mathrm{III}}, \quad (17)$$

$$(a_{\mathrm{ZnO}}a_{\mathrm{Nb_2O_5}})_{\mathrm{III}} = (a_{\mathrm{ZnO}}a_{\mathrm{Nb_2O_5}})_{\mathrm{II}}, \quad (18)$$

$$(a_{\mathrm{Nb_2O_5}})_{\mathrm{II}} = (a_{\mathrm{ZnO}}a_{\mathrm{Nb_2O_5}})_{\mathrm{III}}/(a_{\mathrm{ZnO}})_{\mathrm{II}}. \quad (19)$$

The calculated niobium oxide activities in the areas [$ZnO + Zn_3Nb_2O_8$] (**I**), [$Zn_3Nb_2O_8 + ZnNb_2O_6$] (**II**), and [$ZnNb_2O_6 + Zn_2Nb_{34}O_{87}$] (**III**) and the experimentally determined zinc oxide activities (Tables 1, 2) enabled us to determine the standard Gibbs energies of zinc niobates. Once the absolute entropies of zinc [37, 38] and niobium [37, 38] simple oxides and of mixed oxides estimated according to Kelley and Latimer [39–42] were known (see above), we could determine the enthalpies of formation of zinc niobates from simple oxides (Table 6). The uncertainty in the thus-calculated enthalpies arises from estimates of the entropies of mixed oxides and our accepted condition of the temperature-independent entropy change of zinc niobates formation reactions from simple oxides. The enthalpies of formation were referred to 298.15 K in

Table 6. Gibbs energies and enthalpies of formation of zinc niobates from simple oxides (kJ/mol)

Compound	$-\Delta_f G^\circ_{1400}$	$-\Delta_f H^\circ_{298}$ (from oxides)	$-\Delta_f H^\circ_{298}$ (from oxides; Recommended value)
$Zn_3Nb_2O_8$(cr)	48.2 ± 8.1	49.6 ± 9.0	50.0 ± 20.0
$ZnNb_2O_6$(cr)	32.2 ± 10.5	32.6 ± 11.5	40.5 ± 15.0
$Zn_2Nb_{34}O_{87}$(cr)	84.5 ± 10.5	92.1 ± 11.5	90.9 ± 15.0

the same manner as the enthalpies of reactions (5)–(9) were.

The consistency of the values of standard enthalpies of formation of zinc niobates found by three independent methods (calculated from the second and third laws of thermodynamics and from the Gibbs energy of formation) signifies the correctness of our studies performed to determine component partial vapor pressures and activities.

CONCLUSIONS

The thermodynamic characteristics of the ZnO–Nb_2O_5 system determined in this study can be very useful in the manufacture of dielectric ceramics with high physical characteristics, which can be an alternative to the more expensive tantalum oxide ceramics. As mentioned above, zinc niobates are distinguished by high sensing sensitivity to hydrogen [2], and the hydrogen gas selectivity strongly depends on the single-phase state of the material, e.g., $ZnNb_2O_6$, whose preparation and performance with the maintenance of the initial characteristics is impossible unless the main thermodynamic characteristics of the sensor are known.

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CONFLICT OF INTERESTS

The authors declare that they have no conflicts of interests.

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