

Thermodynamic assessment of phase relations in the system PbO–RuO₂–TiO₂

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Lead ruthenate (Pb₂Ru₂O_{6.5}) with pyrochlore structure is one of the phases that form in thick-film resistors, which consist of a conducting oxide dispersed in a lead borosilicate glass with minor additions. Lead ruthenate converts to RuO₂ when the PbO concentration in the glass is reduced. TiO₂ is added as a modifier to lower the temperature coefficient of resistance of thick-film resistors. To understand the chemistry of the system, Hrovat et al. [1] examined subsolidus phase relations in the system PbO–RuO₂–TiO₂ by firing mixtures of PbO, RuO₂ and TiO₂ in air and subsequent phase identification by X-ray diffraction (XRD). Along the binary PbO–RuO₂ they identified the compound Pb₂Ru₂O_{6.5}. Strictly the composition of this compound does not fall on the binary join PbO–RuO₂ since it contains excess oxygen. Along the binary PbO–TiO₂ only one ternary compound PbTiO₃ was identified. No new phases were identified along the join RuO₂–TiO₂ or inside the ternary triangle. For all phases negligible solid solubility was indicated. Two tie lines were identified, one connecting TiO₂ and Pb₂Ru₂O_{6.5} and the other between PbTiO₃ and Pb₂Ru₂O_{6.5}. The proposed ternary phase diagram, shown in Fig. 1, indicates that there are no reactions between RuO₂ or Pb₂Ru₂O_{6.5}, which act as conducting phases in thick film resistors, and TiO₂.

Hrovat et al. [1] did not establish the attainment of equilibrium in their samples. Although they identified

the form of TiO₂ as rutile, they did not specify the form of PbO employed and the actual firing temperatures. Recent communication indicates that firing was done at 1,073 K for most samples [2]. The composition of phases that form during firing may be influenced by the kinetics of formation of the two competing ternary oxides Pb₂Ru₂O_{6.5} and PbTiO₃ from their component binary oxides. Phase reversal experiments were not conducted by Hrovat et al. [1]. One way to check attainment of equilibrium is to heat-treat equimolar mixtures of RuO₂ + PbTiO₃ and TiO₂ + Pb₂Ru₂O_{6.5} and identify the products of the reaction in the two samples. The form of PbO used does not influence the thermodynamics of phase formation since the stabilities of both PbTiO₃ and Pb₂Ru₂O_{6.5} are equally impacted. However, the nature of PbO will affect the kinetics of the two competing reactions.

During long exposure of an equimolar mixture of TiO₂ and Pb₂Ru₂O_{6.5} at 1,123 K the authors observed the formation of PbTiO₃ and RuO₂ suggesting that the phase relations suggested by Hrovat et al. [1] are incorrect. Since kinetics of solid-state reactions are sluggish at these temperatures, correct equilibrium phase relations can be better established by thermodynamic calculations. Thermodynamic data for PbTiO₃ is well established in the literature [3–8]. The early high-temperature vapor pressure measurements on PbTiO₃ [3–5] were incorrectly interpreted. The polymeric species of lead oxide (PbO)_n in the gas phase were ignored [3–4]. Shim and Jacob [6] have shown that when the polymeric species are taken into consideration the Gibbs energy of formation calculated from vapor pressure studies are in good agreement with the solid-state emf measurements [6, 7]. According to Shim and Jacob [6], for the reaction

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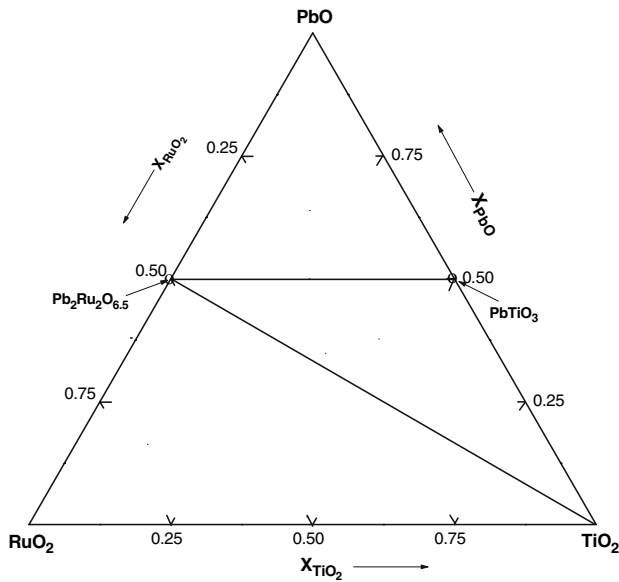
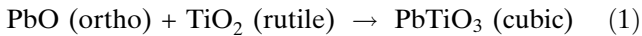
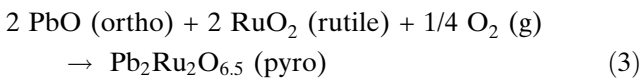


Fig. 1 The ternary phase diagram (subsolidus) of the system PbO–RuO₂–TiO₂ in air according to Hrovat et al. [1]



$$\Delta G^0 = -32510 - 0.995T (\pm 1200) \text{ J mol}^{-1} \quad (2)$$

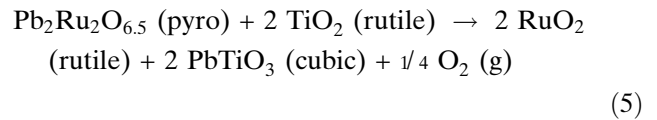
in the temperature range from 1,050 K to 1,350 K. The enthalpy of formation of PbTiO₃ from binary oxides suggested by Eq. 2 is –32.51 kJ/mol, in excellent agreement with the value of –32.06 (±2.7) kJ/mol at 970 K reported more recently by Rane and Navrotsky [8] using high-temperature drop solution calorimetry. Until recently, there was no information in the literature on the Gibbs energy of formation of Pb₂Ru₂O_{6.5}. Using a solid-state electrochemical cell, the oxygen chemical potential over a condensed phase mixture Ru + PbO + Pb₂Ru₂O_{6.5} has now been measured using Ru + RuO₂ as the reference electrode [9]. From the results Gibbs energy of formation of Pb₂Ru₂O_{6.5} from component oxides and oxygen gas according to the reaction



is obtained as

$$\Delta G^0 = -80224 + 75.763 (T/K) - 5.873 (T/K) \ln (T/K) (\pm 524) \text{ J mol}^{-1} \quad (4)$$

The direction of tie lines involving the phases RuO₂, TiO₂, PbTiO₃, and Pb₂Ru₂O_{6.5} is governed by the sign of the Gibbs energy change for the exchange reaction,



The value of ΔG⁰ for the above reaction at 1,073 K is –24.25 kJ/mol. Since solid solubilities at 1,073 K are not very significant, activities of the condensed phases are close to unity. In air the driving force for the reaction is enhanced. The value of ΔG for the reaction in air at 1,073 K is:

$$\Delta G = \Delta G^0 + RT \ln J = \Delta G^0 + 1/4 RT \ln p_{\text{O}_2} = -27730 \text{ J/mol} \quad (6)$$

indicating that Pb₂Ru₂O_{6.5} and TiO₂ will react together to form RuO₂ and PbTiO₃. Hence, the tie line connecting Pb₂Ru₂O_{6.5} and TiO₂ phases in the phase diagram of Hrovat et al. [1] is incorrect. The correct tie lines are between PbTiO₃ and RuO₂ and between Pb₂Ru₂O_{6.5} and PbTiO₃. The modified “ternary phase diagram” is shown in Fig. 2. In air TiO₂, which is added as a modifier in thick film resistors, will react with the conducting phase Pb₂Ru₂O_{6.5} to form PbTiO₃ and RuO₂, unless TiO₂ is dissolved in the glass with ther-

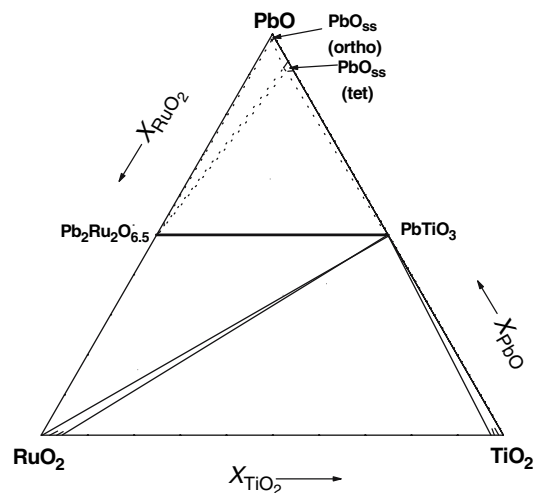


Fig. 2 The “ternary phase diagram” of the system PbO–RuO₂–TiO₂ in air at 1,073 K calculated from thermodynamic data. The diagram is a projection of phase relations in the quaternary shown in Fig. 3

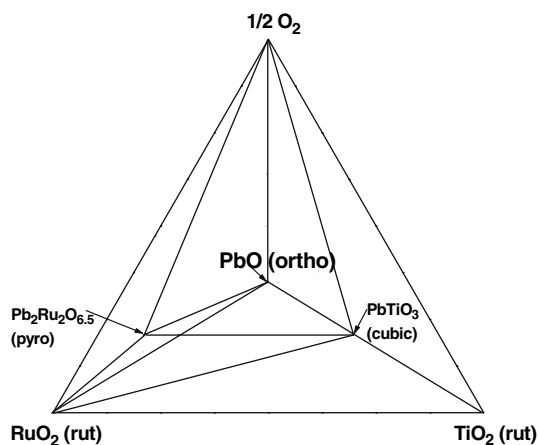


Fig. 3 Phase relations in the quaternary system PbO–RuO₂–TiO₂–O at 1,073 K

dynamic activity less than 0.21 at 1,073 K. Tentative phase relations for PbO-rich compositions shown in Fig. 2 are based on available information on the binary systems [10–12] and estimates of thermodynamic properties for PbO-rich solid solutions with orthorhombic and tetragonal structures. Strictly Fig. 2 is not an isothermal section of a true ternary system, but a projection of phase relations in the quaternary system PbO–RuO₂–TiO₂–O from the oxygen apex onto the PbO–RuO₂–TiO₂ plane at constant temperature as shown in Fig. 3.

The Gibbs energy of formation of PbTiO₃ from binary oxides (Eq. 2) exhibits only a small temperature dependence. However, the Gibbs energy of formation of Pb₂Ru₂O_{6.5} from oxides and oxygen gas (Eq. 4) varies strongly with temperature because one of the

reactant phases is gaseous. Hence, Pb₂Ru₂O_{6.5} will become more stable with decreasing temperature and a reversal in phase relations can occur below 323 (±50) K. Although thermodynamically feasible, at such low temperatures the rates of solid-state reactions are prohibitively negligible. It is unlikely that the predicted reversal can be realized in practice.

In summary, the subsolidus phase diagram for the system PbO–RuO₂–TiO₂ proposed by Hrovat et al. [1] is shown to be incorrect. The correct phase diagram computed from thermodynamic data is presented.

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