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Kinetics and mechanism of the solid-state synthesis of fluorite in ZrO_2–Y_2O_3–Ln_2O_3 (Ln=Ce,Nd,Er) systems

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The mechanisms and kinetics of the solid-state reaction $x\,ZrO_2 + yY_2O_3 + (1-x-y)\,Ln_2O_3 \rightarrow$ ternary fluorite solid solution was studied in the temperature range 1350 to 1650° C by quantitative X-ray diffraction analysis. In the ZrO_2–Y_2O_3–CeO_2 system the fluorite formation process starts with the simultaneous interaction of CeO_2 and Y_2O_3 with ZrO_2, although the reaction rate of ceria with zirconia is more rapid. In the ZrO_2–Y_2O_3–Nd_2O_3 system, the formation of a pyrochlore, $Nd_2Zr_2O_7$, responsible for the formation process of the ternary fluorite solid solution. Finally, in the ZrO_2–Y_2O_3–Er_2O_3 system, a competitive interaction of yttria and erbia occurred in the formation process of the ternary solid solution. The kinetic data were treated using the Avrami equation, and activation energies for the processes studied calculated.

1. Introduction

The study of interactions between oxides is useful in providing fundamental information about factors controlling solid-state reactions. In the case of ZrO_2 and Ln_2O_3, this information is necessary to synthesize new inter-oxide compounds.

Little information exists about the interaction between rare-earth oxides and zirconia. The major contribution in this area was reported by Glushkova *et al.* [1] who studied the kinetics of the formation of ternary solid solutions in the ZrO_2–Y_2O_3–CaO, ZrO_2–Y_2O_3–MgO, ZrO_2–Y_2O_3–Nd_2O_3 and ZrO_2–CaO–Nd_2O_3 systems. Thermochemical data on the synthesis of rare-earth zirconates and hafnates at high temperatures was also reported by Glushkova *et al.* [2]. The kinetics of formation of solid solution of the fluorite type between HfO_2 and Y_2O_3 was studied by Isupova *et al.* [3], and Kuznetsov *et al.* [4] reported the formation kinetics of solid solutions in the ZrO_2–Y_2O_3 and ZrO_2–Y_2O_3–Yb_2O_3 systems. More recently, Glushkova *et al.* [5] have studied the formation kinetics of a Dy_2O_3–$2ZrO_2$ solid solution.

The main purpose of the present work was to study the kinetics of the fluorite solid-solution formation process in the systems ZrO_2–Y_2O_3–CeO_2, ZrO_2–Y_2O_3–Nd_2O_3 and ZrO_2–Y_2O_3–Er_2O_3, to elucidate the overall reaction mechanism.

2. Experimental details

2.1. Sample preparation

The samples were prepared by weighing the oxide components to obtain the desired final composition, intimately mixing in acetone for several hours, drying and pressing in a steel die at about 2000 kg cm^{-2} before heating. The starting materials were 99.9% pure and had a particle size of $< 30\,\mu$m.

2.2. Kinetic studies

The pressed samples were placed in the hot zone of a voltage-stabilized molybdenum- or rhodium-wound furnace, and heated in alumina boats in ambient air at temperatures between 1300 and 1650° C for varying times between 5 min and 24 h. Temperatures were measured with a Pt–Rh 6% Pt–Rh 30% thermocouple to an accuracy of

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about ± 5° C; samples were quenched in air at the end of an experiment. The concentration of the phases was determined by quantitative X-ray diffraction analysis.

2.3. X-ray analysis for $(ZrO_2)_{0.88}(Y_2O_3)_{0.05}(CeO_2)_{0.07}$, $(ZrO_2)_{0.80}(Y_2O_3)_{0.08}(Nd_2O_3)_{0.12}$ and $(ZrO_2)_{0.90}(Y_2O_3)_{0.05}(Er_2O_3)_{0.05}$ compositions

A quantitative study was carried out for the process of formation of the ternary fluorite solid solutions. Samples of the above compositions were synthetized at 1800° C for 7h. Standard mixtures of these solid solutions were prepared with 10 to 90 wt% monoclinic zirconia. The intensity ratios for the main lines of the cubic and monoclinic phases of the diffraction patterns of these mixtures were used to construct a calibration curve (see Fig. 1). The extent of reaction was determined by comparison of X-ray line intensities of the heat-treated samples with the calibration curve. The intensities of the lines scanned were calculated as the product of the height and the half-width of the reflections. The samples were examined several times with an X-ray powder goniometer (goniometer speed, $1/4° \, 2\theta \, \mathrm{min}^{-1}$, and paper speed $2\theta \, \mathrm{mm} \, \mathrm{min}^{-1}$). All determinations were carried out at least twice, the relative error of the X-ray intensity measurements was estimated to be better than 5%.

The amount of monoclinic or cubic phases present in the mixtures were determined using the following expressions:

$$X_m = \frac{1.7 I_m}{1.7 I_m + I_c}$$

$$X_c = \frac{I_c}{1.7 I_m + I_c}.$$

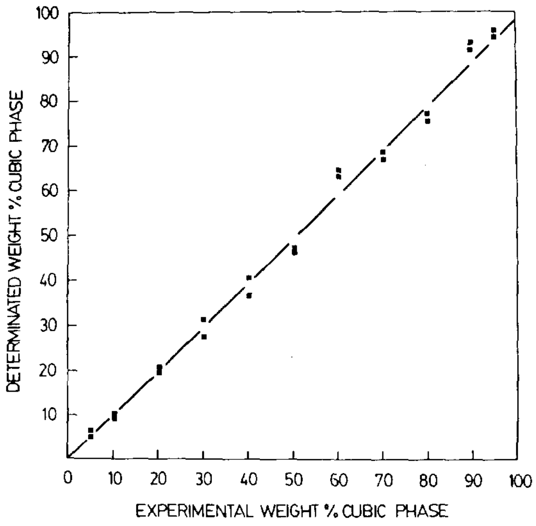

Figure 1 Calibration curve used for cubic-phase analysis.

These simplified expressions are similar to that used by Garvie and Nicholson [6] in the polymorphic method, but in the present case it was assumed that the ratio $I_m(11\bar{1})/I_m(111)$ remains constant. In all samples of the present work this ratio has an average value of 0.7 and therefore $I_m(11\bar{1}) + I_m(111) = 1.7 I_m(11\bar{1})$ [7]. Porter and Heuer [8] introduced several corrections on the intensities to improve the accuracy of the method applied to Mg–PSZ, and obtained a similar formula to that used here.

3. Results and discussion

Fig. 2a to c shows the growth of the ternary fluorite solid solutions for the three systems studied. As can be seen, above 1300° C the reactions proceed at intergranular contacts to form as the final product the ternary cubic solid solution. However, the cubic solid solutions are not always formed in this way. For example, in the X-ray diffraction pattern of products formed at lower temperatures, lines of yttrium oxide were clearly visible, and this was strongly related to the ability of the lanthanide oxide to interact with ZrO_2. Glushkova *et al.* [1], believed this arose because in the initial periods of the reaction, the reactivity of the oxides with ZrO_2 increased in the order $Nd_2O_3 > CeO_2 > Er_2O_3$; this increase correlated with the ability of these oxides to form compounds with zirconia. Actually, as the reaction proceeds, ZrO_2 interacts with Nd_2O_3 or CeO_2 to form $Nd_2Zr_2O_7$, and probably metastable $Ce_2Zr_2O_{7+x}$, respectively, erbium and yttrium oxides produce cubic solid solutions of the fluorite type. The subsequent reactions in which the intermediate product reacts further to form the ternary cubic solid solution must be slower. The sequence of reactions is:

$$ZrO_2 + Y_2O_3 + CeO_2 \rightarrow Ce_2Zr_2O_{7+x} + Y_2O_3 \rightarrow (F_{ss})_T \qquad (1)$$

$$ZrO_2 + Y_2O_3 + Er_2O_3 \rightarrow (F_{ss})_T. \qquad (2)$$

A quantitative X-ray analysis of the products formed in the ZrO_2–Y_2O_3–Nd_2O_3 system was performed as a function of time, and the results shown schematically in Fig. 3. It can be seen

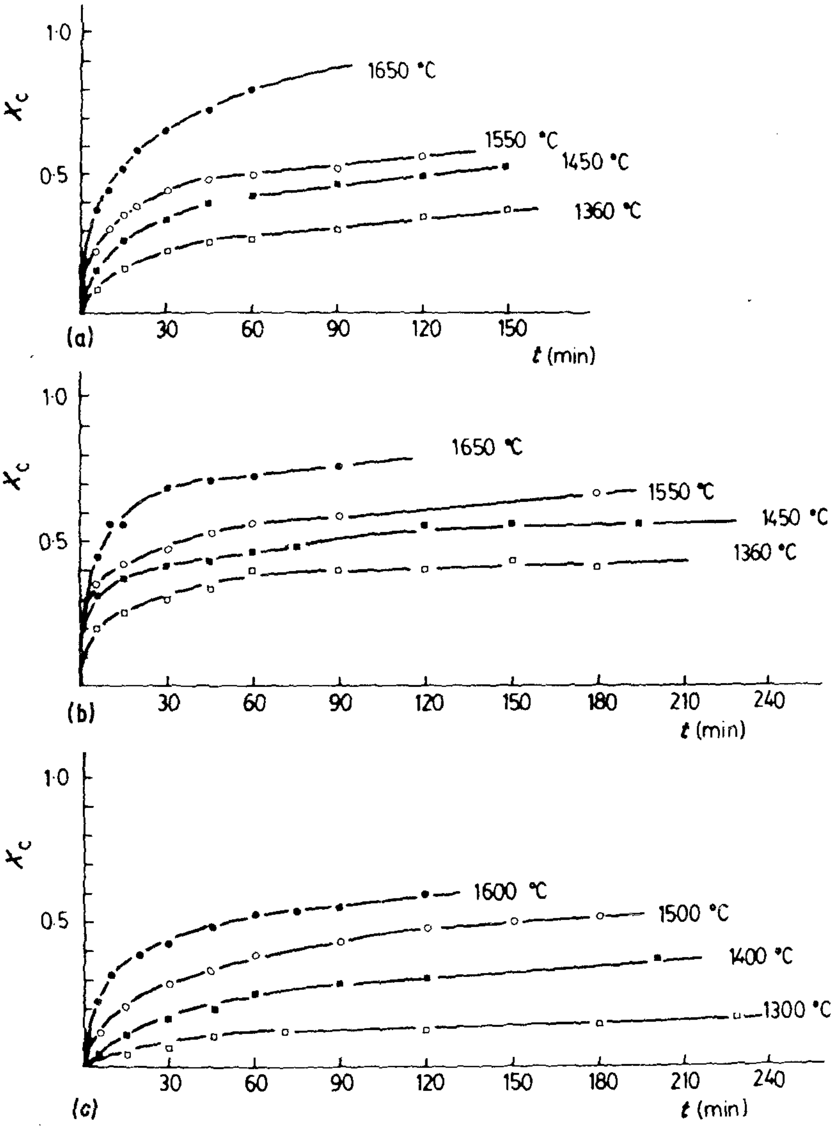

Figure 2 Kinetic growth curves for $(F_{ss})_T$ formation. (a) ZrO_2–Y_2O_3–CeO_2, (b) ZrO_2–Y_2O_3–Nd_2O_3, and (c) ZrO_2–Y_2O_3–Er_2O_3 systems.

that at 1360° C, the reactions for the $(F_{ss})_T$ and $Nd_2Zr_2O_7$ formation proceed simultaneously. Above 1360° C these reactions occurred up to a point when the concentration of $Nd_2Zr_2O_7$ was ~ 20% (below 500 min): in longer heat treatments, the $(F_{ss})_T$ concentration increases rapidly at the expense of $Nd_2Zr_2O_7$. At higher temperatures, formation of $(F_{ss})_T$ is a more rapid process: these reaction paths are summarized in Fig. 4.

The kinetic curves for the growth of $(F_{ss})_T$ (see Fig. 2) show that these are regularly spaced and of a similar shape. Initially, the reactions proceed very rapidly, as indicated by the steep slope of the reaction curves, and no induction or nucleation period was observed.

Several different equations describing the kinetics of solid-state reactions have been proposed [9–12], and their numerical solutions tabulated by Sharp *et al.* [13]. In the present work, the experimental data may be fitted to the Avrami equation:

$$\ln(1/1-x) = (kt)^m,$$

as well as by Jander's equation:

$$F(x) = [1-(1-x)^{1/3}]^2 = (k/r^2)t$$

However, Jander's equation was not particu-

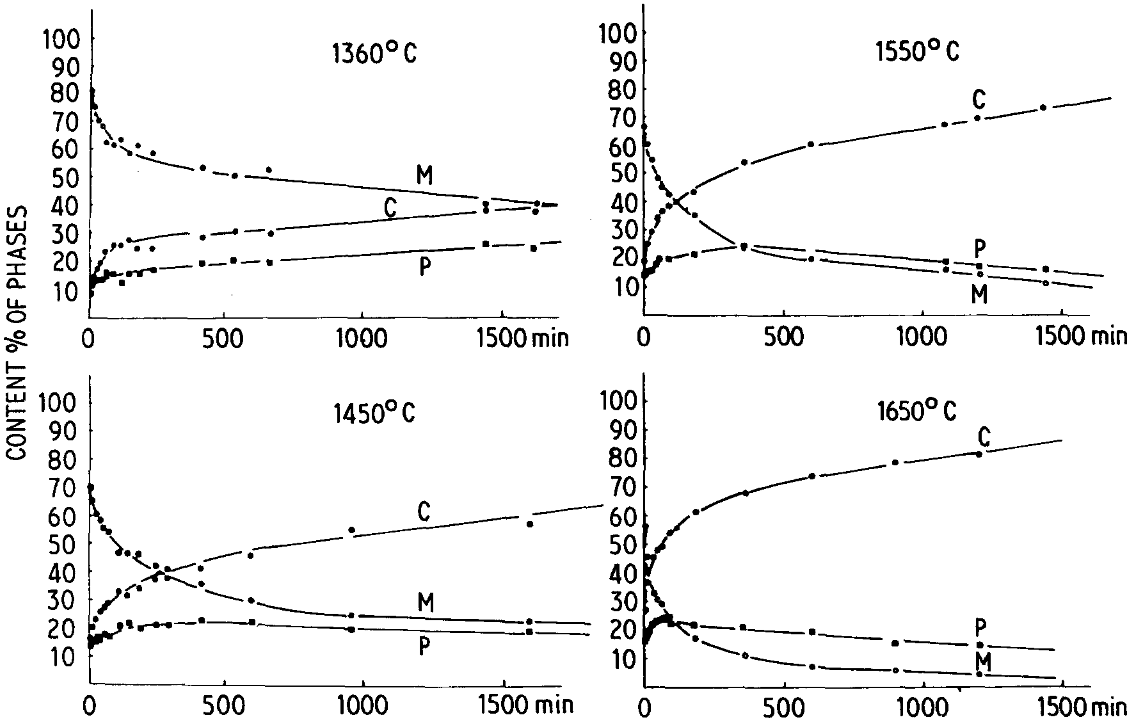

Figure 3 Phase composition of the reacting mixture as a function of time for the ZrO_2–Y_2O_3–Nd_2O_3 system. M, monoclinic phase; C, cubic phase of the fluorite type, and P, cubic phase of the pyrochlore type.

larly applicable to early stages of reactions (see Fig. 5), whereas the Avrami equation gives a slightly better overall fit. Therefore, the data were treated using the Avrami equation. The present data, when plotted as $\ln\ln(1/1-x)$ against $\ln t$ yield a straight line with slope m and intercept $m \ln k$, as shown in Fig. 6, for the ZrO_2–Y_2O_3–CeO_2 system, and a satisfactory fit is obtained. Similar results were obtained for the ternary solid solutions of the ZrO_2–Y_2O_3–Nd_2O_3 and ZrO_2–Y_2O_3–Er_2O_3 systems.

In these systems the value of m, which is related to the reaction mechanism, varied between 0.43 and 0.45 for the ZrO_2–Y_2O_3–CeO_2 system, and 0.21 to 0.25 for the ZrO_2–Y_2O_3–Nd_2O_3 system. For the system ZrO_2–Y_2O_3–Er_2O_3, a value of $m \simeq 0.5$ was obtained.

The plots of the logarithm of the chemical reaction constant, calculated from the Avrami equation, as a function of the inverse temperature, are well described by a straight line (see Fig. 7). Taking into account the Arrhenius equation, $k = C\,e^{-E/RT}$, the activation energy, E, for the formation of the ternary fluorite solid solutions were obtained. The values found for the systems ZrO_2–Y_2O_3–Ln_2O_3 (Ln = Ce, Nd, Er) were

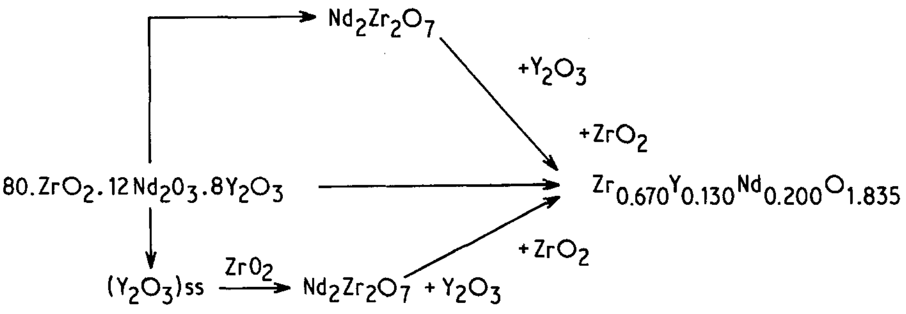

Figure 4 Reaction scheme of the synthesis of $(F_{ss})_T$ in the ZrO_2–Y_2O_3–Nd_2O_3 system.

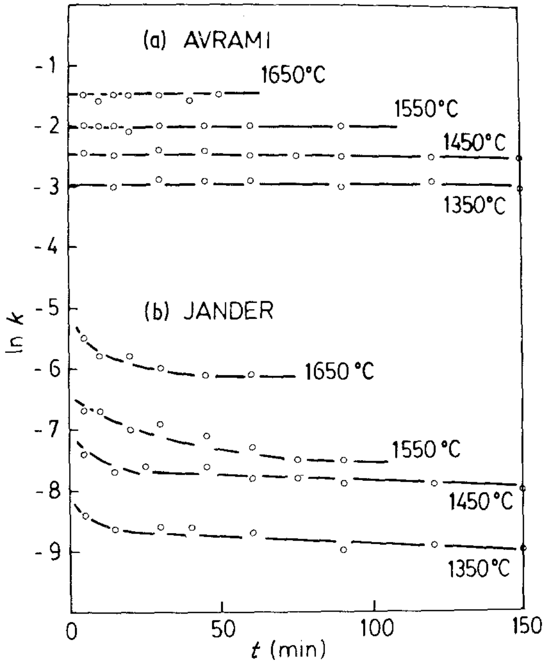

Figure 5 Analysis of Avrami and Jander rate constant.

73, 94 and 72 kcal mol^{-1}, respectively. The high activation energies of these reactions runs parallel to their low reaction rates.

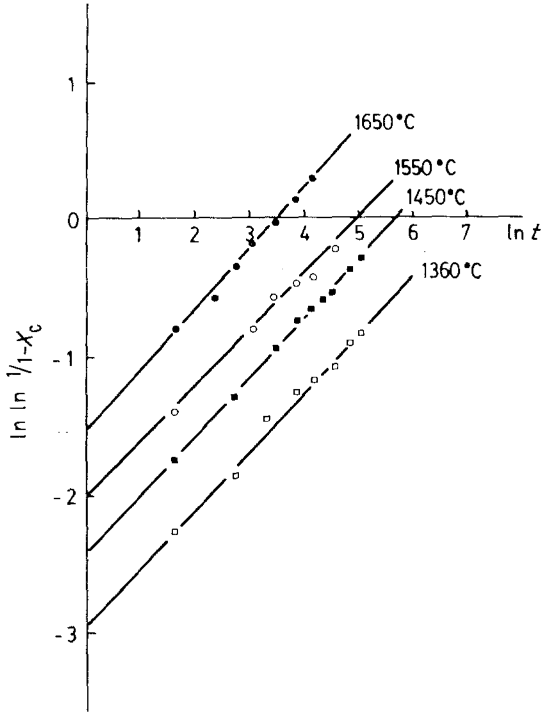

Figure 6 Avrami equation analysis.

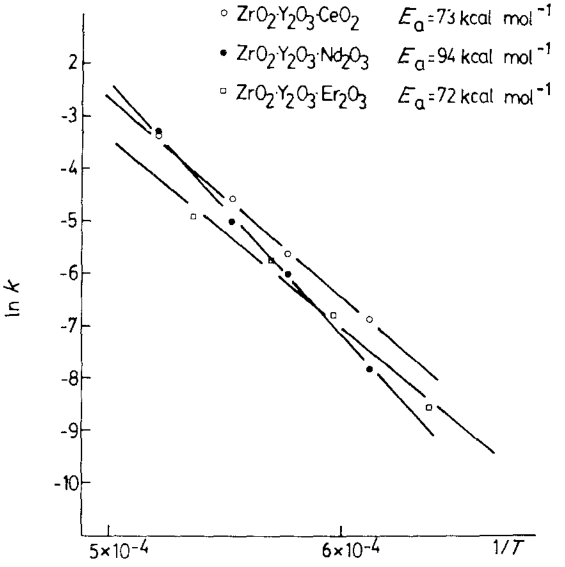

Figure 7 Arrhenius plot of log K against $1/T$.

From the experimental results obtained in the present work, the following interpretation on the interaction between ZrO_2, Y_2O_3 and Ln_2O_3 oxides could be given: above a critical temperature, in the present case monoclinic–tetragonal transformation temperature of ZrO_2, a spontaneous and rapid nucleation in tetragonal matrix takes place. As a consequence of this phenomenon, Ln_2O_3 is rapidly consumed forming metastable $Ce_2Zr_2O_{7+x}$, $Nd_2Zr_2O_7$ or zirconia–erbia solid solution, respectively, which interact simultaneously with yttria to form the final $(F_{ss})_T$ phase. In this rapid formation of $(F_{ss})_T$ phase, two factors seem to play an important role: (a) the presence of "active points" from the beginning of the reaction, probably on the surface or the tetragonal zirconia grains; and (b) the average cation radius of the Ln^{3+} and Y^{3+} to form the ternary cubic solid solution $(F_{ss})_T$.

The "active points" can be considered as "germ nuclei" that, in agreement with the Avrami suggestions, activated by temperature can serve as growth nuclei. In this sense, taking in account the strong resemblance of tetragonal and cubic zirconia structures, the ternary solid solution formation may take place at the more favoured sites of the tetragonal zirconia lattice, and the reaction progress by a diffusion-controlled growth of the $(F_{ss})_T$ crystallites which, on the other hand, are very small at the beginning. In the present case, this monodimensional diffusion-controlled growth could be more favoured in the direction of the c-axis of the tetragonal zirconia unit cell.

At the present time it is very difficult to attain final conclusions on the true mechanism governing these solid-state reactions. More work on the solid-state reactions in these systems is desirable, both to clarify their mechanism and to help in searching for new high temperature materials.

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References

1. V. B. GLUSHKOVA, E. K. KOEHLER, A. K. KUZNENSON and P. A. TIKHONOV, in "Les elements des terres rares", Vol. I, (CNRS, Paris, 1970) p. 209.
2. V. B. GLUSHKOVA and V. A. KRZHIZHANOVSKAYA, in "Etude des transformations cristallines a haute temperature", Colloques internationaux CNRS. no. 205 (1971) p. 469.
3. E. N. ISUPOVA, V. B. GLUSHKOVA and E. K. KOEHLER, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 5 (1969) 1948.
4. A. K. KUZNETSOV, M. D. KRASIL'NIKOV and P. A. TIKHONOV, *ibid.* 8 (1972) 749.
5. V. B. GLUSHKOVA, V. A. KRZHIZHANOVSKAYA and E. K. KOEHLER, *ibid.* 9 (1973) 719.
6. R. C. GARVIE and P. S. NICHOLSON, *J. Amer. Ceram. Soc.* **55** (1972) 303.
7. C. PASCUAL, PhD thesis, Madrid University (1980).
8. D. L. PORTER and A. H. HEUER, *J. Amer. Ceram. Soc.* **62** (1979) 298.
9. W. I. JANDER, *Z. Anorg. Chem.* **162** (1927) 1.
10. A. M. GINSTLING and B. I. BROUNSHTEIN, *J. Appl. Chem. USSR* **23** (1950) 1327.
11. H. DUNWALD and C. WAGNER, *Z. Physik Chem. (Leipzig)* **B24** (1934) 53.
12. M. AVRAMI, *J. Chem. Phys.* 7 (1939) 1102.
13. J. H. SHARP, G. W. BRINDLEY and B. N. NARAHARI AGHAR, *J. Amer. Ceram. Soc.* **49** (1966) 379.

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