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Thermodynamic Properties of Alkaline Earth Titanates, Zirconates, and Hafnates

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We shall review the problems arising during the critical analysis (aimed at selecting recommended values) of the thermodynamic constants of the alkaline-earth titanates, zirconates, and hafnates—a very important class of ferroelectric perovskites, widely used in radio electronics. Recommended values of the following standard thermodynamic quantities are given, with a statement of the uncertainty limits: the specific heat $C_{p,298}$, the enthalpy change $H_{298}-H_0$, the entropy S_{298}, the heat of formation $\Delta H_{f,298}$, the free energy of formation $\Delta G_{f,298}$, and the temperature and heat of phase transformation. The effect of impurities on the thermal constants of the phase transformations is discussed. The relationship between the thermodynamic characteristics and the crystal structure of perovskites is considered, with special reference to the effect of orthorhombic distortion of the ideal lattice on the entropy of the perovskite. In addition to thermodynamic methods we shall consider also other physical methods used to identify phase transformation temperatures, Curie points, and the temperature of the transition from the ferroelectric to the paraelectric state. Physical methods are especially important when the energy changes associated with the phase transformations are very small and cannot be detected by measurements of specific heat. 289 references.

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I. INTRODUCTION

Most of the thermodynamic data for rare-earth titanates, zirconates, and hafnates were obtained during the past 20 or 30 years. In this review we shall critically discuss the data published up to 1976 and we shall make a systematic choice of recommended values of the thermodynmic characteristics of these compounds.

In every case the standard entropy and enthalpy at 298.15 K was recalculated from the experimental data by the method described in Refs. 1 and 2. In these calculations independent interpolations of the specific heat were made at 5 K intervals for the range 5–100 K and at 10 K intervals for the range 100–300 K. Particular attention was paid to the relationship between thermodynamic characteristics and crystal structure. Most of the recommended data are compared with the most recent tabulations [3,4].

We have established a relationship between the thermodynamic formation quantities of the perovskites and the changes in the oxygen co-ordination polyhedron surrounding the cations. We have calculated the energy of the alkaline-earth cations Ca, Sr, Ba in the perovskite oxygen icosahedron, and also the energy of the transition of the zirconium and hafnium ions to an octahedral co-ordination of oxygen ions from the thermodynamically stable modifications of ZrO_2 and HfO_2. We have shown that the heat of formation of the perovskites from the simple oxides is directly proportional to the sum of the energies of the cation transitions involved in the formation of the perovskite structure. We have established a relationship between the uncritical Goldschmidt factor and the entropy change during the formation of perovskites from simple oxides.

II. LOW-TEMPERATURE SPECIFIC HEAT AND ENTROPY

1. Magnesium Titanates

$MgO \cdot TiO_2$. Shomate[5] measured the low-temperature specific heat of a $MgTiO_3$ sample containing 0.8% of $MgSiO_3$ in the temperature range 52.6–296.2 K. His values for the specific heat and the entropy at 298 K are 21.93 and 17.8 ± 0.1 cal mole^{-1} K^{-1}, using the Debye and the Einstein function $D(365/T) + E(383/T) + 3E(711/T)$ for extrapolation to 0 K. An independent calculation using the same data[5] gave $S_{k,298} = 17.8230$ e.u. The value $S_{k,298} = 17.82 \pm 0.10$ e.u. (which is also adopted in Refs. 3 and 4) is therefore recommended. The enthalpy calculated from these results is $H_{298} - H_0 = 3239.2$ cal mole^{-1}, in good agreement with the tabulated value[3,4] 3240 cal mole^{-1}. The rounded-off value, with an uncertainty of ±20 cal mole^{-1}, is recommended. The standard specific heat of $MgTiO_3$ at 298 K is taken[3,4] to be 21.960 cal mole^{-1}: this value differs somewhat from that given by Shomate[5], but no explanation is given. Extrapolation of high-temperature enthalpy measurements[6] gives $C_{p,298} = 21.92$ cal mole^{-1} K^{-1}. The recommended value is $C_{p,298} = 21.96 \pm 0.03$ cal mole^{-1} K^{-1}.

$MgO \cdot 2TiO_2$. The low-temperature specific heat of $MgTi_2O_5$ (99.5% purity) was measured by Todd[7] in the temperature range 52.5–296.4 K. Extrapolation to 0 K was carried out with the Debye and Einstein functions $D(264/T) + 4E(420/T) + 3E(906/T)$. The standard entropy of $MgTi_2O_5$ was rounded off to $S_{k,298} = 30.4 \pm 0.2$ e.u., although direct calculation gives 30.41 e.u. An independent calculation from the same results[7] gave $S_{k,298} = 30.415$ e.u. Ref. 4 gives the value 30.42 e.u., which agrees even better with the independent calculation. The JANAF tables[3] give a tentative value of $S_{k,298} = 32.41 \pm 1.5$ e.u. by allowing for the cation disorder at 0 K and for congruent melting of the compound $MgTi_2O_5$.

The correction for non-zero entropy at 0 K requires a detailed consideration of the crystal structure of $MgTi_2O_5$ and of the disposition of the cations in the polyhedra. Magnesium dititanate is stable with respect to $MgTiO_3$ and TiO_2 only at high temperatures, decomposing into geikielite and rutile at low temperatures. This effect arises from the possibility of disorder in the positions of the Mg^{2+} and Ti^{4+} ions in the crystallographically non-equivalent sites of $MgTi_2O_5$. If we assume that all the Mg^{2+} and Ti^{4+} ions are randomly located we must add $\Delta S = 3R \ln 2 = 3.79$ e.u. to $S = 30.41$ e.u. This gives us the best entropy value $S_{k,298} = 34.2$ e.u., which we shall use in the following calculations as well as the JANAF value[3]. If we assume that all the Mg^{2+} ions and one-half the Ti^{4+} ions are randomly positioned we obtain $S_{k,298} = 30.4 + 2.75 = 33.15$ e.u. X-Ray diffraction analysis of $MgTi_2O_5$ quenched from 1500°C indicates a distribution corresponding to the formula $(Mg_{0.684}Ti_{0.316})_{4C} \cdot (Mg_{0.316} \cdot Ti_{1.684})_{8t}O_5$, i.e. a disorder factor $x = 0.316$ ($x = 0$ for the normal cation distribution, $x = 2/3$ for a fully disordered distribution, and $x = 1$ for an inverted cation distribution).

Todd[7] obtained $C_{p,298} = 35.15$ cal mole^{-1} K^{-1} for the standard specific heat of $MgTi_2O_5$. This value is adopted in Ref. 4: it is consistent with high-temperature enthalpy measurements[8] but it differs from the JANAF value[3] of 35.10. We recommend the value $C_{p,298} = 35.15 \pm 0.05$ cal mole^{-1} K^{-1}.

Todd did not calculate the enthalpy of magnesium dititanate. A calculation from his results gives $H_{298} - H_0 = 5361$ cal mole^{-1}. The values 5363 and 5428 cal mole^{-1} are given in Ref. 3 and 4 respectively: the latter value is inconsistent with the independent calculation of the entropy. We recommend the value $H_{298} - H_0 = 5360 \pm 40$ cal mole^{-1}.

$2MgO \cdot TiO_2$. The low-temperature specific heat of Mg_2TiO_4 ($[MgTi]MgO_4$ spinel, of 99.5% purity) was measured by Todd[7] in the temperature range 52.38–296.5 K. The results were extrapolated to 0 K by using the Debye and Einstein functions $D(305/T) + 3E(447/T) + 3E(823/T)$. He obtained a standard entropy of $S_{k,298} = 24.76 \pm 0.15$ e.u., which is exactly confirmed by an independent calculation using his results. Ref. 4 gives $S_{k,298} = 26.13$ e.u., and Ref. 3 gives 27.51 ± 1.5 e.u. The difference arises from different estimates of the configurational entropy due to disorder. Magnesium orthotitanate is an inverted spinel, with the magnesium ions in tetrahedral (A) and in octahedral (B) positions. The cation distribution can be expressed as $Mg[MgTi]O_4$, where the square bracket denotes the ions octahedrally surrounded by oxygen ions. Therefore the entropy obtained from specific heat data must be corrected by adding the ordering entropy of the cations in B positions ($2R \ln 2 = 2.75$ e.u.), which gives $S_{k,298} = 27.51$ e.u. This is the value which we recommend. We note that an intermediate value is quoted in Ref. 4, with an ordering correction of $R \ln 2 = 1.38$ e.u.

The standard specific heat quoted by Todd is $C_{p,k,298} = 30.76$ cal mole^{-1} K^{-1}, with a probable error of ±0.02 cal mole^{-1} K^{-1}. This value is consistent with high-temperature measurements of enthalpy[8], and differs only slightly from the value (30.75) adopted in Ref. 4.

The enthalpy of the orthotitanate was not computed by Todd. A calculation based on his results gives $H_{298} - H_0 = 4502$ cal mole^{-1}, which is identical to the value quoted i Refs. 3 and 4. We recommend the rounded-off value $H_{298} - H_0 = 4500 \pm 30$ cal mole^{-1}.

2. Calcium Titanates

$CaO \cdot TiO_2$. The low-temperature specific heat of $CaTiO_3$ (purity better than 99%) was measured by Shomate[5] in the range 52.5–296.3 K. Extrapolation to 0 K was made by using the sum $D(256/T) + 2E(375/T) + 2E(768/T)$. Shomate calculated $S_{k,298} = 22.38$ e.u. for the standard entropy of $CaTiO_3$, in very good agreement with an independent calculation based on his results and also with the JANAF value[4]. We recommend this value, with an uncertainty of ±0.10 e.u.

The standard specific heat of $CaTiO_3$ at 298 K was found[5] to be 23.34 cal mole^{-1} K^{-1}. The same value is quoted in Refs. 4 and 9. Extrapolation from high-temperature measurements of enthalpy[6] gives 23.35 cal mole^{-1} K^{-1}. We recommend the value $C_p = 23.34 \pm 0.05$ cal mole^{-1} K^{-1}, the rather wide uncertainty reflecting the absence of corrections for impurities in the sample[5].

Shomate did not calculate the standard enthalpy of $CaTiO_3$. A calculation based on his results gives $H_{298} - H_0 = 3800.7$ cal mole^{-1}. We recommend the rounded-off value 3800 ± 20 cal mole^{-1}.

$3CaO \cdot 2TiO_2$. The low-temperature specific heat of $Ca_3Ti_2O_7$ was measured by King[10] in the range 52.6 to 296.9 K. Chemical analysis of his sample gave 48.61% TiO_2 (theoretical value 48.71%). Extrapolation to 0 K was by the sum of functions $D(158/T) + 5E(333/T) + 5E(652/T) + E(781/T)$. The standard entropy recommended by King is $S_{k,298} = 56.1 \pm 0.4$ e.u., with which we concur. This value coincides, after rounding off, with the value (56.057 e.u.) obtained by an independent calculation from the same results[10]. It is also adopted in Ref. 4.

King's measurements[10] give $C_{p,298} = 57.20$ cal mole^{-1} K^{-1} for the standard specific heat of $Ca_3Ti_2O_7$, with an uncertainty of ±0.05 cal mole^{-1} K^{-1}. The enthalpy of the com-

pound was not calculated by King, and is not given in Ref. 4. A calculation based on King's results gives $H_{298} - H_0 = 9418.6$ cal mole^{-1}. We recommend the rounded-off value $H_{298} - H_0 = 9420 \pm 70$ cal mole^{-1}.

3. Strontium Titanates

$SrO \cdot TiO_2$. $SrTiO_3$ undergoes four clearly defined low-temperature phase transformations of the second kind: at 0.06, 35, 65, and 107 K.

1) The transition from the high-temperature cubic structure to a tetragonal structure in the temperature range 100–110 K has been noted in more than 50 investigations.

The first report of this transition was made in 1956 by Gränicher [11], who noted anisotropy of the dielectric constant below 100 K, and subsequently by Müller [12], who observed tetragonal domains in $SrTiO_3$ crystals doped with Fe^{3+} by ESR measurements below 100 K. According to the ESR results [12-21] the low-temperature phase is tetragonal, with a c/a ratio of 1.0003 at 77 K. After a number of unsuccessful attempts [13,20,25] this structural change was demonstrated directly by X-ray diffraction [22-24]. However it was pointed out [26] that neither the axial ratio nor its temperature dependence [23] agrees with the ESR results. It was shown that the main contribution to the change in the pseudo-cubic structure with $c/a = 1.00008$ is a rotation of neighbouring oxygen octahedra around the original cubic axis [23]. The angle of rotation φ is treated as an ordering parameter for this phase transformation of the second kind. This conclusion was confirmed by neutron diffraction work [26-31]. The cubic structure of the $SrTiO_3$ perovskite is assigned O_h symmetry, and the low-temperature tetragonal structure D_{4h} symmetry [20,32,33]. The phase transformation is accompanied by marked changes in elastic constants [34-53], Rayleigh [38] and Raman spectra [32,33,54-59], double refraction [22,24], and by a decrease in the amplitude of the $^{87}Sr^{60}$ NMR spectrum, increased thermal diffusivity and thermal conductivity [61], and a slight broadening of the ESR spectra of crystals containing magnetic impurities [12,13,15-21]. The high-temperature $SrTiO_3$ cubic structure is shown to be imperfect by the anisotropy of its electrical properties [11,62-66] and of the thermal stress [67,68]. The transition temperature varies with sample purity, pressure, and degree of reduction [45,47,69].

The mechanism of the transformation is discussed in almost all the above-mentioned papers. The most detailed analysis is given by Reshchikova [70], who assigns this $O_h \rightleftharpoons D_{4h}$ phase transition (accompanied by a fourfold increase in volume of the unit cell) to the displacement type of transition, arising from the presence of soft modes of lattice vibration in the cubic phase with a non-zero wave vector, which become "frozen" during the phase transition. Another group of papers deals with the mechanism of the transformation and with the structure of the equilibrium phases without attempting to specify the exact temperature of the transition [71-84]. Some workers failed to observe any anomalies in the electrical [85,86] and optical properties [87] in the transition region. Luthi and Moran [47] have discussed the reasons for this discrepancy.

The specific heat of $SrTiO_3$ has been measured directly in the transition region [61,66,69,88]. Garnier [69] found that the transition region extends over 2 K, and that T_{tr} is lowered by almost 1 K if the sample is annealed. The transition is also more gradual with an annealed sample. These effects are ascribed to a 0.05% decrease in the concentration of oxygen. Subsequently Salamon and Garnier [61] observed a change in specific heat at 110 K on a sample supplied by Sakudo and Unoki [65], and they also noted a 2% change in thermal diffusivity and a 1% change in thermal conductivity at the same temperature.

In most of these papers the anomalous changes in property are presented graphically, and the T_{tr} values are obtained by interpolation. Values indicated by the work of different authors range from 99.5 K [31] to 112 K. [34,35]. Averaging all the data on the temperature of this transformation gives 107.2 K. However we can identify a group of papers [17,26,30,47,48,61,67,69,88] in which special attention is paid to the precise measurements of T_{tr}, by a variety of methods. Averaging these results gives $T_{tr} = 106.9$ K. The difference between the two averages is less than the width of the transition region (2 K). Therefore we recommend the rounded-off value $T_{tr} = 107 \pm 3$ K. The quoted uncertainty encompasses most of the experimental data and corresponds to the scatter of results obtained with different samples.

2) The second low-temperature transition in $SrTiO_3$ is most clearly shown by measurements of the thermal hysteresis of $1/\epsilon$ (62 K [89], 65 K [65]), of double refraction (50 K [22], 60 K [24]), of X-ray diffraction (50 K [22], 55–65 K [23]), and of Raman (67 K [32]) and ESR spectra (65 K [21,90]). Below 65 K $SrTiO_3$ has a rhombic structure [23,32,65], of the D_{2h} type, with $a:b:c = 0.9998:1:1.0002$. Transition from the antiferromagnetic to the paramagnetic state has been demonstrated [91] experimentally: this could be due to conversion of the domain configuration in the sample from c-plate to a-plate [65].

By giving greater weight to the wider-ranging investigations [21,65,90] we select $T_{tr} = 65 \pm 5$ K as the recommended value. It should be noted that the existence of this transition is still controversial. It is not confirmed by spectroscopic measurements [33] or by studies of acoustic properties [49].

3) The Curie temperature has been obtained from measurements of the temperature dependence of dielectric constant [11,86,89,92-95], of neutron diffraction [96], of acoustic [34,45] and i.r. absorption [71], and of electrostriction [32,45,64,92-97]. The calculated values of T_c range from 28 K [96] to 50 K. [92] The transition has been observed experimentally only in three laboratories: Lytle [23] obtained $T_c = 35$ K from X-ray diffraction measurements, O'Shea and coworkers [32] observed a change in the Raman spectra at 34 K, and Sorge and Hegenbarth [98] obtained $T_c = 36$ K from measurements of elastic constants. From these results we recommend the value $T_c = 35 \pm 2$ K, in good agreement with the value (36.3 K) obtained by averaging all the above calculated and experimental results.

The only work which explicitly denies all phase transformations below 105 K is an acoustic investigation [49] at temperatures in the region 4–130 K. Bogdanov and coworkers [24] identified three temperature regions in which the double refraction of $SrTiO_3$ obeys different laws: 110–60, 60–20, and 20–4.2 K. The latter region has a maximum at 10 K, confirming a previous report [23]. We should stress that this observation has been repeated only once [22], again by measurements of X-ray diffraction and of double refraction. Hence the information on thermal characteristics in the region 4–20 K is insufficient for a recommended value to be selected. The limit of 20 K, which is only approximate, was taken from Ref. 24, where the parameter being measured was practically linear in the region 15–50 K. The results of Kirkpatrick and Müller [14] therefore would appear to confirm the existence of a phase transformation.

4) The superconductivity of $SrTiO_3$ was first observed by Schooley and coworkers[99]. In three monocrystalline samples, reduced in different ways, the temperature of the superconducting transition was found to be 0.1, 0.25, and 0.28 K. A subsequent series of investigations[100-104] established that superconductivity is present in $SrTiO_3$ samples doped with Nb as well as in reduced samples. The T_{tr} value depends on the concentration of charge carriers n_c in the region 8×10^{18}–5×10^{20} cm^{-3}. T_{tr} increases at first with n_c, reaching a maximum at intermediate values of n_c, and then decreases. The n_c values were measured by the Hall effect, and T_{tr} from the magnetic susceptibility and electrical resistivity of the samples. With reduced samples the T_{tr} maximum was found at 0.3 K, with Nb-doped samples at 0.4 K. The lowest value of T_{tr} was 0.06 K.[101] For many samples the width of the transition region was 0.1 K. The transition to the superconducting state has been observed also by measurements of low-temperature specific heat[105,106].

We choose as the recommended value of the transition temperature $T_{tr} = 0.06$ K, i.e. the value obtained[101] for a $SrTiO_3$ sample with the smallest deviation from stoichiometry, the smallest degree of reduction, and the lowest concentration of charge carriers ($n_c = 8 \times 10^{18}$ cm^{-3}). Allowing for the observed width of the transition region we estimate the uncertainty as ± 0.03 K. We note that the highest value ($T_{tr} = 0.3$ K) was obtained for $n_c = 7 \times 10^{19}$ cm^{-3}.

Todd and Lorenson[107] measured the low-temperature specific heat of $SrTiO_3$ over the widest temperature range (55–296 K). No anomalies could be detected in their plot of specific heat against temperature. Below 51 K the specific heat was determined by using the sum $D(182/T) + 2E(319/T) + 2E(776/T)$. For 298 K the authors obtained $C_p = 23.51$ cal mole K^{-1} and $S^0 = 26.0 \pm 0.2$ e.u. The C_p value coincides with the extrapolation from measurements of enthalpy at high temperature[108]. The good agreement with Refs. 107 and 108 is pointed out by Narayanan and Vedam[109], who obtained calculated values of C_V for the region 55–1800 K. Thus we can choose $C_{p,k,298} = 23.51 \pm 0.02$ cal mole^{-1} K^{-1} as the recommended value.

The specific heat has been measured in the region of the transition to the superconducting state[105,106,110] with $SrTiO_3$ samples containing different charge carrier concentrations. The temperature dependence of C_p obtained in this work over the narrow range 0.5–4.0 K, and also the value $\Delta S_{tr} = 0.12$ mJ mole^{-1} K^{-1},[105] are not suitable for calculating the entropy and enthalpy of stoichiometric $SrTiO_3$.

Many workers have found[50,61,66,68-70,88] that the change in specific heat in the region of the phase transition at 107 K is also negligibly small, amounting to 0.5–1.3% of the lattice contribution. These values are smaller than the error in the calculation of $H_{298} - H_0$ and S°_{298} introduced by the extrapolation to the low-temperature region.

From Todd and Lorenson's results[107] we calculate $H_{298} - H_0 = 4120$ cal mole^{-1} and $S_{298} = 25.98$ e.u. The latter value agrees well with that obtained by the authors[107]: the discrepancy is very small, and can be ascribed to differences in the computational methods. Hence we can adopt $S_{298} = 26.0 \pm 0.2$ e.u. as the recommended value. The quoted uncertainty undoubtedly allows for the entropies of the low-temperature phase transitions, which are accompanied by very small changes in C_p. To the same degree of confidence we can recommend the value $H_{298} - H_0 = 4120 \pm 40$ cal mole^{-1} for the enthalpy of $SrTiO_3$, which was not calculated by Todd and Lorenson[107].

$2SrO \cdot TiO_2$. The low-temperature specific heat of Sr_2TiO_4 was measured by Todd and Lorenson[111] in the temperature range 53.6–296.7 K on a sample of 99.5% purity. Extrapolation to 0 K was done by using the sum of functions $D(162/T) + 3E(280/T)$ and $3E(664/T)$. The standard entropy obtained[111] (38.01 e.u.) agrees exactly with an independent calculation based on their experimental results (38.013 e.u.). We choose $S_{k,298} = 38.0 \pm 0.3$ e.u. as the recommended value: the same value is tabulated in Ref. 4.

Todd and Lorenson's value[111] for the standard specific heat of Sr_2TiO_4 is $C_{p,298} = 34.34$ cal mole^{-1} K^{-1}, which agrees with the extrapolation from high-temperature measurements of enthalpy on the same sample[108], and is tabulated in Ref. 4. We adopt this as the recommended value, with an uncertainty of ±0.03 cal mole^{-1} K^{-1}.

The standard enthalpy of Sr_2TiO_4 has not been calculated before. Using the results of Ref. 111 we calculate $H_{298} - H_0 = 6060 \pm 60$ cal mole^{-1}, which we proposed as our recommended value.

4. Barium Titanates

$BaO \cdot TiO_2$. Barium titanate has five polymorphic modifications: trigonal $\xrightarrow{80^\circ C}$ rhombic $\xrightarrow{5^\circ C}$ tetragonal $\xrightarrow{120^\circ C}$ cubic $\xrightarrow{1250^\circ C}$ hexagonal, all three low-temperature modifications being pseudo-cubic because the differences in the positions of the ions are not large. We shall discuss these transitions individually.

1) The ferroelectric $BaTiO_3$ transition. Most of the work on the properties of $BaTiO_3$ has been done near 120°C (the temperature of the transition from the non-ferroelectric to the ferroelectric phase). The thermodynamic theory of this transition was developed by Ginzburg[112,113] and elaborated by other workers[114-116]. Ginzburg discusses two variants of the theory, corresponding to observed facts. According to the first variant the phase transition near 120°C should be treated as a transition of the second kind but approaching a transition of the first kind; according to the second variant it should be treated as a transition of the first kind but approaching the second kind. Some workers[114,117-127,278] have treated it as a transition of the first kind, others[108,112,115,116,128-136] as a transition of the second kind. In view of the strong discrepancies between the experimental results of different workers (for example, on the temperature dependence of the spontaneous polarisation, the constant in the Curie–Weiss law, the discontinuity in specific heat, the temperature of the transition, and its hysteresis), and in view of the strong dependence of the results on the method of preparation and on the purity of the samples, we can conclude that different types of transition were observed by different workers.

The method most commonly used to determine the transition temperature was dictated by the most outstanding feature of barium titanate: the temperature dependence of the dielectric constant, which was studied on ceramic[117-120,122,126,129,137-165] and on single-crystal samples[118,123,126,127,134,135,159-161,167-173] in different fields[138]. In parallel with this work, several authors carried out X-ray structural[124,130,142,146,152,164,166,167,174-183], crystallographic[118,142,166,184], thermochemical[108,122,123,128,133,144,146,151,153,154,185-187,279,280,281], differential thermal[121,125,175,186,188-190], and dilatometric studies[124,130,144,147,151,153,164,174,177], and measured the tangent of the loss angle[143,154,173], the spontaneous polarisability[126,167,191], the refractive index and the double refraction[118,167,169,176,179,182,192,193,283], the

ESR spectra[194], the acoustic properties[123,165,278], the ferromagnetic hysteresis[119,156], the thermal diffusivity[195], and the variation of the electric properties[114,136,166,170] and of the transition temperature[126,196,197] with pressure and with field, applied in different crystallographic directions.

Many of the reported values[133,138,140,141,148,155,177] of T_{tr} are clearly unacceptable and will not be considered further. This is specially true of values in the region of 80°C, which are reported as probably too low as a result of the presence of impurities in the samples. This transition appears to be particularly sensitive to heat treatment conditions[155] as well as to the purity of the sample, since some of the other transitions (e.g. in Ref. 148) agree well with data obtained elsewhere. The lowest values of T_{tr} are ascribed[144,175] to the impurity effect of the binders added to improve the sintering properties of the samples. One paper[149] stands alone in suggesting that the ferroelectric properties of barium titanate are due entirely to the presence of impurities: unlike every other sample previously examined in that laboratory[137,138,140,141], a sample of $BaTiO_3$ prepared from chemically pure compounds was found to have a dielectric permeability which was not only constant over a wide temperature range but also relatively small. Thus the pure sample of $BaTiO_3$ was a dielectric, but not a ferroelectric. We stress that this conclusion[149] has not been confirmed by the extensive subsequent work on a wide variety of sample types.

Hysteresis of the transition temperature has been observed repeatedly[117,119-121,124,125,142,151,153,154,169,176,177]: the hysteresis is more marked for the cubic than for the tetragonal modification[176]. The existence of a temperature region of coexistence of two phases, of width (10–11 K) depending on the thermal history of the sample[151,177], is well established, but Harwood[146] points out that this region extends over 1–2 K for monocrystalline samples and ~10 K for polycrystalline samples. Roi[117] observed an even wider transition region (104–128°C) for a ceramic sample. He suggests that a transition region of finite width should be present only in polycrystalline samples, in which the simultaneous transition in all the microcrystals of the ceramic is prevented by internal stresses. The widest reported transition region (110–135°C) was observed in a ceramic sample[153]. Meyerhofer[169] found hysteresis (4.3 K) in single-crystal $BaTiO_3$, and pointed out various possible types of transition kinetics as a function of the applied field. Cross[119] observed different transition temperatures in different parts of a polycrystalline sample.

The effect of impurities on the transition temperature has been shown by several workers[171,182,283], T_{tr} decreasing with increase in impurity concentration. Variations in T_{tr} have also been noted by other workers[126,128,144,151,155,281]. The dependence of T_{tr} on experimental conditions has been clearly demonstrated[144,146,151,154].

No regularity has been observed in the behaviour of the transition temperature on changing from ceramic to monocrystalline samples. For example, Shirane and Takeda[153] obtained T_{tr} = 127 and 115°C for a ceramic and a monocrystalline sample, whereas Samara[126] obtained 112.5°C for a ceramic sample and 118.0, 120.0, 111.0, and 122.5°C for a series of four monocrystalline samples.

Many workers[117,134,137,147,150,152,157,158,160-162,170,181,184,185,191,194,196,279,280,283] were not interested in locating the temperature of the transition, and did not quote its numerical value. In these cases we have made an estimate of the transition temperature by noting the extremum of the anomaly presented graphically by each author. The average of 98 reported values of T_{tr} and of our estimates, but rejecting some unacceptable values, is T_{tr} = 119.2°C. By taking only the values obtained in special measurements of T_{tr},[108,114,118-130,135,136,138,139,142-146,151,153-156,159,163-169,171-176,178-180,182,183,186-193,195,197,198] and giving double statistical weight to the values obtained in investigations involving two or more methods[118,122,123,146,151,153,164,169], we obtain the average value T_{tr} = 119.6°C. This is close to the transition temperature usually quoted by physicists ("in the neighbourhood of 120°C").

Values of $T_{tr} \leq 115$°C were probably obtained with relatively impure or imperfect samples, or may have been due to unsatisfactory measurement methods. We stress that higher values of T_{tr} correspond to smaller amounts of impurity. The mean of the values chosen by this criterion[108,114,118-130,135,136,138,139,142-146,153-155,159,163-169,171-174,178-180,182,183,187-190,192,193,195,197,198] is T_{tr} = 121.5°C. We take this as the recommended value for the transition temperature, with an uncertainty of ± 5 K which allows for the thermal hysteresis of the transition as well as the error in the measurements.

The heat of the ferroelectric transition has been obtained by direct calorimetric measurements[121-123,153,154,279], by DTA,[190] and from measurements of the temperature dependence of the thermal expansion coefficient in conjunction with the Clausius–Clapeyron equation[125-127,162,188,191]. The anomalous temperature dependence of the specific heat in the region of the transition has also been investigated[133,136,140,141,144,146,151,187,280], but these workers did not attempt to calculate ΔH_{tr} as they considered the method insufficiently accurate[151]. An estimate of ΔH_{tr} can nevertheless be made from the published graphs of C_p against temperature or from the maximum values of ΔC_p. The mean of 24 values obtained in this way is ΔH_{tr} = 53.5 cal mole^{-1}. By averaging only the direct thermochemical determinations of ΔH_{tr}[121-123,153,154,190,279] we obtain 48.1 cal mole^{-1}, and by averaging only the values obtained from the Clausius–Clapeyron equation we obtain 46.8 cal mole^{-1}. The last two values agree reasonably well. Estimates of ΔH_{tr} made from plots of C_p are very inaccurate (from 15 to 100 cal mole^{-1}) and should be rejected. We also reject the value given by Roberts[121] (ΔH_{tr} = 15 cal mole^{-1}) as the lower limit of the latent heat of the transformation, estimated from measurements of the temperature change which occurs when the transition is induced by applying an electric field under adiabatic conditions. Averaging the other 13 values gives ΔH_{tr} = 47.4 cal mole^{-1}. We choose as the recommended value ΔH_{tr} = 47.5 ± 3 cal mole^{-1}, where the quoted uncertainty describes the error in the calorimetric measurements. Using T_{tr} = 394.65 K we obtain ΔS_{tr} = 0.12 e.u. for the entropy of the transformation.

2) Low-temperature transitions of $BaTiO_3$. The temperatures of these transitions were determined by measurements of specific heat[107,122,123,153,154], by microscopic[166], X-ray diffraction[131,166,176,178,179,199-201], and dilatometric studies[135,153,177], and by measurements of dielectric constant[123,129,135-137,148,153,155,164,166,167,170,173,185,202-205], of piezoelectric[166], acoustic[148,159], optical[131,173,176,179,193,201,203,206,283], and magnetic properties[205,207], as well as by studies of NMR[194] and luminescence spectra[208]. Some workers[153,159,166,176,204,205] used monocrystalline samples. Some[203,208] examined only the low-temperature transition at −80°C, others[122,129,136,137,164,170,177,194] ignored it and studied the transition at a higher temperature in the region of 10°C. Much of the work is devoted to physical investigations, with the aim of explaining the anomalies in the physical properties. Little effort was devoted to determining exactly the temperature of the transition.

Many workers treat the transition as a phase transformation of the first kind[117] in spite of the λ-shaped plot of C_p against temperature. The lack of a definite latent heat compels us to treat the thermodynamic characteristics of these transitions as phase transformations of the second kind. A review[135] of the anomalous properties of $BaTiO_3$ identifies the low-temperature transition temperature with the Curie point.

By averaging all the data on the two transition temperatures we obtain $T_{tr} = -75.5$ and 4.58°C. Some of the values[153,154] were assigned a double statistical weight because they were obtained by several methods, and two values[107] ($T_{tr} = -71.55 \pm 0.2$ and 11.75 ± 0.2°C) were given triple weight because this was the only investigation aimed at absolute measurements of the specific heat of $BaTiO_3$. Our averaging did not include values which had not been directly quoted by the authors but estimated by us from published property–temperature plots[129,136,137,167,170,185,194,202,204,207,208]. We quote that the dilatometric measurements[177] failed to detect any anomaly between −10 and 20°C. Averaging the values obtained by calorimetric measurements[107,123,153,154] specially aimed at determining the transition temperature gives −72.75 and 11.43°C, whereas averaging all the other values gives −76.9 and 1.47°C. The discrepancy between the two sets of data is specially large for the transition at the higher temperature. Accepting only the calorimetric measurements, we recommend the values $T_{tr} = 11.4 \pm 5$°C = 284.55 ± 5 K and $T_{tr} = -73 \pm 5$°C = 200.15 ± 5 K. The quoted uncertainty allows for the thermal hysteresis of the transitions and for the scatter of the physical measurements.

The enthalpies of these transitions have been calculated[107,123,153,154] from the anomalies in the temperature dependence of the specific heat. The most careful calorimetric study of $BaTiO_3$, in the range from 53 to 103 K, was reported by Todd and Lorenson[107]. In the range 278–293 K they obtained $\Delta H_{tr} = 26$ cal mole^{-1}, and in the range 196–206 K $\Delta H_{tr} = 12$ cal mole^{-1}. An independent treatment of their results by the method described in Refs. 1 and 2 gives $\Delta H_{tr} = 22.635$ (278–293 K) and 13.03 cal mole^{-1} (180–210 K). The former value agrees well with Ref. 153, less well with Ref. 107, and badly with Refs. 123 and 144. Rejecting the latter two values and averaging the others we arrive at the recommended value $\Delta H_{tr} = 23.5 \pm 4$ cal mole^{-1} for the heat of the transition in the region of 278–293 K. The quoted uncertainty corresponds to the estimate made in Ref. 153. For the region 180–210 K we recommend $\Delta H_{tr} = 13 \pm 1$ cal mole^{-1} by averaging the values most consistent[107,154] with our calculation and rejecting an unacceptable value[153].

Low-temperature measurements[154] of C_p show considerable scatter and discontinuities, and they cannot easily be fitted to a "normal" curve. Results[282] for the range 2–37 K are presented only graphically. Hence we shall use only the data from Ref. 107 to calculate the enthalpy and entropy of $BaTiO_3$, together with the suggested[107] sum of functions $D(198/T) + 2E(351/T) + 2E(669/T)$ for extrapolating to the low-temperature region. Our calculation based on the data of Ref. 107 gives $S_{k,298} = 25.79$ e.u., and therefore we recommend the value $S_{k,298} = 25.8 \pm 0.2$ e.u. obtained in Ref. 107. The enthalpy of $BaTiO_3$ was not calculated[107]. From the published results[107] we calculate $H_{298} - H_0 = 4230$ cal mole^{-1}, and we recommend this value with error limits of ±40 cal mole^{-1}.

The standard specific heat at 298 K was found[107] to be 24.49 cal mole^{-1} K^{-1}. A different set of data[154] gives 24.31 cal mole^{-1} K^{-1} by interpolation. Extrapolation from high-temperature measurements of enthalpy[108] gives a value identical to that of Ref. 107. Hence we choose $C_{p,k,298} = 24.49 \pm 0.02$ cal mole^{-1} K^{-1} as the recommended value.

Blunt and Love[209] observed a dielectric loss peak at 70 K with a ceramic sample of $BaTiO_3$, but no anomaly in the dielectric constant. A large increase in coercive force at temperatures below 20 K was reported[210] for a multidomain sample. However a special investigation[203] failed to confirm these observations. Neither the dielectric constant nor the ferromagnetic hysteresis had any anomalies in the region from 4.2 to 180 K. Hence we are unable to recommend any values for transitions in this temperature range.

$2BaO \cdot TiO_2$. The low-temperature specific heat of Ba_2TiO_4 has been measured[111] in the temperature range 54–307 K with a sample of 99.2% purity. Extrapolation to 0 K was by the sum of functions $D(104/T) + 3E(207/T) + 2E(523/T) + E(858/T)$. The recommended[111] standard entropy $S_{k,298} = 47.0 \pm 0.5$ e.u. agrees very well with the value (46.92 e.u.) obtained by an independent recalculation.

Extrapolation of the high-temperature enthalpy measurements[108] on the same Ba_2TiO_4 sample gives a standard specific heat of $C_{p,k,298} = 35.647$ cal mole^{-1} K^{-1}. Unlike the corresponding results for $BaTiO_3$, $SrTiO_3$, and Sr_2TiO_4 this value differs significantly from the directly measured[111] value $C_{p,298} = 36.48$ cal mole^{-1} K^{-1}. We choose the latter as the recommended value, with an uncertainty of ±0.1 cal mole^{-1} K^{-1} to allow for this discrepancy and for the inadequate purity of the sample.

The standard enthalpy of Ba_2TiO_4 has not been calculated previously. We obtain $H_{298} - H_0 = 6842.8$ cal mole^{-1} by using the data of Ref. 111, and we propose the rounded-off value 6840 ± 60 cal mole^{-1} as the recommended value.

5. Mixed Barium and Strontium Titanates

$BaTiO_3 - SrTiO_3$. Todd and Lorenson[107] measured the specific heat of $Ba_{0.543}Sr_{0.457}TiO_3$ in the range 53–298 K. They obtained $C_{p,k,298} = 23.98$, which we accept as the recommended value with an uncertainty of ±0.02 cal mole^{-1} K^{-1}. The sum of functions $D(192/T) + 2E(399/T) + 2E(676/T)$ was used to extrapolate the results below 51 K. The entropy value obtained[107], $S_{k,298} = 27.4 \pm 0.2$ e.u., is recommended. This value includes an enthalpy of mixing of 1.37 e.u. An independent calculation based on the same data[107] gave good agreement when the C_p values at 45, 50, and 51 K were obtained by graphical interpolation, but not when they were computed using the functional sum. The authors[107] did not calculate the standard enthalpy. Our calculation, using their experimental data, gave $H_{298} - H_0 = 4210$ cal mole^{-1}; we recommend this value, with an uncertainty of ±40 cal mole^{-1}.

Calculation by a linear combination of the enthalpies of $BaTiO_3$ and $SrTiO_3$ gives $H_{298} - H_0 = 4180$ cal mole^{-1}, which agrees with the recommended value within the error limits. The temperature plot of the specific heat of $Ba_{0.543}Sr_{0.457}TiO_3$ does not show the two transition effects observed in $BaTiO_3$ in this temperature region. Measurements of dielectric constant[211] on various mixed titanates suggest the possibility of a transition at 248 K, the dielectric constant peak observed in $BaTiO_3$ at 393 K shifting gradually towards lower temperatures as the mole fraction

of strontium titanate in solid solution increases. A special series of measurements [107] in the region 232–262 K failed to reveal any anomaly in C_p. The authors [107] point out that the temperature coefficient of the specific heat for the solid solution above 248 K is lower than expected, and this could be interpreted as anomalous behaviour. A very small anomaly was noted [279] in the plot of C_p against temperature for a sample of $Ba_{0.5}Sr_{0.5}TiO_3$ in the region 100–400 K. However no numerical values are quoted [279], and we are unable to make an estimate of the transition temperature.

$BaSrTiO_4$. The low-temperature specific heat of the $BaSrTiO_4$ solid solution was measured by Todd and Lorenson [111] in the range 53–296.5 K. The results were extrapolated to 0 K by using the sum $D(116/T) + 3E(239/T) + 3E(646/T)$. The calculated [111] value $S_{298} = 45.79$ e.u. coincides with our independent calculation based on the same data (45.795 e.u.). We therefore recommend the value $S_{k,298} = 45.8 \pm 0.4$ e.u., which includes the term $S_0 = 2.75$ e.u. calculated [111] on the assumption of a fully disordered distribution of Ba and Sr cations in the crystal lattice of the solid solution of their titanates.

For the standard specific heat we recommend the reported [111] value $C_{p,k,298} = 34.95$ with an uncertainty of ± 0.1 cal mole^{-1} K^{-1} (corresponding to the uncertainty previously suggested for Ba_2TiO_4).

From the published data [111] we calculate a standard enthalpy of 6477.9 cal mole^{-1}, and we recommend the rounded-off value $H_{298} - H_0 = 6480 \pm 60$ cal mole^{-1}. By assuming linearly additive enthalpies for these solid solutions we obtain $H_{298} - H_0 = 6450$ cal mole^{-1} for $BaSrTiO_4$, which agrees with the adopted value within the error limits.

6. Calcium, Strontium, and Barium Zirconates

$CaO \cdot ZrO_2$. King and Weller [212] measured the specific heat of $CaZrO_3$ in the range 52.81–296.10 K. The extrapolation to 0 K was done by using the sum of functions $D(233/T) + 2E(355/T) + 2E(722/T)$. The reported [212] value $C_{p,k,298} = 23.88$ is recommended, with an uncertainty of ± 0.02 cal mole^{-1}. The calculated [212] $S_{k,298}$ value was 23.92 e.u. (the value tabulated in Ref. 4). An independent calculation, using the same data [212], gave 23.915 e.u. The value recommended by the authors [212] is 23.9 ± 0.2 e.u. A calculation of the standard enthalpy of $CaZrO_3$ from King and Weller's results [212] gives 3991.5 cal mole^{-1}: we recommend the rounded-off value $H_{298} - H_0 = 3990 \pm 40$ cal mole^{-1}.

$SrO \cdot ZrO_2$. The same authors [212] measured the specific heat of $SrZrO_3$ in the range 53.4–295.8 K, extrapolating their results to 0 K by the sum of functions $D(177/T) + 2E(308/T) + 2E(678/T)$. We recommend their value [212] $C_{p,k,298} = 24.71$, with an uncertainty of ± 0.02 cal mole^{-1} K^{-1}. This value is adopted in Ref. 4. The reported [212] value of $S_{k,298}$ is 27.52 e.u.: our independent recalculation gives 27.533 e.u. The recommended value [212] is $S_{k,298} = 27.5 \pm 0.2$ e.u. (the value quoted in Ref. 4). The standard enthalpy calculated from the same results [212] is 4362.2 cal mole^{-1}: we recommend the rounded-off value $H_{298} - H_0 = 4360 \pm 40$ cal mole^{-1}.

$BaO \cdot ZrO_2$. King and Weller [212] also measured the specific heat of $BaZrO_3$ in the range 53.6–296.1 K, extrapolating their results to 0 K by using the sum of functions $D(144/T) + 2E(273/T) + 2E(692/T)$. They obtained [212] $C_{p,k,298} = 24.31$ cal mole^{-1} K^{-1}, which we recommend (with an uncertainty of ±0.02). Their calculated value [212] of $S_{k,298}$ is 29.83 e.u., which agrees well with our independent recalculation (29.835 e.u.). We recommend the value $S_{k,298} = 29.8 \pm 0.2$ e.u. The same values of specific heat and entropy are adopted in Ref. 4. For the enthalpy of $BaZrO_3$ we recommend the value $H_{298} - H_0 = 4515 \pm 40$ cal mole^{-1}, calculated from King and Weller's results [212].

III. HIGH-TEMPERATURE SPECIFIC HEAT AND PHASE TRANSFORMATIONS

1. Magnesium Titanates

The high-temperature enthalpies of $MgTiO_3$ have been measured by drop calorimetry ("method of mixtures") in the range 298–1720 K, [6] those of $MgTi_2O_5$ and Mg_2TiO_4 in the range 298–1800 K. [8] The results are described by the equations

Compound	Equation (cal mole^{-1})	Precision
$MgTiO_3$	$H_T - H_{298} = 28.29\,T + 1.64 \cdot 10^{-3}T^2 + 6.530 \cdot 10^5/T - 10\,771$	0.4%
$MgTi_2O_5$	$H_T - H_{298} = 40.68\,T + 4.60 \cdot 10^{-3}T^2 + 7.35 \cdot 10^5/T - 15\,003$	0.3%
Mg_2TiO_4	$H_T - H_{298} = 35.96\,T + 4.27 \cdot 10^{-3}T^2 + 6.89 \cdot 10^5/T - 13\,412$	0.3%

No solid-state transformation have been detected in the magnesium titanates.

Table 1. Melting points of magnesium titanates.

$2MgO \cdot TiO_2$	$MgO \cdot TiO_2$	$MgO \cdot 2TiO_2$	Reference
1840	—	1680	250
—	—	1645	213
1732±10	1630±10	1652±10	214
1740±20*	1680±20*	1690±20	215–217
1756*	1630*	1662	218
1750±10*	1680±10*	1690±10	219, 220

*Incongruent melting.

Melting-point data for the magnesium titanates, obtained in studies of the $MgO-TiO_2$ phase diagram, are given in Table 1 in chronological order. The incongruent melting of $2MgO \cdot TiO_2$ and $MgO \cdot TiO_2$ was recognised in all the work after 1956.

For Mg_2TiO_4 we reject the result of Ref. 250, which is clearly too high, and that of Ref. 214, which assumes congruent melting: unsatisfactory methods were used in these investigations, especially in the MgO-rich region. In both cases the phase diagram was constructed from measurements with an optical pyrometer, relying on visual observation of melting. The difficulty of visually determining the melting point further complicated the problem (common to all these investigations) caused by the partial reduction of TiO_2 in spite of the presence of an oxidising atmosphere. The precision of these measurements depends on the viscosity of the melt (which is very high in the presence of an excess of MgO), on the composition of the melt, on the presence of a eutectic or a compound, and also on the skill of the experimenter. We note that the melting of $MgTiO_3$ was not even detected in Ref. 250. The

mean of the other three values given in Table 1, obtained by a quenching method and with a hot-stage microscope, is $T_f = 1750°C$, which can be taken as the recommended value (with an uncertainty of ±15 K) for the incongruent melting point of Mg_2TiO_4 (equilibrium solid phase MgO). We note that Circular 500,[9] quoting Ref. 250, gives 1835 °C as the recommended value.

For $MgTiO_3$ we can average all the data in Table 1 (rejecting Ref. 214) and we obtain $T_f = 1660°C$, which we propose as the recommended value of the incongruent melting point with error limits of ±20 K. Simple averaging is used because there is no reason to assign greater statistical weight to any of the results. The composition of the liquid phase is not specified—the equilibrium solid phase is $2MgO·TiO_2$. The JANAF tables[3] give $T_f = 1953 \pm 20$ K, but the value obtained in Ref. 214 is also mentioned. Because of the subsequent, careful work by the quenching method we cannot agree with the JANAF recommendation[3].

By averaging all the values in Table 1 for $MgO·TiO_2$ we obtain $T_f = 1670°C$ which we propose as the recommended value, with an uncertainty of ±20 K, which includes almost all the experimental values. Circular 500,[9] quoting Ref. 250, gives $T_f = 1680°C$, and the JANAF tables[3], quoting Refs. 215–217, give $T_f = 1690 \pm 20°C$. We prefer to average all the experimental results, for the reasons given above under $MgTiO_3$.

The enthalpies of melting of $MgTiO_3$ and $MgTi_2O_5$ are given[3] as 21.6 and 35 kcal mole^{-1} by analogy with data on sodium titanates and calcium titanate silicates. In the absence of direct experimental determinations we cannot accept these as recommended values. We note that premelting effects, arising from disordering of the solid phase at temperatures below the melting point, could have a significant influence on the true enthalpy of melting.

2. Calcium Titanates

Naylor and Cook[6] measured the high-temperature enthalpy of $CaTiO_3$ in a drop calorimeter for the temperature range 298–1794 K. A phase transformation, with a heat of 550 cal mole^{-1}, was detected at 1530 K. The following enthalpy values were obtained for α- and β-$CaTiO_3$ respectively: $H_T - H_{298} = 30.47T + 0.68 \times 10^{-3}T^2 + 6.690 \times 10^5/T - 11\,389$ cal mole^{-1} (298–1530 K, 0.6%) and $H_T - H_{298} = 32.03T - 11\,197$ cal mole^{-1} (1530 to 1800 K, 0.2%). We can accept the quoted[6] values $T_{tr} = 1530$ K and $\Delta H_{tr} = 0.550$ kcal mole^{-1} as recommended values, with error limits of ±5 K and ±0.010 kcal respectively. The entropy of the transformations, according to these data, is 0.36 e.u. These characteristics of the $CaTiO_3$ transition are quoted in Ref. 9, whereas Ref. 3 does not list any phase transformation in calcium titanates.

The results of the most important thermal investigations of the $CaO–TiO_2$ system are compared in Table 2; the dashes denote absence of data from certain laboratories on certain compositions. Explicit statements concerning the presence or absence of a particular compound are also listed in Table 2.

Work prior to 1954 was largely fragmentary, and aimed mainly at establishing the presence of various compounds and their formation during heat treatment[222–223,225–228], or at estimating the melting points of various titanates[221,224,225] by visual observations of drop formation during melting. Work reported since 1954 is more complex, including critical analyses of previously published data and attempts to explain or eliminate inconsistencies.

The first X-ray structural study of the whole of the $CaO·TiO_2$ system[229] was reported in 1954. Other measurement techniques used in that work included the quenching method, visual observation of the melting of specially prepared pellets in an oxy-hydrogen flame, and differential thermal analysis (up to 1720°C) coupled with microstructural analysis of the samples. Only two compounds were identified: their melting points are given in Table 2. Similar results were obtained[230] by the cone softening method, the compositions being identified by X-ray diffraction. It was noted that the compound $3CaO·2TiO_2$ does not readily form below 1500°C, which explains the failure to detect this compound in some investigations (e.g. Ref. 225). Some workers[229] interpreted the diffraction patterns of intermediate compositions by assuming dissolution of CaO in the solid titanates. Others[230] deny this hypothesis, and assign more complex diffraction patterns to the stoichiometric titanate.

Table 2. Reported compound formation and thermal data for the $CaO–TiO_2$ system (m.p., °C).

Eutectic with TiO_2	$Ca_2Ti_3O_8$	$CaTiO_3$	$Ca_4Ti_3O_{10}$	$Ca_3Ti_2O_7$	Ca_2TiO_4	Ca_3TiO_5	Ca_4TiO_6	Eutectic with CaO	Method**	Reference
1400	no	1740	—	—	—	—	—	1620	1	221
—	yes	yes	—	yes	no	no	no	—	2	222
1437	no	yes	—	—	—	—	no	—	3	223
1410	no	1970	—	—	1800	1870	no	—	4	224
—	no	1725	—	yes	no	—	no	—	2,5	225
—	no	yes	—	no	no	no	no	—	2	226
—	—	yes	—	yes	no	no	—	—	2	227
—	—	—	—	yes	—	—	—	—	6,7	228
1460	no	1954	—	1750	no	no	no	—	1, 3, 6	229
1475	no	1915	—	1750*	no	no	no	1725	1,6	230
—	—	—	1755	1740*	—	—	—	—	1,6	231
—	—	yes	no	yes	—	—	—	—	6	232
1460	no	1989	1870	—	no	no	no	1740	8	233, 234

*Incongruent melting, equilibrium solid phase $CaTiO_3$.
**The numbers denote: 1) visual observation, 2) heat treatment, 3) quenching method, 4) visual observation of drop formation, 5) observation of drop formation in a $H_2–O_2$ flame, 6) X-ray diffraction analysis, 7) petrological study, 8) hot stage microscopy.

More recently Roth[231] extended previous work[230] by analysing the diffraction patterns of mixtures[229] in this system and comparing them with data for the $SrO–TiO_2$ system. He concluded that an additional compound is formed, of composition $4CaO·3TiO_2$, rather than solid solutions. Roth demonstrated the thermodynamic stability of this compound by special X-ray studies of samples annealed at, or quenched from, 1550–1745°C. Relative measurements of the melting points of $3CaO·2TiO_2$ and $4CaO·3TiO_2$ gave incongruent melting points of 1740 and 1755 °C respectively. These results were confirmed by visual observations of melting in different atmospheres and by the quenching method. Roth used these results to correct previously published phase diagrams[229,230].

Imlach and Glasser[232], in their study of the $CaO–TiO_2–Al_2O_3$ phase diagram, re-checked the work of Roth[231] and concluded that the compound $4CaO·3TiO_2$ does not exist. Their X-ray work showed that slightly different diffraction patterns are obtained by varying the heat treatment procedure, suggesting a definite homogeneity region for the compound $3CaO·2TiO_2$. Their ternary phase diagram[232] uses values identical to those of Ref. 229 for the binary $CaO–TiO_2$ system.

Jongejan and Wilkins[233] published a critical analysis of the phase diagrams and the experimental methods previously reported[229-232], and they pointed out that liquidus temperatures cannot be accurately determined by the visual method because of the difficulty of discerning the disappearance of the last crystals, particularly since the dendritic CaO crystals tend to float in the melt. They constructed a phase diagram[233] from observations in a hot-stage microscope. In addition to the congruently melting $CaTiO_3$ they detected $4CaO \cdot 3TiO_2$, which melts incongruently at 1870°C (equilibrium solid phase $CaTiO_3$). The possibility that this temperature could apply merely to a solid-state transformation of $CaTiO_3$ is admitted[233], but a specially detailed study of the liquidus line in the TiO_2-rich region confirmed the existence of the compound $4CaO \cdot 3TiO_2$. The incongruently melting compound $3CaO \cdot 2TiO_2$ was also assumed to be present, but the solidus line was not accurately studied in this region and a break in the liquidus line was not detected. The composition ordinate for this compound and the liquidus line in the same region are shown as broken lines in the phase diagram. These results[233] were confirmed in a later paper[234].

The existence of the compound $CaO \cdot TiO_2$ is indicated by all the data on the $CaO-TiO_2$ system listed in Table 2. Among the melting-point data for this compound those from Refs. 221 and 225 are clearly unacceptable: this is not surprising in view of the inaccurate methods used. By averaging the remaining values we obtain $T_f = 1957$°C. Our recommended value is rounded off to $T_f = 1960 \pm 30$°C, the suggested uncertainty including most of the experimental data and reflecting the low precision of work at these very high temperatures.

The reported[222] existence of the compound $2CaO \cdot 3TiO_2$ should be treated as unconfirmed.

Information on the CaO-rich part of the $CaO-TiO_2$ phase diagram is even more complex and contradictory.

The compound $4CaO \cdot TiO_2$ was not detected in any of the investigations which included this composition. The titanates $2CaO \cdot TiO_2$ and $3CaO \cdot TiO_2$ are indicated in one phase diagram[224], but melting points are not quoted, and the values in Table 2 were simply read off the diagram. All the other workers (see Table 2) deny the existence of these titanates. We must conclude that it would be premature to attempt a recommendation on their melting points.

Most of the structural studies which have been reported point to the existence of the compound $3CaO \cdot 2TiO_2$, melting incongruently at a well defined temperature[229-231]. The temperature reported[233] as the melting point of the eutectic with CaO (1740°C) may have been a misinterpretation of the incongruent melting of $3CaO \cdot 2TiO_2$. Basing our choice on the work of Roth[231], who made a special comparative study of the melting points of the neighbouring compositions $4CaO \cdot 3TiO_2$ and $3CaO \cdot 2TiO_2$ by several methods, we propose $T_f = 1740 \pm 15$°C as the recommended value for the incongruent melting point of $3CaO \cdot 2TiO_2$. The suggested error limits include the other reported values[229,230]. The equilibrium solid phase is taken to be $CaTiO_3$, as shown by the following arguments.

The existence of the compound $4CaO \cdot 3TiO_2$, discussed in three publications, is more controversial. Some deny it[232] on the basis of a special X-ray study and of the results[229] of De Vries and coworkers. On the other hand Roth[231] convincingly proves its existence by combining the same results[229] with those of his own investigations. However the break in the liquidus line[233] cannot be ascribed unequivocally to incongruent melting of a compound of the same composition. Furthermore the incongruent melting point of $4CaO \cdot 3TiO_2$ quoted in Ref. 233 differs by more than 100 K from that quoted in Ref. 231, even though the latter phase diagram[231] agrees in other respects with those of other workers. We should add that the liquidus line of Ref. 233 does not show a break for the compound $3CaO \cdot 2TiO_2$, in direct contradiction to other reports[229-232]. The authors[233] also cannot explain the serious discrepancy in their melting point for the eutectic composition rich in CaO. Because of all these inconsistencies we must conclude that the proof[233] of the existence of the compound $4CaO \cdot 3TiO_2$ is not entirely convincing. Equally, there are no grounds for accepting the results of Ref. 231 in preference to the more recent results of Ref. 232. We must therefore await more definite confirmation of the existence of the compound $4CaO \cdot 3TiO_2$, and more precise measurements of its phase characteristics.

Borisenko and Shirokova[235] observed a polymorphic transition at 765°C in their study of the compound $3CaO \cdot 2TiO_2$ by a complex thermal analysis method. The thermal effect was small, and no volume change was detected. A structural study by X-ray ionisation analysis at 700 and 800°C revealed only a small change in the degree of tetragonal distortion of the lattice in this temperature range. An alternative explanation of the reported effect is possible, based on kinetic arguments. For example, a slight dependence of crystal structure on heat treatment conditions has been noted[232]. This transition is not confirmed by any of the other investigations by X-ray diffraction or thermal anslysis, and therefore we cannot include the transition temperature quoted in Ref. 235 in our list of recommended values.

3. Strontium Titanates

$SrO \cdot TiO_2$. No solid-state transformations have been observed in the measurement[108] of the enthalpy change $H_T - H_{298}$ for $SrTiO_3$. In the region 298–1800 K the results are described by the expression[108] $H_T - H_{298} = 28.23T + 0.88 \times 10^{-3}T^2 + 4.66 \times 10^5/T - 10\,058$ (cal mole^{-1}). The melting point of $SrTiO_3$ has been measured only in one laboratory[236,237], using a combination of thermal, X-ray diffraction, and microscopic methods[237], and found to be $T_f = 2040 \pm 20$°C. This must be taken as the recommended value in preference to the estimated values 2100°C [109] and 1910°C.[238]

Sr_2TiO_4. The high-temperature specific heat of Sr_2TiO_4 also was measured[108] in the range 384–1831 K. Between 298 and 1800 K the experimental results are described with 0.4% precision by the expression $H_T - H_{298} = 38.45T + 1.92 \times 10^{-3}T^2 + 4.67 \times 10^5/T - 13\,201$ (cal mole^{-1}).

An earlier[236] phase diagram for the $SrO-TiO_2$ system shows a maximum in the liquidus curve corresponding to the composition Sr_2TiO_4 ($T_f = 1800 \pm 20$°C). A more detailed investigation by the same authors[237] produced a revised phase diagram for the $SrO-TiO_2$ system in the composition range 33–100 mole % TiO_2. The left-hand boundary of this diagram corresponds to Sr_2TiO_4, with $T_f = 1860 \pm 20$°C, but the authors[237] do not discuss the type of melting or the discrepancy with their previous result. A polymorphic $\alpha-\beta$ transformation with $T_{tr} = 1600 \pm 10$°C is also reported[237] for Sr_2TiO_4.

A microstructural study[238] of the $SrO-TiO_2$ system has confirmed the stability of Sr_2TiO_4 up to T_f. A sample quenched from 1860°C showed signs of melting and traces

of SrO. A polymorphic transformation was observed between 1500 and 1550°C. The structure of the samples was studied after a first anneal at 1600°C and a second anneal at 1500°C for 75 h or at 1550°C for 10 h. The first sample had the low-temperature structure, the second had the high-temperature structure. This work achieved a closer approach to equilibrium than that of Ref. 237, in spite of the large temperature step. Hence we take T_{tr} = 1525 ± 20°C as the recommended value. We note a slight discrepancy with the high-temperature enthalpy measurements of Coughlin and Orr[108], who did not attempt to detect polymorphic transformations. Since our adopted T_{tr} value lies at the boundary of the temperature range covered in Ref. 108 it is not surprising that equilibrium was not achieved in that work. Alternatively, the transition could have been masked by the interpolation procedure used in the drop calorimeter technique.

The results of Refs. 237 and 238 for the melting point of Sr_2TiO_4 are satisfactorily consistent, but those of Ref. 236 are unconfirmed. Therefore we take T_f = 1860 ± 20°C as the recommended value.

$Sr_3Ti_2O_7$. Drys and Trzebiatowski[237] detected, in addition to strontium meta- and orthotitanate, the compound $Sr_3Ti_2O_7$, which decomposes into solid strontium meta- and orthotitanate at 1640 ± 10°C. The decomposition temperature was determined by X-ray diffraction analysis of samples annealed at 1630, 1640, 1650, and 1660°C. The first two samples consisted of $Sr_3Ti_2O_7$, the last two of a two-phase mixture of $SrTiO_3 + Sr_2TiO_4$. The existence of $Sr_3Ti_2O_7$ was confirmed by microstructural studies[238], but the decomposition temperature was found in the range 1550–1600°C. A sample heat treated at 1600°C and again annealed for 10 h at 1550°C contained only $Sr_3Ti_2O_7$, whereas a sample annealed at 1600°C showed the presence of metatitanate and of the high-temperature form of Sr_2TiO_4. The work of Ref. 238 was done under conditions more closely approaching equilibrium. We therefore accept these results, and we give T_{tr} = 1580 ± 20°C as the recommended value for the decomposition temperature of $Sr_3Ti_2O_7$ into $SrTiO_3$ and β-Sr_2TiO_4.

Sr_3TiO_5. Cocco and Massazza[238] found yet another compound in this system: $3SrO{\cdot}TiO_2$, stable in the region of 1560–1760°C. Thus, a sample annealed at 1550°C contained Sr_2TiO_4 and SrO, a sample annealed at 1600 or 1750°C contained only the phase Sr_3TiO_5, and a sample annealed at 1770°C again consisted of SrO and Sr_2TiO_4. The transformation temperatures quoted by the authors[238], T_{tr} = 1560 and 1760°C, are recommended with an uncertainty of ±20 K. We note that this region of compositions was not examined in Ref. 237.

4. Barium Titanates

$BaTiO_3$. The high-temperature enthalpy of $BaTiO_3$ was measured[108] in the range 400–1800 K: $H_T - H_{298} = 29.03T + 1.02 \times 10^{-3}T^2 + 4.58 \times 10^5/T - 10\,282$ cal mole^{-1} (0.3% precision).

The melting point of $BaTiO_3$ is generally agreed[180,183,239–243] to lie in the range 1610–1620°C. There is only one substantially different value: T_f = 1700°C, reported in Ref. 244 and quoted in Refs. 108 and 135. The shortcomings of the method[244] are discussed in Ref. 241. By averaging all the values except that of Ref. 244 we obtain the recommended value T_f = 1616 ± 5°C.

The high-temperature transition of $BaTiO_3$ from the perovskite to the hexagonal structure has been studied by microscopic[180,183,239], thermal[180,183,239,240,243], X-ray diffraction[183,240,243], and kinetic methods[245]. The dependence of the transition temperature on impurity concentration and on heat-treatment atmosphere was investigated by Glaister and Kay[242]. With two exceptions[239,245], giving a transition temperature of 1450°C, all the other workers give T_{tr} = 1460°C. The discrepancy arises from the different temperature intervals chosen for the heat treatment experiments (50 K in Ref. 239). We recommend the value T_{tr} = 1460 ± 5°C. It should be noted that a series of enthalpy measurements up to 1800 K [108] failed to reveal any thermal effect in the neighbourhood of T_{tr}.

$BaTi_2O_5$, $BaTi_3O_7$, $BaTi_4O_9$. The liquidus diagram of the $BaO-TiO_2$ system was first reported in 1951 by Statton[244], who used an optical pyrometer to study the melting of various compositions on a molybdenum strip in a vacuum. The diagram shows clear peaks for $BaTi_2O_5$ (1675°C), $BaTi_4O_9$ (1640°C), and also for $BaTiO_3$ and Ba_2TiO_4, but the graphical presentation is not accompanied by numerical tabulations. Corrections had to be applied for the interaction of BaO with Mo, which affected the results. All the compounds were identified by X-ray diffraction.

Trzebiatowski and coworkers[239] constructed the phase diagram of this system in the composition region 33 to 100 mole % TiO_2. They used visual and differential thermal analysis methods, combined with microscopic and X-ray studies of the quenched samples. They quote 1315 and 1465°C respectively for the congruent melting points of $BaTi_2O_5$ and $BaTi_4O_9$, but congruent melting is not clearly shown in their diagram. Furthermore the presence of the compound $BaTi_3O_7$ is suggested both by the liquidus curve in the region of ~75 mole % TiO_2 and by the diffraction pattern of this composition.

Rase and Roy[240] made a careful study of the phase composition of the $BaO-TiO_2$ system at high temperatures, and analysed the results of previous work in great detail. From their study of quenched samples, and their visual and thermographic observations of melting on a platinum strip, they obtained the phase diagram of the system and they established methods of preparing the compounds in polycrystalline or monocrystalline forms, as well as their stability conditions. The existence of $BaTi_2O_5$ and $BaTi_4O_9$ was confirmed, but these compounds were found to melt incongruently at 1322 and 1428°C respectively. The equilibrium solid phases are reported to be $BaTiO_3$ and TiO_2 respectively. The same workers[240] also convincingly identified the compound $BaTi_3O_7$, with T_f = 1357°C (equilibrium solid phase $BaTi_4O_9$). We take this as the recommended value, with error limits of ±10 K.

Shchepochkina[241] critically discussed the experimental shortcomings of Statton's work[244] and obtained more precise values of the phase transition temperatures in the $BaO-TiO_2$ system by a method relying on the softening of rod tips. For $BaTiO_3$ she obtained T_f = 1615°C, which is very close to our recommended value of 1616°C, and for the congruent melting of $BaTi_2O_5$ and $BaTi_4O_9$ she obtained 1385 and 1445°C respectively.

Judging by the general standard of the work, both in quality and in quantity, we accept the result of Rase and Roy[240], and we conclude that the melting of barium dititanate and tetratitanate is incongruent. Statton's results[244] are clearly inconsistent with later work, probably because of the serious compositional changes aggravated by the use of a vacuum and by the incongruent

melting of the samples. Comparison of the T_f values for $BaTiO_3$, given as 1610°C in Ref. 239 and 1618°C in Ref. 240, with the recommended value of 1616°C suggest the possibility of a large systematic error in Ref. 239. We note that Statton obtained an unacceptable value (T_f = 1700°C) even for $BaTiO_3$. By averaging the results of Refs. 239, 241, and 240, but giving the latter a doubtful statistical weight, we arrive at the rounded-off temperatures 1340 ± 20 and 1440 ± 15°C for the incongruent melting of $BaTi_2O_5$ and $BaTi_4O_9$, which are recommended. The different uncertainty limits reflect the reproducibility of the two sets of results.

Ba_2TiO_4. The incongruent melting point of the orthotitanate in Statton's liquidus diagram[244] is 1692°C. T_f values of 1820, 1860, and 1880°C are obtained in Refs. 239, 240, and 241 respectively. The experimental details of the procedures used are discussed above. Rase and Roy[240] consider Ba_2TiO_4 to be too reactive towards platinum at its melting point for a reliable identification of the type of melting. The increase in the T_f value from Ref. 244 to Ref. 241 does not line up with the results of those same workers for $BaTiO_3$ and other titanates, and it is difficult to select any particular value as the preferred one, especially in view of the experimental difficulties and of the very high value of T_f. However Statton's value[244] is probably unacceptable. By averaging the other values, giving double weight to Rase and Roy's[240], we arrive at the recommended value T_f = 1855 ± 20°C.

The high-temperature enthalpy of Ba_2TiO_4 has been measured[108] in the range 398–1831 K by a drop calorimeter method. No solid-phase transitions were noted. The experimental results are described with a precision of 0.6% by the expression $H_T - H_{298} = 43.00T + 0.80 \times 10^{-3}T^2 + 6.96 \times 10^5/T - 15\,226$ (cal mole^{-1}).

5. Magnesium Zirconate

The existence of the compounds $MgO \cdot ZrO_2$ and $2MgO \cdot 3ZrO_2$ has been suggested by a structural study[263] of the $MgO-ZrO_2$ system. The liquidus line of the $MgO-ZrO_2$ system given in Ref. 254 on the basis of a visual thermal study differs from that of Ref. 263: the compound $2MgO \cdot 2ZrO_2$ is not found on the liquidus line, and the compound $MgZrO_3$ has a congruent melting point. The melting point is not quoted, but it can be estimated from the published diagram as T_f = 2130°C. Circular 500,[9] quoting Ref. 254, gives T_f = 2120°C. Von Wartenberg[250], referring to his previous work[254,264], gives T_f = 2150°C. We note that the melting of magnesium zirconate was not studied in Ref. 264.

All these values originate from the same laboratory. Our recommended value is obtained by averaging them: T_f = 2130 ± 20°C. The suggested uncertainty allows for the likely error in the various estimates.

6. Calcium Zirconates

$CaZrO_3$. The values reported by different authors for the congruent melting point of $CaZrO_3$ are in good agreement: 2350°C,[246,247] 2325°C,[248] and 2370°C.[249] We take their mean as the recommended value: T_f = 2350 ± 20°C.

The high-temperature enthalpy of $CaZrO_3$, measured[251] in a drop calorimeter, was found to be $H_T - H_{298} = 30.41T + 0.62 \times 10^{-3}T^2 - 3.46 \times 10^5/T - 10\,290$ cal mole^{-1} (0.8%) for the range 491–1066 K. No phase transformations were observed in this temperature region.

X-ray structural analysis[252] revealed two modifications of $CaZrO_3$: a low-temperature form, stable below 1200°C, and a high-temperature form, stable above 1250°C. The transition was found to be gradual[252], occurring in the range 1100–1250°C on heating and in the range 1100–900°C on cooling the sample. The authors conclude[252] from published data that the lattice parameter of this compound depends on the temperature at which the sample was synthesised. These results are semi-quantitative and cannot be used as a basis for a recommendation on this phase transformation.

$CaZr_4O_9$. Garvie[253] carried out an X-ray structural analysis of the $CaO-ZrO_2$ system along the 1305, 1400, 1500, 1600, 1700, and 1765°C isotherms in the region rich in CaO. The variation of lattice parameter with composition revealed a sharp boundary to the formation of cubic solid solutions of CaO in ZrO_2 at 20 mole % CaO, corresponding to the compound $CaZr_4O_9$. The change in lattice parameter of this composition at ~1650°C is interpreted by Garvie as a phase transition giving a different defect structure. The existence region of $CaZr_4O_9$ in the phase diagram lies above 1270°C: below this temperature the co-existing phases are ZrO_2 and $CaZrO_3$. The recommended temperatures for the equilibrium formation and for the phase transformation of $CaZr_4O_9$ are 1270 ± 30 and 1650 ± 30°C respectively.

7. Strontium Zirconates

$SrZrO_3$. The congruence of the melting of $SrZrO_3$ was shown in Ref. 254, but the authors found the melting point inaccessible and estimated it as above 2600°C.

Berezhnoi and Belik[255] quote T_f = 2750°C for $SrZrO_3$ without disclosing the method of measurement. The same value was obtained by Travers and Foex[249], who used a solar furnace to study the $SrO-ZrO_2$ phase diagram. Noguchi and coworkers[256] also used a solar furnace in their work on the liquidus curve of the $SrO-ZrO_2$ system, and obtained T_f = 2646 ± 20°C for $SrZrO_3$.

Both these phase diagrams[249,256] indicate congruent melting of the compound $SrZrO_3$. However the melting point given in Ref. 256 is inconsistent with those of Ref. 255 and with the independent measurements of Ref. 249, and therefore we take as our recommended value T_f = 2750 ± 20°C. We note that Carlsson's review[259] gives the melting point of $SrZrO_3$ as approximately 2800°C.

Berezhnoi and coworkers[260] calculated the enthalpy and entropy of melting of $SrZrO_3$ from the phase diagram of the $SrO-ZrO_2$ system: 16.7 kcal mole^{-1} and 5.5 e.u. We recommend their ΔH_f value with an uncertainty of ±2 kcal mole^{-1}. The corresponding value of the entropy of melting is ΔS_f = 5.52 e.u.

Carlsson[259] investigated the high-temperature solid-phase transitions of $SrZrO_3$. Differential thermal analysis at 550–950°C gave two endotherms corresponding to transitions at 730 and 860°C. These measurements are found to be poorly reproducible. The transition temperature is assumed to be the point at which the heating curve begins to deviate from its normal shape. The presence of different crystal structures at 600, 820, 1000, and 1200°C was confirmed by high-temperature X-ray diffraction. A rhombic modification was found to exist from room temperature up to 700°C, when it converts into a pseudo-tetragonal form with $c/a < 1$. Above 830°C another pseudo-tetragonal modification is formed, with $c/a < 1$, and at 1170°C the structure becomes cubic. Carlsson

quotes the temperatures of the first two transitions, from DTA results, as 730 ± 25 and 860 ± 25°C, stressing the satisfactory agreement with the X-ray results. The temperature dependence of the lattice parameters was studied for the high-temperature transition with T_{tr} = 1170°C. The plot of dielectric constant against temperature has a peak at ~700 and 850°C. The transformation at 1170°C is thought to be either ferroelectric–paraelectric or antiferroelectric–paraelectric, the latter being the more likely. The temperature dependence of electrical resistance of $SrZrO_3$ has no anomaly at 1170°C, though the compound behaves as a semiconductor above 1000°C.

Peaks at 762, 846, and 1095°C have been reported[261] on the DTA curve of $SrZrO_3$ (the quoted temperatures corresponding to the peak maxima, unlike those of Carlsson[259]). The same reference shows breaks at 745, 1060 (very weak), and 1480°C in the temperature dependence of electrical resistance.

The T_{tr} value of the low-temperature transition[261] agrees well with Carlsson's value[259] in view of the different methods of identifying the transition point on the DTA curve. Therefore we choose T_{tr} = 730 ± 25°C as the recommended value. The two sets of data for the second transition are also in very good agreement: we choose T_{tr} = 860 ± 25°C. For the last transition we average the DTA value[261] and the value obtained[259] from the temperature dependence of the lattice parameters, and we obtain T_{tr} = 1135 ± 35°C as the recommended value.

Further confirmation is needed of the possible transition at 1480°C [261] suggested by the electrical resistance curve, because it occurs at the very limit of the temperature range of the experiment, and it has not so far been detected by any other method.

The high-temperature enthalpy of $SrZrO_3$ has been measured by drop calorimetry[284] at temperatures in the range 562–2318 K. The results are described with 0.3% precision by the expression $H_T - H_{298} = 147.072T - 2.077 \times 10^{-3}T^2 + 4.148 \times 10^6/T - 57\,277$ (J mole^{-1}). Other workers[285] used the same method in the range 298–1620 K and obtained the following expression (1% precision): $H_T - H_{298} = 29.79T + 0.70 \times 10^{-3}T^2 + 4.89 \times 10^5/T - 10\,584$ (cal mole^{-1}). Neither of these investigations detected the polymorphic transformations of $SrZrO_3$, obviously because of the rather large temperature step between the measurements (80–120°C). Furthermore the accuracy of these results is in doubt, the former[284] being higher than the latter[285] by 5.7–7.1% in the range 700–1600 K. We should also note that existing information on the polymorphic transformations of $SrZrO_3$ is completely ignored in both these publications[284,285].

Sr_2ZrO_4, $Sr_3Zr_2O_7$, $Sr_4Zr_3O_{10}$. Noguchi and coworkers[256] studied the liquidus diagram of the $SrO–ZrO_2$ system with a solar furnace. The phase composition of the samples was checked by chemical analysis and by X-ray diffraction after quenching. The evaporation rate of some of the samples was also measured. Three compounds were found in the system in addition to $SrZrO_3$: Sr_2ZrO_4, $Sr_3Zr_2O_7$, and $Sr_4Zr_3O_{10}$. The congruent melting points of Sr_2ZrO_4 and $Sr_4Zr_3O_{10}$ are given as 2325 and 2674°C respectively. We take the latter value as the recommended T_f for $Sr_4Zr_3O_{10}$, with an uncertainty of ±20 K.

Travers and Foex[249] also studied the $SrO–ZrO_2$ phase diagram by differential thermal analysis, using a solar furnace. Special attention was paid to the compound $SrZrO_3$. The compound $Sr_4Zr_3O_{10}$ is not shown on their phase diagram, and Sr_2ZrO_4 and $Sr_3Zr_2O_7$ are stated to melt incongruently. T_f = 2250°C is quoted for $Sr_3Zr_2O_7$, and the melting of Sr_2ZrO_4 is shown as a broken line on the diagram, from which we estimate T_f = 2220°C. It is stressed[249] that all the compounds were identified by X-ray diffraction.

Evidence on the type of melting of Sr_2ZrO_4 is contradictory[249,256], and therefore we cannot give a ruling on this problem. However the direct experimental determination[256] should be the more reliable. We therefore recommend, after rounding off, T_f = 2300 ± 30°C for the melting point of Sr_2ZrO_4.

The compound $Sr_3Zr_2O_7$ was first identified[262] after heating the corresponding mixture at 1700°C. Noguchi and coworkers[256] obtained the same diffraction pattern after a similar preparation. However a 2 hour anneal at 1800 and 1900°C followed by air quenching gave only the diffraction lines of $Sr_4Zr_3O_{10}$, with small amounts of $SrZrO_3$ and SrO. The stability region of $Sr_3Zr_2O_7$ therefore appears to extend only up to 1700°C.[256] This region is shown as a broken line in the phase diagram[256], $Sr_3Zr_2O_7$ decomposing into Sr_2ZrO_4 and $Sr_4Zr_3O_{10}$ at 1700°C. We note that this decomposition is not inconsistent with the incongruent melting of the composition $Sr_3Zr_2O_7$ observed[249] at 2250°C (equilibrium solid phase $SrZrO_3$), since those workers[249] did not observe the compound $Sr_4Zr_3O_{10}$. The stability of $Sr_3Zr_2O_7$ is not discussed[249], but it is pointed out that the diffraction pattern of a sample quenched from a melt of this composition does not contain lines of the compound $Sr_3Zr_2O_7$.

Since the tentative result of Ref. 256 appears to reconcile the inconsistency of the other data we take T_{tr} = 1700 ± 50°C as the recommended temperature for the decomposition of $Sr_3Zr_2O_7$ into $SrZrO_4$ and $Sr_4Zr_3O_{10}$.

8. Barium Zirconate

$BaZrO_3$. The congruent melting of $BaZrO_3$ has been demonstrated in a study[254] of the $BaO–ZrO_2$ system. From the published phase diagram[254] the melting point of $BaZrO_3$ is estimated as T_f = 2860°C. Circular 500,[9] referring to this work[254], gives T_f = 2700°C. By averaging these two estimates we arrive at the recommended value T_f = 2690 ± 20°C.

In 1976 Levitskii and coworkers[285] measured the high-temperature enthalpy of $BaZrO_3$ in the range 298–1606 K using a drop calorimeter. The normal temperature step of 80–120 K was decreased to 10–30 K in the region of the C_p anomaly. Temperatures of 758 ± 1 K and 1175 ± 1 K were obtained for the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$-$BaZrO_3$ polymorphic transformations. The experimental results are described by the expressions

Compound	Equation (cal mole^{-1})	Temperature, K
α-$BaZrO_3$	$H_T - H_{298} = 25.63\,T + 3.12 \cdot 10^{-3}T^2 + 2.82 \cdot 10^5/T - 8865$	298—758
β-$BaZrO_3$	$H_T - H_{298} = 27.77\,T + 0.09 \cdot 10^{-3}T^2 - 8272$	758—1175
γ-$BaZrO_3$	$H_T - H_{298} = 24.75\,T + 2.21 \cdot 10^{-3}T^2 - 7576$	1175—1606

Tentative values of the heats of these phase transitions, defined as the difference between the enthalpies of the two forms at $T = T_{tr}$, are quoted as $\Delta H_{758}(\alpha \rightarrow \beta) = 0$ and $\Delta H_{1175}(\beta \rightarrow \gamma) = 330$ cal mole^{-1}. The authors conclude[285] that the $\alpha \rightarrow \beta$ transformation is a phase transition of the second kind. We take the published[285] characteristics of these transitions as recommended values. The entropy of the $\beta \rightarrow \gamma$ transition is $\Delta S = 0.28$ cal mole^{-1} K^{-1}.

9. Strontium Hafnate

$SrHfO_3$. Berezhnoi and Belik[255] state that $SrHfO_3$ melts at 3163 K without mentioning the method of measurement. We take this as the recommended value, with an uncertainty of ±30 K.

Berezhnoi and coworkers[260] studied solid solutions of $SrZrO_3$ and $SrHfO_3$, and they calculated the heat and entropy of melting of $SrZrO_3$ from the phase diagram of the $SrO-ZrO_2$ system. They took $\Delta S_f = 5.5$ e.u. for the fusion of $SrHfO_3$ (equal to the value for $SrZrO_3$). Using their previous value[255] of T_f they calculated $\Delta H_f = 17.5$ kcal mole^{-1} for $SrHfO_3$. Assuming an error of ±1 e.u. in the estimate of ΔS_f we obtain an uncertainty of ±3 kcal mole^{-1} for ΔH_f. We propose these as the recommended values for ΔH_f, and 5.53 e.u. for the entropy of melting.

The high-temperature enthalpy of $SrHfO_3$ in the temperature range 675–2337 K was measured by Fomichev and coworkers[284] at 100 K intervals by the drop calorimetric method. Their results are described by the expression $HT - H_{298} = 109.509T + 13.266 \times 10^{-3}T^2 - 1.260 \times 10^6/T - 27\,516$ (J mole^{-1}). No polymorphic transformations were observed in this work.

IV. ENTHALPY AND FREE ENERGY OF FORMATION

Kelley and coworkers[265] measured the enthalpy of formation of these compounds in a solution calorimeter (73.7°C, mixture of hydrochloric and hydrofluoric acid). Samples of mechanical mixtures of the oxides and of the compounds, contained in gelatin capsules, were introduced into the calorimeter at an initial temperature of 25°C. The heat of formation of the compound from its oxides at 25°C was obtained from the difference between the thermal effects accompanying the dissolution of the two samples. The thermochemical cycle for the hypothetical compound $MO \cdot TiO_2$, where M is an alkaline earth metal, is illustrated by the scheme

TiO_2 (cr., 25°) + 4 H^+ (sol., 73.7°) → Ti^{4+} (sol., 73.7°) + $2H_2O$ (sol., 73.7°) (ΔH_1)
MO (cr., 25°) + $2H^+$ (sol; 73.7°) → M^{2+} (sol., 73.7°) + $2H_2O$ (sol., 73.7°) (ΔH_2)
$MO \cdot TiO_2$ (cr., 25°) + $6H^+$ (sol., 73.7°) → M^{2+} (sol., 73.7°) + Ti^{4+} (sol., 73.7°) + $3H_2O$ (sol., 73.7°) (ΔH_3).

The heat of formation of $MO \cdot TiO_2$ from the oxides at 25°C is $\Delta H = \Delta H_1 + \Delta H_2 - \Delta H_3$. The composition of the acid mixture was 10.05 wt.% HCl + 10.05 wt.% HF. The experimental results were corrected for the heat of dissolution of the capsule in the acid. The error of the measurement of the heat of formation of the compound from the oxides was 0.3–0.5 kcal mole^{-1}.

Feodos'ev and coworkers used the method of combustion in a bomb calorimeter under standard conditions. A mixture of the alkaline earth carbonate MCO_3 and of the dioxide M_1O_2 (where M_1 = Ti, Zr, Hf) was pelleted with powdered graphite, used as an initiator in the proportion of 1:5. The reaction was

$$MCO_3 + M_1O_2 = MM_1O_3 + CO_2.$$

The heat of formation of MM_1O_3 from the elements was calculated by using the known heats of formation of the carbonates and of the oxides. The experimental results were corrected for the heat of formation of the nitric acid found among the combustion products, which were tested for completeness of the reaction and examined by X-ray diffraction. The unburned graphite was determined calorimetrically. The results for the titanates were in good agreement with those of Kelley and coworkers. The error of the measurements of heat of combustion was 0.3 to 0.8 kcal.

The original calorimetric results have been recalculated in this review by using the heats of formation of the oxides, carbonates, and CO_2 previously chosen during the compilation of Ref. 2.

1. Magnesium Titanates

$MgTiO_3$. Kelley and coworkers[265] obtained $\Delta H = -6.35 \pm 0.25$ kcal by solution calorimetry for the heat of formation of $MgTiO_3$ from MgO and TiO_2. Panfilov and Feodos'ev[266] measured in a bomb calorimeter the heat of combustion of air-dry MgO and TiO_2 mixed with graphite:

$$MgO \cdot x\,H_2O \cdot y\,CO_2 + TiO_2 = MgTiO_3 + x\,H_2O + y\,CO_2$$

and also the heat of combustion of MgO mixed with graphite:

$$MgO \cdot x\,H_2O \cdot y\,CO_2 = MgO + x\,H_2O + y\,CO_2.$$

Chemical and phase analyses of the combustion products were carried out[266]: the TiO_2 was determined as the insoluble residue after two extractions in boiling hydrochloric acid (1 h). The molar amounts of MgO and TiO_2 entering into the reaction were equal. $\Delta H = -5.5 \pm 0.1$ kcal was found[266] for the heat of formation of $MgTiO_3$ from the oxides. The discrepancy between the two results[265,266] exceeds the quoted experimental errors. In our choice of a recommended value we gave preference to Kelley's results[265], because they were obtained with a very pure sample of MgO (99.8%) containing small amounts of CaO, SiO_2, Fe_2O_3, and alkaline earths. The composition of the magnesium oxide used in Ref. 266 is more indeterminate. Using $\Delta H_f(MgO) = -143.76$ and $\Delta H_f(TiO_2$, rutile) = -225.59 kcal mole^{-1} we obtain $\Delta H_f(MgTiO_3) = -375.7$ kcal mole^{-1} from Kelley's result[265]. By combining this value with recommended entropy data we arrive at $\Delta G_f = -354.6$ kcal mole^{-1}. The error in ΔH_f and ΔG_f is less than 0.3 kcal mole^{-1}.

Mg_2TiO_4. The heat of formation of magnesium orthotitanate (spinel) from the oxides is given[265] as $\Delta H = -4.1 \pm 0.25$ kcal mole^{-1}. Using the heats of formation of the oxides assumed above we obtain $\Delta H_f = -517.2$ and $\Delta G_f = -493.8$ kcal mole^{-1} for Mg_2TiO_4, with an uncertainty not exceeding 0.5 kcal mole^{-1}.

$MgTi_2O_5$. Kelley[265] obtained $\Delta H = -4.45 \pm 0.25$ kcal mole^{-1} for the formation of the dititanate from the oxides. From this value we calculate $\Delta H_f = -599.2$ and $\Delta G_f = -566.2$ kcal mole^{-1} for $MgTi_2O_5$ by using the value $S(MgTi_2O_5) = 34.19$ e.u., or $\Delta G_f = -565.7$ kcal mole^{-1} by using the value $S(MgTi_2O_5) = 32.4$ e.u. (see Chapter II). The uncertainty in ΔH_f and ΔG_f is less than 0.7 kcal mole^{-1}.

2. Calcium Titanates

$CaTiO_3$. Kelley and coworkers[265] obtained $\Delta H = -19.35 \pm 0.25$ kcal for the reaction $CaO + TiO_2$(rutile) = $CaTiO_3$(perovskite). Panfilov and Feodos'ev[266] found $\Delta H = 22.5 \pm 0.2$ kcal for $CaCO_3 + TiO_2$(rutile) = $CaTiO_3 + CO_2$. The extent of the combustion reaction was 99%. Calculation from Kelley's result gives $\Delta H_f(CaTiO_3$, perovskite) = -396.7 kcal mole^{-1}, whereas from Ref. 266 we obtain $\Delta H_f = -397.6$ kcal mole^{-1}. The uncertainty of

both values is ~0.5 kcal mole^{-1}. The value obtained by solution calorimetry is the more reliable because the reaction was quantitative, and we choose it as the recommended value. By combining this with entropy data we obtain $\Delta G_f = -376.3$ kcal mole^{-1}.

$\Delta G_f(CaTiO_3)$ data have been obtained by the e.m.f. method with a solid electrolyte. The e.m.f. of the cell $O_2, Pt \mid CaO \parallel CaF_2 \parallel CaTiO_3, TiO_2 \mid Pt, O_2$ has been measured[267] at 873 K. From the result we calculate $\Delta G_{298} = -19.11$ kcal for the potential-determining reaction $CaO + TiO_2 = CaTiO_3$, and $\Delta H = -18.86$ kcal, which gives $\Delta H_{f,298} = -396.2$ kcal mole^{-1}. E.m.f. measurements are reported also[268] for the galvanic cell $Pt, CaTiO_3, CaO, TiO_{0.5} \parallel ThO_2 + La_2O_3 \parallel M, MO, Pt$, where M = Fe or Nb, in the range 1180–1290 K. From the results the authors calculated $\Delta H_f(CaTiO_3) = -398$ kcal mole^{-1} for the reaction $0.667CaO + 0.667TiO_{0.5} + MO = 0.667CaTiO_3 + M$ by using published values of the thermodynamic functions. This value is probably inaccurate because many data, covering a wide range of temperature, were used in the calculation.

Ca_2TiO_4. The functions ΔH_f and $S(Ca_2TiO_4)$ have been evaluated by the comparative calculation method[288]. The data used for the calculation are mutually inconsistent, and the work is of doubtful value.

$Ca_3Ti_2O_7$. Measurements[269] of the heat of dissolution of a mixture of oxides and of $Ca_3Ti_2O_7$ have given $\Delta H_f(Ca_3Ti_2O_7) = -943.8$ kcal mole^{-1}. By using the chosen value of $S_{298}(Ca_3Ti_2O_7)$ we obtain $\Delta G_{f,298} = -896.1$ kcal mole^{-1}. The error in ΔH and ΔG is less than 1 kcal.

3. Strontium Titanates

We have previously reviewed[274] the thermodynamic properties of $SrTiO_3$, and chosen the values $\Delta H_{f,298} = -402.2$ kcal mole^{-1} and $\Delta G_{f,298} = -382.3$ kcal mole^{-1}, with an uncertainty not greater than 0.5 kcal mole^{-1}.

Sr_2TiO_4. Kelley[265] obtained -37.85 ± 0.25 kcal for $\Delta H_f(Sr_2TiO_4)$ from the oxides, which gives $\Delta H_{f,298}(Sr_2TiO_4) = -552.2$ kcal mole^{-1}. Using $S_{298} = 38.0$ e.u. we arrive at $\Delta G_{f,298} = -524.6$ kcal mole^{-1}. The error in ΔH and ΔG is less than 2 kcal mole^{-1}.

4. Barium Titanates

The thermodynamic properties of $BaTiO_3$ have already been reviewed[274]. The values $\Delta H_{f,298} = -395.2$ kcal mole^{-1} and $\Delta G_{f,298} = -374.3$ kcal mole^{-1} were recommended, with an error of less than 0.5 kcal mole^{-1}.

Ba_2TiO_4. Kelley's value[265] of the heat of formation from the oxides is $\Delta H = -45.7 \pm 0.3$ kcal. Using the accepted values of ΔH_f for BaO and TiO_2 gives $\Delta H_{f,298}(Ba_2TiO_4) = -533.3$ kcal mole^{-1} and $\Delta G_{f,298} = -507.0$ kcal mole^{-1}. The error is less than 2 kcal mole^{-1}.

$0.543BaTiO_3 \cdot 0.457SrTiO_3$. The same reference[265] gives $\Delta H_{f,298} = -397.9$ kcal mole^{-1} for this solid solution. Using the S_{298} value recommended here leads to $\Delta G_{f,298} = -377.7$ kcal mole^{-1}; the error of ΔH and ΔG is less than 2 kcal mole^{-1}.

$BaSrTiO_4$. The value -540.2 kcal mole^{-1} is recommended[265] for $\Delta H_{f,298}(BaSrTiO_4)$ from the elements. With the S_{298} value recommended here we obtain $\Delta G_{f,298} = -514.2$ kcal mole^{-1}, with an error not greater than 2 kcal mole^{-1}.

5. Calcium Zirconate

The function $\Delta H_f(CaZrO_3)$ has been determined[270] from the heat of combustion of a pelleted mixture of $CaCO_3$, ZrO_2, and graphite. An enthalpy change of $\Delta H = 35.2 \pm 0.2$ kcal was obtained for the reaction $CaCO_3 + ZrO_2 = CaZrO_3 + CO_2$, which took place in 85% yield. By combining this result with $\Delta H_f(CaCO_3) = -288.46$ kcal mole^{-1}, $\Delta H_f(CO_2) = -94.05$ kcal mole^{-1}, and $\Delta H_f(ZrO_2) = -263.04$ kcal mole^{-1} the value $\Delta H_f(CaZrO_3) = -422.3$ kcal mole^{-1} was obtained. The uncertainty, due mainly to the failure of the calorimetric reaction to go to completion, is less than 2 kcal mole^{-1}.

The heat of combustion of a mixture of CaO + Zr in a bomb under an oxygen pressure of 25 atm has been measured[287]. The value $\Delta H_f(CaZrO_3) = -400.3$ kcal mole^{-1} was obtained[287], and good agreement with the result of Ref. 270 (-398 kcal mole^{-1}) was claimed. However the value -398 kcal mole^{-1} quoted in Ref. 270 is not ΔH_f but $\Delta G_f(CaZrO_3)$, and therefore the claim is groundless.

6. Strontium Zirconate

The function $\Delta H_f(SrZrO_3)$ has been determined[270] from the combustion of a mixture of $SrCO_3$, ZrO_2, and graphite (95% yield). The heat of this reaction was found to be $\Delta H = 38.2 \pm 0.2$ kcal. Using the value $\Delta H_{f,298}(SrCO_3) = -294.5$ kcal mole^{-1}, the standard enthalpy $\Delta H_{f,298}(SrZrO_3) = -425.3$ kcal mole^{-1} was calculated. Khekimov and coworkers[271] measured the e.m.f. of the galvanic cell $O_2, Pt \mid SrO, SrF_2 \parallel CaF_2 \parallel SrZrO_3, ZrO_2, SrF_2 \mid Pt, O_2$, in which the potential-determing reaction is $SrO + ZrO_2 = SrZrO_3$, in the temperature range 1180–1370 K. The heat of formation of $SrZrO_3$ from the oxides was calculated as $\Delta H = -18.6 \pm 1.5$ kcal, corresponding to $\Delta H_f(SrZrO_3) = -426$ kcal mole^{-1} (from the elements), in good agreement with the thermochemical value. However the thermodynamic functions of $SrZrO_3$ used in this calculation[271] were not the experimental values but estimated values, taken to be equal to the corresponding functions for $SrTiO_3$. Hence we shall ignore this result in choosing the recommended value of $\Delta H_f(SrZrO_3)$, and we give $\Delta H_{f,298} = -425.3$ kcal mole^{-1} and $\Delta G_{f,298} = -405.0$ kcal mole^{-1} for $SrZrO_3$, with an uncertainty of less than 1 kcal.

7. Barium Zirconate

The heat of the reaction $BaCO_3 + ZrO_2 = BaZrO_3 + CO_2$ has been measured[273] under the same conditions as the heat of combustion of $SrCO_3$. The result, combined with the accepted ΔH_f and entropy values of the oxides, leads to $\Delta H_{f,298} = -425.3 \pm 2$ kcal mole^{-1} and $\Delta G_{f,298} = -405.0 \pm 2$ kcal mole^{-1}. The heats of the reactions $Ba_3Al_2O_6 + 2ZrO_2 = BaAl_2O_4 + 2BaZrO_3$ and $ZrO_2 + BaF_2 + CaO = BaZrO_3 + CaF_2$ have been measured[288] by the e.m.f. method at 980–1120 K with a fluoride ion electrolyte. The calculated value[288] $\Delta H_f(BaZrO_3) = -423.4 \pm 2.6$ kcal mole^{-1} agrees very well with the thermochemical value.

The heats of formation of $CaHfO_3$ and $SrHfO_3$ have not been measured. Estimated values[289] of ΔH_f for the hafnates, calculated by the equation $\Delta H_f(MHfO_3) = 1.001\ \Delta H_f(MSiO_3) - 34.2$ (kcal mole^{-1}), agree within 1% with the experimental value[272] in the case of $BaHfO_3$.

8. Barium Hafnate

The measured[272] heat of combustion of a mixture of $BaCO_3$, HfO_2, and graphite gave $\Delta H = 32.3 \pm 0.8$ kcal for the reaction $BaCO_3 + HfO_2 = BaHfO_3 + CO_2$ (97% yield). BaO was not detected among the reaction products, showing that $BaCO_3$ is stable under the conditions of the calorimetric experiment. The enthalpy $\Delta Hf_{,298}(BaHfO_3) = -431.5$ kcal mole^{-1} is calculated from the result[272]. Taking $\Delta S_f(BaZrO_3) \simeq \Delta S_f(BaHfO_3) = -68$ e.u. for the formation from the elements we calculate $\Delta Gf_{,298}(BaHfO_3) = -411$ kcal mole^{-1}. The uncertainty of ΔH and ΔG is less than 2 kcal mole^{-1}.

The thermodynamic constants chosen in this review are summarised in Table 3.

Table 3. Recommended values of $\Delta H_{f,298}$, $\Delta G_{f,298}$, $H_{298} - H_0$, S_{298}, and $C_{p,298}$ for the alkaline-earth titanates, zirconates, and hafnates.

Compound	$\Delta H_{f,298}$, cal mole^{-1}	$\Delta G_{f,298}$, cal mole^{-1}	$H_{298}-H_0$, cal mole^{-1}	S_{298}, e.u.	$C_{p,298}$, cal mole^{-1} K^{-1}
$MgTiO_3$	−375.7±0.3	−354.6±0.3	3240±20	17.82±10	21.96±0.03
$MgTi_2O_5$	−599.2±0.7	−566.2±0.7	5360±40	34.2	35.15±0.05
$MgTi_3O_8$	—	−567.5	—	32.4	—
Mg_2TiO_4	−517.2±0.5	−493.8±0.5	4500±30	27.5	30.76±0.02
$CaTiO_3$	−396.7±0.5	−376.3±0.5	3800±20	22.38±0.10	23.34±0.05
$Ca_3Ti_2O_7$	−943 8±1	−896.1±1	9420±70	56.1±0.4	57.20±0.05
$SrTiO_3$	−402.4±0.5	−382.3±0.5	4120±40	26.0±0.2	23.51±0.02
Sr_2TiO_4	−552.2±2	−524.6±2	6060±60	38.0±0.3	31.34±0.03
$BaTiO_3$	−395.2±0.5	−374.3±0.5	4230±40	25.8±0.2	24.49±0.02
Ba_2TiO_4	−533.3±2	−507.0±2	6840±60	47.0±0.5	36.48±0.10
$BaSrTiO_4$	−540.2±2	−514.2±2	6480±60	45.8±0.4	34.95±0.10
$CaZrO_3$	−422.3±2	−401.7±2	3990±40	23 9±0.2	23.88±0.02
$SrZrO_3$	−425.3±1	−405.0±1	4360±40	27.5±0.2	24.71±0.02
$BaZrO_3$	−425.3±2	−405.0±2	4515±40	29.8±0.2	24.31±0.02
$CaHfO_3$	—	—	—	25.9*	—
$SrHfO_3$	—	—	—	29.6*	—
$BaHfO_3$	−431.5±2	−411±2	—	31 8*	—
$Ba_{0.543}Sr_{0.457}TiO_3$	−397.9±2	−377.7±2	4210±40	27.4±0.2	23.38±0.02

*Estimated.

V. DISCUSSION OF THE THERMODYNAMIC CHARACTERISTICS OF PEROVSKITES

The great majority of the compounds discussed here have the perovskite ABO_3 structure, where A is an alkaline earth element, and B is an element of the titanium subgroup. $MgTiO_3$ alone belongs to another structure type: ilmenite. All the other metatitanates are perovskites. According to Goldschmidt the transition from one structure to the other is determined by the tolerance factor $t = [R(A) + R(O)]\sqrt{2}[R(B) + R(O)]$, where $R(A)$, $R(B)$, and $R(O)$ are the ionic radii of the elements and of oxygen. Within the perovskite structure two types of co-ordination of the oxygen polyhedra are possible: the icosahedron, with a co-ordination number (c.n.) of 12, and the octahedron, with a c.n. of 6. The large ion of the alkaline earth element is surrounded by an icosahedron, the B^{4+} ion by an octahedron. The perovskite structure is stable for $0.8 < t < 1.0$, and for $t = 1$ it becomes ideal, with the closest contact between the A and B ions and the oxygen ions. For other values of t the ideal structure becomes distorted. The ilmenite structure, stable for $t < 0.8$, is characterised by an octahedral co-ordination of the O^{2-} ions around the cations. The case of $t < 1$ corresponds to free permutation of the type A cations in the co-ordination polyhedron, and the case of $t > 1$ corresponds to free permutation of the type B cations[277].

We shall examine the thermodynamics of the formation of an icosahedron (c.n. 12) around a large cation. There are compounds of the ABO_3 type which can exist in both polymorphic modifications (ilmenite and perovskite): for example, $CdTiO_3$. The energy relationships which determine the metal–oxygen bond in the octahedron and the icosahedron can be formulated. According to both theoretical and experimental crystal chemistry, compounds of a given type tend to have a definite metal–oxygen distance which is constant for a given c.n. It may be possible to calculate the energetics of the co-ordination polyhedra by using the heat of atomisation ΔH_a of the oxides $(MO_i)_c$ for the cases c.n. = 6 and c.n. = 12.

By definition, $\Delta H_a[(MO_i)_c] = \Delta H_a(M) + i/2D(O_2) - \Delta H_f[(MO_i)_c]$, where $\Delta H_a(M)$ is the heat of sublimation of the metal, $D(O_2)$ is the dissociation energy of O_2, and $\Delta H_f[(MO_i)_c]$ is the heat of formation of the oxide MO_i with a co-ordination number of 6 or 12. Consider the ratio $E_c = \Delta H_a[(MO_i)_c]/k$, where k is the co-ordination number, which characterises the energy of a single bond in the co-ordination polyhedron, and the quantity $A_c = E_c/R_c$, where R_c is the characteristic M–O distance in this polyhedron. It is convenient to express the thermochemical quantities in kcal, and the distances in Å. Characteristic distances are systematically reviewed in Ref. 275, and the thermochemical quantities are given in this review and in Ref. 2. In the oxides MgO, CaO, SrO, BaO, and CdO the cations under standard conditions are in an octahedral co-ordination of O^{2-} ions, with a c.n. of 6. In TiO_2(rutile) the Ti^{4+} ion also has a co-ordination number of 6, but Zr^{4+} and Hf^{4+} in their MO_2 compounds[276] have the very rare c.n. 7. When metatitanates are formed from the oxides the c.n. of M^{2+} can change, but the co-ordination polyhedron of Ti remains the same. When metazirconates and metahafnates are formed the oxygen polyhedra of both cations can change.

According to the published thermochemical data for Mg, Mn, Fe, Co, Ni, and Cd titanates the heat of formation of the ilmenites from their oxides is almost constant: $\Delta\bar{H} = -6 \pm 0.8$ kcal. In the case of $CdTiO_3$ we know ΔH_f for both the perovskite and the ilmenite modification: perovskite is the less stable by 3.6 kcal. The following thermochemical cycle can be used to evaluate the preference energy of the ion for the icosahedral co-ordination:

$$(CdO)_{[6]} + TiO_2 = Cd_{[6]}TiO_3 \text{ −6.6 kcal (ilmenite)}$$
$$(CdO)_{[12]} + TiO_2 = Cd_{[12]}TiO_3 \text{ −3.0 kcal (perovskite)}$$
$$(CdO)_{[6]}TiO_3 = (CdO)_{[12]}TiO_3 + 3.6 \text{ kcal}$$

The subscripts [6] and [12] denote the c.n. of the Cd^{2+} ion. To this approximation the preference energy of Cd^{2+} for the icosahedral co-ordination is 3.6 kcal g-ion^{-1}.

The preference energy of the other ions can be estimated by assuming a ΔH_f of −6 kcal mole^{-1} for the formation of the hypothetical ilmenite $ATiO_3$ from the oxides without change in the c.n. of the A ion, i.e. by taking the average of the heats of formation of the known ilmenites. With this assumption the preference energy of the ions

for the icosahedral co-ordination of the perovskites is given by the expression $\epsilon = \Delta H_f + 6$ (kcal), where ΔH_f is the heat of formation from the oxides in the standard state. By using the ΔH_f values for the oxides and the titanates we obtain the following preference energies ϵ for some doubly charged cations:

Cation	Ca^{2+}	Sr^{2+}	Ba^{2+}	Cd^{2+}
ϵ, kcal g-ion^{-1}	−13.3	−26.4	−32.6	+3.6

From these ϵ values we can calculate $\Delta H_a(MO)_{12}$ in the hypothetical co-ordination with a c.n. of 12, and hence we can evaluate the quantity E_{12} which characterises the energy of a single M–O bond in the icosahedron and compare it with E_6 for the oxide in the standard state (Table 4).

Table 4. Heats of atomisation and energies of a single M–O bond in the octahedron and the icosahedron.

Cation in $MTiO_3$	ΔH_a $(MO)_6$, kcal mole^{-1}	ΔH_a $(MO)_{12}$, kcal mole^{-1}	E_6, kcal mole^{-1}	E_{12}, kcal mole^{-1}	A_6/A_{12}	R_{12}/R_6
Ca^{2+}	253.9	267.2	42.32	22.27	2.177	1.146
Sr^{2+}	243.0	269.4	40.50	22.45	1.997	1.107
Ba^{2+}	234.3	266.9	39.05	22.24	1.909	1.087

The transition of the alkaline-earth ion to the icosahedral configuration produces a remarkable levelling of the single-bond energy: the mean value is 22.32 ± 0.09 kcal per bond, i.e. within ±0.4%, as compared with a spread of 8% in the E_6 values.

The formation of Ca, Sr, and Ba metazirconates and metahafnates produces a change in the c.n. of both cations, and the heats of formation from the oxides are much lower than those for the corresponding titanates. This is evidently due to the expenditure of energy in transferring the Zr^{4+} and Hf^{4+} ions from polyhedra with a c.n. of 7 in the oxides to octahedra in the perovskites. Assuming a constant preference energy for the Ca^{2+}, Sr^{2+}, and Ba^{2+} ions to the icosahedral co-ordination from the original octahedra we can determine the energy of the transition of Zr^{4+} and Hf^{4+} to the octahedral co-ordination from the configuration with a c.n. of 7, which is characteristic of their dioxides. We assume that the heats of formation of the zirconates and hafnates from AO and the hypothetical oxide MO_2 with a c.n. of 6 are equal to the ΔH_f value of the corresponding titanates, which are formed without change in the c.n. of the B^{4+} ion. For $CaZrO_3$ (for example) we arrive at the following thermochemical cycle:

$$CaO + (ZrO_2)_{[6]} = CaZr_{[6]}O_3 \quad -19.3 \text{ kcal}$$
$$CaO + (ZrO_2)_{[7]} = CaZr_{[6]}O_3 \quad -7.5 \text{ kcal}$$
$$(ZrO_2)_{[7]} = (ZrO_2)_{[6]} \quad +11.8 \text{ kcal}$$

A similar calculation gives the energies of the transitions of the Zr^{4+} and Hf^{4+} ions in other compounds:

Cation in perovskite	Ca^{2+}	Sr^{2+}	Ba^{2+}
$\epsilon(Zr^{4+})$, kcal g-ion^{-1}	11.8	14.8	7.3
$\epsilon(Hf^{4+})$, kcal g-ion^{-1}	11.7	13.7	5.2

In spite of the significant difference between the $\epsilon(B^{4+})$ values, which is not surprising in view of the approximations made in the calculation, we think it legitimate to average these values, which gives $\epsilon(Zr^{4+}) = 11$ kcal g-ion^{-1} and $\epsilon(Hf^{4+}) = 10$ kcal g-ion^{-1} with a possible error of ±3 kcal g-ion^{-1}.

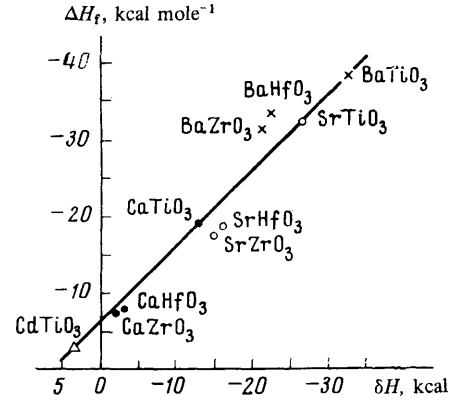


Figure 1. Heat of formation of perovskites from the oxides (ΔH_f) against energy of cation transitions (δH).

Table 5. Thermochemical and crystal chemical properties of perovskites.

Perovskite	ΔH_f, kcal mole^{-1} (from the oxides)	ΔS_f, e.u. (from the oxides)	t	Perovskite	ΔH_f, kcal mole^{-1} (from the oxides)	ΔS_f, e.u. (from the oxides)	t
$CaTiO_3$	−19.3	1.25	0.968	$SrHfO_3$	−18.7	—	0.938
$CaZrO_3$	−7.5	2.76	0.917	$BaTiO_3$	−38.6	−3.47	1.056
$CaHfO_3$	−7.7	—	0.922	$BaZrO_3$	−31.3	0.52	1.001
$SrTiO_3$	−32.4	0.72	0.985	$BaHfO_3$	−33.4	—	1.006
$SrZrO_3$	−17.6	2.21	0.934	$CdTiO_3$	3.6	1.75	0.954

Thus we may conclude that the heat of formation of the perovskite ABO_3 from the oxides depends on the energy of the cation transitions resulting from the change in the co-ordination of the oxygen ions surrounding the metal cation. The linear variation of ΔH_f with the quantity δ (the sum of the energies of the cation transitions accompanying the formation of the perovskite) is illustrated in Fig. 1.

In addition to the enthalpy of formation from the oxides, the entropy change is another important thermodynamic parameter of perovskites. ΔH_f, ΔS_f, and t values for a number of compounds are listed in Table 5. In most cases $t < 1$, denoting free ordering of the large cations in the icosahedra. The titanates should be treated separately from the zirconates, because there is no change in the c.n. of Ti (see Fig. 2). On going from $CaTiO_3$ ($t < 1$) to $BaTiO_3$ ($t < 1$) the ΔS_f value for the formation from the oxides changes sign and becomes negative. The tendency for the entropy of formation from the oxides to fall is found also in the zirconate group from $CaZrO_3$ to $BaZrO_3$. The stiffness of the M–O bond in the icosahedra increases as we approach the $t > 1$ region. This leads to greater ordering and to limited freedom of motion of large cation in the icosahedron, i.e. to a smaller entropy of formation

from the oxides. In Ca, Sr, and Ba zirconates the freedom of the large cation increases from Ba to Ca, and the ΔS_f value increases in the same order. Although the entropy of the metahafnates of these elements has not been determined experimentally we can expect a similar behaviour. We should stress that the value of the tolerance factor t is strongly dependent on the choice of the system of ionic radii. We have chosen the system of Shannon and Prewitt[275], which is the most detailed and takes into account the spin state of the ion as well as the state of oxidation and the co-ordination number.

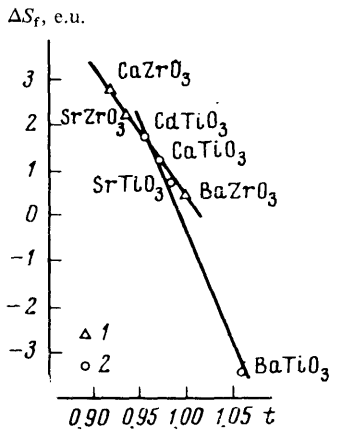


Figure 2. Entropy of formation of perovskites from the oxides (ΔS_f) against tolerance factor for (*1*) titanates and (*2*) zirconates.

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