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Interaction between Ni/NiO and $PbTiO_3$: Phase Reversal with Redox Switching

K.T. Jacob and V.S. Saji

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In some applications it is useful to have $Pb(Zr,Ti)O_3$ (PZT) films printed and fired on metallic substrates because of low cost, ease of handling, and mechanical flexibility of the substrate. As part of the systematic studies on phase compatibility of metallic substrates with PZT ceramics, studies have been conducted on the interaction between Ni and $PbTiO_3$ under oxidizing and neutral conditions at 1123 K. Phase relations in the pseudoternary system NiO-PbO-TiO_2 and quaternary Ni-Pb-$NiTiO_3$-$PbTiO_3$ were explored by equilibrating compacted mixtures of component oxides and/or metals in air and prepurified Ar gas. The equilibrium phases were identified by x-ray diffraction and energy dispersive spectroscopy. The results suggest that NiO is phase compatible with $PbTiO_3$. When nickel surface is oxidized, NiO is in direct contact with $PbTiO_3$ and there is no displacement reaction between NiO and $PbTiO_3$. However, in neutral and reducing conditions metallic Ni reacts with $PbTiO_3$ to form $NiTiO_3$ and a lead-rich alloy, with catastrophic consequences in device applications. The results are rationalized using a thermodynamic analysis. The nature of phase relations in the system Ni-Pb-Zr-O is elucidated using thermodynamic data.

Keywords displacement reaction, metal/ceramic interaction, NiO-PbO-TiO_2 system, Ni-Pb-$NiTiO_3$-$PbTiO_3$ system, phase diagram

1. Introduction

The ferroelectric ceramic $Pb(Zr,Ti)O_3$, abbreviated as PZT, used in sensors, activators, and electromechanical transducers, is often deposited or printed on ceramic substrates. In some applications, metallic substrates are required. When fired in air, the metallic surface is oxidized and PZT is in direct contact with the oxide. If fired in neutral or reducing conditions the PZT is in contact with the metal. Hence it is necessary to study interaction of PZT with both the substrate metal and its oxide. Most high-temperature alloys in common use are based on iron, cobalt, or nickel. Of these three metals, nickel has the lowest affinity for oxygen. Reduction of PZT by the metal is least likely when using nickel as the substrate. Hence, this study was conducted on the interaction between Ni and NiO with PZT.

Known phases in the quaternary system Pb-Ni-Ti-O are represented on the equilateral tetrahedron (Fig. 1), in which apices represent the pure components and the edges represent the six binary systems under isothermal and isobaric conditions. The four triangular faces represent the four ternary systems. Quaternary compositions are represented by points in the interior of the tetrahedron. The shaded triangle in Fig. 1, with Ni, Pb, and TiO_2 as corners, divides the quaternary into two halves. The lower portion of the quaternary containing titanium alloys and lower oxides of titanium, associated with very low oxygen chemical potentials, was not explored in this study. The upper portion containing Pb-Ni alloys, oxides of Pb and Ni, and titanates at relatively higher oxygen potentials was experimentally investigated at 1123 K. Oxygen chemical potentials for three-phase equilibria M-$MTiO_3$-TiO_2 (M = Pb, Ni) in the bounding ternary systems M-Ti-O depicted in Fig. 2 were measured earlier as a function of temperature using solid-state electrochemical

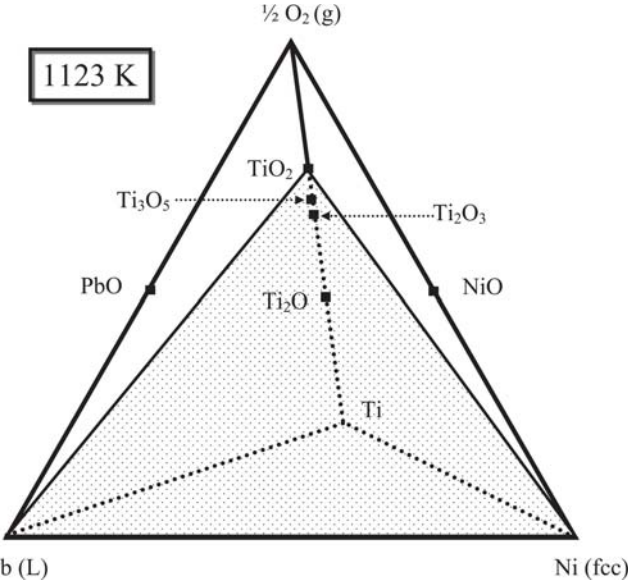

Fig. 1 Quaternary system Ni-Pb-Ti-O under isothermal and isobaric conditions represented by an equilateral tetrahedron. The shaded triangle with Ni, Pb, and TiO_2 as corners divides the quaternary into two halves. The upper portion containing Pb-Ni alloys, oxides of Pb and Ni, and titanate phases at relatively high oxygen chemical potentials was experimentally investigated at 1123 K.

K.T. Jacob and **V.S. Saji,** Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India. Contact e-mail: katob@met.iisc.ernet.in.

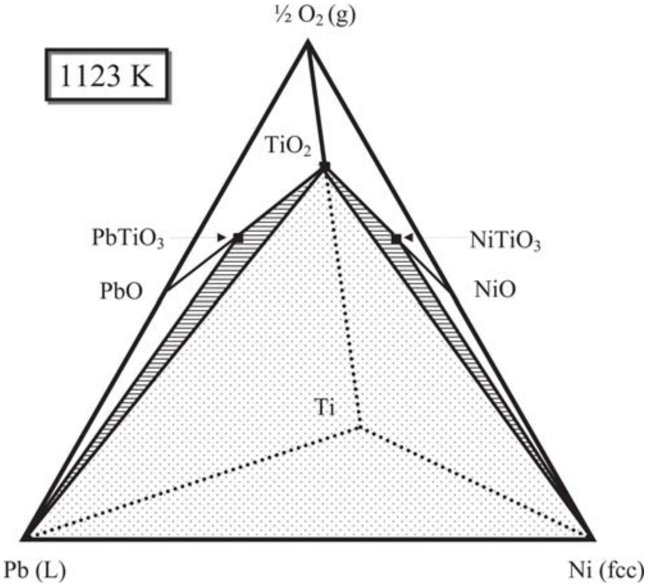

Fig. 2 Three-phase equilibria M-$MTiO_3$-TiO_2 (M = Ni, Pb) in the bounding ternary systems M-Ti-O, which were investigated earlier (Ref 1, 2).

cells.[1,2] The standard Gibbs energies of formation of $PbTiO_3$ and $NiTiO_3$ were deduced from these measurements.

In this study, phase equilibria between Ni-Pb alloys and $MTiO_3$ titanate phases (M = Ni, Pb) represented by the shaded region in Fig. 3 were explored. Ten mixtures of metals and oxides of different average composition were equilibrated at 1123 K in argon atmosphere to prevent oxidation of the metal phase. Phase composition of quenched samples was determined by x-ray diffraction (XRD) and energy dispersive spectroscopy (EDS). Also explored were phase relations in air between monoxide (MO) phases and titanate ($MTiO_{3)}$ (M = Ni, Pb) phases in the shaded plane of Fig. 4. The oxide samples were equilibrated in air.

2. Experimental Procedure

2.1 Materials

$NiTiO_3$ and $PbTiO_3$ were prepared from fine powders of NiO, PbO, and TiO_2 of 99.9% purity. Yellow PbO with orthorhombic structure and rutile form of TiO_2 were used for synthesis. The oxides were dried at 450 K and then passed through a 325 mesh screen. An equimolar mixture of PbO/NiO and TiO_2 was mixed in an agate mortar using isopropyl alcohol as the vehicle. $NiTiO_3$ was prepared by heating the compacted mixture of NiO and TiO_2 at 1373 K for 72 h in air. The pellet was ground, pelletized, and reacted again under identical conditions for a further period of 72 h. Yellow $NiTiO_3$ had the ilmenite structure with lattice parameters a = 0.50301 nm and c = 1.37898 nm. The mixture of PbO and TiO_2 was pelletized and heated at 1373 K for 3 h and 1125 K for 20 h in a closed platinum crucible in air. The pellet was burned in a loose powder mixture of the same composition. The small loss of PbO by volatilization occurred preferentially from the loose powder. The composition of the pellet was thus unaffected. The product was reground and heated for a further 3 h at 1200 K under similar conditions. The formation of lead titanate was confirmed by XRD analysis. At room temperature and ambient pressure, yellow-brown $PbTiO_3$ had tetragonal symmetry (*P4mm*) with lattice parameters a = 0.3898 nm and c = 0.4152 nm. It was ferroelectric exhibiting the characteristic hysteresis loop. Differential scanning calorimetry studies showed that tetragonal $PbTiO_3$ transforms to cubic perovskite at 764 K on heating with an associated enthalpy change

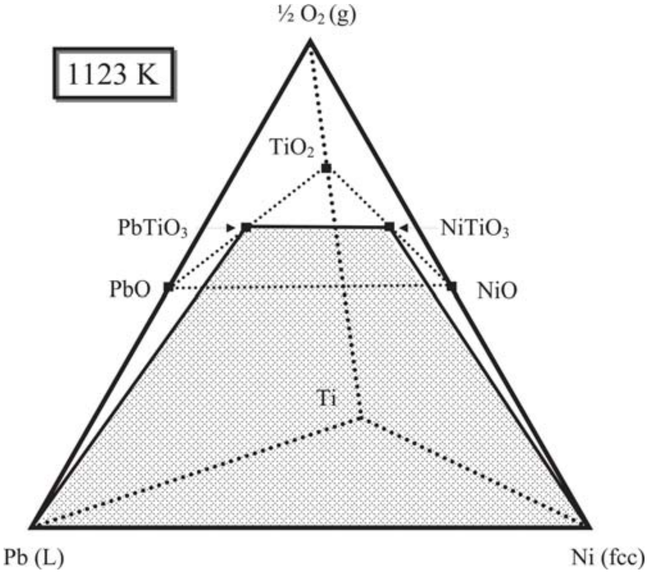

Fig. 3 Section of the quaternary diagram containing Ni-Pb alloys and $MTiO_3$ (M = Ni, Pb) titanate phases is represented by the shaded region.

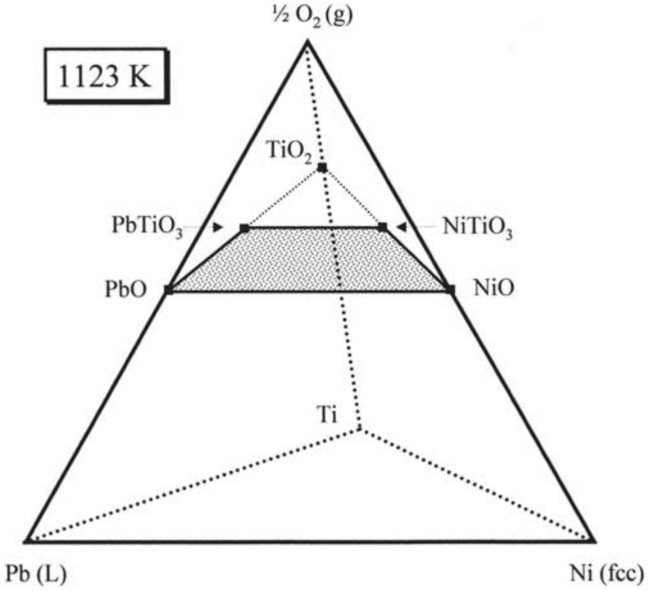

Fig. 4 Section of the quaternary diagram containing monoxide (MO) and titanate ($MTiO_{3)}$ (M = Ni, Pb) phases is represented by the shaded region.

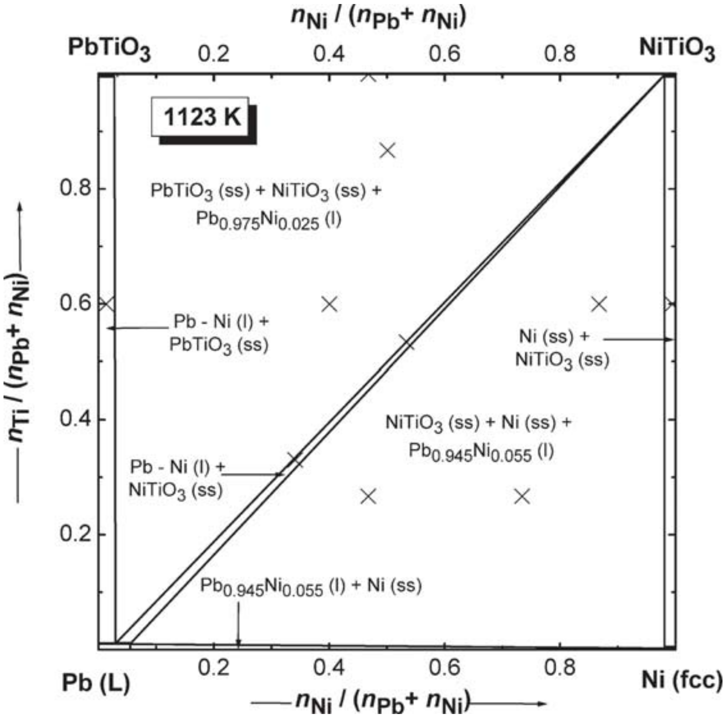

Fig. 5 Phase relations in the quaternary Pb-Ni-$PbTiO_3$-$NiTiO_3$ at 1123 K obtained by analysis of equilibrated samples. The average composition of the equilibrated samples is shown by X.

of 2.0 (±0.1) kJ/mol. Fine powders of Pb and Ni used in this study, ranging in size from 2 to 6 μm, were of 99.99% purity. Argon gas of 99.999% purity was dried by passing through anhydrous phosphorous pentoxide and deoxidized by copper wool at 723 K.

2.2 Equilibration

Precisely weighed quantities of selected metal (Ni/Pb) and metal titanate ($MTiO_3$, M = Ni, Pb) or metal oxide (MO, M = Ni, Pb) and titanate powders were pressed into pellets and placed in zirconia crucibles. Each crucible was packed with loose powder of the same composition. The crucible covered with a lid was put into a quartz tube, which was rinsed three times under vacuum (~1 Pa) with prepurified argon gas and then flame sealed under reduced pressure (~2×10^4 Pa) of argon. Initially, powders were mixed in approximately equimolar ratio and pelletized at 200 MPa in a steel die. In subsequent experiments, different ratios of the coexisting phases were used. Mixtures of $PbTiO_3$ and Ni, Pb and $NiTiO_3$, PbO and $NiTiO_3$, and NiO and $PbTiO_3$ were equilibrated to determine equilibrium phase relations. Additional samples were chosen for equilibration to refine the phase diagram obtained from preceding experiments. The overall compositions of samples used are identified by cross mark in Fig. 5 and 7. The samples were equilibrated at 1123 K for a total duration of 120 h, with intermediate grinding.

2.3 Chemical Analysis

Part of the quenched samples were mounted and polished for EDS and optical microscopy. Part of the sample was analyzed by XRD. Mixed with powder sample for XRD was metallic silicon, which acted as an internal standard, so that accurate cell dimensions can be obtained by least squares refinement of lattice spacing. Quantitative analysis of individual phases was done by EDS on JEOL 7830F Auger Microprobe (JEOL, Tokyo, Japan). A narrow electron beam was focused on either the oxide or metal phase to minimize the interference from neighboring phases. Pure Pb, Ni, NiO, and TiO_2 were used for calibration.

3. Results and Discussion

3.1 Phase Relations between Alloy and Titanates

Phase relations in the quaternary Pb-Ni-$PbTiO_3$-$NiTiO_3$ obtained by analysis of nine samples is shown in Fig. 5. The mean compositions of the ten samples studied are displayed by the symbol X. No new phases were detected in this section of the phase diagram. The most striking result is the incompatibility between Ni and $PbTiO_3$. When Ni is in contact with $PbTiO_3$, there will be a displacement reaction at the interface giving rise to $NiTiO_3$ and Pb-rich alloy phase. Liquid Pb dissolves about 5.5 mol% Ni and a small amount of oxygen. There is a three-phase region involving $PbTiO_3$ (ss) + $NiTiO_3$ (ss) + Pb liquid containing 2.5 mol% Ni. A second three-phase region involving $NiTiO_3$ (ss), liquid Pb containing 5.5 mol% Ni, and solid Ni containing 3 mol% Pb also exists at 1123 K. Even when Pb-rich alloys are in equilibrium with oxides, there was little tendency for the heavy metal phase to segregate by gravity flow. The small lead spherical particles (~3 μm) were held between oxide grains of the pellet by surface tension forces.

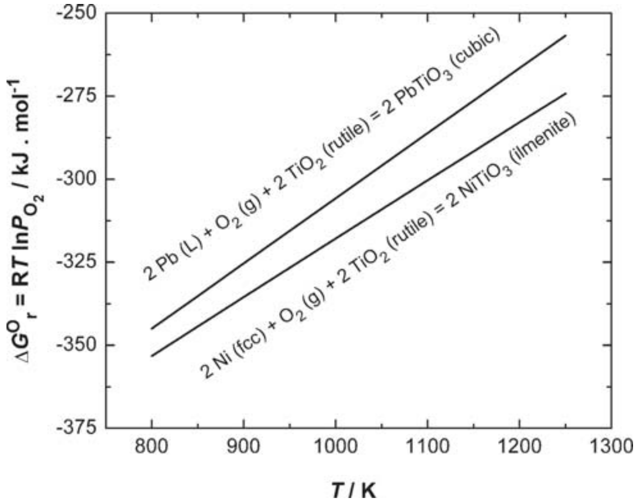

Fig. 6 Variation of the standard Gibbs energy changes, (ΔG°_r) for reactions $2M + O_2 + 2TiO_2 = 2MTiO_3$ (M = Ni, Pb) with temperature

The phase equilibrium results can be rationalized on the basis of thermodynamic data on $PbTiO_3$ and $NiTiO_3$.[1-3] For the reaction:

$$2\,Pb(L) + O_2(g) + 2\,TiO_2\,(rutile) = 2\,PbTiO_3\,(cubic) \qquad (Eq\ 1)$$

$$\Delta G^0_{(1)} J \cdot mol^{-1} = -501{,}860 + 196.11\,(T/K) \qquad (Eq\ 2)$$

$$2\,Ni\,(fcc) + O_2(g) + 2\,TiO_2\,(rutile) = 2\,NiTiO_3\,(ilmenite) \qquad (Eq\ 3)$$

$$\Delta G^0_{(3)}/J \cdot mol^{-1} = -503{,}468 + 253.28\,(T/K) - 9.80\,T \ln (T/K) \qquad (Eq\ 4)$$

Standard Gibbs energy changes associated with the formation reactions of $PbTiO_3$ and $NiTiO_3$ are plotted as a function of temperature in Fig. 6. The line for $NiTiO_3$ is below that for $PbTiO_3$ at all temperatures shown on the diagram. The data indicate that Ni will displace Pb from $PbTiO_3$ forming two separate phases $NiTiO_3$ and Pb(L) at the interface. In PZT ceramics, the activity of $PbTiO_3$ is less than unity. This will displace Gibbs energy curve of $PbTiO_3$ in the negative direction toward the curve for $NiTiO_3$ by 2 $RT \ln a_{PbTiO_3}$, but will not change the overall qualitative picture. For the $Pb(Ti_{0.5}Zr_{0.5})O_3$ composition, the activity of $PbTiO_3$ at 1123 K is 0.753,[4] resulting in a downward displacement of oxygen potential by −5.3 kJ/mol. With decrease in temperature, positive deviation from ideality will become more pronounced and hence the absolute value of 2 $RT \ln a_{PbTiO_3}$ will become smaller. The results clearly indicate that PZT ceramic films deposited and fired on Ni substrates cannot give stable performance.

3.2 Phase Relations in the System PbO-NiO-TiO$_2$

Based on phase identification of 19 samples of different overall composition equilibrated at 1123 K, an isothermal section of the phase diagram is composed (Fig. 7). Along the binary PbO-NiO, there were no solid solutions (ss) or interoxide compounds. Along the binary NiO-TiO_2, there is some limited terminal solid solubility and a ternary oxide $NiTiO_3$. Along the binary PbO-TiO_2 there are several PbO phases and a ternary oxide $PbTiO_3$. PbO has small solid solubility in TiO_2. The stable phase of PbO has the ortho–rhombic structure. However, addition of TiO_2 stabilizes the low-temperature tetragonal structure over a limited compositional range. A liquid phase of PbO containing dissolved TiO_2 is also located along the binary. Both $NiTiO_3$ and $PbTiO_3$ have a small homogeneity range. No quaternary oxide was detected. The most important feature of the diagram is the compatibility of NiO with $PbTiO_3$. $PbTiO_3$ deposited on an oxidized Ni substrate is therefore stable.

There is only limited terminal solid solubility along the join $PbTiO_3$-$NiTiO_3$. At 1123 K, $PbTiO_3$ has cubic or perovskite structure ($Pm\bar{3}m$), and $NiTiO_3$ has the ilmenite structure ($R\bar{3}$). The limited solubility is understandable in terms of the structural incompatibility of the end members. Isothermal section of the phase diagram contains five three-phase regions. These are: (a) TiO_2 (ss) + $PbTiO_3$ (ss) + $NiTiO_3$ (ss), (b) $PbTiO_3$ (ss) + $NiTiO_3$ + NiO (ss), (c) $PbTiO_3$ (ss) + NiO + PbO (Ls), (d) NiO + PbO (Ls) + PbO (t) (ss), and (e) NiO + PbO (t) (ss) + PbO (o) (ss). During deposition of $PbTiO_3$ on oxidized Ni surfaces, it is desirable to avoid PbO-rich $PbTiO_3$ composition so that the risk of formation of a liquid phase is minimized. Thin films (10 to 1000 nm) of PZT are usually deposited by sputtering, evaporation, or sol-gel processes. Thicker layers up to 100 μm can be obtained using the screen printing technique.

The major features of the phase diagram can be rationalized on the basis of thermodynamic data for $PbTiO_3$ and $NiTiO_3$.[1,2] Depicted in Fig. 8 are the standard Gibbs energies of formation of $PbTiO_3$, $NiTiO_3$, and $PbZrO_3$ from component binary oxides as a function of temperature.[1-3] For the reaction:

$$PbO\,(orthorhombic) + TiO_2\,(rutile) = PbTiO_3\,(cubic) \qquad (Eq\ 5)$$

$$\Delta G^0_{(5)}/J \cdot mol^{-1} = -32{,}510 - 0.995\,(T/K) \qquad (Eq\ 6)$$

$$NiO\,(rock\ salt) + TiO_2\,(rutile) = NiTiO_3\,(ilmenite) \qquad (Eq\ 7)$$

$$\Delta G^0_{(7)}/J \cdot mol^{-1} = -12{,}250 + 2.44\,(T/K) \qquad (Eq\ 8)$$

$$PbO\,(orthorhombic) + ZrO_2\,(monoclinic) = PbZrO_3\,(cubic) \qquad (Eq\ 9)$$

$$\Delta G^0_{(9)}/J \cdot mol^{-1} = -4540 - 6.76\,(T/K) \qquad (Eq\ 10)$$

The lines for $PbTiO_3$ and $PbZrO_3$ show change in slope at the melting point of PbO. Above the melting point, the standard Gibbs energies of formation of $PbTiO_3$ and $PbZrO_3$ can be represented as:

$$PbO\,(L) + TiO_2\,(rutile) = PbTiO_3\,(cubic) \qquad (Eq\ 11)$$

$$\Delta G^0_{(11)}/J \cdot mol^{-1} = -59{,}660 + 23.06\,(T/K) \qquad (Eq\ 12)$$

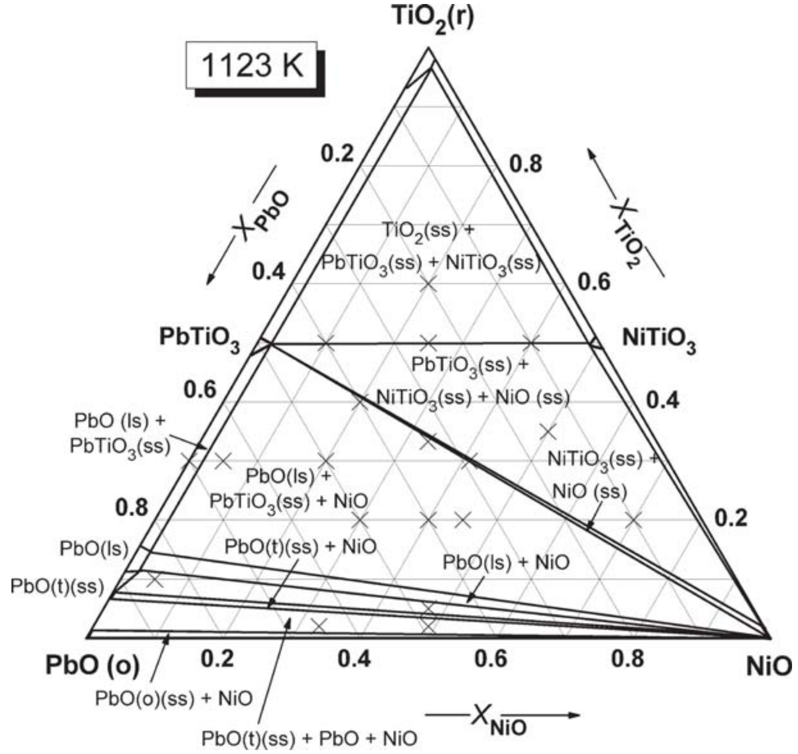

Fig. 7 Experimental phase equilibria for the system PbO-NiO-TiO_2 at 1123 K. The average overall composition of the equilibrated samples is shown by X.

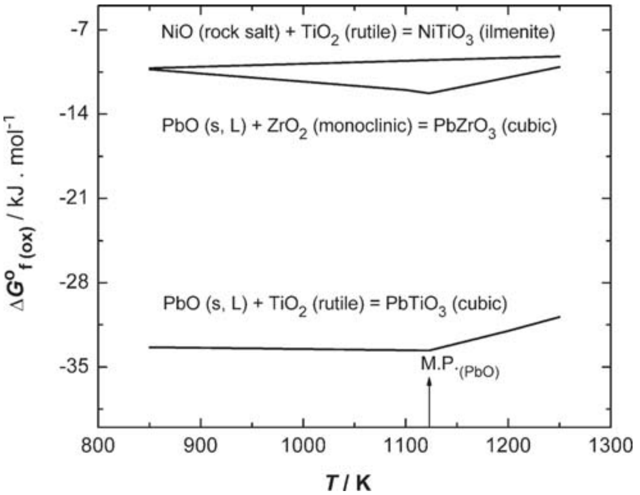

Fig. 8 Variation with temperature of the standard Gibbs energy of formation from component binary oxides, ($\Delta G^{\circ}_{f(ox)}$) for $NiTiO_3$, $PbTiO_3$, and $PbZrO_3$

$$PbO\ (L) + ZrO_2\ (\text{monoclinic}) = PbZrO_3\ (\text{cubic}) \qquad (\text{Eq 13})$$

$$\Delta G^0_{(13)}/\text{J} \cdot \text{mol}^{-1} = -31{,}690 + 17.29\ (T/\text{K}) \qquad (\text{Eq 14})$$

It can be seen from the figure that Gibbs energy of formation of $PbTiO_3$ from binary oxides is significantly more negative than that of $NiTiO_3$. Thus NiO cannot react with $PbTiO_3$ to give $NiTiO_3$ and a PbO-rich phase.

The two-phase equilibria NiO + $PbTiO_3$ and $PbTiO_3$ + $NiTiO_3$ identified in this study are in agreement with the results of Hrovat et al.,[5] who investigated subsolidus phase relations in the system PbO-NiO-TiO_2 at 1073 K. However, they did not report on the stability of the various PbO-rich phases and their solubility limits.

3.3 Phase Relations in the System PbO-NiO-ZrO_2

Based on the results obtained for the system Pb-NiO-TiO_2 and thermodynamic properties of $PbZrO_3$,[3] a qualitative picture of phase relations in the system PbO-NiO-ZrO_2 can be obtained. Along the binary PbO-ZrO_2, there is a stable phase corresponding to the composition $PbZrO_3$. At room temperature and ambient pressure, $PbZrO_3$ is antiferroelectric with orthorhombic symmetry, *Pbam/Pba*2. Since there is no other competing phase, NiO will coexist with $PbZrO_3$, as shown in Fig. 9. The stability of $PbZrO_3$ in contact with Ni can be evaluated from the Gibbs energy changes for the oxidation reactions shown in Fig. 10.

$$2Pb(L) + O_2(g) + 2\ ZrO_2(\text{monoclinic}) = 2\ PbZrO_3\ (\text{cubic}) \qquad (\text{Eq 15})$$

$$\Delta G^0_{(15)}/\text{J} \cdot \text{mol}^{-1} = -445{,}920 + 184.58\ (T/\text{K})^{[3]} \qquad (\text{Eq 16})$$

$$2\ Ni\ (\text{fcc}) + O_2(g) = 2\ \text{Nio}\ (\text{rock salt}) \qquad (\text{Eq 17})$$

$$\Delta G^0_{(17)}/\text{J} \cdot \text{mol}^{-1} = -478{,}968 + 248.404\ (T/\text{K}) - 9.80\ T \ln\ (T/K)^{[6]} \qquad (\text{Eq 18})$$

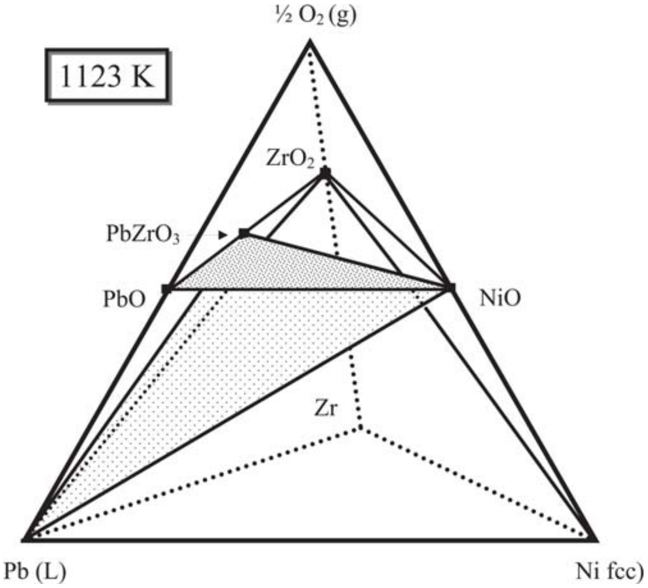

Fig. 9 Subsolidus phase equilibria in the system Zr-Pb-Ti-O

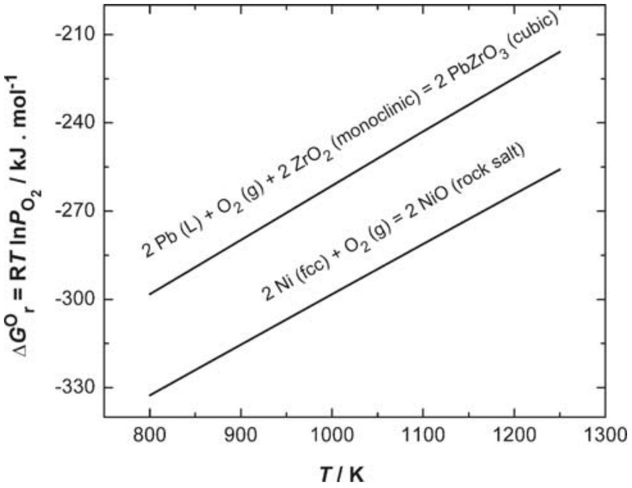

Fig. 10 Variation with temperature of the standard Gibbs energy change (ΔG_r°) for oxidation reaction involving Pb and Ni in the presence of ZrO_2

Since there is no stable ternary oxide of Ni, it can only be oxidized to NiO, whereas Pb is oxidized to $PbZrO_3$ in the presence of ZrO_2. The oxygen potential to oxidation of Ni to NiO[6] is considerably lower than that for the decomposition of $PbZrO_3$ to Pb and ZrO_2.[3] Therefore Ni will react with $PbZrO_3$ to form NiO, ZrO_2, and Pb. Thus lead zirconate, even when present at reduced activity in PZT ceramics, would not be stable in contact with metallic Ni as depicted in Fig. 9. The actual products formed by reaction of PZT ceramics with Ni metal depend on the composition of PZT and temperature. Although the driving force for reaction of $PbZrO_3$ with Ni is larger than for $PbTiO_3$, the kinetics of these competing reactions is expected to be dependent on composition and temperature.

The other three-phase equilibria represented by tie-triangles in Fig. 9 are Pb + PbO + NiO, Pb + ZrO_2 + NiO, Ni + NiO + ZrO_2, and Pb + Ni + ZrO_2. Four phase equilibria, represented by tie-tetrahedra are Pb + PbO + NiO + $PbZrO_3$ and Pb + $PbZrO_3$ + ZrO_2 + NiO. Any composition within each tetrahedron will separate into the four phases; the composition of the phases are given by the apices. Four three-phase regions adjoin the four-phase tie-tetrahedron. The nature and extend of solid solubility in the system cannot be computed from thermodynamic information now available and must be obtained by experiment.

4. Conclusions

Phase equilibrium measurements in the appropriate sections of the phase diagram for the system Pb-Ni-Ti-O and thermodynamic considerations indicate PZT ceramics are not stable in contact with metallic Ni. They will react to form several phases at the interface that include $NiTiO_3$, Pb-rich alloy, and/or ZrO_2. Formation of an oxidized layer on Ni can prevent the degradation reaction since NiO is compatible with both $PbTiO_3$ and $PbZrO_3$. However, NiO does not have sufficient electrical conductivity to act as an electrode for PZT ceramics. Hence the use of NiO barrier layer between Ni and PZT ceramics has only limited potential in device applications. It will be useful to explore the use of either doped-NiO or other NiO-containing buffer layers with higher conductivity.

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