

Eliminating chemical effects from thermal expansion coefficient measurements

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Abstract A new approach for measuring coefficient of thermal expansion (CTE) in materials that exhibit chemical expansion as well is introduced. This allows separating the expansion that is induced by temperature changes alone from the total expansion, which is induced by temperature *and* chemical changes in the material. Combining this with measurements that are done at constant temperature and in controlled oxygen environment can yield better understanding of the subject of solid expansion in oxides. In order to understand whether the oxygen partial pressure has an influence on the CTE or not, measurements were carried out on three different oxide materials at several oxygen activities. A comparison between SrTiO₃, SrZrO₃ and Al₂O₃ was done by a single push-rod dilatometer equipped with a system that allows purging with different gas mixtures and a pO₂ monitoring device. In order to make the experiment within a reasonable timeframe, very porous samples have been used. The experiments were done at three different temperatures: 722, 822 and 1022 °C. The pO₂ was controlled by CO–CO₂–Ar gas mixture, and monitored with an in house built zirconia sensor. The main results reveal that the CTE of the perovskites is influenced by the pO₂ while that of alumina, as expected, is not. The CTE of SrTiO₃ is more sensitive to changes in the pO₂ than that of SrZrO₃. In some of the measurements there exists a clear change of the behavior of the CTE vs. log(pO₂) at a certain oxygen partial pressure.

Keywords Thermal expansion · Dilatometry · Chemical expansion · Perovskites · Modulated temperature

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1 Introduction

When a device is composed of materials that have different mechanical properties, a mismatch exists and the resultant strain can be followed by an internal stress. This internal stress can lead to mechanical failure [1, 2]. For example, this phenomenon is well known in solid oxide fuel cells (SOFC) and poses a major constraint to the realization of SOFC in applications. Such a cell consists of at least four different materials in constant contact with each other. The match between the thermal expansion of the cathode, the electrolyte, the anode and the interconnect is one of the most important criteria for mechanical stability of such multicomponent system [3, 4]. This problem is also related to the thermal cycling; the SOFC undergoes many thermal cycles between an operating temperature and room temperature. The shrinkage behavior of the different parts cause stress in the SOFC [5, 6].

It is known that there is a strong connection between the oxygen partial pressure and the thermal expansion of the unit cell of some mixed-valence oxides. Thermal expansion of solid oxide materials is a function of temperature and oxygen vacancy concentration. These parameters have been quantified by Adler in terms of “volumetric thermal expansivity” (β_T) and “volumetric chemical expansivity” (β_C):

$$\beta_T = \left(\frac{\partial \ln V}{\partial T} \right)_{x_v, P} \quad (1)$$

$$\beta_C = \left(\frac{\partial \ln V}{\partial x_v} \right)_{T, P} \quad (2)$$

Here, V is the volume, T is the temperature, P is the total pressure and x_V is the oxygen vacancy mole fraction. So, the strain that a solid oxide is subjected to (without external forces) is composed of two parts: volumetric chemical expansivity (chemical expansion) and volumetric thermal expansivity [7].

$$d\varepsilon(T, x_V) = \frac{1}{3}\beta_T dT + \frac{1}{3}\beta_C dx_V \quad (3)$$

Many researches have been done in order to realize the influence of the oxygen partial pressure on the thermal expansion. In addition there are a lot of works that checked the direct influence of oxygen partial pressure on the chemical expansion. Nevertheless, we are not aware of references that checked the direct influence of the oxygen partial pressure on the coefficient of thermal expansion without connection to the chemical expansion. For instance, the CTE of $La_{0.3}Sr_{0.7}Fe_{1-x}Ga_xO_{3-\delta}$, was examined as a function of temperature at several oxygen partial pressures in a dilatometer [8]. For each pO_2 a curve of thermal expansion as a function of temperature (900–1200 °C) was built. The CTE was calculated from the slope of each curve. This work demonstrates very clearly that this slope is also pO_2 -dependant and not only temperature-dependant. Similar experiments were also done on $Sr_{0.3}La_{0.7}TiO_{3-\delta}$, $La_{1-x}Sr_xCr_{1-y}Ti_yO_{3-\delta}$ and other perovskites [9, 10]. However, this kind of experiments reveals a total coefficient, which results from both thermal and chemical expansions. Since the oxygen activity is determined both by the oxygen partial pressure and by the temperature, it does not allow to deduce separately the influences of these two degrees of freedom on the CTE. For better understanding of the thermal properties and behavior of oxide ceramic materials as a function of temperature and composition, especially as a function of oxygen nonstoichiometry, this discrimination is important. Moreover, by measuring CTE while eliminating the chemical expansion during the measurement at different pO_2 s, one can check whether CTE itself depends on the oxygen partial pressure or not. Being a “thermodynamic constant” it could be, in principle, a function of the degrees of freedom of the system, including the pO_2 . Hence, an approach for measuring CTE directly that is based on modulated temperature dilatometry [11] has been applied.

2 Experimental

2.1 Measuring method

In order to eliminate the chemical expansion influence, and by that to investigate the direct influence of pO_2 on CTE,

samples were examined in a dilatometer (BÄHR DIL801) as follows. The sample was heated to certain temperature in certain pO_2 . When the sample approached equilibrium (thermally and chemically), small changes of temperature around that base-temperature were done. The dilatometer temperature was programmed to decrease and increase by 10 °C from the base-temperature toward both directions, in a rate of 5 $\frac{^\circ C}{min}$ several times. After these temperature changes, the dilatometer was programmed to return to the base-temperature. As the sample returned to equilibrium, the pO_2 was changed and the same process was repeated again: getting new equilibrium, changes in temperature, back to steady temperature. Figure 1 represents temperature profile as a function of time in constant pO_2 . In this example the temperature changes are around 1022 °C. If the sample’s response to temperature changes is much faster as compared to its response to changes in the chemical potential, which require ionic diffusion over few microns distances, this procedure should reveal the CTE solely. This has been pointed out previously by Johansen in a more general sense: “...the disturbance produced by irrelevant monotonic effects can be eliminated” [12].

It can be seen from Fig. 1 that the recorded changes in temperature are between 1016–1027 °C instead of the nominal change of 1012–1032 °C. The reason for that is the fact that there is a difference between the temperature of the furnace (the programmed one), and the temperature at the sample. This measuring was made for five different oxygen partial pressures. Three pressures in the decreasing direction and two on the way back (increasing the oxygen partial pressure), and at three different temperatures: 722, 822 and 1022 °C. The pO_2 was controlled by CO–CO₂–Ar gas mixture with total flow rate of 55 $\frac{ml}{min}$ and monitored with an in house built zirconia sensor. The sensor temperature was lower, in some measurements, than the dilatometer temperature for technical reasons. Hence the

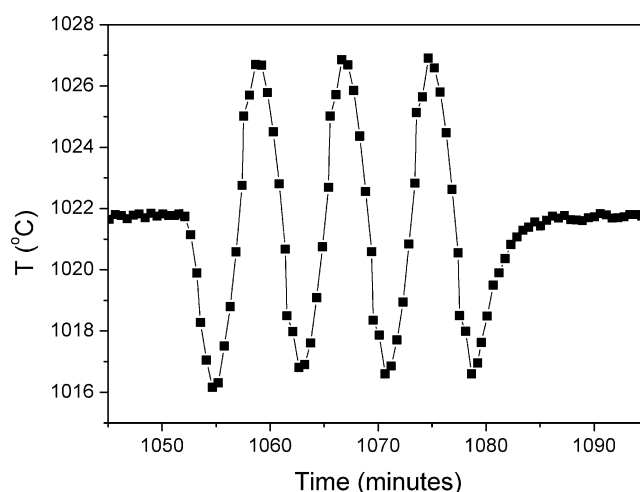


Fig. 1 A typical temperature profile as a function of time

pO_2 in the dilatometer was calculated using the correction developed by Riess and Porat [13]. In order to get information on the CTE at higher oxygen partial pressures, similar measurements were done in air and in Ar atmospheres. The CTE was calculated from the slopes of the linear changes in dimension (at the times of changing temperature). Figure 2 is an example for one of the measurements that were done to calculate the CTE. Each slope of increasing and decreasing of dimension is due to change in temperature, so the slope $\frac{d(\ln L)}{dt}$ multiplied by $(\frac{dT}{dt})^{-1}$ is the “true” CTE. The changes are too fast and the temperature changes are too small for significant chemical changes to occur. This can be verified by checking for possible hysteresis between the increasing and decreasing temperature parts. By doing a weighted averaging between the slopes that belong to the same temperature and oxygen partial pressure an average CTE and error assessments are received. Another check that was done is to verify that the slopes of the increasing and decreasing temperature parts are the same, within the experimental errors. Since no significant difference was observed in all temperatures and pO_2 -s that were measured, we can conclude that chemical changes are too slow to occur.

2.2 Sample preparation

Powders of $SrTiO_3$ and $SrZrO_3$ were prepared by conventional solid state reaction. In order to get equilibrium during the experiments as fast as possible, the samples need to be porrosive to allow short distances for the migration of oxygen ions. On the other hand, the samples must have stiffness to be able to withstand the measurement in the dilatometer (self-weight of about 2 g and force of 4 mN that is activated on the sample by the push-rod). For that reason, in-situ measurements of sintering were done in the dilatometer to decide for the appropriate temperature and duration of the sintering process, to get samples with relative density between 60–70%.

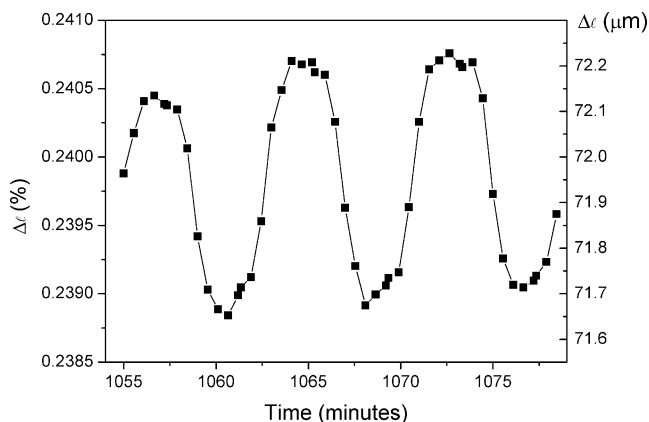


Fig. 2 Change of linear dimensions of $SrZrO_3$ as a function of time in $pO_2 = 1.4 \cdot 10^{-13}$ atm, at $T = 1022$ °C

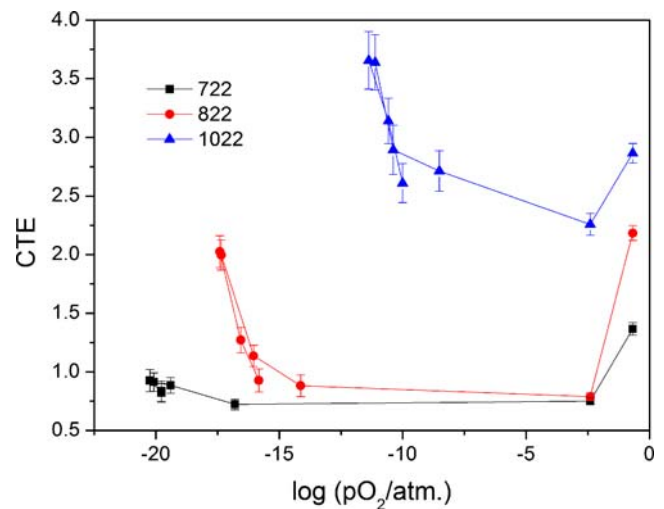


Fig. 3 Change of CTE of $SrTiO_3$ as a function of pO_2 , at $T = 722$, 822 and 1022 °C (the lines are added to assist the eye and to show the order of measurements)

The relative density is calculated by:

$$\% \rho_{\text{relative}} = \frac{\rho_{\text{real}}}{\rho_{\text{theoretical}}} 100 \quad (4)$$

Following these measurements, $SrTiO_3$ samples were sintered at 1227 °C for 24 h and $SrZrO_3$ samples were sintered at 1477 °C for 24 h. In both procedures, the heating and the cooling rates were $3 \frac{^\circ\text{C}}{\text{min}}$. During the sintering process air was flowed through the system for the initial 15 h, then the gas changed to wet $N_2 + H_2$ in order to decrease the oxygen partial pressure to 1.1×10^{-11} atm for the next 5 h, and then the gas changed again to air for additional 4 h. The reason we decrease the pO_2 during the sintering process is to ensure that changing the partial pressure later during the dilatometry measurements at lower temperature will not be accompanied with further sintering [14].

3 Results and discussion

In order to investigate the influence of the oxygen partial pressure on CTE, isotherms for $SrTiO_3$, $SrZrO_3$ and also Al_2O_3 as a reference were made. Figure 3 shows the change of CTE as a function of $\log(pO_2)$ in three different temperatures for $SrTiO_3$. First of all it is possible to see that the values of the CTE are higher as the temperature is higher. In all three temperatures there is a minimum point at $\log(pO_2) \sim -4$. The actual minimum may well be at lower pO_2 , but there has been an experimental range of oxygen partial pressure that we could not obtain, between the one we got with Ar and the partial pressures we got with $CO-CO_2$ mixtures. In isotherm 1022 in the area of low oxygen partial pressure there is a sharp increase of the CTE at

$\log(pO_2) \sim -11$. In isotherm 822 there exists such sharp increase at $\log(pO_2) \sim -16$. These sharp increases may indicate the points were the concentration of oxygen vacancies is high enough and their influence is significant. It does make sense that as the temperature is higher, the low oxygen partial pressure causes more oxygen loss. In isotherm 722 after the minimum point, there is only a small change between the different CTEs at different pO_2 . Two reasons for that are possible. The first one is that in such temperature, the oxygen partial pressure that is associated with significant concentration of oxygen vacancies is lower than the checked range. The second possible reason is that in such temperature there is no influence of low oxygen partial pressure on the CTE at all, or in other words there is a low limit temperature to the phenomenon by which oxygen partial pressure (or oxygen vacancies) influence CTE.

Figure 4 shows the change of CTE as a function of $\log(pO_2)$ in three different temperatures for $SrZrO_3$. In this figure it is possible to see clearly that for $SrZrO_3$ the values of CTE at $\log(pO_2) \sim -1$ and $\log(pO_2) \sim -2.5$ are higher as the temperature increases. The other CTE measurements, for all three temperatures, are in between $0.7-1.1 \times 10^{-6} K^{-1}$, which is a narrow range in comparison to the $SrTiO_3$ CTE measurements. Isotherm 1022 has a minimum point at $\log(pO_2) \sim -11$. Although the exact point of partial pressure that have minimum CTE could not be determined from these graphs, we can clearly say that this point is placed at a much lower partial pressure as compared to the situation that was observed for $SrTiO_3$. In addition, the increase of CTE in lower pO_2 is not as sharp as in $SrTiO_3$.

Isotherm 822 does not have an observed minimum point; same holds for isotherm 722. Again, both explanations as discussed for isotherm 722 in $SrTiO_3$ are possible. We

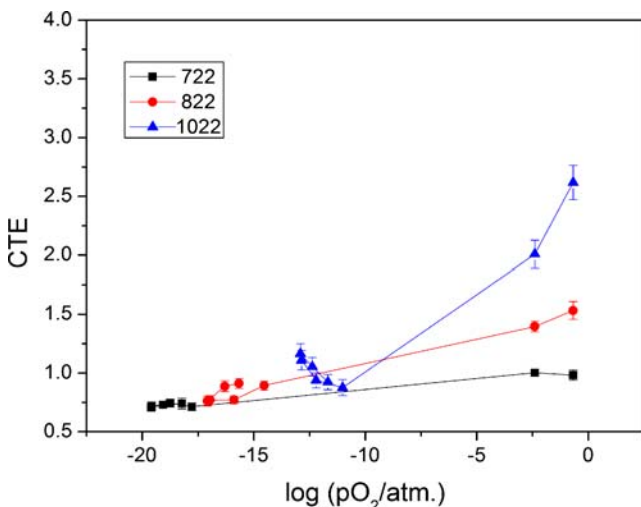


Fig. 4 Change of CTE of $SrZrO_3$ as a function of pO_2 at $T=722, 822$ and 1022 °C (the lines are added to assist the eye and to show the order of measurements)

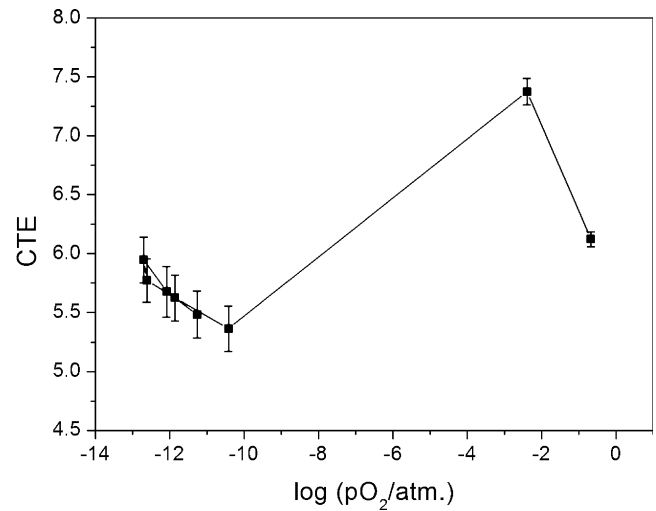


Fig. 5 Change of CTE of Al_2O_3 as a function of pO_2 , at $T=1022$ °C

believe that the reason for much less difference between CTEs at different pO_2 for each isotherm and between the isotherms, is due to the fact that probably in $SrZrO_3$ oxygen vacancies creation is not as easy as in $SrTiO_3$.

Figure 5 shows the change of CTE as a function of $\log(pO_2)$ in $T=1022$ °C for Al_2O_3 . In this figure there are a maximum in $\log(pO_2) \sim -2.5$ and a minimum in $\log(pO_2) \sim -10.5$ (with a gap between them where no experimental point measured due to experimental limitations). It is very difficult to characterize the CTE of Al_2O_3 behavior due to the surprising maximum point. Without this point it is possible to say as a first approximation that the change in CTE is negligible in comparison to the changes of CTE of both $SrTiO_3$ and $SrZrO_3$. We are almost sure that the maximum point does not reflect the real behavior, but rather is an experimental error. This assumption is based on Fig. 6 that shows an experiment that the problematic point is calculated from. Figure 6 describes the relative change in length of Al_2O_3 sample in three different temperatures vs.

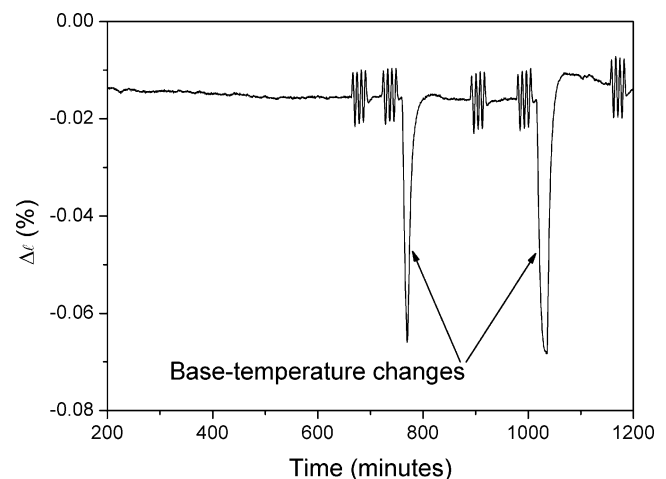


Fig. 6 Relative change in length of Al_2O_3 sample vs time under Ar flow in three different temperatures: $722, 822$ and 1022 °C

time. The experiment was done under Ar gas flow, and hence the problematic point at 1022 is calculated from here. The sample heated to 722 °C, equilibrated and only then the CTE measurement has started (small decreases and increases in temperature). When the CTE measurement was finished the sample was heated to the next temperature, 822 °C, and the same stages as in 722 °C were performed. The same procedure was also repeated at 1022 °C. It can be seen from this figure that each time the base-temperature was changed, there was a sharp decrease in the measured linear dimension and a sharp increase right after that. Repeated experiments under Ar showed similar behavior as in Fig. 6. This may have connection to the low heat transport in Ar, but we do not have a sound explanation for that behavior yet. However it is important to know that this behavior was observed only with an alumina sample, when the experiment was done under Ar gas flow and to less extent under air flow. The alumina sample is a non-porous standard that is provided with the dilatometer.

4 Conclusion

The coefficient of thermal expansion is influenced both by temperature changes and by chemical expansion that is driven by temperature changes. The influence of pO_2 on the CTE of $SrTiO_3$ and $SrZrO_3$ was investigated. A critical pO_2 exists, beneath it this influence becomes apparent and a sharp increase in the CTE occurs. The critical pO_2 is a function of temperature. When the temperature increases, the critical pO_2 increases as well. It is possible that the sharp increase in the CTE at reduced conditions results from oxygen loss. Oxygen loss increases the degree of anharmonicity, which is known to increase the CTE. On the other hand, it is associated also with cationic radius increase that can reduce the anharmonicity. Oxygen loss also reduces the Pauling bond strength (PBS), since on the average we get for the B-site instead of +4 ion with 6 nearest neighbors (i.e., $PBS=0.67$), +3 ion with 5.5 nearest neighbors (i.e., $PBS=0.55$). It is known that weaker PBS for a specific system results in higher CTE. For instance, in Fluorite the relevant relation is CTE proportional to $(PBS)^{-2}$ (see [1], Section 11.3).

Our measurements show that for both perovskites examined, the CTE does not depend on the pO_2 at 722°C. Two possible explanations for this behavior might be suggested. (1) The critical pO_2 may be below our experimental available range. (2) There may be a low limit temperature to the phenomenon by which oxygen partial pressure influences CTE.

Apparently in $SrZrO_3$, oxygen vacancies creation is not as easy as in $SrTiO_3$. This assumption is based on the fact that much more difference between the CTEs at different pO_2 was measured for $SrTiO_3$ in comparison to $SrZrO_3$ at each isotherm, and larger differences between the isotherms in those materials were also observed. The change in CTE as a function of pO_2 for Al_2O_3 is negligible in comparison to the change of CTE of both $SrTiO_3$ and $SrZrO_3$.

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References

1. R.E. Newnham, *Properties of Materials: Anisotropy, Symmetry, Structure* (Oxford University Press, New York, 2005)
2. J.F. Nye, *Physical Properties of Crystals: Their Representation by Tensors and Matrices*, 2nd edn. (Oxford University Press, New York, 1985)
3. B.C.H. Steele, Oxygen-transport and exchange in oxide ceramics *J. Power Sources* **49**(1–3), 1–14 (1994)
4. A. Bieberle, L.J. Gauckler, in Thermal and isothermal expansion, ed. by H.L. Tuller, J. Schoonman, I. Riess. *Oxygen Ion and Mixed Conductors and their Technological Applications*, vol. 368 (Kluwer, Dordrecht, 2000), pp. 347–358
5. J. Larminie, A. Dicks, *Fuel Cell Systems Explained*, 2nd edn. (Wiley, Sussex, 2003), p. 428
6. M. Mori, Effect of B-site doping on thermal cycle shrinkage for $La_{0.8}Sr_{0.2}Mn_{1-x}M_xO_{3+\delta}$ perovskites (M=Mg, Al, Ti, Mn, Fe, Co, Ni) *Solid State Ionics* **174**, 1–8 (2004)
7. X.Y. Chen, J.S. Yu, S.B. Adler, Thermal and chemical expansion of Sr-doped lanthanum cobalt oxide ($La_{1-x}Sr_xCoO_{3-\delta}$) *Chem. Mater.* **17**, 4537–4546 (2005)
8. V.V. Kharton, A.A. Yaremchenko, M.V. Patrakeev, E.N. Naumovich, F.M.B. Marques, Thermal and chemical induced expansion of $La_{0.3}Sr_{0.7}(Fe, Ga)O_{3-\delta}$ ceramics *J. Eur. Ceram. Soc.* **23**(9), 1417–1426 (2003)
9. S. Hashimoto, L. Kindermann, P.H. Larsen, F.W. Poulsen, M. Mogensen, Conductivity and expansion at high temperature in $Sr_{0.7}La_{0.3}TiO_{3-\alpha}$ prepared under reducing atmosphere *J. Electroceram.* **16**(2), 103–107 (2006)
10. M. Mori, Y. Hiei, Thermal expansion behavior of titanium-doped $La(Sr)CrO_3$ solid oxide fuel cell interconnects *J. Am. Ceram. Soc.* **84**(11), 2573–2578 (2001)
11. Y. Kraftmakher, Modulation calorimetry and related techniques *Phys. Repts.* **356**, 1–117 (2002)
12. T.H. Johansen, An ac-dilatometer for thermal expansivity measurements *High Temp. High Press.* **19**, 77–87 (1987)
13. I. Riess, O. Porat, Oxygen partial-pressure measurements under more demanding conditions *Solid State Ionics* **86–8**, 1075–1078 (1996)
14. R.D. Levi, Y. Tsur, The effect of oxygen vacancies in the early stages of $BaTiO_3$ nanopowder sintering *Adv. Mater.* **17**(13), 1606–1608 (2005)