

Calorimetric and Analytical Investigations on Nonstoichiometric Lead Lanthanum Titanates

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Lead lanthanum titanates with different molar fractions of lanthanum were investigated by solution calorimetry in hydrochloric acid, drop calorimetry, and differential scanning calorimetry. The nonstoichiometry of the phases was determined by chemical analysis. The maximum PbO deficiency of lead lanthanum titanates decreases slowly with increasing molar fraction of lanthanum. The molar enthalpies of formation from lead titanate and lanthana are positive for small lanthanum concentrations, but negative for higher lanthanum contents. These results are interpreted on the basis of the defect reactions and equilibria of the substances. © 1992 Academic Press, Inc.

1. Introduction

For many years, lead titanate (PT) and lead lanthanum titanates (PLT) have found widespread technical applications. Current research aims are mainly directed to their electrooptic and piezoelectric properties; new developments related to these materials can still be expected. Recently, random access memories based on ferroelectric materials have become a subject of great interest in computer technology, and the use of lead titanate and lead lanthanum titanates has been discussed (1).

Lead titanate and lead lanthanum titanates are phases with perovskite structure and a broad homogeneity range: $\text{Pb}_{1-y}\text{TiO}_{3-y}$ and $\text{Pb}_{1-x-y}\text{La}_{2x/3}\text{TiO}_{3-y}$ (x : La content, see later). The PbO decomposition

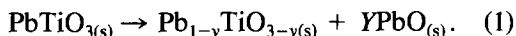
pressure of the substances decreases from high values when the "intrinsic" PbO-deficiency y increases. Stoichiometric lead titanate ($y=0$) exists in equilibrium with solid solutions of TiO_2 in PbO (2, 3). The maximum PbO-deficiency Y of lead titanate and lead lanthanum titanates is reached in two-phase samples with excess TiO_2 . The value of Y for lead titanate depends on the temperature of preparation. Data were reported by Holman and Fulrath (2) and Flohr and Schwitzgebel (3). The maximum PbO-deficiency of lead lanthanum titanates, which according to the phase rule depends on two independent variables, lanthanum content and temperature, has hitherto not been determined.

It has been shown several times that in lead lanthanum titanates the lanthanum ions, whose ionic radius ($r = 1.02 \text{ \AA}$ (4)) is intermediate between that of lead ($r = 1.2 \text{ \AA}$ (4)) and that of titanium ions ($r = 0.61 \text{ \AA}$ (4)), occupy exclusively lead ion sites (5-8).

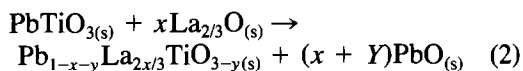
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The excess positive charge of La^{3+} with regard to Pb^{2+} must be compensated, so that electroneutrality is preserved. Different types of charge compensation can be discussed: maintenance of electroneutrality by reduction of Ti^{4+} ions to Ti^{3+} is observed only in reducing atmospheres and is perceptible by a deep color and high electrical conductivity of the samples (5). The reduction can be excluded by sintering in air or under a gas atmosphere containing lead oxide. Under these conditions, an equivalent number of vacancies are formed on the cation lattices for preservation of electroneutrality. This leads to another type of nonstoichiometry, formally called "extrinsic" in the following. Vacancies on the Ti^{4+} ion lattice, however, are only formed when sintering under a high partial pressure of lead oxide. If the substances are under their PbO decomposition pressure in equilibrium with TiO_2 , it was concluded from different studies that only lead ion vacancies are formed (6–8). "Doping" with lanthana $\text{La}_{2/3}\text{O}$ results in the formation of an equivalent amount of lead oxide and, hence, as many as two-thirds of the lead ion sites are occupied by lanthanum substitutionals and one-third of the sites must be vacant, as expressed in the formula $\text{Pb}_{1-x-y}\text{La}_{2x/3}\text{TiO}_{3-y}$.

The energetics of formation of intrinsic nonstoichiometry in lead titanate have been investigated by solution calorimetry in hydrochloric acid at 363 K, drop calorimetry, and differential scanning calorimetry (9). The formation reaction of the PbO deficiency has been written as a solid-state reaction:



The energetics of the formation of lead lanthanum titanates according to the solid-state reaction



are studied by the same techniques. The first

step of this investigation is the determination of the maximum PbO -deficiency Y as a function of the molar fraction x of lanthana by analytical methods, because the extrinsic and the maximum intrinsic nonstoichiometry can be expected to be interrelated.

2. Experimental

2.1. Substance Preparation

Lead lanthanum titanates were prepared by wet blending of orthorhombic lead oxide (99.9%, Kelpin), titania (99.8%, Ventron), and lanthana (99.9%, Ventron) for 2 hr in a polyamide beaker with corundum balls. Lanthana was calcined at 1300 K before use to decompose contaminating lanthanum carbonate and hydroxide. The homogenized powder mixtures were dried to completeness and fired in alumina crucibles with plane polished covers in two stages. During the first step (8 hr at 1123 K), an excess of 2 mol% PbO was added to the mixtures in order to enhance the rate of the solid-state reaction. The absence of unreacted TiO_2 in the product was controlled by X-ray diffraction. Then, the milled product was fired for 48–72 hr at 1523 K in air.

During this second sintering, PbO was evaporated until the two-phase limit was reached and excess TiO_2 appeared. The sintered pellet was milled after half of the second sintering to promote additional homogeneity of the samples and a quicker reaction. The appearance of TiO_2 was checked by X-ray diffraction; furthermore, TiO_2 was found as a white residue after dissolution of the sample in hydrochloric acid. The PbO losses during sintering were determined by difference weighings. The final products were finely ground in an agate mortar and sieved to ensure a regular particle diameter. This is important for solution calorimetry.

2.2. Chemical Analysis of Nonstoichiometry

The chemical analysis was performed to ensure the chemical composition of the two-

phase samples and to determine the maximum PbO-deficiency reached in samples with different molar fraction of lanthanum oxide.

The amount of excess TiO₂ was determined by weighing the residue after dissolution of the two-phase samples in hot concentrated hydrochloric acid. Dissolved titanium was analyzed gravimetrically with cupferron (10). Gravimetric determinations of the lead content with thionalide (10) and as lead sulphate (11) gave identical results. It is not easy to determine lanthanum with the necessary precision. Three different procedures were compared: titrimetry with ethylenediamine tetraacetate ("complexone II"), UV spectroscopy with alizarine-S, and gravimetry as basic lanthanum oxalate (12, 13). It was found that the last technique could be applied to the filtrate of the hydrochloric acid solution without separation of titanium and dissolved lead chloride. After a correction for the solubility of lanthanum oxalate, the results were the most reproducible as compared with those of the other determinations. Detailed analytical procedures can be found elsewhere (12).

2.3. Solution Calorimetry

Up to 0.5 g of the educts or the products of reaction (2) were dissolved in 5 M hydrochloric acid at (363 ± 0.01) K in an isoperibolic solution calorimeter. The solution calorimeter, which has been described elsewhere (9, 12), was calibrated electrically after each experiment. The enthalpies of solution depended on the composition and concentration of the solutions. Therefore, it was necessary to dissolve educts or products in stoichiometric amounts to obtain solutions of identical composition and identical thermodynamic final state. The enthalpies of reaction (2) can then be calculated as the difference of the enthalpies of solution of educts and of products.

2.4. Drop Calorimetry and Differential Scanning Calorimetry

The enthalpy differences [$H(673 \text{ K}) - H(320 \text{ K})$] of lead lanthanum titanates were determined by aneroid drop calorimetry. The isoperibolic copper block calorimeter, which has already been described (12, 14), was calibrated with α -alumina. The temperatures of the ferroelectric phase transition ("Curie point") were tentatively investigated by differential scanning calorimetry (DSC-2, Perkin-Elmer).

3. Results

In Table I the maximum PbO-deficiencies Y of the investigated lead lanthanum titanates are summarized as a function of the molar fraction x of lanthana La_{2/3}O, as obtained from the described analytical procedures. The molar enthalpies of formation of lead lanthanum titanates according to reaction (2) at 363 K, their molar enthalpy differences [$H(673 \text{ K}) - H(320 \text{ K})$], and temperatures of the ferroelectric phase transition are also listed in Table I. The stated experimental errors are standard deviations for calorimetry and are estimated for the analytical results.

4. Discussion

4.1. Maximum PbO Deficiency of Lead Lanthanum Titanates

The general behavior of Y can be clarified by the following thermodynamic considerations on the defect equilibria. Using the Kroeger-Vink nomenclature, the results of Table I can be interpreted on the basis of the defect reaction (3), according to which at regular lattice sites of lead Pb_{Pb} and oxygen O_O vacancies V''_{Pb} and V''_O are formed ("Schottky defects") in equilibrium with gaseous lead oxide,

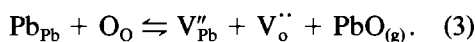
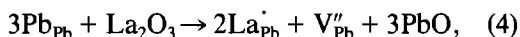


TABLE I

MAXIMUM PbO DEFICIENCY Y , MOLAR ENTHALPY OF FORMATION $\Delta_R H_2$ (REACTION (2)) AT 363 K, MOLAR ENTHALPY DIFFERENCE $[H(673 \text{ K}) - H(320 \text{ K})]$, AND TEMPERATURE OF FERROELECTRIC PHASE TRANSITION T_c OF LEAD LANTHANUM TITANATES $\text{Pb}_{1-x-y}\text{La}_{2x/3}\text{TiO}_{3-y}$

$x \pm 0.02$	$Y \pm 0.02$	$\Delta_R H_2$ (kJ mole ⁻¹)	$[H(673 \text{ K}) - H(320 \text{ K})]$ (kJ mole ⁻¹)	T_c (K)
0.04	0.11	+4.6 ± 1.8	39.4 ± 0.7	>700
0.08	0.10	+1.4 ± 1.5	45.7 ± 0.7	640 ± 20
0.15	0.11	-4.9 ± 1.8	42.6 ± 0.7	540 ± 20
0.29	0.07	-18.3 ± 3.6	40.2 ± 0.6	<300

Doping with lanthana leads to the formation of further lead vacancies, according to the doping reaction (4),



which could change the equilibrium of defect reaction (3). Its equilibrium constant can be expressed using the stoichiometric indices of the complete chemical formula $\text{Pb}_{1-x-y}\square_{y+x/3}\text{La}_{2x/3}\text{TiO}_{3-y}\square_y$, if concentrations (written as square brackets), which are proportional to these indices, are used instead of activities:

$$K = \frac{([\text{V}_{\text{Pb}}''][\text{V}_{\text{O}}'']P)/([\text{Pb}_{\text{Pb}}][\text{O}_{\text{O}}])}{= P(y + x/3)y/((1 - x - y)(3 - y))}. \quad (5)$$

The dependence of the PbO decomposition pressure P on the dopant concentration has been determined from e.m.f. of solid electrolyte cells (15). If $\text{Pb}_{1-x}\text{La}_{2x/3}\text{TiO}_3$ is considered as a solid solution of $\text{La}_{2/3}\text{TiO}_3$ in PbTiO_3 , only slight deviations from ideal behaviour have been found at 1023 K (15). At the higher preparation temperature of our samples (1523 K), we can suppose that the PbO pressure fulfills Raoult's law even better (P_0 : PbO pressure of pure lead titanate):

$$P = P_0(1 - x). \quad (6)$$

The value of Y at this temperature can be calculated from the known value at 1364 K (2) and its temperature dependence (2, 3): $Y(1523 \text{ K}) = 0.12$. One obtains then for pure

$\text{Pb}_{1-y}\text{TiO}_{3-y}$ ($x = 0$) $K/P_0 = 5,7 \cdot 10^{-3}$. In first approximation, a constant value of K was assumed for the whole solid solution series. Equation (5) can then be solved for $Y(x)$, i.e., the maximum PbO-deficiency Y of a sample with a given lanthana content x . The calculation shows that $Y(x)$ decreases slowly with increasing lanthana content (Table II). In the case of lead lanthanum zirconate titanates, Holman (16) has shown that doping with 8% of lanthana did not change the value of Y . Within the limits of uncertainty, the calculated values are in agreement with the experiment.

4.2. Enthalpies of Formation of Lead Lanthanum Titanates

We can calculate mean molar heat capacities of lead lanthanum titanates from the molar enthalpy differences $[H(673 \text{ K} -$

TABLE II

COMPARISON OF MAXIMUM PbO DEFICIENCIES AND ENTHALPIES OF REACTIONS (8) FOR LEAD LANTHANUM TITANATES $\text{Pb}_{1-x-y}\text{La}_{2x/3}\text{TiO}_{3-y}$ WITH CALCULATED VALUES (SEE TEXT)

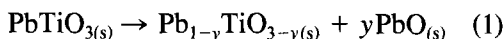
x	$Y(\text{exp})$	$Y(\text{calc})$	$\Delta_R H_{8,\text{exp}}$ (kJ mole ⁻¹)	$\Delta_R H_{8,\text{calc}}$ (kJ mole ⁻¹)
0.04	0.11	0.11	-1.5	-2
0.08	0.10	0.11	-4.7	-4
0.15	0.11	0.10	-11.0	-7
0.29	0.07	0.08	-24.4	-13

$H(320\text{ K})$], when no phase transition occurs in this temperature interval. The calculated values $(111.6 + 1.8)\text{ J K}^{-1}\text{ mole}^{-1}$ ($x = 0.04$) and $(113.8 + 1.6)\text{ J K}^{-1}\text{ mole}^{-1}$ ($x = 0.29$) are in accordance with values assessed from molar heat capacities of the oxide components (17) using Neumann-Kopp's rule, which assumes additivity of molar heat capacities. Thus, for reaction (2) $\Delta C_p = 0$; the enthalpies of formation in Table I are valid at 298.15 K. The higher molar enthalpy differences of the two other lead lanthanum titanates ($x = 0.08$ and 0.15, cf. Table I) are due to the occurrence of the ferroelectric phase transition in the investigated temperature interval; the difference of about 6 or 3 kJ mole^{-1} can be attributed to the enthalpy of the ferroelectric phase transition. The transitions occur over a large temperature interval ("diffuse phase transitions"), probably because of the large defect concentration of lead lanthanum titanates. This phenomenon is reflected in the relatively high uncertainties of the Curie temperatures (Table I).

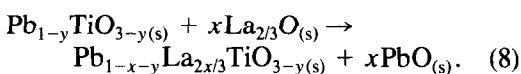
The molar enthalpies of formation of lead lanthanum titanates according to reaction (2) are positive at lower molar fractions of lanthanum, but clearly negative at higher concentrations (Table I). A linear relation between the molar enthalpy of formation $\Delta_R H_2$ (the index refers to the reaction number) and the molar fraction of lanthanum x can be written

$$\Delta_R H_2 = 6.1 - 81x. \quad (7)$$

This result can be interpreted by separating the formation of the "intrinsic" nonstoichiometry



from the "extrinsic" nonstoichiometry



The constant in Eq. (7) represents the enthalpy of reaction (1) ($x = 0$). Division of

this value by $Y = 0.12$ leads to the enthalpy of formation of one mole vacancy pairs V_{Pb}'' and V_{O}'' , the so-called "Schottky enthalpy": $\Delta H_{\text{Sch}} = 50\text{ kJ mole}^{-1}$. This result is in agreement with values previously calculated from calorimetry or estimated from the temperature dependence of Y for pure lead titanate (9). The consistency of the calorimetric values and the predictions of the model is emphasized. The enthalpy of reaction (1) can be subtracted from the experimental enthalpies of reaction (2) to obtain the enthalpies of reaction (8): $\Delta_R H_8$.

The enthalpies $\Delta_R H_8$ can be compared with independent values calculated from the lattice energies ($\Delta_L U$). Neglecting the small difference between energy and enthalpy for condensed phases, we can write

$$\Delta_R H_8 = \Delta_L U(\text{PLT}) - \Delta_L U(\text{PT}) + x[\Delta_L U(\text{PbO}) - \Delta_L U(\text{La}_{2/3}\text{O})]. \quad (9)$$

Literature values for the lattice energies of lead oxide (3565 kJ mole^{-1} (18)) and lanthana $\text{La}_{2/3}\text{O}$ (4150 kJ mole^{-1} (19)) are known. The lattice energies of lead titanate and lead lanthanum titanates were computed using the Born-Mayer equation (Avogadro number: $N = 6.022045 \times 10^{23}\text{ mole}^{-1}$, permittivity of vacuum: $\epsilon_0 = 8.854 \times 10^{-12}\text{ F m}^{-1}$, elementary charge: $e = 1.60219 \cdot 10^{-19}\text{ C}$):

$$\Delta_L U = -NMe^2/(4\pi\epsilon_0 R_0)(1 - r/R_0). \quad (10)$$

The lattice parameters a of the compounds with maximum PbO -deficiency were taken from Kling ($R_0 = a/2$ (15)). The Madelung constant M of tetragonal perovskites could be calculated using the formula of Saltzman and Schor (20). The repulsion parameter r of lead perovskites was determined using the procedure proposed by Baughan (21). The lattice energy of lead titanate ($y = 0.100$) was then calculated to $\Delta_L U(\text{PT}) = -1536\text{ kJ mole}^{-1}$ (12). A linear relationship between the lattice energy of lead lanthanum titanates and the lanthanum content x was derived (12):

$$\Delta_L U(\text{PLT})/(\text{kJ mole}^{-1}) \\ = -15,360 - 630x. \quad (11)$$

The intercept is in agreement with the calculated lattice energy of pure lead titanate. We obtain finally

$$\Delta_R H_8 = -45x. \quad (12)$$

The values calculated with this formula are tabulated together with the experimental results in Table II.

5. Conclusion

Lead lanthanum titanates with different lanthanum contents were investigated by calorimetric and analytical techniques.

1. The maximum PbO-deficiency of lead lanthanum titanates decreases slowly with increasing molar fraction of lanthanum.

2. The molar enthalpies of formation of lead lanthanum titanates from lead titanate and lanthana are positive at low, negative at higher lanthanum concentrations.

Both results can be interpreted by a model based on defect reactions and equilibria at the temperature of preparation.

Acknowledgment

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