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Influence of composition on the T→M transformation in the systems ZrO_2–Ln_2O_3 (Ln = La, Nd, Sm, Eu)

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The systems ZrO_2–Ln_2O_3 have been studied on samples annealed at 600, 1170, 1450 °C in the 0–15 mol % Ln_2O_3 (where Ln is the rare-earth La, Nd, Sm or Er) range using X-ray diffraction, thermal analysis and dilatometry. The microstructure of annealed samples was examined mainly by electron microscopy. It was found that rare-earth oxides-doped zirconia formed monoclinic, tetragonal, cubic and pyrochlore-type phases. The existing region of the tetragonal phase is 1–15 mol % Ln_2O_3, which is independent of the species but dependent on the dopant content and temperature. The equilibrium phase diagrams and non-equilibrium diagrams have been deduced. The temperature and composition of eutectoid $ZrO_{2,ss}$ (T)→$ZrO_{2,ss}$ (M) + Py, as well as interconnection between grain size, Ln_2O_3 content and the martensitic transformation temperature, (M_s), were determined.

1. Introduction

It is known that zirconia undergoes a martensitic-type phase transformation on heating and cooling. Reversible transition from the high-temperature tetragonal modification (T) to the low-temperature monoclinic (M) phase is accompanied by a volume change of about 9% [1]. Additions of IIA–IIIB group oxides exert a stabilizing influence on the tetragonal modification of zirconia; metastable tetragonal solid solutions exist at room temperature; however, the equilibrium temperatures of their transformation are considerably higher. These solid solutions are the base of partially stabilized zirconia ceramics. For the stabilization of CaO, MgO, Y_2O_3 oxides, by some rare-earth oxides, the equilibrium and metastable phase diagrams, heat-treatment conditions, concentration and grain-size dependencies of T-phase stabilization were carefully studied [2–5]. For instance, it was stated [6], that the higher the annealing temperature and the longer the annealing duration, the larger was the grain size. The last circumstance results in an increase of the monoclinic phase volume after cooling. Some of the most interesting results are connected with the prevention of the T → M transformation by means of rare-earth dopants [6–10]. However, phase equilibria in the zirconia-rich region (eutectoid area) of the ZrO_2–Ln_2O_3 systems, as well as the transformability of the T-phase as a function of ion radius of the dopant, has been insufficiently studied. Moreover, the temperatures of the martensitic transformation depend on the presence of intermediate phases or metastability. So, the rapid quenching of the PSZ–ZrO_2 melts is accompanied by the crystallization of the metastable solid solutions, ordered phases in which (according to the equilibrium diagram, the pyrochlore-type compound should be formed) were not observed [7–10]. Pyrochlore-type phase stabilization in the systems with rare-earth of the cerium subgroup and its instability or absence for the yttrium subgroup, results in essential differences between conditions of tetragonal crystal stabilization. Furthermore, only the high-temperature fields of the phase diagrams of zirconia with rare-earth oxides are established [11–13], although the eutectoid (T → M) area has been investigated for lanthana and erbia [6, 7].

The main phase equilibria differences between the two subgroups of lanthanides is determined by pyrochlore phase stability. For oxides of the cerium subgroup, the homogeneity field of pyrochlore compound $Zr_2Ln_2O_7$ (Py) becomes narrower as the lanthanide ion radius decreases. So, for La_2O_3 and Pr_2O_3, the pyrochlores melt congruently, but for Nd_2O_3, melting is incongruent. Moreover, the preparation of $Zr_2Nd_2O_7$ in pure form (without fluorite-type phase impurities) is not a trivial task [14]. Samaria forms pyrochlore as well, but the area of stability is less than for neodymia due to the presence of a fluorite phase. In the system ZrO_2–Eu_2O_3, the temperature range of the pyrochlore-phase stability is unknown. One can see the problem of fluorite-type solid solution ordering and its influence on martensitic transformation is worthy of investigation.

This investigation was directed to estimate the low-temperature phase equilibria in the zirconia-rich area of the phase diagrams ZrO_2–Ln_2O_3 (where Ln = La, Nd, Sm, Eu), and to study the martensitic transformation and their interconnection.

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2. Experimental procedure

The samples, containing 0–15, 33 mol % Ln_2O_3, were prepared by a chemical method: preliminary synthesized ZrO_2-powders by hydrothermal high-temperature hydrolysis of $ZrOCl_2 \cdot 8H_2O$ (active monodisperse spherical powders ZrO_2, $S_{sp} = 20–40\ m^2\ g^{-1}$, $d_{av} = 30$ nm) were mixed with Ln_2O_3 solution in nitric acid. The mixtures were evaporated and the precipitate dried in air at 100–150 °C (5 h) and decomposed at 600 °C (2 h). Annealed powders were ground in isopropyl alcohol medium using zirconia balls in a polyethylene container (5–8 h) and then pressed to tablets 5 mm diameter, 5 mm long at a pressure of 10 MPa. The samples were heated to 600, 1170, 1250 and 1450 °C at a heating rate of 10 °C min^{-1}, then held for 2 h and finally furnace cooled. Phase analysis was carried out by X-ray diffraction with nickel-filtered CuK_α radiation and a goniometer scanning speed of 0.005 °C s^{-1} over the 2θ range 15–80 °C at room temperature.

The percentage of the monoclinic phase in lanthana- and neodymia-stabilized zirconia was calculated from X-ray diffraction lines corresponding to pyrochlore and monoclinic phases [11]

$$\bar{V}_m = \frac{1.603[I_m(11\bar{1})]}{1.603[I_m(11\bar{1})] + I_c(111)} \qquad (1)$$

Similar calculations were carried out in the case of samaria and europia, but the reflection intensities of m- and t-phases were used [6]

$$\bar{V}_m = \frac{I_m(111) + I_m(11\bar{1})}{I_m(111) + I_m(11\bar{1}) + I_t(111)} \qquad (2)$$

where $I_m(111)$, $I_m(11\bar{1})$, $I_t(111)$, $I_c(111)$ are the integral intensities of reflections (1 1 1) and $(11\bar{1})$ of the monoclinic and the (1 1 1) reflections of the tetragonal and cubic phases, respectively. Differential thermal analysis, as well as precision dilatometry, were utilized for determination of phase-transformation temperatures on heating, A_s, and on cooling, M_s. The heating and cooling rates of both methods were about 10 °C min^{-1}.

3. Results and discussion

3.1. Phase analysis: metastable states at 600 and 1170 °C

The results of X-ray analysis of the samples annealed at 600, 1170, 1250 and 1450 °C are presented in Fig. 1. At low annealing temperatures, phase equilibrium was only achieved in the case of lanthana. Other rare-earth oxides formed non-equilibrium mixtures of the phases within a wide range of addition concentrations. X-ray analysis showed that the zirconia powder prepared at 600 °C crystallized in the monoclinic form independent of the concentration of lanthana (0–15 mol % La_2O_3). In contrast, the extent of this phase formation in the systems with neodymia, samaria and europia was only 0.5, 1.0, 0.75 mol % Ln_2O_3, respectively. At higher dopant concentrations, two-phase mixtures of monoclinic and tetragonal zirconia were detected.

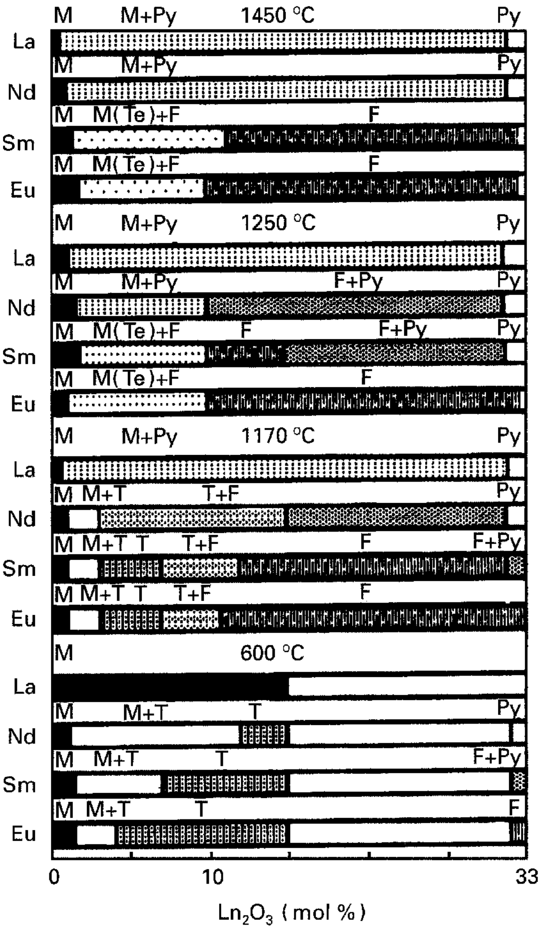

Figure 1 Phase composition in the systems ZrO_2–Ln_2O_3 (Ln = La, Nd, Sm, Eu) for the samples heat treated 2 h at 600, 1170, 1250, 1450 °C on X-ray analysis data at room temperature.

Decreasing the lanthanide ionic radius ($La^{3+} = 0.114$, $Nd^{3+} = 0.105$, $Sm^{3+} = 0.100$, $Eu^{3+} = 0.098$ nm) results in extension of the tetragonal phase area, e.g. 12–15 mol % Nd_2O_3, 8–15 mol % Sm_2O_3, 4–15 mol % Eu_2O_3. Compositions containing 33 mol % Ln_2O_3 include pyrochlore-type phase (neodymia), two-phase mixture of pyrochlore- and fluorite-type phases (samaria) and fluorite-type solid solution (europia). It is known that the T-phase may be stabilized in ultrafine zirconia powders obtained by decomposition of chemical compounds. The metastable tetragonal form is a consequence of the great surface energy of the small particles [15, 16] and on heating and increasing the particle size, the T → M transformation occurs. T-phase stability at low temperatures can be also caused by lattice defects due to the solution of the rare-earth oxide. Both variations of steric factor (decreasing lanthanide ionic radius) and the specific charge on a lattice defect can influence T-phase stability. Clearly, the larger the ionic radius of the addition, the lower is the stability of the tetragonal lattice. Increasing the annealing temperature to 1170 °C does not violate the general tendency of stabilization.

Powders containing up to 1.0 mol % La_2O_3 and annealed at 1170 °C for 2 h consist of monoclinic zirconia, but a two-phase mixture of Py + M is detected at higher lanthana content. Negligible traces of the tetragonal phase appear with 12–15 mol % La_2O_3.

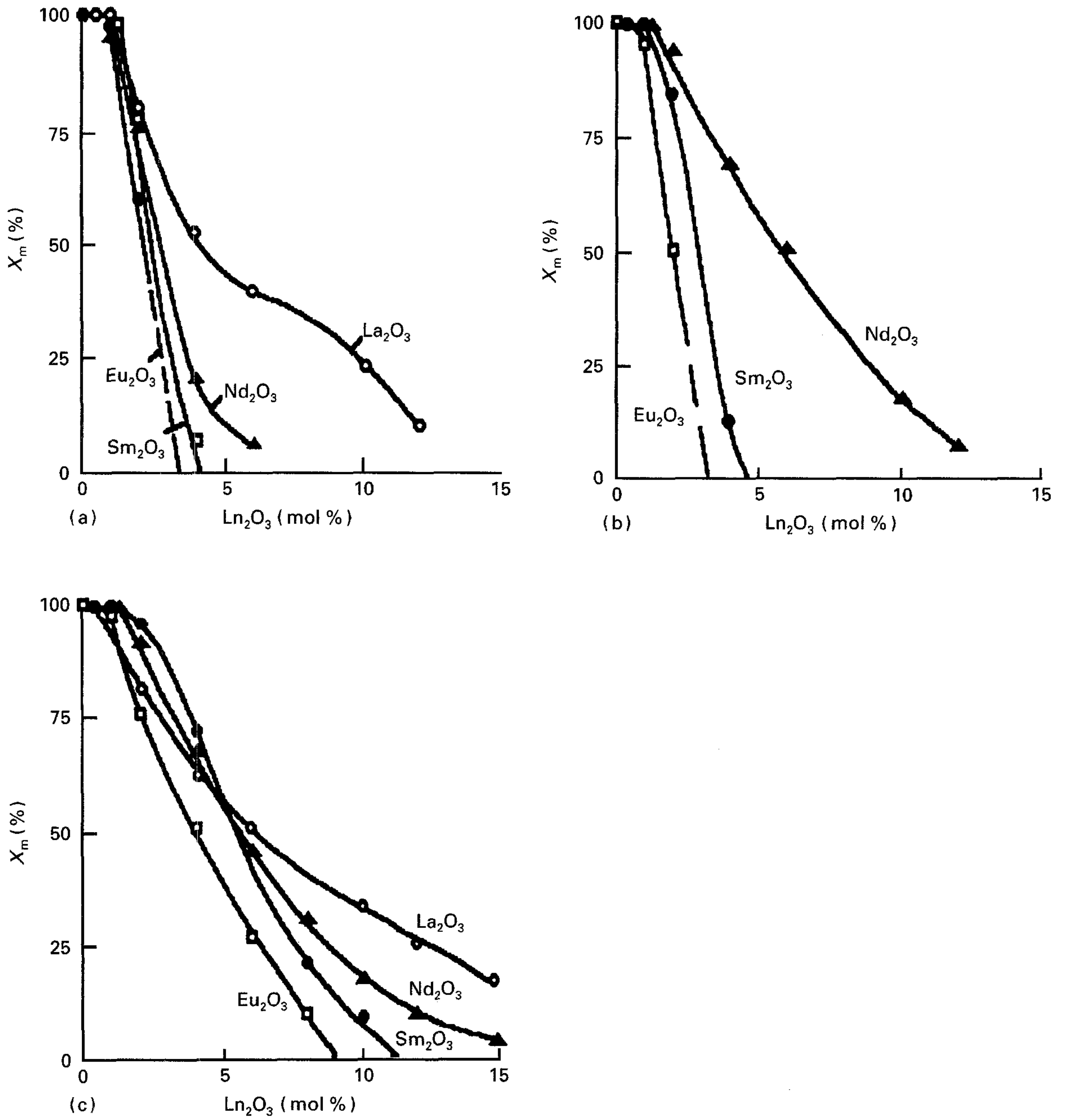

Figure 2 Percentage of the monoclinic phase versus concentration of lanthanide oxides after different annealing temperatures: (a) 1170, (b) 1250, (c) 1450 °C (2 h).

The present results are in contradiction with the data of Bastide *et al.* [6]. According to them, in the samples containing more then 12 mol % La_2O_3 (after annealing at ~ 1200 °C, 2 h) two-phase mixtures Py + T were observed rather than monoclinic solid solution. Moreover, initially prepared zirconia powder (750 °C) was only tetragonal in 2 mol % La_2O_3 and richer compositions. Such divergence with the present results is apparently connected with the powder preparation techniques. On the other hand, additions of neodymia, samaria and europia stabilized T-phase. Two phase mixtures M + T are formed within the concentration range 1–3 mol % Nd_2O_3 and 1.5–3 mol % $Sm_2O_3(Eu_2O_3)$. There was no pure T-phase after heat treatment at 1170 °C in the system ZrO_2–Nd_2O_3 and at neodymia contents more than 15 mol %, a fluorite-type phase was formed. However, the tetragonal phase is stabilized by Sm_2O_3 and Eu_2O_3 over the range 3–6 mol %. Two-phase T + F fields are observed at 7–11.5 mol % Sm_2O_3, 7–10 mol % Eu_2O_3 and 3–15 mol % (instead of the expected T + Py). Such behaviour can be explained by the low rate of ordering processes in these systems. As has been shown [17], the perfection of the pyrochlore lattice is a function of annealing time and temperature. At low temperatures (1000–1200 °C) 100 h exposure was required for the complete ordering of fluorite solid solutions in the ZrO_2–Sm_2O_3 system. When annealed at higher temperatures to 1450 °C the ordering occurs rapidly but the degree of order becomes lower. The coexistence of fluorite, small amounts of pyrochlore phase and stabilized tetragonal zirconia, is evidence of metastability. In the samples sintered at 1170 °C the tetragonal phase was not detected simultaneously with $Zr_2La_2O_7$. On the contrary, a new type of PSZ based on the tetragonal solid solutions and stabilized by pyrochlore phase has been confirmed elsewhere [6]. It was probably not stoichiometric pyrochlore

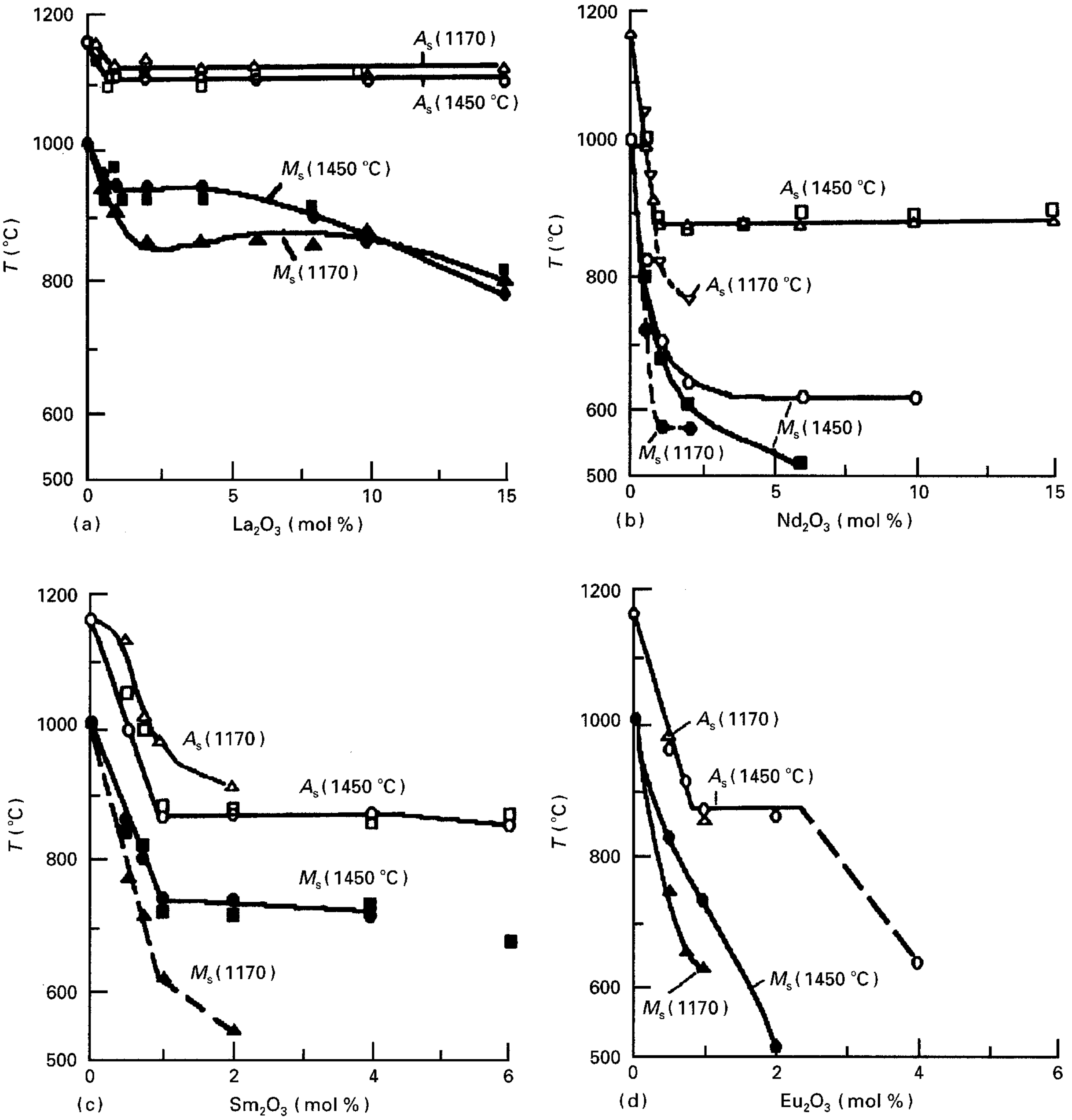

Figure 3 Composition dependencies of transformation temperatures A_s and M_s after 2 h annealing at 1170 and 1450 °C, for the systems (a) $ZrO_2–La_2O_3$, (b) $ZrO_2–Nd_2O_3$, (c) $ZrO_2–Sm_2O_3$, (d) $ZrO_2–Eu_2O_3$. (▲, △, ●, ○) DTA, (■, □) dilatometry.

phase, because its lattice parameter is very close to that of fluorite-type solid solutions; remarkable widening of (1 1 1)-fluorite, (2 2 2)-pyrochlore reflections may be the result of both partial ordering and phase coexistence in the non-equilibrium state. The formation of non-stoichiometric pyrochlore with partially ordered anion and cation sublattice is determined by the lanthanide ion radius [18]. It is well known that Py-phase is obtained with volume variation. As far as the T → M transformation occurs with increasing volume, the ordering reaction F → Py, activating the tensile stresses, caused the unstable tetragonal phase to form.

3.2. Phase analysis: annealing at 1250 and 1450 °C

Homogenization at temperatures of 1250 °C and higher in the systems containing La_2O_3 and Nd_2O_3 results in invariable phase composition. It should be pointed out that tetragonal zirconia completely transforms to the monoclinic phase on cooling. On the other hand, the lanthanides of the yttria subgroup promote the stabilization of T-phase (designated as T_e-equilibrium phase in Fig. 1). As will be shown below, the amount of stabilized non-equilibrium tetragonal crystals markedly increases with rare-earth concentration. Thus, the comparison of phase relationships at 1450 and 1250 °C revealed that absolute homogenization had not been achieved at lower temperature, especially for neodymia- and samaria-rich compositions in which pyrochlore synthesis had not been completed. In the system $ZrO_2–Eu_2O_3$, pyrochlore-type phase was not detected although it has been referred to by other authors [19, 20]. Perhaps, the phase $Zr_2Eu_2O_7$ is stable at temperatures lower than 1250 °C and forms under long firing times.

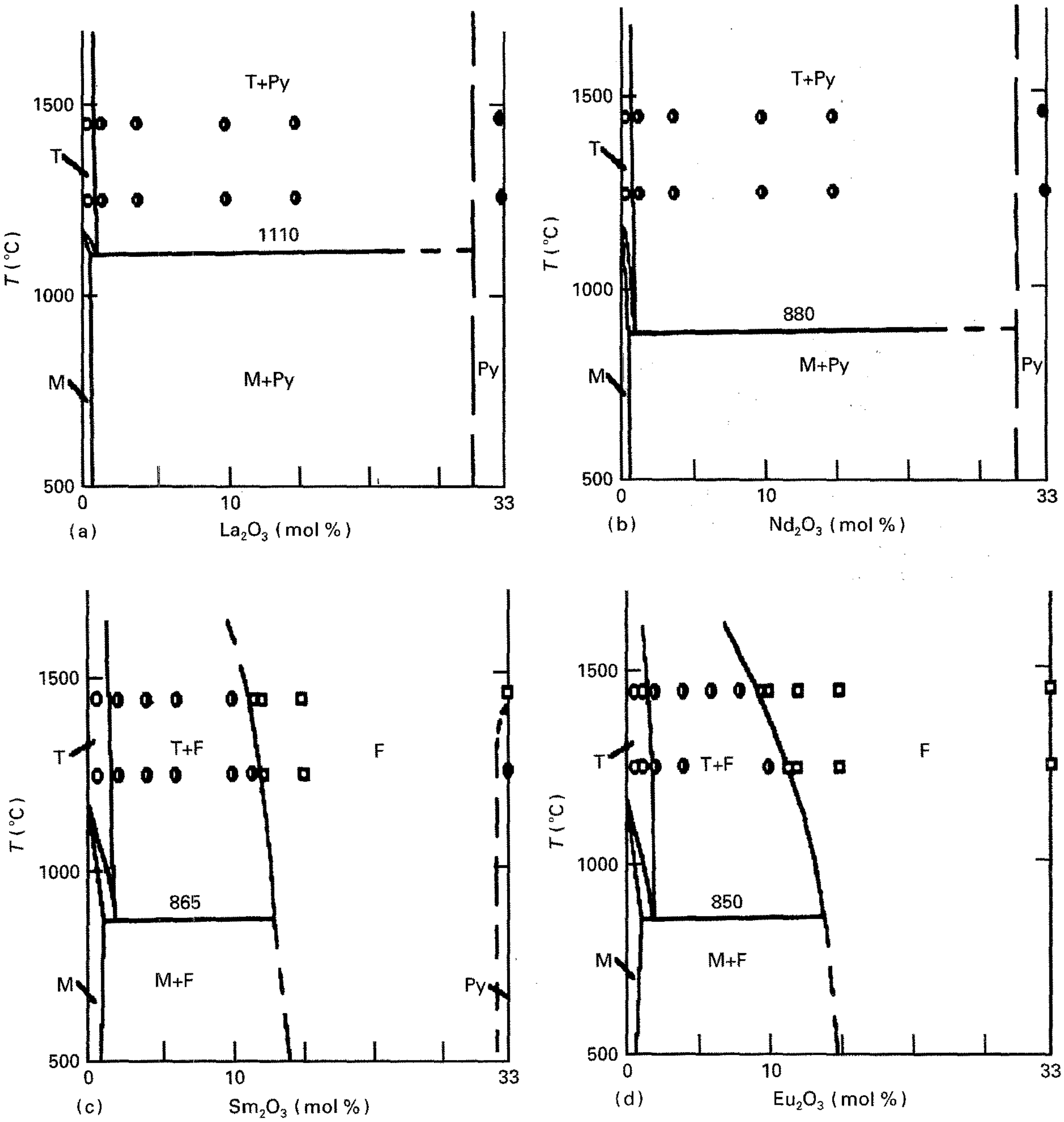

Figure 4 Tentative phase diagrams of ZrO_2–Ln_2O_3 in the concentration range 0–33 mol % Ln_2O_3 obtained by DTA, X-ray diffraction and dilatometry data: (a) ZrO_2–La_2O_3, (b) ZrO_2–Nd_2O_3, (c) ZrO_2–Sm_2O_3, (d) ZrO_2–Eu_2O_3.

Concentration dependencies of the monoclinic phase content at different annealing temperatures are presented in Fig. 2. Concentration boundaries of tetragonal phase stability (for samaria and europia) became wider as the temperature increased from 1170 °C to 1250 °C. Similar to Sm_2O_3 and Eu_2O_3, the neodymia stabilizes the T-phase at 1200 °C; however, at higher temperatures the tetragonal phase is stable in neither the Nd_2O_3 in nor the La_2O_3 systems.

TABLE I. Characteristics of the eutectoid transformations in the ZrO_2–Ln_2O_3 systems.

System	Eutectoid coordinates		Eutectoid reaction
	T °C	Ln_2O_3 (mol%)	
ZrO_2–La_2O_3	1110	0.75	T → M + Py
ZrO_2–Nd_2O_3	880	1.0	T → M + Py
ZrO_2–Sm_2O_3	865	1.5	T → M + F
ZrO_2–Eu_2O_3	850	1.5	T → M + F

3.3. Thermal analysis

Fig. 3 presents the concentration dependencies of transformation temperatures of zirconia on heating, A_s, and on cooling, M_s. Both DTA and dilatometry data are in excellent agreement with each other. For all investigated systems, the higher the rare-earth oxide concentration and the smaller the ionic lanthanide radius, the lower is the temperature of the martensitic transformation, M_s. After low-temperature homogenization, DTA and dilation effects were negligible and not fixed at high dopants content, especially for the yttria subgroup. According to Bastide *et al.* [6] for equilibrium samples ($T_s = 1450$ °C) the temperature of the eutectoid reaction is equal to A_S and certainly, the concentration dependencies A_s have a clear range of constancy of transition temperature. The slope of the curves increases inversely with the ionic radius of lanthanide. The equilibrium phase diagrams in the zirconia-rich area constructed from the present results are given in Fig. 4. It can be seen from the diagrams and from the data of Table I that the smaller is the ionic radius of the dopant, the lower is the eutectoid temperature.

4. Conclusion

The features of tetragonal–monoclinic martensitic transformation in the systems ZrO_2–Ln_2O_3 were considered as both equilibrium and non-equilibrium phase interactions. In these systems the stability of T-zirconia depended on pyrochlore-type compound formation. It was stated that pyrochlore phase synthesis as well as its degree of ordering, are determined by the ionic radius of lanthanide, the dopant concentration and the annealing conditions.

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