Oxygen – Lead – Zirconium

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Introduction

Experimental studies of the O-Pb-Zr system are confined to the investigation of $ZrPbO_3$ and the PbO-ZrO_2 section [1962Ike, 1967Fus, 1967Har, 1981Jac]. Thermodynamic properties and the phase diagram of the PbO-ZrO_2 system have been critically assessed by [1999Koo]. Extensive studies on the crystal structure, thermodynamic properties and phase transitions in lead zirconate are listed in Table 1.

Binary Systems

The binary O-Zr phase diagram is adopted from [Mas2]. The thermodynamic assessment of the O-Zr system reported by [2001Lia] is consistent with the accepted phase diagram.
The binary O-Pb phase diagram (Fig. 1) is taken from the critical assessment [1998Ris], with some modifications in the liquid phase region [2005Can]. There are no reports about the oxygen saturation limit in solid Pb, but it is certainly extremely small and could never be detected [1988Wri]. The liquid phase exhibits a large miscibility gap.
The accepted Pb-Zr phase diagram (Fig. 2) is taken from the critical evaluation of [1996Ari] later reviewed by [1999Oka]. This diagram is not definitively established due to very limited experimental information. There is no experimental information regarding the melting temperature of Zr_5Pb_3. This temperature was estimated to be ~1650°C by [1996Ari]. The value of ~2000°C was accepted by [1986Dal].

Solid Phases

Data pertinent to the PbO-ZrO_2 section are listed in Table 2.
Three stable perovskite type phases have been found at the $ZrPbO_3$ composition: the orthorhombic low temperature (up to 231°C) phase is antiferroelectric, the intermediate (from 231 to 234°C) is ferroelectric, and the cubic high temperature (up to the melting point T_m = 1570°C) phase is paraelectric [1979Wha] (Table 2). The paraelectric ⇌ ferroelectric ⇌ antiferoelectric phase transition temperatures depend on the oxygen nonstoichiometry and on the compositional deviations caused by the sublimation of PbO [1985Ujm]. Until now, the basic structure parameters have mainly been investigated for the antiferroelectric phase.
It was under debate for many years whether the room temperature phase of lead zirconate, α$ZrPbO_3$(r) is ferroelectric or antiferroelectric and hence whether the crystal structure belongs to the centrosymmetric or non-centrosymmetric space group. The crystal structure of the lead zirconate modifications was first proposed by [1951Saw] and the space group of the antiferroelectric phase was reported to be *Pbam* or *Pba*2. The authors were unable to locate the position of Zr or O ions, or to detect any displacement of the Pb ions out of the (001) planes. [1957Jon] made a more detailed study. Positions of the Zr and O ions were located to some extent, but they were not sure if the cations were displaced out of the (001) plane. The structure of α$ZrPbO_3$(r) has been reinvestigated by [1982Fuj, 1984Fuj]. These authors found a better reliability factor for space group *Pbam* than for *Pba*2. Also [1982Tan1, 1982Tan2] suggested the *Pbam* space group and determined the oxygen coordinates. In all these crystal studies it was assumed that the structure is fully ordered. However, according to [1993Gla] α$ZrPbO_3$(r) exhibit a disorder in the oxygen sites, whereas the ZrO_6 octahedra are considerably more regular. Later [1997Cor] found the true ordered oxygen structure, while [1998Tes] characterized structure by distortion of the ZrO_6 octahedra which is smaller then in the previous study [1993Gla]. The space group *Pbam* was also confirmed by [1997Cor, 1998Tes]. Moreover, the disorder in Pb ions displacements along *z* axis [1997Cor, 1997Sic, 1998Tes, 2000Fuj, 2001Fuj, 2002Fuj, 2003Fuj1, 2003Fuj2] and Zr-displacements were observed [1998Yam, 1997Soe]. There is a possibility, however, that the observed disorder is simply an artifact of pseudosymmetry. Whatever the space group is, one of the main problems in an accurate structure determination is the strong

pseudosymmertic character of the Pb and Zr sites and the relatively high scattering factor of the cations compared to the oxygen anions [1996Cor]. The difficulties to grow high quality large single crystals poses an additional problem. Thus, questions regarding the existence of polarization and the true crystal structure of lead zirconate are still open.

The structural instabilities and electronic properties of antiferoelectric $\alpha ZrPbO_3(r)$ were investigated by local-density total-energy calculations [1995Sin] using the atomic positions of [1982Fuj, 1984Fuj]. Results of [1995Sin] demonstrated the coexistence of both ferroelectric and antiferoelectric instabilities in lead zirconate, with a very delicate balance between them and correctly predicted a centrosymmetric *Pbam* group as the most stable structure, but a ferroelectric rhombohedral structure was very close in energy. Based on the new experimental data of [1997Fuj] a reexamination of crystal structure of antiferroelectric $\alpha ZrPbO_3(r)$ using density functional calculation [2002Rod, 2005Joh] showed small, but significant changes in cation positions compared to [1995Sin]. The relative stability of the antiferroelectric and ferroelectric phases in lead zirconate was also studied by [1998Ley], where the antiferoelectric dipole configuration was reported to be energetically more favorable than the ferroelectric one.

There is very little structural information about the paraelectric phase [1951Saw, 1979Koc, 1995Sin, 2001Kwa, 2002Aoy]. [1979Koc] found the existence of two phase transitions at 325 and 390°C in cubic paraelectric lead zirconate. [2002Aoy] detected the distinct disorder of Pb at twelve sites toward the neighboring O, which proves the existence of electron hybridization between O and disordered Pb in cubic $\beta ZrPbO_3(h_2)$. [2001Kwa] preformed experiments and model calculations reporting the strong indication of the displacement of Pb in cubic high temperature lead zirconate. The local density calculations by [1995Sin] showed a very strong instability of the cubic perovskite structure, which involve the changes in Pb-O distances with substantial hybridization between O and Pb. Results of [2002Rod] are very close to those obtained by [1995Sin]. Covalent nature of Pb and O bonds is also revealed in first principles study of [2005Wan].

Many authors reported the presence of a transient phase, $\gamma ZrPbO_3(h_1)$ [1951Saw, 1984Fuj, 1985Ism, 1986Rol, 1989Rol, 1992Fuj, 1998Tes] apart from the orthorhombic antiferroelectric and cubic paraelectric phases. However, the results and conclusions vary in details. [1951Saw] described the intermediate phase as antiferroelectric one with the tetragonal symmetry and occurring on cooling only. [1979Wha] reported the rhombohedral symmetry of the ferroelectric transient phase. [1984Fuj, 1992Fuj] supposed that the intermediate phase has an antiferroelectric character, while [1989Dec, 1982Tan2] reported that the transient phase has a ferroelectric character. Ferroelectric character of the intermediate phase was confirmed by dielectric measurements of [1986Rol, 1989Rol]. Authors of [1982Tan2] were the first who determined the space group of the transient phase as *F*$\bar{4}$2*mm*. At the same time, Rietveld analyses with *Pba*2 and *Pbam* settings made by [1998Tes] gave poor fits with large thermal factors on all atomic sites, what excluded these space groups.

In the purest samples of $ZrPbO_3$ the stability range of the intermediate phase is very narrow. Usually it has been detected between 230 and 235°C on heating and between 234 and 225°C on cooling. This temperature range depends on the purity of reagents or solvent used [1979Wha], but within the given class of reagents also on the preparation conditions [1989Dec]. Effect of preparation conditions, *i.e.*, sintering temperature, on phase transitions in lead zirconate was also investigated by [2004Puc1, 2004Puc2], while [1996Fes] reported the effect of the chemical etching on the phase transition and electrical hardening. It was also found that external DC electric field broadened and stabilized the transient ferroelectricity but that hydrostatic pressure rapidly removed it [1981Han].

The temperature dependence of permittivity and remaining polarization in monocrystaline and ceramic $ZrPbO_3$ and the temperature of the phase transitions between ferro-, antiferro-, and paraelectric phases are influenced by applied electric field and hydrostatic pressure. Under external electric field, $ZrPbO_3$ undergoes a series of phase transitions [1979Fes]. Although many studies have been performed [1981Han, 1978Fes, 1979Fes, 1984Leo, 1985Ism, 1992Shu, 1996Shu] no complete structural analysis of the field induced phases has been made so far. The lack of structural information on these phases is hindering the elucidation of the mechanisms of phase transition of this kind. [1984Leo] and [1992Shu, 1996Shu] reported the existence of a ferroelectric phase arising at room temperature under electric field of about 220 kV/cm.

The space group of this EFI (Electric Field Induced) phase is *Cm*2*m* and its ferroelectric properties are due to the ordering of Pb displacements relative to the oxygen framework along the polar axis [1996Shu].
Before 1995, there were only few studies focused on the influence of hydrostatic pressure on the phase transitions in lead zirconate [1981Han, 1985Ujm]. The ferroelectric phase was found to occur only at pressures less than 26 MPa for monocrystals and 40 MPa for the ceramics [1981Han]. Recently, the behavior at room temperature and much higher pressures has been studied in terms of structure and dielectric properties [1994Men, 1999Kob, 1999Fur1, 1999Fur2]. [1994Men] performed the high pressure experiments on the nanocrystalline $ZrPbO_3$ (with grain size of 94 nm). The transition pressure from ferro- to antiferroelectric as well as from para- to ferroelectric phases was found to be 0.79 and 4.12 GPa, respectively. [1999Kob] found that the orthorhombic phase ($\alpha ZrPbO_3$) transforms into the monoclinic one with almost no volume change at 37 GPa. This study also suggested a subtle structural change occurring in the monoclinic phase at about 75 GPa. On the other hand, dielectric constant measurements showed two anomalies at around 3 and 19 GPa for the polycrystalline samples, which suggested the existence of two transitions in the orthorhombic phase. Two phase transitions at about 2.3 and 17.5 GPa were confirmed by [1999Fur1, 1999Fur2]. Results of *ab initio* molecular dynamics and pseudopotencials calculations for the pressure influence on phase transitions [2002Leu] are in reasonable agreement with experiments. Local density calculations of [2000Coc] show that all the modes determining the orthorhombic antiferroelectric phase become more unstable in the range of lattice parameters corresponding to positive pressures.

Quasibinary Systems

The PbO-ZrO_2 section was first investigated by [1962Ike] and published by [1967Fus]. Decomposition of cubic $\beta ZrPbO_3(h_2)$ to tetragonal βZrO_2 and a liquid phase containing 93 mol% PbO at 1570°C [1967Fus] was also confirmed by [1981Jac]. A few investigations has been performed in the PbO rich part of PbO-ZrO_2 system [1967Fus, 1981Jac, 1967Har] but results are contradictory. [1967Har] reported that X-ray analysis of the samples PbO + ZrO_2 in 1:1 molar ratio heated to 1294°C indicated the presence of $ZrPbO_3$, αZrO_2, and αPbO. The last phase had a tetragonal structure of the red αPbO rather than the orthorhombic structure of the yellow βPbO. This finding was confirmed by [1981Jac] by heating an equimolar mixture of βPbO and αZrO_2 up to 955°C, followed by cooling in air and X-ray analysis. This observation is not in accord with the phase diagram by [1967Fus], but consistent with the assessed phase diagram by [1999Koo] which is accepted in the present assessment (Figs. 3a, 3b). A detailed study of the PbO rich side of the PbO-ZrO_2 phase diagram is required to check the temperature boundaries and phase composition of the various phase fields.

Invariant Equilibria

Table 3 lists the three-phase equilibria in the PbO-ZrO_2 system calculated using the thermodynamic description of [1999Koo]. The temperatures of the peritectic formation of $\beta ZrPbO_3(h_2)$, αPbO solid solution and that of the PbO rich eutectic were measured by [1967Fus] and are reproduced very exactly by calculations. No other invariant equilibria are known. The temperature of the L + $ZrO_2 \rightleftharpoons \beta ZrPbO_2$ reaction was calculated to be 1538°C [1999Koo], that is lower than experimental value of 1570°C [1967Fus, 1981Jac].

Thermodynamics

Thermodynamic properties of $ZrPbO_3$ were investigated by several groups [1969Hae, 1973Hol, 1979Sch, 1981Jac, 1993Gos, 1996Ono]. The experimental investigations were mainly performed on the high temperature cubic modification, β (Tables 4, 5 and 6) except the study of [1993Gos] on the low temperature orthorhombic modification, α. [1996Ono] measured the heat capacity of single crystals of antiferroelectric $\alpha ZrPbO_3$(r) in a wide temperature region (from room temperature to 377°C) by AC calorimetry, but have drawn the curve in arbitrary units. Heat capacity curve showed a sharp change at 231.5°C, due to transformation into the high temperature modification. [1993Gos] reported the thermodynamic functions (C_p, S, $H_T - H_{298}$) of the low temperature orthorhombic modification (α) from room temperature to 207°C.

The low temperature heat capacity data of $\alpha ZrPbO_3$(r) are missing. The Gibbs energy of formation of lead zirconate calculated from the vapor pressure studies (assuming that the vapor phase consists entirely of monomeric PbO molecules) [1969Hae, 1973Hol, 1979Sch] is inconsistent with the emf measurements reported by [1981Jac] and the PbO-ZrO_2 phase diagram, which suggests decomposition of lead zirconate to tetragonal ZrO_2 and a liquid phase containing 93 mol% PbO at 1570°C. Since the vapor phase over pure solid and liquid PbO consist of polymeric species of type Pb_nO_n ($1 < n < 6$) results based on the vapor pressure measurements differ significantly from those obtained by EMF measurements [1981Jac]. Recently, the enthalpy of formation of $\beta ZrPbO_3(h_2)$ was measured by [2001Ran]. The heat content and entropy of $\beta ZrPbO_3(h_2)$ are not known. Thermodynamic data for the other phases in the O-Pb-Zr system (liquid, PbO solid solutions, (αZr), (βZr), etc.) are completely missing.

[1999Koo] reported the thermodynamic assessment of the PbO-ZrO_2 system, where $ZrPbO_3$ was modeled as a stoichiometric compound based on the results of [1981Jac]. However, the only cubic high temperature phase $\beta ZrPbO_3(h_2)$ was included in the assessment. The Gibbs energy of cubic lead zirconate was described as $G_m^{ZrPbO3} = G(h)_{PbO2} + G_{\alpha ZrO2} - 4540 - 676T$ (J·mol^{-1}). The calculated heat capacity ($C_p = 110.6 + 2.5\cdot10^{-2}\,T - 7.8\cdot10^{5}\,T^{-2}$ J·mol^{-1}·K^{-1}), molar enthalpy and entropy for the cubic $ZrPbO_3$ are presented in Figs. 4 - 6. Figure 7 shows the calculated PbO vapor pressures compared with experimental data [1979Sch, 1973Hol, 1969Hae]. The standard enthalpy and the Gibbs energy of formation of $\beta ZrPbO_3(h_2)$ from elements and its entropy at 298 K, which were calculated using the thermodynamic description of [1999Koo] are presented in Table 7.

Notes on Materials Properties and Applications

Because of dielectric, pyroelectric and electro-optical properties lead zirconate ceramics has long been studied from both physical and technical point of view (Table 8). Especially, lead zirconate thin films have been studied extensively [1992Wan, 1999Bha, 2000Bae, 2000Bha, 2001Dob, 2004Ste]. Intensive research work has been carried out on ferroelectric and paraelectric thin films for commercial applications such as memory devices, infrared detectors and non-linear optoelectronics. Recently, antiferroelectric thin films [1992Wan, 1999Bha, 2000Bha] have been proposed for the new generations of “smart” systems such as high charge coupled devices (MEMs) consisting of sensors and actuators. Antiferroelectric materials are characterized by the antiparallelly aligned adjacent dipoles with zero polarization in equilibrium. The transformation of antiferroelectric to ferroelectric phase by a sufficient applications of electric field could be utilized for the high charge coupled devices and transducer applications. In addition, the highly oriented antiferroelectric $ZrPbO_3$ thin films were investigated in view of their possible application as a temperature sensitive element in an alternative bolometer system for fusion devices such as the International Thermonuclear Experimental Reactor to quantitatively determine the total power of incident radiation over a wide range of wavelengths [2004Bit, 2004Ste].

Miscellaneous

The *E-T* phase diagram of lead zirconate and schematic isothermal dependences of the dielectric polarization on the electric field are presented in Fig. 8 [1978Fes, 1979Fes]. [1989Hau] reported the thermodynamic theory to model the phase transition and properties of lead zirconate where its free energy was expressed as a power series of the ferroelectric and antiferroelectric polarization including all possible terms up to the sixth power and first-order cross-coupling terms and couplings to elastic stress. Morphologies of thin films and single crystals were also studied. Preferred orientation in $ZrPbO_3$ thin films prepared by sol-gel technique was studied by [2000Bae], while [1992Top] investigated the S type of twining boundaries in ferro- and antiferro- ferroelectric $ZrPbO_3$ crystals.

References

[1951Saw] Sawaguchi, E., Maniwa, H., Hoshino, S., "Antiferroelectric Structure of Lead Zirconate", *Phys. Rev.*, **83**, 1078 (1951) (Crys. Structure, Electronic Structure, Experimental, 5)

[1957Jon] Jona, F., Shirane, G., Mazzi, F., Pepinsky, R., "X-ray and Neutron Diffraction Study of Antiferoelectric Lead Zirconate", *Phys. Rev.*, **105**, 849-856 (1957) (Crys. Structure, Experimental, Phys. Prop., 24)

[1962Ike] Ikeda, T., Okano, T., Watanabe, M., "A Ternary System PbO-TiO_2-ZrO_2", *J. Appl. Phys. (Japan)*, **1**, 218-222 (1962) (Experimental, Phase Relations, 6)

[1967Fus] Fushimi, S., Ikeda, T., "Phase Equilibrium in the System PbO-TiO_2 -ZrO_2 ", *J. Am. Ceram. Soc*., **50**, 129-132, (1967) (Experimental, Phase Diagram, Phase Relations, 13)

[1967Har] Harris, N.H., "Solid State Reactions Forming the (Pb,Sr) (Ti,Zr) O Solutions", *Ph. D. Thesis*., University of Illinois, (1967) (Experimental, Phase Diagram, Phase Relations) as quoted in [1981Jac]

[1969Hae] Haerdtl, K.H., Rau, H., "PbO Vapor Pressure in the $Pb(Ti_{1-x}Zr_x)O_3$ System", *Mater. Res. Bull*., **3**, 41-45, (1968). (Experimental, Thermodyn., 7)

[1973Hol] Holman, R., Fulrath, R.M., "Intrinsic Nonstoichiometry in the Lead Zirconate-Lead Titnate System Determined by Knudsen Effusion", *J. Appl. Phys.,* **44**, 5227-5236, (1973) (Experimental, Thermodyn., 24)

[1978Fes] Fesenko, O.E., Kolesova, R.V., Sindeyev, Yu.G., "The Structural Phase Transitions in Lead Zirconate in Super-High Electric Fields", *Ferroelectrics*, **20**, 177-178 (1978) (in Russian) (Experimental, Phase Relations, 7)

[1979Fes] Fesenko, O.E., Kolesova, R.V., Sindeev, Yu.G., "Structural Phase Transitions in Lead Zirconate in Very High Electric Fields", *Sov. Phys. - Solid State (Engl. Transl.)*, **21**, 668-672 (1979), translated from *Fiz. Tverd. Tela (Leningrad)*, **21**, 1152-1159, (1979) (in Russian) (Crys. Structure, Electr. Prop., Experimental, Phase Relations, 18)

[1979Koc] Kochetkov, V.V., Venevtsev, Yu.N., Vostrikov, N.A., "New Phase Transitions in Lead Zirconate", *Sov. Phys.-Crystallogr. (Engl. Transl.)*, **24**, 494-495 (1979), translated from *Kristallografiya*, **24**, 858-859, (1979) (Crys. Structure, Experimental, 9)

[1979Nur] Nuritdinov, B., Kalashnikov, A.A., "Study of Lead Zirconate ($PbZrO_3$) Evaporation by Mass-Spectrometric Method" (in Russian), *Nauch. Issled. Obl. Mat. Fiz.,* Tashkent, 59-62 (1979) (Experimental, Thermodyn.)

[1979Sch] Schmahl, N.G., Schwitzgebel, G. Kling, H., Speck, E., "Thermodynamic Investigations of the Solid Solution of Lead Zirconate - Lead Titanate", *Mat. Res. Bull.*, **14**, 1213-1218 (1979). (Experimental, Thermodyn., 12)

[1979Wha] Whatmore, R.W., Glazer, A.M., "Structural Phase Transitions in Lead Zirconate", *J. Phys. C. Solid State Physics*, **12**, 1505-1519 (1979) (Crys. Structure, Electr. Prop., Experimental, 20)

[1981Han] Handerek, J., Pisarski, M., Ujma, Z., "The Influence of an Electric Field and Hydrostatic Pressure on Dielectric Properties and Phase Transitions in $PbZrO_3$", *J. Phys. C. Solid State Physics*, **14**, 2007-2016 (1981) (Electronic Structure, Experimental, 15)

[1981Jac] Jacob, K.T., Shim, W.W., "Gibbs Energy of Formation of Lead Zirconate", *J. Am. Ceram. Soc.*, **64**, 573-578 (1981) (Experimental, Phase Diagram, Phase Relations, Thermodyn., 16)

[1982Fuj] Fujishita, H., Shiozaki, Y., Achiwa, N., Sawagushi, E., "Crystal Structure Determination of Antiferroelectric $PbZrO_3$ - Application of Profile Analysis Method to Powder Method of X-ray and Neutron Diffraction", *J. Phys. Soc. Jpn*., **11**, 3583-3591 (1982) (Crys. Structure, Experimental, 21)

[1982Tan1] Tanaka, M., Saito, R., Tsuzuki, K., "Determinations of Space Group and Oxygen Coordinates in Antiferroelectric Phase of Lead Zirconate by Convencional and Convergent-Beam Electron Difraction", *J. Phys. Soc. Jpn.,* **51**, 2635-2640, (1982) (Crys. Structure, Experimental, 25)

[1982Tan2] Tanaka, M., Saito, R., Tsuzuki, K., "Electron Microscopic Studies on Domain Structure of $PbZrO_3$", *Jpn. J. Appl. Phys.,* **21**, 291-298, (1982) (Crys. Structure, Experimental, 18)

[1984Fuj] Fujishita, H., Hoshino, S., "A Study of Structural Phase Transitions in Antiferroelectric $PbZrO_3$ by Neutron Diffraction", *J. Phys. Soc. Jpn.*, **53**, 226-234 (1984) (Crys. Structure, Electronic Structure, Experimental, 24)

[1984Leo] Leont'ev, N.G., Kolesova, R.V., Fesenko, O.E., Smotrakov, V.G., "X-Ray Structural Investigation of Electric-Field-Induced Orthorhombic Phase of Lead Zirconate", *Sov. Phys. Crystallogr.*, **29**, 240-241 (1984), translated from *Kristallografiya*, **29**, 398-400 (1984) (in Russian) (Crys. Structure, Experimental, 9)

[1985Hil] Hill, R.J., "Refinement of the Structure of Orthorhombic PbO (missicot) by Rietveld Analysis of Neutron Powder Diffraction Data", *Acta Crystallogr. C*, **41**, 1281-1284, (1985) (Crys. Structure, Experimental)

[1985Ism] Ismailzade, I.H., Samedov, O.A., "The Nature of the Intermediate Phase of $PbZrO_3$", *Phys. Status Solidi A*, **89A**, 133-136 (1985) (Electr. Prop., Experimental, 15)

[1985Ujm] Ujma, Z., Handerek, J., Pisarski, M., "Changes in Phase Transition Temperatures in $PbZrO_3$ with Pb and O Vacancies under the Influence of Hydrostatic Pressure", *Ferroelectrics*, **64**, 237-245 (1985) (Electr. Prop., Experimental, Phase Relations, 15)

[1986Abr] Abriata, J.P., Garces, J., Versaci, R., "The O-Zr (Oxygen - Zirconium) System", *Bull. Alloy Phase Diagrams*, **7**, 116-124 (1986) (Crys. Structure, Phase Diagram, Review, #, 48)

[1986Dal] Dalle Donne, M., Dorner, S., Lupton, D.F., "Fabrication and Properties of Zr_5Pb_3, A New Neutron Multiplier Material for Fusion Blankets", *J. Nucl. Mater.*, **141-143**, 369-372, (1986) (Phase Diagram, Experimental, 11)

[1986Rol] Roleder, K., Handerek, J., Ujma, Z., Kania, A., "Problem of the Transient Phase Between the Paraelectric and the Antiferroelectric Phase in $PbZrO_3$", *Ferroelectrics*, **70**, 181-190 (1986) (Electr. Prop., Electronic Structure, Experimental, 19)

[1988Wri] Wriedt, H.A., "The O-Pb (Oxygen-Lead) System", *Bull. Alloy Phase Diagrams*, **9**, 106-127, (1988). (Crys. Structure, Phase Diagram, Review, 174)

[1989Cie] von Cieminski, J., Roleder, K., Handerek, J., "Electromechanical Properties of Lead Zirconate in the Vicinity of Intermediate Phase", *Ferroelectrics Letter*, **10**, 9-22 (1989) (Experimental, Phys. Prop., 16)

[1989Dec] Dec, J., Kwapulinski, J., "Crystallogeometry of Phase Transitions in $PbZrO_3$ Single Crystals", *J. Phys.: Condens. Matter*, **1**, 3389-3396 (1989) (Crys. Structure, Electronic Structure, Experimental, 19)

[1989Hau] Haun, M.J., Harvin, T.J., Lanagan, M.T., Zhuang, Z.Q., Jang, S.J., Cross, L.E., "Thermodynamic Theory of $PbZrO_3$", *J. Appl. Phys.*, **65**, 3173-3180 (1989) (Theory, Thermodyn., 20)

[1989Rol] Roleder, K., Dec, J., "The Defect-Induced Ferroelectric Phase in thin $PbZrO_3$ Single Crystals", *J. Phys.: Condens. Matter*, **1**, 1503-1510 (1989) (Electronic Structure, Experimental, Optical Prop., 15)

[1992Fuj] Fujishita, H., "Crystal Structure and Phase Transitions of Intermediate Phase of $PbZrO_3$", *J. Phys. Soc. Jpn.*, **61**, 3606-3612 (1992) (Crys. Structure, Electr. Prop., Electronic Structure, Experimental, Phase Relations, 23)

[1992Shu] Shuvaeva, V.A., Antipin, M.Yu., Fesenko, O.E., Smotrakov, V.G., Struchkov, Yu.T., "X-Ray Diffraction Investigation of the Ferroelectric Phase $PbZrO_3$, Induced by a Strong Electric Filed", *Sov. Phys.-Crystallogr. (Engl. Transl.)*, **37**, 551-552 (1992), translated from *Kristallografiya*, **37**, 1033-1035, (1992) (in Russian) (Crys. Structure, Experimental, 8)

[1992Top] Topolov, V.Yu., Balyunis, L.E., Turik, A.V., Eremkin, V.V., Sori, B.I., "S-Type Twinning (Domain) Boundaries in $PbZrO_3$ Crystals", *Sov. Phys.-Crystallogr. (Engl. Transl.)*, **37**, 223-226 (1992), translated from *Kristallografiya*, **37**, 433-438 (1992) (in Russian) (Crys. Structure, Experimental, 11)

[1992Wan] Wang, F., Li, K.K., Haertling, G.H., "Transverse Electro-Optic Effect of Antiferroelectric Lead Zirconate thin Films", *Opt. Letters*, **17**, 1122-1124 (1992) (Electr. Prop., Experimental, Optical Prop., 15)

[1993Gla] Glazer, A.M., Roleder, K., Dec, J., "Structure and Disorder in Single-Crystal Lead Zirconate, $PbZrO_3$", *Acta Crystallogr., Sect. B: Struct. Crystallogr. Crys. Chem.*, **B49**, 846-852 (1993) (Crys. Structure, Electronic Structure, Experimental, 23)

[1993Gos] Gospodinov G.G., Marchev V.M., "The Temperature Relations of the Thermodynamic Quantities of Ca, Sr, Ba and Pb Zirconates", *Thermochim. Acta*, **222**, 137-141 (1993) (Experimental, Thermodyn., 11)

[1993Rol] Roleder, K., Jankowska, I., Dec, J., "Polar Relaxation Mode in $PbZrO_3$ Crystals", *Phase Transitions*, **42**, 241-250 (1993) (Electr. Prop., Experimental, 18)

[1994Men] Meng, J., Zou, G., Cui, Q., Zhu, Z., Du, Z., "Raman Spectra and Pressure-Induced Phase Transition in Nanocrystalline $PbZrO_3$", *Solid State Commun.*, **91**, 519-521 (1994) (Experimental, Optical Prop., 15)

[1995Dai] Dai, H., Li, J.F., Viehland, D., "Weak Ferroelectricity in Antiferroelectric Lead Zirconate", *Phys. Review B*, **51**, 2651-2655, (1995) (Experimental, Phys. Prop., 18)

[1995Sin] Singh, D.J., "Structure and Energetics of Antiferroelectric $PbZrO_3$", *Phys. Rev. B*, **52**, 12559-12563 (1995) (Crys. Structure, Electronic Structure, Experimental, 27)

[1996Ari] Arias, D., Abriata, J., Gribaudo, L., "Critical Evoluation and Thermodynamic Assessment of the Zr-Pb System", *J. Nucl. Mater.*, **229**, 24-28, (1996) (Assessment, Calculations, Phase Diagram, Thermodyn., 16)

[1996Cor] Corcer, D.L., Glazer, A.M., "An Investigation Into the Crystal Structure and Disorder of $PbZrO_3$", *Acta Crystallogr., Sect. A: Found. Crystallogr., Suppl. C*, **A52**, C324 (1996) (Crys. Structure, Experimental, 4)

[1996Fes] Fesenko, O.E., "On Electrical Hardening and Phase Transitions in $PbZrO_3$ Crystals Thinned by Chemical Etching", *Sov. Phys. - Solid State (Engl. Transl.)*, **38**, 520-521 (1996), translated from *Fiz. Tverd. Tela (St. Petersburg)* **38**, 941-943, (1996) (in Russian) (Electr. Prop., Experimental, Phase Relations, 6)

[1996Ono] Onodera, A., Kawamura, Y., Tamaki, N., Fujishita H., Roleder, K., Dec, J., Molak, A., "AC Calorimetric Study of Single Crystals of Antiferroelecrtic $PbZrO_3$ and $PbZr_{1-x}Ti_xO_3$ ($x = 0.01$)", *J. Korean Phys. Soc.* (Proc. Suppl.), **29**, S691-S694, (1996) (Experimental, Thermodyn., 18)

[1996Shu] Shuvaeva, V.A., Antipin, M.Yu., Fesenko, O.E., Struchkov, Yu.T., "An X-Ray Diffraction and EXAFS Study of the Electric-Field-Induced $PbZrO_3$ Ferroelectric Phase", *J. Phys.: Condens. Matter*, **8**, 1615-1620 (1996) (Crys. Structure, Electronic Structure, Experimental, 10)

[1997Cor] Corker, D.L., Glazer, A.M., Dec, J., Roleder, K., Whatmore, W., "A Re-investigation of the Crystal Structure of the Perovskite $PbZrO_3$ by X-ray and Neutron Diffraction", *Acta Crystallogr., Sect. B: Struct. Crystallogr. Crys. Chem.*, **B53**, 135-142 (1997) (Crys. Structure, Experimental, 17)

[1997Fuj] Fujishita, S., Katano, S., "Re-Examination of the Antiferroelectric Structure of $PbZrO_3$", *J. Phys. Soc. Jpn.*, **66**, 3484-3488 (1997) (Crys. Structure, Experimental, 8)

[1997Sic] Sicron, N., Yacoby, Y., Stern, E.A., Dogan, F., "XAFS Study of the Antiferroelectric Phase Transition in $PbZrO_3$", *J. Phys. IV France, Colloque*, **7**, 1047-1049 (1997) (Electronic Structure, Experimental, 9)

[1997Soe] Soejima, Y., Yamasaki, K., Fischer, K.F., "Use of X-Ray Anomalous Dispersion: the Superstructure of $PbZrO_3$", *Acta Crystallogr., Sect. B: Struct. Crystallogr. Crys. Chem.*, **B53**, 415-419 (1997) (Electronic Structure, Experimental, 10)

[1998Ley] Leyderman, A.V., Leont'ev, I.N., Fesenko, O.E., Leont'ev, N.G., "Dipole Order and Stability of the Ferroelectric and Antiferroelectric States in Lead Zirconate", *Phys. Solid State*, **40**, 1204-1207 (1998), translated from *Fiz. Tverd. Tela (St. Petersburg)*, **40**, 1324-1327 (1998) (in Russian) (Crys. Structure, Experimental, 15)

[1998Ris] Risold, D., Nagata I.J., Suzuki O.R., "Thermodynamic Description of the Pb-O System", *J. Phase Equilib.*, **19**, 213-233, (1998) (Calculation, Phase Diagram, Thermodyn., #, 154)

[1998Tes] Teslic, S., Egami, T., "Atomic Structure of $PbZrO_3$ Determined by Pulsed Neutron Diffraction", *Acta Crystallogr., Sect. B: Struct. Crystallogr. Crys. Chem.*, **B54**, 750-765 (1998) (Crys. Structure, Electronic Structure, Experimental, 35)

[1998Yam] Yamasaki, K., Soejima, Y., Fischer, K.F., "Superstructure Determination of $PbZrO_3$", *Acta Crystallogr., Sect. B: Struct. Crystallogr. Crys. Chem.*, **B54**, 524-530 (1998) (Crys. Structure, Experimental, 10)

[1999Bha] Bharadwaja, S.S.N., Krupanidhi, S.B., "Growth and Study of Antiferroelectric Lead Zirconate thin Films by Pulsed Laser Ablation", *J. Appl. Phys.*, **86**, 5862-5869 (1999) (Electr. Prop., Experimental, 38)

[1999Fur1] Furuta, H., Endo, S., Ming, L.C., Kobayashi, M., "Raman Scattering Study of $PbZrO_3$ under High Pressure", *Physica B*, **B263**, 816-818 (1999) (Experimental, Optical Prop., 13)

[1999Fur2] Furuta, H., Endo, S., Ming, L.C., Fujishita, H., "Phase Transitions in $PbZrO_3$ under High Pressure Studied by Raman Scattering", *J. Phys. Chem. Solids*, **60**, 65-67 (1999) (Experimental, Optical Prop., Phase Relations, 13)

[1999Kob] Kobayashi, S., Endo, S., Ming, L.C., Deguchi, K., Ashida, T, Fujishita, H., "X-Ray Diffraction and Dielectric Measurements on $PbZrO_3$ at High Pressure: A Phase Transformation Study", *J. Phys. Chem. Solids*, **60**, 57-64 (1999) (Crys. Structure, Experimental, Phys. Prop., 15)

[1999Koo] Koo, B.K., Liang, P., Seifert, H.J., Aldinger, F., "Thermodynamic Assessment of the PbO-ZrO_2 System", *Korean J. Ceram.*, **5**, 205-210 (1999) (Calculation, Phase Relations, Phase Diagram, Thermodyn., #, 35)

[1999Kor] Korniyenko, S.M., Bykov, I.P., Glinchuk, M.D., Laguta, V.V., Jastrabik, L., "Structure of Lead Zirconium Oxide: Evidence from NMR", *Eur. Phys. J. AP*, **7**, 13-17 (1999) (Crys. Structure, Electronic Structure, Experimental, Optical Prop., 17)

[1999Oka] Okamoto, H., "Pb-Zr (Lead - Zirconium)", *J. Phase Equilib.*, **20**, 353 (1999) (Crys. Structure, Phase Diagram, Review, #, 2)

[2000Bae] Bae, S.-H., Jeon, K.-B., Jin, B.M., "Preferred Orientation in $PbZrO_3$ thin Film Prepared by Sol-Gel Technique", *Mater. Res. Bull.*, **35**, 2245-2251 (2000) (Experimental, Morphology, 10)

[2000Bha] Bharadwaja, S.S.N., Krupanidhi, S.B., "Dielectric Relaxation in Antiferroelectric Multigrain $PbZrO_3$ thin Films", *Mater. Sci. Eng. B*, **B78**, 75-83 (2000) (Electr. Prop., Experimental, 35)

[2000Bou] Bouvier, P., Djurado, E., Lucazeau, G., Le Bihan, T., "High-Pressure Structural Evolution of Undoped Tetragonal Nanocrystalline Zirconia", *Phys. Review B,* **62**, 8731-8737 (2000) (Crys. Structure, Experimental, 44)

[2000Coc] Cockayne, E., Rabe, K.M., "Pressure Dependence of Instabilities in Perovskite $PbZrO_3$", *J. Phys. Chem. Solids*, **61**, 305-308 (2000) (Calculation, Crys. Structure, Experimental, Thermodyn., 31)

[2000Fuj] Fujishita, H., Katano, S., "Temperature Dependence of Order Parameters in the Antiferroelectric Phase of $PbZrO_3$", *Ferroelectrics*, **237**, 209-216 (2000) (Crys. Structure, Experimental, 7)

[2001Dob] Dobal, P.S., Katiyar, R.S., Bharadwaja, S.S.N., Krupanidhi, S.B., "Micro-Raman and Dielectric Phase Transition Studies in Antiferroelectric $PbZrO_3$ Thin Films", *Appl. Phys. Lett.*, **78**, 1730-1732 (2001) (Electr. Prop., Experimental, Optical Prop., 18)

[2001Fuj] Fujishita, H., Tanaka, S., "Antiferroelectric Phase Transition and Order Parameters of $PbZrO_3$", *Ferroelectrics*, **258**, 37-46 (2001) (Crys. Structure, Electr. Prop., Experimental, 11)

[2001Kwa] Kwapulinski, J., Kusz, J., Boehm, H., Dec, J., "Thermal Vibrations in $PbZrO_3$ Single Crystals", *J. Phys.: Condens. Matter*, **13**, 1461-1466 (2001) (Crys. Structure, Experimental, 19)

[2001Lia] Liang, P., Dupin, N., Fries, S.G., Seifert, H.J., Ansara, I., Lucas, H.L., Aldinger, F., "Thermodynamic Assessment of the Zr-O Binary System", *Z. Metallkd.*, **92**, 747-756 (2001) (Phase Diagram, Review, Thermodyn., 57)

[2001Ost] Ostapchuk, T., Petzelt, J., Zelezny, V., Kamba, S., Bovtun, V., Porokhonskyy, V., Pashkin, A., Kuzel, P., Glinchuk, M.D., Bykov, I.P., Gorshunov, B., Dressel, M., "Polar Phonons and Central Mode in Antiferroelectric $PbZrO_3$ Ceramics", *J. Phys.: Condens. Matter*, **13**, 2677-2689 (2001) (Electronic Structure, Experimental, Optical Prop., 35)

[2001Ran] Rane, M.V., Navrotsky A., "Enthalpies of Formation of Lead Zirconate Titanate (PZT) Solid Solutions", *J. Solid State Chem.*, **161**, 402-409 (2001) (Experimental, Thermodyn., 21)

[2002Aoy] Aoyagi, S., Kuroiwa, Y., Sawada, A., Tanaka, H., Harada, J., Nishibori, E., Takata, M., Sakata, M., "Direct Observation of Covalency Between O and Disordered Pb in Cubic $PbZrO_3$", *J. Phys. Soc. Jpn.*, **71**, 2353-2356 (2002) (Electronic Structure, Experimental, 23)

[2002Fuj] Fujishita, H., "Order Parameters in the Structural Phase Transition of Antiferroelectric $PbZrO_3$", *Ferroelectrics*, **266**, 27-40 (2002) (Crys. Structure, Experimental, 20)

[2002Leu] Leung, K., Wright, A.F., "Lead Zirconate at Ambient and High Pressure", *Ferroelectrics*, **281**, 171-186 (2002) (Crys. Structure, Experimental, Thermodyn., 44)

[2002Rod] Rodriguez, J.A., Etxeberria, A., Gonzalez, L., Maiti, A., "Structural and Electronic Properties of $PbTiO_3$, $PbZrO_3$ and $PbZr_{0.5}Ti_{0.5}O_3$: First-Principles Density-Funstional Studies", *J. Chem. Phys.*, **117**, 2699-2709 (2002) (Calculation, Crys. Structure, Phys. Prop., 80)

[2002Win] Winterer, M., Delaplane, R., McGreevy, R., "X-ray Diffraction, Neutron Scattering and EXAFS Spectroscopy of Monoclinic Zirconia: Analysis by Rietveld Refinement and Reverse Monte Carlo Simulations.", *J. Appl. Crystallogr.*, **35**, 434-442 (2002) (Calculation, Crys. Structure, Experimental, 33)

[2003Fuj1] Fujishita, H., Ishikawa, Y., "Thermodynamics of Antiferroelectric Phase Transition in $PbZrO_3$", *Ferroelectrics*, **283**, 75-86 (2003) (Crys. Structure, Electr. Prop., Experimental, Thermodyn., 20)

[2003Fuj2] Fujishita, H., Ishikawa, Y., Tanaka, S., Ogawaguchi, A., Katano, S., "Crystal Structure and Order Parameters in the Phase Transition of Antiferroelectric $PbZrO_3$", *J. Phys. Soc. Jpn.*, **72**, 1426-1435 (2003) (Crys. Structure, Experimental, 32)

[2004Bit] Bittner, R., Humer, K., Weber, H.W., Kundzins, K., Sternberg, A., Lesnyh, D.A., Kulikov, D.V., Trushin, Y.V., "Oxygen Vacancy Defects in Antiferroelectric $PbZrO_3$ thin Film Heterostructures After Neutron Irradiation", *J. Appl. Phys.*, **96**, 3239-3248 (2004) (Electr. Prop., Experimental, 39)

[2004Ost] Ostapchuk, T., Petzelt, J., Rychetsky, I., Porokhonskyy, V., Malic, B., Kosec, M., Vilarinho, P., "Influence of Porosity on the Dielectric Response and Central-Mode Dynamics in $PbZrO_3$ Ceramics", *Ferroelectrics*, **298**, 211-218 (2004) (Experimental, Morphology, Electr. Prop., 14)

[2004Puc1] Puchmark, C., Jiansirisomboon, S., Rujijanagul, G., Tunkasiri, T., "Effect of Sintering Temperatures on Phase Transition of Lead Zirconate Ceramics", *Current Appl. Phys.*, **4**, 179-181 (2004) (Experimental, Morphology, 8)

[2004Puc2] Puchmark, C., Rujijanagul, G., Jiansirisomboon, S., Tunkasiri, T., "Effect of Sintering Temperature on Phase Transition and Mechanical Properties of Lead Zirconate Ceramics", *Ferroelectrics Letters*, **31**, 1-13 (2004) (Electr. Prop., Experimental, Phase Reltions, Mehan. Prop., 16)

[2004Ste] Sternberg, A., Kundzins, K., Zauls, V., Aulika, I., Cakare, L., Bittner, R., Weber, H., Humer, K., Lesnyh, D., Kulikov, D., Trushin, Y., "Antiferroelectric $PbZrO_3$ Thin Films: Structure, Properties and Irradiation Effects", *J. Eur. Ceram. Soc.*, **24**, 1653-1657 (2004) (Crys. Structure, Electr. Prop., Experimental, Phys. Prop., 14)

[2005Can] Cancarevic, M., Zinkevich, M., Aldinger, F., "Thermodynamic Assessment of Cu-Pb-O System", *Z. Metallkd.*, **96**, 879-887 (2005) (Calculation, Phase Diagram, Phase Relations, Thermodyn., 59)

[2005Joh] Johannes, M.D., Singh, D.J., "Crystal Stucture and Electric Field Gradients of $PbZrO_3$ from Density Functional Calculations", *Phys. Rev. B*, **B71**, 212101-1-212101-4 (2005) (Calculation, Crys. Structure, 35)

[2005Wan] Wang, Y.X., Arai, M., Sasaki, T., Wang, C.L., Zhong, W.L., "First-Principles Study on the (001) Surface of Cubic $PbZrO_3$ and $PbTiO_3$", *Surf. Sci.*, **585**, 75-84 (2005) (Calculation, Crys. Structure, Electronic Structure, Thermodyn., 21)

Table 1: Investigation of the O-Pb-Zr Phase Relations, Structures and Thermodynamics

References	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1951Saw]	Polarization microscopy X-ray diffraction	Single crystals of the antiferroelectric and cubic $ZrPbZrPbO_3$
[1962Ike]	Solid state reactions X-ray diffraction	PbO to ZrO_2, fired at 1150-1200°C, > 850°C for PbO rich compositions, 1300°C for ZrO_2 rich ones
[1967Fus]	Quenching X-ray diffraction DTA	1100, 1200 and 1300°C Phase relations in PbO rich side of the PbO-ZrO_2 phase digram
[1967Har]	Solid state reactions X-ray diffraction	1290°C, PbO:ZrO_2 = 1:1
[1973Hol]	Knudsen effusion mass spectroscopy	850 to 1150°C PbO vapor pressure over the $ZrPbO_3$ + αZrO_2 and $ZrPbO_3$ + PbO(l) region
[1979Nur]	Knudsen effusion mass spectroscopy	712 to 1023°C Pb vapor pressure over the $ZrPbO_3$ + αZrO_2 region
[1979Sch]	Dynamic thermobalance method (transportation technique) and EMF measurements	400, 450, 650 and 1027°C PbO vapor pressure over the $ZrPbO_3$ + αZrO_2 and $ZrPbO_3$ + PbO(l) region
[1979Wha]	X-ray (continuously recording X-ray diffraction)	20 to 228°C Crystal structure of the antiferroelectric, ferroelectric and paraelectric $ZrPbO_3$ phases
[1979Koc]	X-ray diffraction	230 and 480°C Crystal structure of the paraelectric $ZrPbO_3$ phase
[1981Jac]	EMF measurements	527 and 1127°C PbO potential over the $ZrPbO_3$ + αZrO_2 region
[1982Fuj]	X-ray diffraction Neutron diffraction	25°C Crystal structure of the antiferroelectric $ZrPbO_3$ phase
[1982Tan1]	X-ray diffraction Electron microscopy (JEM, CBED)	25°C Crystal structure of the antiferroelectric $ZrPbO_3$ phase
[1982Tan2]	X-ray diffraction Electron microscopy (JEM)	25°C Crystal structure of the antiferroelectric $ZrPbO_3$ phase

References	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1984Fuj]	Neutron diffraction	25°C Crystal structure of the antiferroelectric $ZrPbO_3$ phase
[1984Leo]	X-ray diffraction	25°C Crystal structure of the electric field induced ferroelectric lead zirconate
[1989Dec]	Polarization microscopy X-ray diffraction	25, 460 and 550°C Single crystals of the antiferroelectric and cubic $ZrPbO_3$
[1992Fuj]	X-ray diffraction Neutron diffraction Rietveld method	230°C Crystal structure of the intermediate $ZrPbO_3$ phase
[1992Shu]	X-ray diffraction	25°C Crystal structure of the electric-field induced ferroelectric lead zirconate
[1993Gos]	X-ray diffraction Gravimetry Differential scanning calorimetry	127 to 207°C The molar heat capacity of the antiferroelectric $ZrPbO_3$
[1993Gla]	Polarization microscopy X-ray diffraction	24°C Crystal structure of the antiferroelectric $ZrPbO_3$ phase
[1994Men]	Raman scattering method TEM	25°C Structure of the pressure-induced phase transition in nanocrystalline antiferroelectric $ZrPbO_3$ phase
[1996Ono]	AC calorimetry	25 to 377°C The heat capacity of the single crystals of lead zirconate
[1996Shu]	X-ray diffraction EXAFS	25°C Crystal structure of the electric-field induced ferroelectric lead zirconate
[1996Cor]	X-ray diffraction Neutron diffraction	25°C Crystal structure of the antiferroelectric $ZrPbO_3$ phase
[1997Fuj]	Neutron diffraction Reitveld method	25°C Crystal structure of the antiferroelectric $ZrPbO_3$ phase
[1997Sic]	X-ray (XAFS)	–100 to 550°C Crystal structure of antiferoelectric, intermediate and paraelectric $ZrPbO_3$ phases
[1997Cor]	X-ray diffraction Neutron diffraction	–173°C Crystal structure of the single crystals of antiferoelectric $ZrPbO_3$ phase
[1997Soe]	X-ray diffraction	25°C Single crystals of the antiferoelectric $ZrPbO_3$

References	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1998Tes]	Pulsed neutron diffraction	–253, 25, 200 and 235°C Crystal structure of antiferoelectric, intermediate and paraelectric $ZrPbO_3$ phases
[1998Yam]	X-ray diffraction	25°C Crystal structure of the antiferoelectric $ZrPbO_3$
[1999Fur1]	Raman spectroscopy	25°C, pressure up to 30 GPa Structure and phase transitions of $ZrPbO_3$
[1999Fur2]	Raman spectroscopy	25°C, pressure up to 30 GPa Pressure-induced phase transition in $ZrPbO_3$
[1999Kor]	NMR	At 25°C, pressure up to 30 GPa Pressure-induced phase transition in $ZrPbO_3$
[1999Kob]	X-ray diffraction	25°C, pressure up to 75 GPa Crystal structure and phase transition of $ZrPbO_3$
[2000Fuj]	X-ray diffraction Neutron diffraction (Rietveld method)	25 to –188°C Crystal structure of the antiferoelectric $ZrPbO_3$ phase
[2001Fuj]	X-ray diffraction Neutron diffraction (Rietveld method)	25 to –265°C Crystal structure of the antiferoelectric $ZrPbO_3$ phase
[2001Ost]	IR reflectivity measurements	623 to –263°C Structure of the antiferoelectric $ZrPbO_3$ phase
[2001Kwa]	X-ray diffraction	250 to 600°C Crystal structure of the cubic $ZrPbO_3$ phase
[2002Aoy]	X-ray diffraction Rietveld method	247°C Crystal structure of the cubic $ZrPbO_3$ phase
[2003Fuj1]	X-ray diffraction	25 to –265°C Crystal structure of the antiferoelectric $ZrPbO_3$

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γZrO_{2-x} 2710 - ~1525	*cF*12 $Fm\bar{3}m$ CaF_2		61.0 to 66.6 at.% 63.6 at.% at 1525°C 62 at.% at 2052°C [1986Abr, Mas2]
		a = 494.72	[2000Bou]
		a = 509	[1986Abr]
βZrO_{2-x} 2377 - 1205	*tP*6 $P4_2/nmc$ HgI_2		66.5 to 66.6 at.% O [1986Abr, Mas2]
		a = 359.482 c = 518.247	[2000Bou]
		a = 358.82 c = 518.82	[1986Abr]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αZrO$_2$	*mP*12		[Mas2, 1986Abr]
< 1205	$P2_1/c$	*a* = 514.513	baddeleyite [2002Win]
		b = 520.234	
		c = 532.194	
		β = 99.153°	
		a = 516.9	[1986Abr]
		b = 523.2	
		c = 534.1	
		β = 99.15°	
βPbO	*oP*8		[1998Ris]
886 - 489	*Pbcm*	*a* = 589.31	massicot [1985Hil, V-C2]
	βPbO	*b* = 549.04	
		c = 475.28	
		a = 561.12	[V-C2]
		b = 560.91	
		c = 499.35	
αPbO	*tP*4		[1998Ris, V-C2]
< 489	*P*4/*nmm*		dissolves up to 3.41 at.% Zr
	αPbO		(7.058 mol% ZrO$_2$) [1999Koo]
			dissloves 4 mol% ZrO2 [1967Fus]
		a = 397.44	at 25°C [V-C2]
		c = 502.20	
* βZrPbO$_3$ (h$_2$)	*cF**		[1967Fus, 1979Wha]
1570 - 234	$Fm\bar{3}m$	*a* = 415	[1951Saw]
* γZrPbO$_3$ (h$_1$)	*cF**	-	[1979Wha, 1982Tan1, 1982Tan2]
234 - 231	*F*2*mm*		
* αZrPbO$_3$ (r)	*oP*40	*a* = 588.194	at 25°C [1979Wha, 1998Tes]
< 231	*Pbam*	*b* = 1178.206	
		c = 822.946	
* δZrPbO$_3$ (I)	*oC*10	*a* = 589.01	at 25°C [1992Shu, 1996Shu]
< 234	*Cm*2*m*	*b* = 589.71	Electric field induced phase
		c = 413.41	
* εZrPbO$_3$ (II)	*hR**	-	[1979Fes, 1996Fes]
< 210	$R\bar{3}m$		Electric field induced phase
* ϕZrPbO$_3$ (III)	*hR**	-	[1979Fes,1996Fes]
< 20	$R\bar{3}c$		Electric field induced phase

Table 3: Invariant Three-Phase Equilibria

Reaction	T [°C]	Type	Phase	Composition, (at.%)		
				Pb	Zr	O
L + βZrO_2 ⇌ $\beta ZrPbO_3(h_2)$	1538	p	L	47.504	1.664	50.832
			βZrO_2	0.0	33.333	66.667
			$\beta ZrPbO_3(h_2)$	20.00	20.00	60.00
L + $\beta ZrPbO_3(h_2)$ ⇌ αPbO	909.8	p	L	49.992	0.0054	50.003
			$\beta ZrPbO_3(h_2)$	20.00	20.00	60.00
			αPbO	44.887	3.409	51.704
L ⇌ αPbO + βPbO	885.8	e	L	49.998	0.0014	50.000
			αPbO	47.82	1.45	50.73
			βPbO	50.00	0	50.00

Table 4: Thermodynamic Data of Reaction or Transformation

Phase	T [°C]	Quantity per mole of atoms H, G: [kJ·mol^{-1}]; S: [J·mol^{-1}·K^{-1}]	Comments
$\alpha ZrPbO_3(r)$ ⇌ $\beta ZrPbO_3(h_2)$	231.5	ΔS = 1.65	[1996Ono], AC calorimetry
βPbO + αZrO_2 ⇌ $\beta ZrPbO_3(h_2)$	25	ΔH = 5.24 ΔS = 19 ΔG= 0.5	[1979Sch] derived from EMF measurements
$\beta ZrPbO_3(h_2)$ ⇌ αZrO_2 + Pb(g) + $0.5O_2$(g)	712 - 1023	ΔH = 191.36 ± 12.48	[1979Nur], mass-spectrometry
αZrO_2 + βPbO ⇌ $\beta ZrPbO_3(h_2)$	527 - 1127	ΔG= – 4.54 – 6.76·10^{-3} T (± 0.8)	[1981Jac], derived from emf measurements
αZrO_2 + βPbO ⇌ $\beta ZrPbO_3(h_2)$	973	ΔH = –2.63 ± 4.22	[2001Ran], solution calorimetry

Table 5: Thermodynamic Properties of Single Phases

Phase	Temperature [°C]	Property per mole of atoms H: [J·mol^{-1}]; S, C_p: [J·mol^{-1}·K^{-1}]	Comments
$\alpha ZrPbO_3(r)$	25 - 207	C_p = 1845 – 2.244 T – 1.045·10^8 T^{-2} (± 0.23)	[1993Gos] DSC
	25	$^\circ S$ = 119.7	
	25 - 207	$H_T - H_{298}$ = 47224.35	at T = 480 K

Table 6: Vapor Pressure Measurements

Phase(s)	Temperature Range [°C]	Pressure [bar]	Coments
$\beta ZrPbO_3(h_2) + \alpha ZrO_2$	712	$p_{Pb} = 0.188 \cdot 10^{-4}$	[1979Nur] mass-spectrometry
	785	$p_{Pb} = 0.466 \cdot 10^{-4}$	
	832	$p_{Pb} = 0.912 \cdot 10^{-4}$	
	852	$p_{Pb} = 0.101 \cdot 10^{-3}$	
	872	$p_{Pb} = 0.152 \cdot 10^{-3}$	
	912	$p_{Pb} = 0.249 \cdot 10^{-3}$	
	935	$p_{Pb} = 0.284 \cdot 10^{-3}$	
	1023	$p_{Pb} = 0.679 \cdot 10^{-3}$	
$\beta ZrPbO_3(h_2) + \alpha ZrO_2$	1077	$p_{PbO} = 8.10532 \cdot 10^{-4}$	[1979Sch] dynamic thermobalance method
	1061	$p_{PbO} = 6.38543 \cdot 10^{-4}$	
	1029	$p_{PbO} = 3.67096 \cdot 10^{-4}$	
	984	$p_{PbO} = 1.64153 \cdot 10^{-4}$	
$\beta ZrPbO_3(h_2) + \alpha ZrO_2$	1133	$p_{PbO} = 1.86 \cdot 10^{-3}$	[1973Hol] Knudsen effusion
	1105	$p_{PbO} = 1.38 \cdot 10^{-3}$	
	1094	$p_{PbO} = 9.87131 \cdot 10^{-4}$	
	1073	$p_{PbO} = 7.34905 \cdot 10^{-4}$	
	1053	$p_{PbO} = 2.089 \cdot 10^{-4}$	
	992	$p_{PbO} = 5.48935 \cdot 10^{-5}$	
$\beta ZrPbO_3(h_2) + \alpha ZrO_2$	935	$p_{PbO} = 6.70008 \cdot 10^{-5}$	[1969Hae] Knudsen effusion
	923	$p_{PbO} = 5.04917 \cdot 10^{-5}$	
	897	$p_{PbO} = 3.03886 \cdot 10^{-5}$	
	883	$p_{PbO} = 2.2327 \cdot 10^{-5}$	
	874	$p_{PbO} = 1.67641 \cdot 10^{-5}$	
	862	$p_{PbO} = 1.24062 \cdot 10^{-5}$	
	849	$p_{PbO} = 8.35468 \cdot 10^{-6}$	
	830	$p_{PbO} = 6.94496 \cdot 10^{-6}$	
	826	$p_{PbO} = 5.06501 \cdot 10^{-6}$	

Table 7: Calculated Termodynamic Functions of $\beta ZrPbO_3(h_2)$ at 298 K

$\Delta_f°H$ [kJ· mol^{-1}]	$°S$ [J·mol^{-1}· K^{-1}]	$\Delta_f°G$ [kJ· mol^{-1}]
–1322.960	126.147	–1360.552

Table 8: Investigations of the O-Pb-Zr Materials Properties

References	Method/Experimental Technique	Type of Properties
[1979Wha]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric constant
[1979Koc]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric constant
[1981Han]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric permittivity

References	Method/Experimental Technique	Type of Properties
[1985Ujm]	Inductance-Capacitance-Resistance measurements (LCR meter)	Electric permittivity
[1985Ism]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric permittivity
[1986Rol]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric and pyroelectric
[1989Rol]	Polarization microscopy Inductance-Capacitance-Resistance measurements (LCR meter)	Optic, dielectric and pyroelectric
[1989Cie]	Capacitance measurement	Dielectric permittivity
[1992Fuj]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric constant
[1992Wan]	Phase detection technique in transmission mode	Electro-optic (thin films)
[1993Rol]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric permittivity
[1995Dai]	Inductance-Capacitance-Resistance measurement (LCR meter) Sawyer-Tower circuit	Dielectric permittivity Polarization
[1995Sin]	Local density calculation	Electric
[1999Bha]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric
[1999Kob]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric
[2000Bha]	Inductance-Capacitance-Resistance measurements (LCR meter)	Dielectric constant
[2000Coc]	Local density calculation	Electric
[2001Dob]	Metal-isolator-metal configuration; Optical microscopy;	Dielectric (dielectric impendence) electric and polarization
[2001Fuj]	Inductance-Capacitance-Resistance measurements (LCR measurements)	Dielectric constant
[2001Ost]	Microwave dielectric spectrometry Terahertz transmission measurements	Dielectric
[2004Ost]	HF dielectric spectrometry	Dielectric permittivity
[2004Puc2]	Vickers and Koop microhardness test Inductance-Capacitance-Resistance measurement (LCR meter)	Hardness, fracture toughness and dielectric properties
[2004Ste]	Inductance-Capacitance-Resistance measurement (LCR meter)	Dielectric permittivity
[2004Bit]	Inductance-Capacitance-Resistance measurements	Dielectric permittivity
[2005Wan]	Local density calculation	Electric

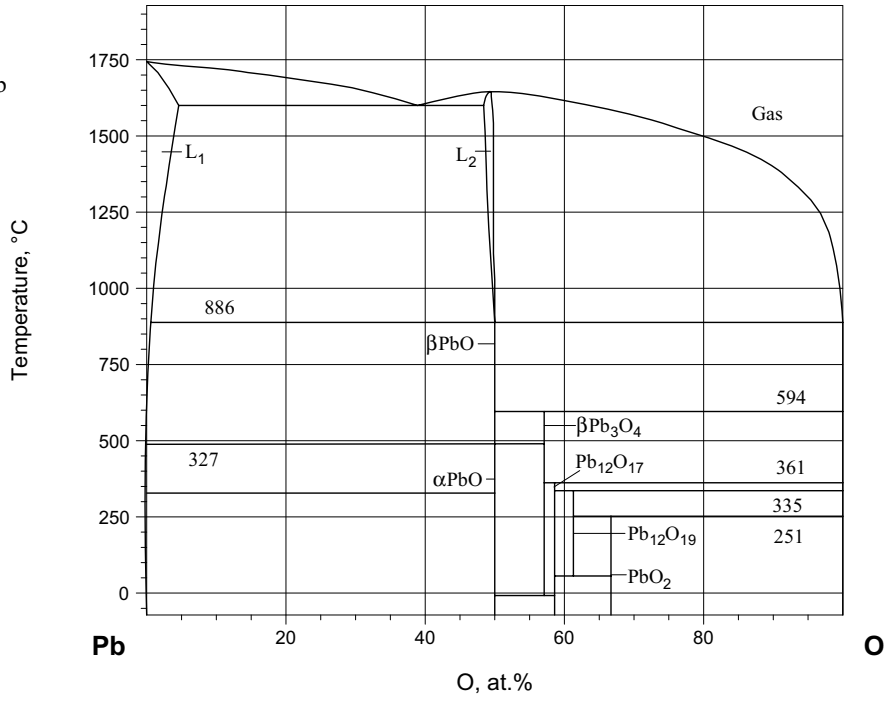

Fig. 1: O-Pb-Zr. Assessed phase diagram of the O-Pb system

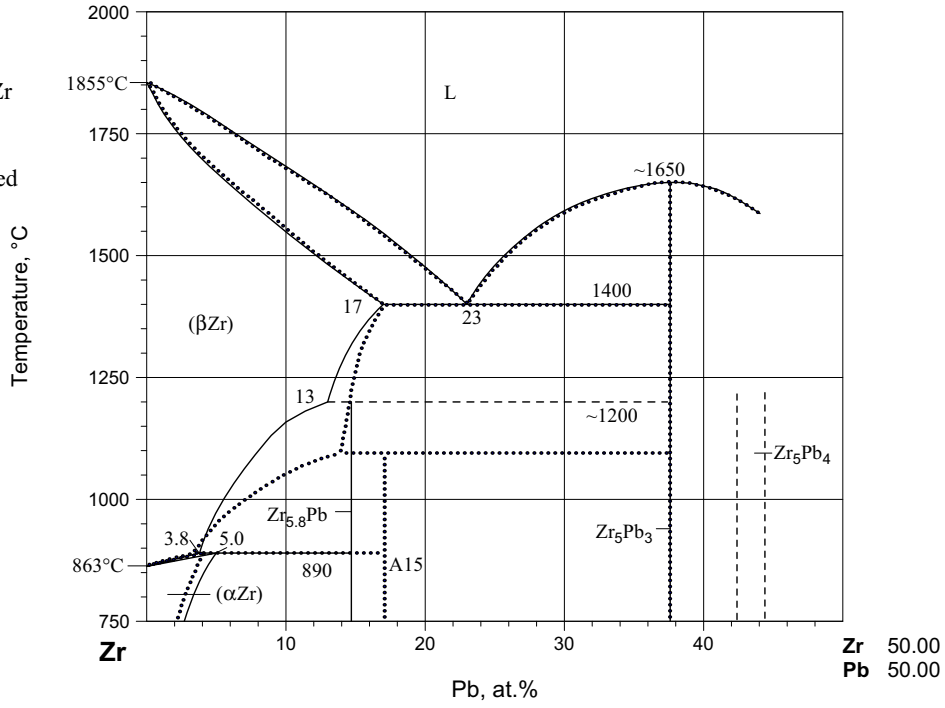

Fig. 2: O-Pb-Zr. Assessed phase diagram of the Pb-Zr system (solid lines) compared with the calculated one (dotted lines)

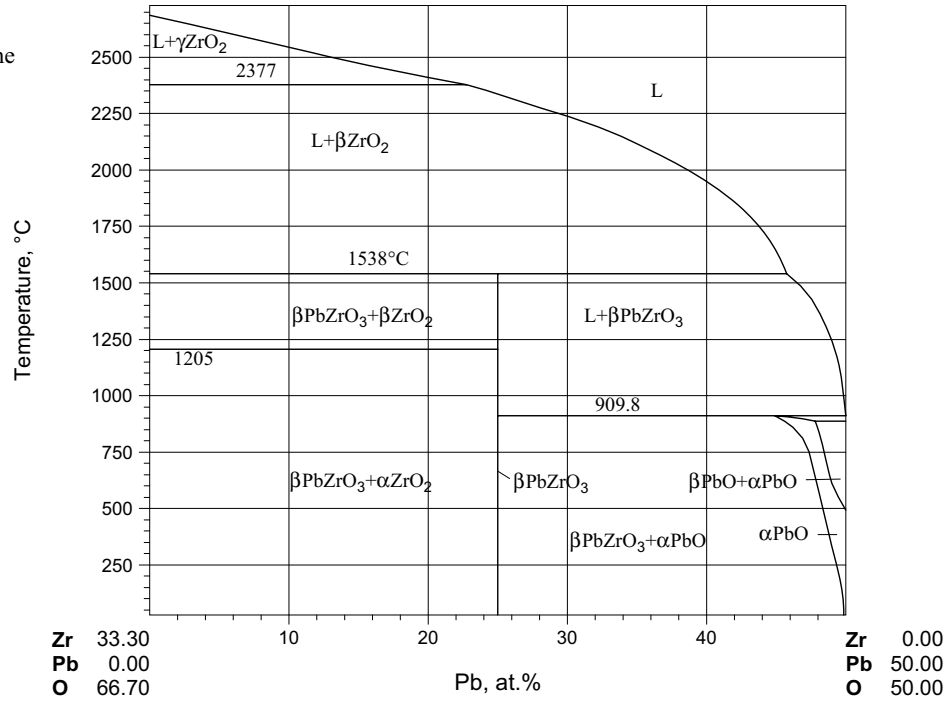

Fig. 3a: O-Pb-Zr. Phase diagram of the PbO-ZrO_2 system

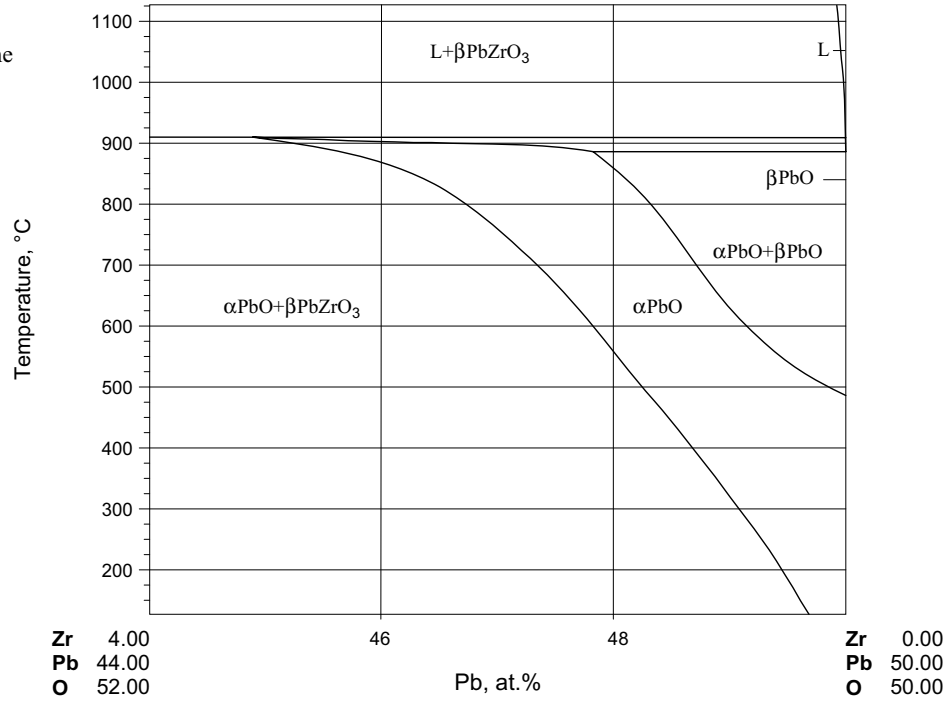

Fig. 3b: O-Pb-Zr. Enlarged view of the PbO rich region

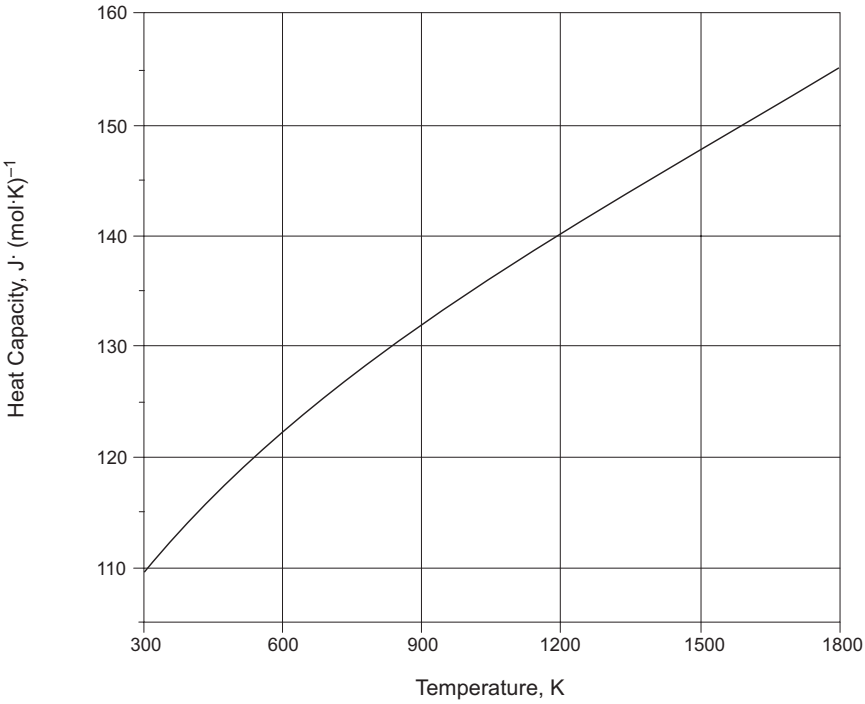

Fig. 4: O-Pb-Zr. Calculated heat capacity of the cubic $\beta ZrPbO_3$

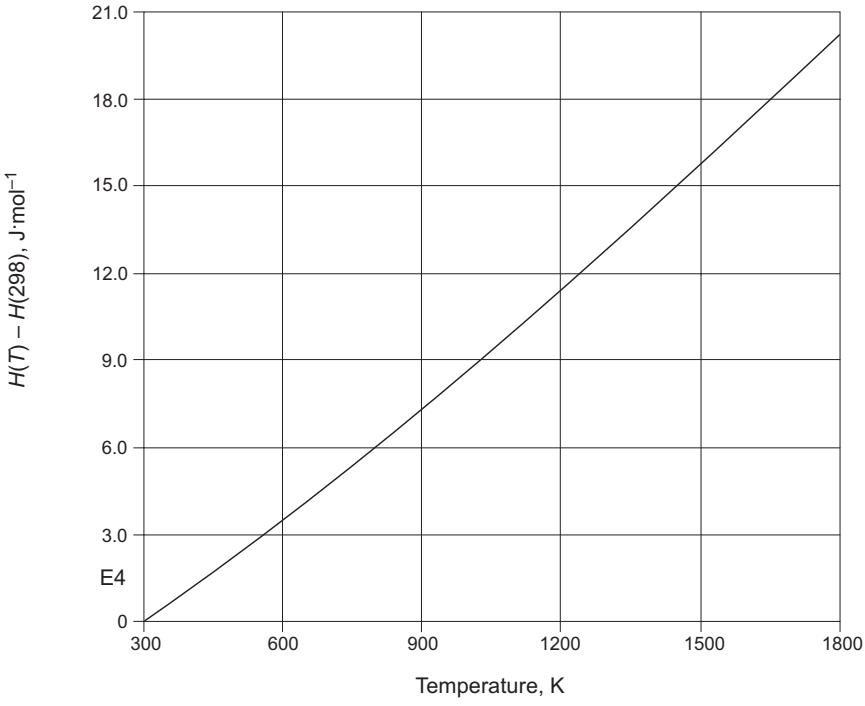

Fig. 5: O-Pb-Zr. Calculated enthalpy increment of cubic $\beta ZrPbO_3$

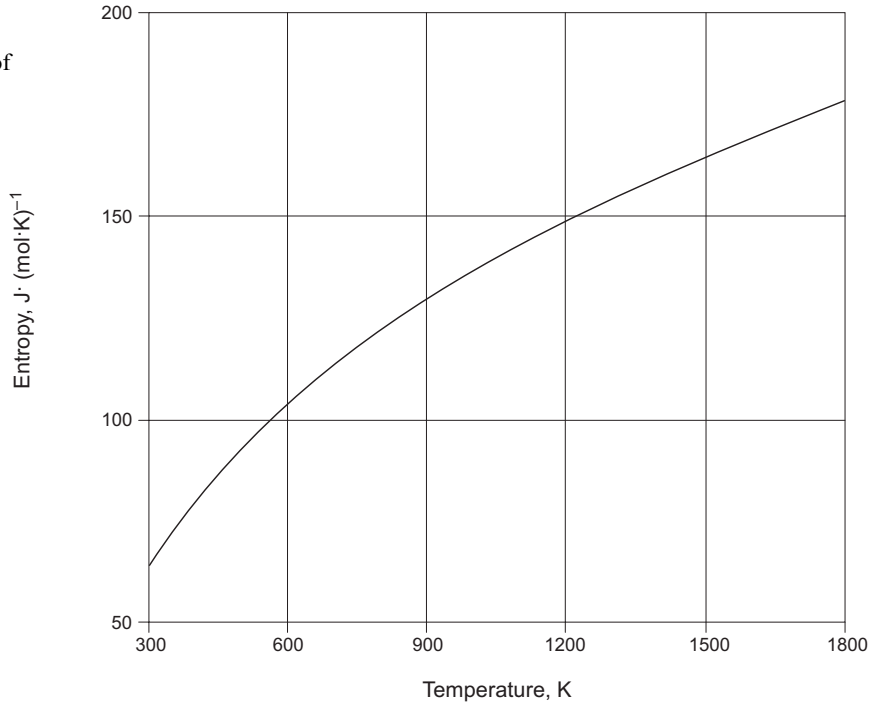

Fig. 6: O-Pb-Zr. Calculated entropy of cubic $\beta ZrPbO_3$

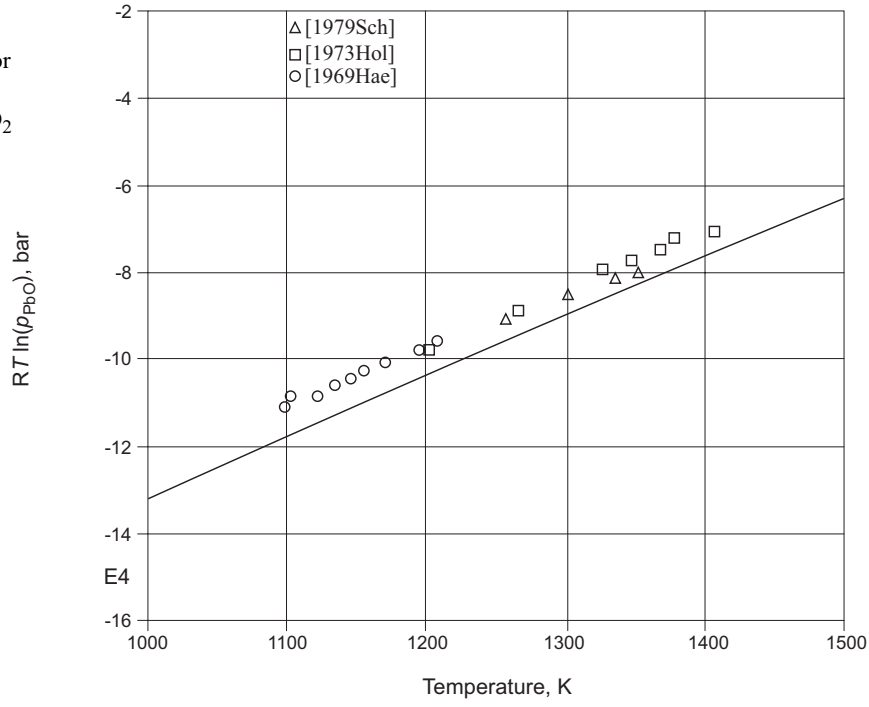

Fig. 7: O-Pb-Zr. Calculated PbO vapor pressure over $\beta ZrPbO_3(h_2) + \alpha ZrO_2$ in comparison with experimental data

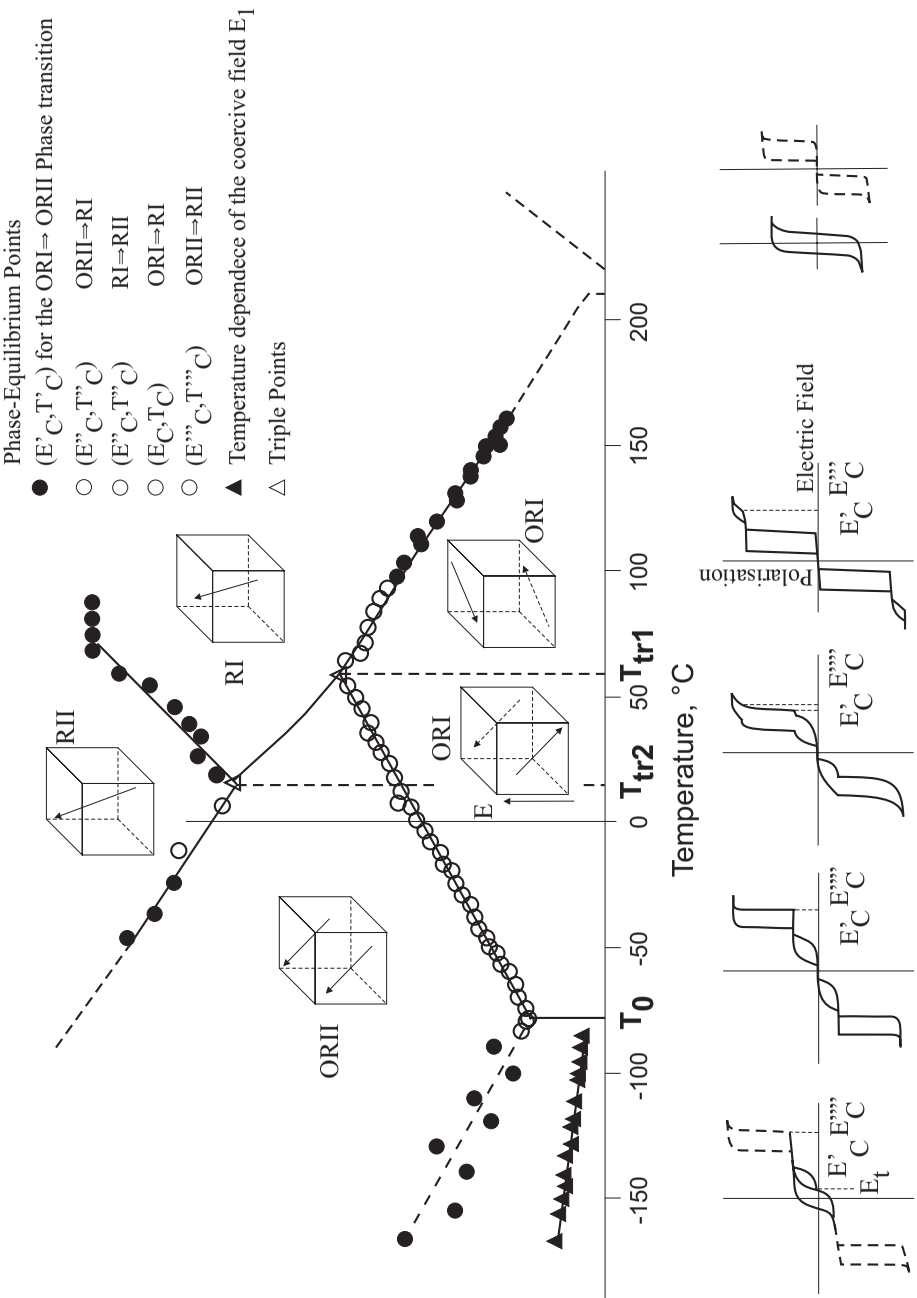

Fig. 8. **O-Pb-Yr.** The E–*T* phase diagram and schematic isothermal dependences of the dielectric polarization on the electric field; ORII = $\delta ZrPbO_3$ (I), RI = $\varepsilon ZrPbO_3$ (II), RII = $\phi ZrPbO_3$ (III).