

## Defect Structures in the Brannerite-Type Vanadates. II. Mechanism of the Solid-State Synthesis of $\text{Mn}_{1-x}\phi_x\text{V}_{2-2x}\text{Mo}_{2x}\text{O}_6$ ( $0 \leq x \leq 0.33$ )

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The mechanism of solid-solid reactions in mixtures of the three components  $\text{Mn}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{MoO}_3$  has been studied by X-ray and thermogravimetric methods. The synthesis of  $\text{Mn}_{1-x}\phi_x\text{V}_{2-2x}\text{Mo}_{2x}\text{O}_6$  (*MV-100x*) solid solutions proceeds along three main reaction paths: (a) direct formation from oxides due to efficient surface diffusion of  $\text{MoO}_3$  and  $\text{V}_2\text{O}_5$  over  $\text{Mn}_2\text{O}_3$  grains, (b) formation of  $\text{MnMoO}_4$  followed by its reaction with  $\text{V}_2\text{O}_5$  to *MV-33* and dilution of the obtained phase with  $\text{V}_2\text{O}_5$  and  $\text{Mn}_2\text{O}_3$ , and (c) reaction of preformed  $\text{MnV}_2\text{O}_6$  and  $\text{MnMoO}_4$  with  $\text{V}_2\text{O}_5$  in which *MV-20* appears as an intermediate (valid for  $x > 0.20$ ). The contribution of these paths to the overall reaction depends on the composition of the initial mixture ( $x$ ), temperature, and surface area of  $\text{Mn}_2\text{O}_3$ . If the synthesis of a single-phase solid solution in a  $\text{MoO}_3$ -poor region ( $x < 0.20$ ) is aimed at, thermal treatment parameters should be selected in such a way as to prevent the preformation of  $\text{MnV}_2\text{O}_6$ , which, once formed, is not subsequently converted to the equilibrium phase.

### Introduction

In our recent work we found that  $\text{MnV}_2\text{O}_6$  of brannerite-type structure is particularly amenable to substitution of  $\text{Mo}^{6+}$  for  $\text{V}^{5+}$  ions, the charge compensation being accomplished by generation of an equivalent number of cationic vacancies ( $\phi$ ) at  $\text{Mn}^{2+}$  sites (1). The series of solid solutions obtained had the general formula  $\text{Mn}_{1-x}\phi_x\text{V}_{2-2x}\text{Mo}_{2x}\text{O}_6$ . The maximum value of  $x$  was found to be 0.45 at 583°C.

This work was undertaken as a study of the nature of solid-solid reactions between  $\text{Mn}_2\text{O}_3$ ,  $\text{MoO}_3$ , and  $\text{V}_2\text{O}_5$  and was aimed at determining the optimum parameters for preparation of a  $\text{Mn}_{1-x}\phi_x\text{V}_{2-2x}\text{Mo}_{2x}\text{O}_6$  solid solution from oxides.

Our preliminary experiments revealed that solid-solid reactions in the system

investigated began with considerable efficiency at about 500°C. Higher temperatures are required, however, to ensure their completion. On the other hand, the reaction temperature should not surpass the upper limit of the brannerite solid-solution stability field. This limit is represented by curve ABC in Fig. 1, which reproduces the relevant portion of the previously determined (1) phase diagram of the  $\text{MnV}_2\text{O}_6$ - $\text{MoO}_3$  system. In our experiments, thus,  $x$  ranged from 0 to 0.33 and the calcination temperature ranged as a rule from 500 to 600°C.

Our symbolism for homogeneous  $\text{Mn}_{1-x}\phi_x\text{V}_{2-2x}\text{Mo}_{2x}\text{O}_6$  solid-solution samples includes *MV* to define the solvent, followed by a numeral *X* ( $=100x$ ) which specifies the mole percentage of vanadium replaced by molybdenum in a  $\text{MnV}_2\text{O}_6$  structure. The same symbols placed within quotation marks denote the overall composition of a sample in which reaction is not

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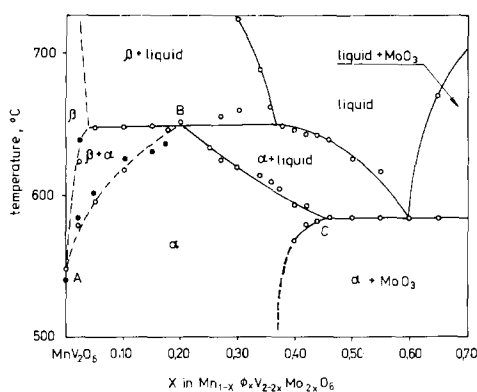


FIG. 1. A portion of the phase diagram of the  $\text{MnV}_2\text{O}_6\text{-MoO}_3$  system. After (1).

complete. A solid solution of stoichiometry corresponding to the overall composition of a given sample is referred to as a nominal one and denoted as  $MV\text{-}X_n$ .

### Experimental

**Materials.**  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  were p.a. grade commercial oxides, and  $\text{Mn}_2\text{O}_3$ (I) and (II) were obtained by pyrolysis of  $\text{MnCO}_3$  at  $700^\circ\text{C}$  and  $\text{Mn}/\text{CH}_3\text{COO}/2 \cdot 4\text{H}_2\text{O}$  at  $500^\circ\text{C}$ , respectively. Their BET surface areas amounted to 9.31 (I) and 1.05 (II)  $\text{m}^2/\text{g}$ . For both samples, microscopic examination showed approximately the same grain size distribution, the predominating grain diameter being  $1.5 \mu\text{m}$ . The syntheses were performed with  $\text{Mn}_2\text{O}_3$ (I) if not indicated otherwise. Reaction mixtures of appropriate composition, thoroughly ground in a mortar, were air heated using alumina crucibles. Details of the thermal treatment program are indicated under Results and Discussion. An elemental analysis (1) has shown that there is no loss of components during heating.

**Methods.** Phase identification by the X-ray diffraction method was performed as described in (1). Shifting of the brannerite (020) reflection was used to determine the Mo content in solid-solution phases appear-

ing in the reaction mixtures. Relevant calibration data are given in (1), the accuracy of the  $x$  determination being  $\pm 0.01$ .

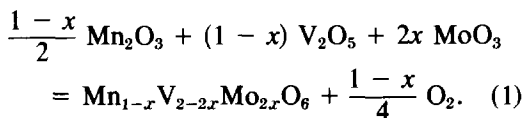
The progress of some solid-solid reactions was monitored in a high-temperature camera. The conversions were calculated from the intensities of reactant X-ray lines by using the patterns of pure substances and their mixtures of known compositions as calibrants.

Thermogravimetric experiments were performed with a Paulik-Paulik-Erdey derivatograph. Samples of about 1 g were placed in platinum crucibles and air heated at the rate of  $2.5^\circ\text{C}/\text{min}$ .

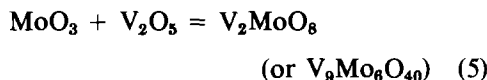
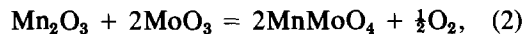
### Results and Discussion

#### Binary Reactions

The synthesis of solid solutions under study may be described by the overall equation



Reactions of solid-solid type start and develop usually at the initial intergranular contacts. In our powder mixture three types of such contacts exist, namely,  $\text{Mn}_2\text{O}_3\text{-MoO}_3$ ,  $\text{Mn}_2\text{O}_3\text{-V}_2\text{O}_5$ , and  $\text{MoO}_3\text{-V}_2\text{O}_5$ . It is thus to be expected that the intermediate binary products



will be formed, which will then react further to form  $MV\text{-}X_n$  of a composition corresponding to the stoichiometry of the starting mixture. As shown below, the intermediates quoted above are really

formed without  $V_2MoO_8$  ( $V_9Mo_6O_{40}$ ), which according to the literature data is synthesized effectively on more prolonged heating, or at higher temperatures (2). Thus, solid-solid reactions in the  $Mn_2O_3$ - $MoO_3$  and  $Mn_2O_3$ - $V_2O_5$  systems with molar ratios of components of 1:1 and 1:2 were studied using the thermogravimetric method and X-ray diffractometry. The product of the reaction between  $Mn_2O_3$  and  $MoO_3$  was  $MnMoO_4$ . Both  $Mn_2O_3$ - $V_2O_5$  systems produced only  $MnV_2O_6$  at temperatures below about  $600^\circ C$ . At  $600^\circ C$  (or above)  $Mn_2V_2O_7$  was formed along with  $MnV_2O_6$  and a single compound corresponding in stoichiometry to the composition of the mixture was formed sequentially in the later stages of the reaction.

Figure 2 shows the curves of thermogravimetric analysis for systems containing  $Mn_2O_3$ (I) or (II) differing in surface areas.

The weight loss observed in the  $Mn_2O_3$ - $MoO_3$  system is a result of reaction (2) progress. The thermogravimetric curves of the  $Mn_2O_3$ - $V_2O_5$  systems are considered to be a complex result of reactions (3) and (4) in the respective temperature ranges. From these results, it may be concluded that

1° reaction (2) is always much faster than (3) or (4),

2° the reaction rate for the  $Mn_2O_3$ - $MoO_3$  and  $Mn_2O$ - $V_2O_5$  systems is proportional to the content of  $Mn_2O_3$  in the initial mixture and to its surface area.

The effect of the surface area and reaction mixture composition on the reaction rate can be considered to be due to the two-step reaction mechanism as described in previous work for  $Mn_2O_3$ - $MoO_3$  systems (3). This mechanism involves a rapid diffusion of  $MoO_3$  or  $V_2O_5$ , which spread over the surface of  $Mn_2O_3$  grains, and gradually react with it, forming radially growing layers of product.

On monitoring the synthesis of  $MnV_2O_6$  in a high-temperature camera we observed that diffraction intensities of  $Mn_2O_3$  maxima decrease more rapidly than those of  $V_2O_5$  as the reaction progresses. This effect may account for the increasing coverage of the  $Mn_2O_3$  surface with  $V_2O_5$  and  $MnV_2O_6$  during reaction and may be considered to give additional support for the suggested reaction mechanism. It seems worth noticing that the above-discussed processes of surface diffusion of  $MoO_3$  and

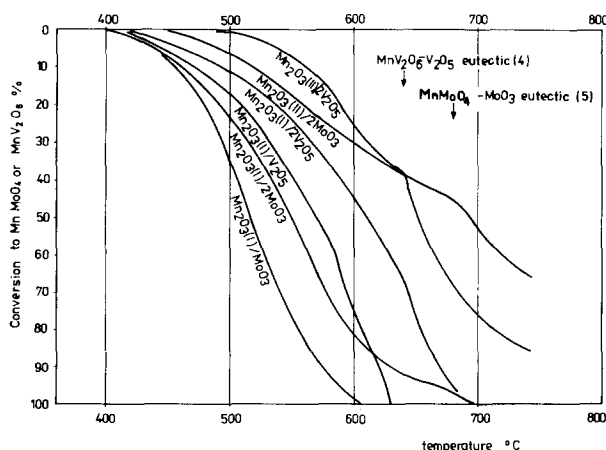


FIG. 2. Results of TGA of  $Mn_2O_3$ - $MoO_3$  and  $Mn_2O_3$ - $V_2O_5$  mixtures. The apparently abnormal increase in the reaction rate at later stages may be ascribed to the appearance of liquids above the eutectic temperatures indicated in the figures.

$V_2O_5$  over the surface of  $Mn_2O_3$  render possible, in the tricomponent mixtures, the ternary molecular contacts  $Mn_2O_3-V_2O_5-MoO_3$  and may give rise to the direct formation of certain  $MV-X$  solid solutions according to Eq. (1).

#### Ternary Reactions, Annealing at 500–520°C

Figure 3 shows the reaction progress in the mixture "MV-10" as studied with a high-temperature X-ray camera at 520°C. The calculated conversions are merely approximate, due to the screening effect of  $V_2O_5$ . It may be said, however, that, after only 90 min of annealing,  $MoO_3$  is completely converted to  $MnMoO_4$  and to a certain  $\alpha$ -MV-phase, with both compounds appearing in comparable amounts. X-Ray lines of the  $\alpha$ -MV-phase obtained are somewhat broadened, indicating nonhomogeneity in the Mo distribution with a predominant composition of  $x = 0.12$ . Fair quantities of  $V_2O_5$  and  $Mn_2O_3$  remain unreacted. After 2–3 hr the reaction is hindered and its further progress is hardly observed on heating at 520°C up to 70 hr. Similar results were obtained for mixtures of other  $x$  parameters ranging from 0.05 to 0.33. Formation of  $MV-X$  with  $X$  close to the nominal one is always accompanied by

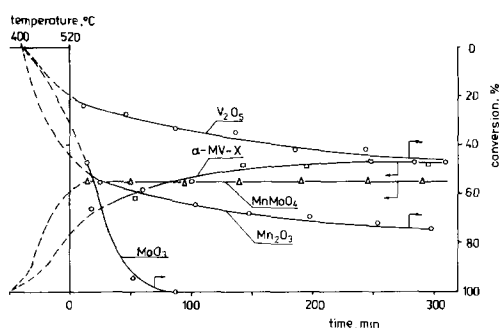


FIG. 3. Reaction progress in the "MV-10" mixtures as determined in a high-temperature X-ray camera at 520°C.

$MnMoO_4$  and unreacted  $Mn_2O_3$  and  $V_2O_5$ . Apparently the last two oxides do not react, as they are isolated by  $MnMoO_4$  and  $MV-X$  covering the surface of  $Mn_2O_3$  grains.

#### Ternary Reactions, Annealing at 600°C

The results obtained on heating the reaction mixtures at 600°C enable one to distinguish two composition ranges in which some differences in the reaction path and the reaction rate are observed, namely,  $0.02 \leq x < 0.20$  and  $0.20 \leq x \leq 0.33$ .

(i)  $0.02 \leq x < 0.20$ .

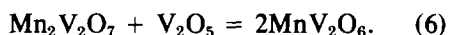
Table I summarizes the results of X-ray phase analyses of samples of the first range calcined at 600°C for 70 and 140 hr, to study

TABLE I  
PHASE COMPOSITION OF "MV-2", "MV-5", "MV-10", AND "MV-15" AFTER ANNEALING AT 600°C FOR 70 AND 140 HR

Designed $x$	Phase composition <sup>a</sup> after annealing		
	70 hr at 600°C		140 hr at 600°C
	Principal phases	Minor phases	
0.02	$MV-0$ , $Mn_2V_2O_7$	$MnMoO_4$ , $V_2O_5$	$MV-0$ , $MV-20$
0.05	$MV-0$ , $MnMoO_4$	$Mn_2V_2O_7$ , $V_2O_5$	$MV-0$ , $MV-20$
0.10	$MnMoO_4$ , $MV-0$	$V_2O_5$	$MV-19$ , $MV-3$
0.15	$MnMoO_4$ , $MV-2$	$MV-20$ , $V_2O_5$	$MV-20$ , $MV-3$

<sup>a</sup> The contents of  $MnMoO_4$  and  $\sim MV-20$  increase and those of  $\sim MV-0$  and  $Mn_2V_2O_7$  decrease monotonously along the series studied.

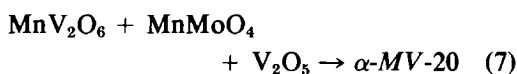
the early and later stages of the reactions. The direct synthesis of solid solution clearly detectable at 500°C is no longer observed. In the early stages of the reaction at 600°C,  $\text{Mn}_2\text{O}_3$  is totally consumed in reactions (2), (3), and (4). Reaction (2), producing  $\text{MnMoO}_4$ , proceeds at the highest rate, as proved before, and stops after complete exhaustion of  $\text{MoO}_3$ . The rest of  $\text{Mn}_2\text{O}_3$  is consumed in reactions (3) and (4), yielding  $\text{MnV}_2\text{O}_8$  and  $\text{Mn}_2\text{V}_2\text{O}_7$  as products; the  $\text{Mn}_2\text{V}_2\text{O}_7$  formation, however, is observed only in Mo-poor preparations with a favorable, high  $(\text{Mn} + \text{V})/\text{Mo}$  ratio. Most probably, the  $\text{Mn}_2\text{V}_2\text{O}_7$  initially formed in the system reacts further with  $\text{V}_2\text{O}_5$  to form  $\text{MnV}_2\text{O}_6$ :



The reaction pattern described above is apparently due to the higher activation energy (and consequently to the higher rate acceleration with increasing temperature) for reactions (3) and (4) than that for (1).

Thus it may be concluded that in the first stage of reaction at 600°C the oxide mixtures of overall composition  $\text{Mn}_{1-x}\text{V}_{2-2x}\text{Mo}_{2x}\text{O}_6$  yield  $2x \text{MnMoO}_4 + 2x \text{V}_2\text{O}_5 + (1 - 3x)\text{MnV}_2\text{O}_6$ . The next reaction step necessarily involves the reaction between these three compounds which leads to the formation of the *MV-20* solid-solution phase. The formation of a solid solution of this particular Mo content, independently of the initial mixture stoichiometry, seems to be due to the particular thermodynamic stability of *MV-20*, which among all possible  $\alpha$ -type solid solutions decomposes at the highest temperature.

The mechanism of the ternary reaction



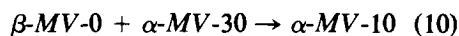
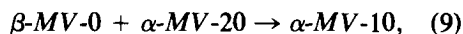
is not quite clear. It could be expected that this reaction will proceed in several binary

steps, the first being a reaction between  $\text{MnMoO}_4$  and  $\text{V}_2\text{O}_5$  or  $\text{MnV}_2\text{O}_6$ . As found in a separate experiment, the reaction

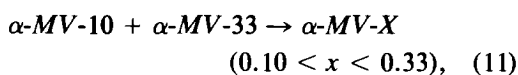


proceeds at 520–600°C, but the *MV-33* phase is not observed in ternary mixtures.  $\text{MnMoO}_4$  and  $\text{MnV}_2\text{O}_6$  could formally react with the formation of *MV-X* (in particular of *MV-20*) with separation of  $\text{Mn}_2\text{O}_3$  or  $\text{Mn}_2\text{V}_2\text{O}_7$  but the progress of this reaction was not observed in binary mixtures, nor were the above-quoted side-products identified in ternary mixtures. It should thus be concluded that reaction (7) may proceed only if all three reactants are simultaneously present in a mixture.

Homogenation reaction of the mixture of *MV-20* and *MV-0* could be expected as the next reaction stage at 600°C resulting in the formation of *MV-X<sub>n</sub>* of the initial mixture stoichiometry. Alternatively for the  $x < 0.10$  region one could envisage the formation of two solid solutions of compositions governed by the thermodynamic equilibrium at 600°C (cf. the phase diagram, Fig. 1). As, however, pure  $\text{MnV}_2\text{O}_6$  is totally converted at 600°C to the high-temperature  $\beta$ -form, the homogenation reactions would require either its phase transformation or decomposition. Apparently the activation energy of this process is too high to be overcome at 600°C. This conclusion seems to be confirmed by independent experiments with binary mixtures which have shown that the reactions



do not proceed at 540–600°C, contrary to another reaction,



in which both reactants show the same  $\alpha$ -structure.

(ii)  $0.20 \leq x \leq 0.33$

The mixtures with compositions richer in Mo than in "MV-20" ( $0.20 \leq x \leq 0.33$ ) yield nominal brannerite solid solutions after heating at 600°C for 40 hr, with one intermediate cooling and grinding.

The first products of incomplete reaction in the mixtures from this range were  $\text{MnMoO}_4$  and  $\text{MnV}_2\text{O}_6$ , an increase in the molybdenum content having the effect of increasing the amount of  $\text{MnMoO}_4$  and decreasing the amount of  $\text{MnV}_2\text{O}_6$ .

In the "MV-20" mixture the consecutive reaction (7) leads to the total consumption of  $\text{MnV}_2\text{O}_6$ ,  $\text{MnMoO}_4$ , and unreacted  $\text{V}_2\text{O}_5$  to the homogeneous MV-20 phase. In the mixtures with  $x > 0.20$  the MV-20 solution formed along the same reaction path reacts further with excess  $\text{MnMoO}_4$  and  $\text{V}_2\text{O}_5$  or with MV-33 preformed according to reaction (8) to produce a homogeneous nominal MV- $X_n$  phase. It is difficult, however, to establish the true reaction mechanism because of the overlapping of the diffraction maxima on X-ray patterns.

#### Ternary Reactions, Stepwise Annealing at 520–600°C

A stepwise annealing procedure was applied for samples with  $x$  ranging from 0.02 to 0.15 for which the preparation under the previously described conditions was unsuccessful. This method consisted in heating the reactant mixtures for 20 hr consecutively at 520 (twice), 540, 560, 580, 600, and 620°C with intermediate grinding between two thermal treatments. The idea was (i) to avoid formation of  $\text{MnV}_2\text{O}_6$  in the early stages of reaction by enhancing the formation of  $\text{MnMoO}_4$  and MV- $X$  (of  $X$  close to  $X_n$ ) at 520°C, and (ii) to accelerate the consecutive reaction of  $\text{MnMoO}_4$  consumption by raising the temperature in the next stages.

Two  $\text{Mn}_2\text{O}_3$  preparations (I) and (II) were used in these experiments. It was expected that due to the weaker reactivity of  $\text{Mn}_2\text{O}_3$ (II) (see Fig. 2) the successive stages of the reaction would be easier to distinguish.

Let us start by describing the behavior of  $\text{Mn}_2\text{O}_3$ (II)-containing mixtures of compositions "MV-15" and "MV-10". After the first stage of annealing (520°C, 40 hr) both samples contained fair amounts of non-reacted  $\text{V}_2\text{O}_5$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{MoO}_3$  accompanied by  $\text{MnMoO}_4$  and small quantities of brannerite-type solid solution with a  $\text{MoO}_3$  concentration considerably exceeding those resulting from the stoichiometry of the mixtures (Fig. 4). On further heating X-ray lines characteristic of initial reactants and  $\text{MnMoO}_4$  decrease in intensity, and the quoted compounds disappear in the following sequence:  $\text{MoO}_3$  (540°C),  $\text{MnMoO}_4$  (560°C),  $\text{Mn}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  (600°C for "MV-15" and 620°C for "MV-10"). At the same time that the content of solid solution increases, it becomes more and more diluted, as can be judged from the shifts of X-ray diffraction lines. The applied procedure

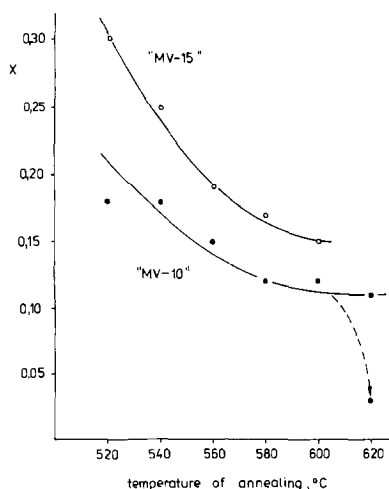
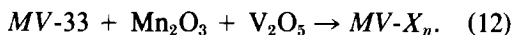


FIG. 4. Changes of  $\text{MoO}_3$  concentration in  $\text{Mn}_{1-x}\text{V}_x\text{V}_{2-x}\text{Mo}_2\text{O}_6$  solid solutions formed on stepwise annealing for 20 hr at temperatures marked on abscissa.

leads to the formation of homogeneous, single-phase *MV*-15. The “*MV*-10” preparation, however, even after calcination at 600°C, contained a small amount of unchanged  $V_2O_5$ . It disappeared completely after the sample was heated at 620°C for 20 hr. An increase, however, of the calcination temperature to 620°C produced—in agreement with the phase diagram—the formation of a small amount of low-doped  $MnV_2O_6$ .

The results presented above show that under present experimental conditions solid solutions are predominantly formed from  $MnMoO_4$  reacting first with  $V_2O_5$  (reaction (8)) to *MV*-33 which is subsequently diluted by  $Mn_2O_3$  and  $V_2O_5$ :



The absence of the direct path (I) may be explained by the much smaller area of  $Mn_2O_3$  surface at which the direct solid-solution formation is supposed to proceed.

A similar stepwise treatment of  $Mn_2O_3$ (I)-containing mixtures of compositions “*MV*-15”, “*MV*-10”, “*MV*-5”, and “*MV*-2” shows faster reaction progress, with only one difference in the mechanism, consisting in the fact that already in the early stages of the reaction some quantities of solid solution of the composition close to the nominal one are formed. After twofold annealing at 600°C for 20 hr the synthesis of *MV*-10 was successful, contrary to the syntheses of *MV*-5 and *MV*-2, for which the temperatures below curve AB in the phase diagram turn out to be insufficient to ensure complete reaction.

## Conclusions

Solid-state reactions which may proceed in mixtures of  $MoO_3$ ,  $Mn_2O_3$ , and  $V_2O_5$  are summarized in Fig. 5. Figure 6 presents a scheme of the reaction zone in this ternary mixture in the early stages of reaction.

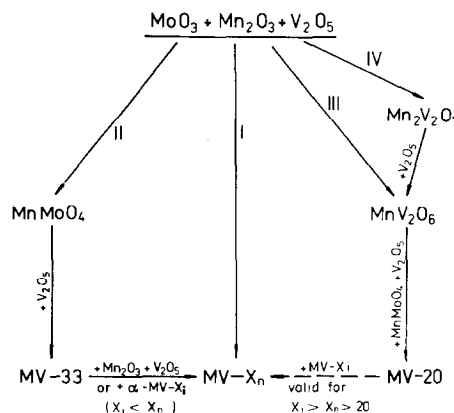


FIG. 5. Reaction pattern in a mixture of  $Mn_2O_3$ ,  $V_2O_5$ , and  $MoO_3$ .

The direct synthesis (path I) of a brannerite-type of solid-solution *MV*- $X$  of a composition very close to the stoichiometry of the initial mixture is possible due to the efficient surface diffusion of  $MoO_3$  and  $V_2O_5$  over  $Mn_2O_3$ . It makes possible the respective ternary molecular contacts indispensable for this reaction. Reaction path I is favored at low temperatures (500–520°C) and at the highly developed  $Mn_2O_3$  surface, as both geometrical and energetic (low activation energy) factors are more advantageous for this reaction than for all others.

However, even under the above-mentioned favorable conditions the formation of a certain amount of  $MnMoO_4$  cannot be avoided (path II).  $MnMoO_4$  reacts further with  $V_2O_5$ , yielding *MV*-33, which can then be diluted with  $Mn_2O_3$  and  $V_2O_5$  (but not with  $MnV_2O_6$  to the nominal *MV*- $X_n$ ). The progress of *MV*-33 synthesis at 520°C, however, is very slow. To accelerate it, a stepwise increase of temperature is advisable to avoid the parallel reaction path III in which weakly reactive  $MnV_2O_6$  could be formed. On stepwise increase of temperature a large conversion to the nominal *MV*- $X_n$ ,  $MnMoO_4$ , and *MV*-33 is reached between 520 and 600°C, the phases obtained protecting the  $Mn_2O_3$  surface against fur-

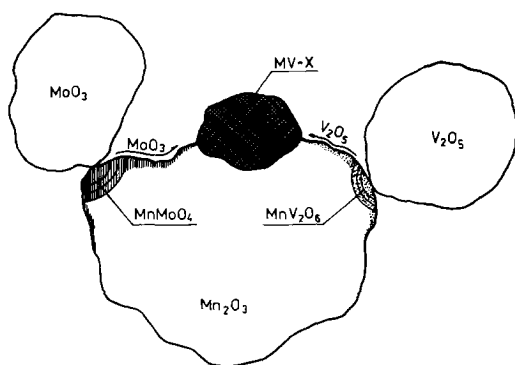


FIG. 6. Scheme of the reaction zone in the early stages of reaction in a mixture of  $\text{Mn}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ , and  $\text{MoO}_3$ .

ther contact with  $\text{V}_2\text{O}_5$  and consumption to  $\text{MnV}_2\text{O}_6$ .

Reaction path III is favored at higher temperatures ( $600^\circ\text{C}$ ).  $\text{MnV}_2\text{O}_6$  formed may be consumed to  $MV-20$  on reacting with  $\text{MnMoO}_4$  and  $\text{V}_2\text{O}_5$ . In the  $\text{MoO}_3$ -rich mixtures ( $x > 0.20$ ) the least reaction leads to total consumption of  $\text{MnV}_2\text{O}_6$  and the  $MV-20$  solution formed may react further with the product of path II to produce a homogeneous nominal  $MV-X_n$  phase. In the  $\text{MoO}_3$ -poor mixtures ( $x < 0.20$ ) the stoichiometry-dependent quantity of  $\text{MnV}_2\text{O}_6$  remains

unreacted and due to the kinetic hindrance it cannot be consumed in any reaction. Thus the equilibration of the mixture is practically impossible.

At  $600^\circ\text{C}$  path IV, in which intermediate formation of  $\text{Mn}_2\text{V}_2\text{O}_7$  is observed may also take place.  $\text{Mn}_2\text{V}_2\text{O}_7$ , however, reacts relatively readily with  $\text{V}_2\text{O}_5$  to form  $\text{MnV}_2\text{O}_6$  and the system returns to path III.

## References

1. R. KOZŁOWSKI, J. ZIÓŁKOWSKI, K. MOCALA, AND J. HABER, *J. Solid State Chem.* **35**, 1 (1980).
2. A. MAGNELI AND B. M. OUGHTON, *Acta Chem. Scand.* **5**, 581 (1951); A. MAGNELI AND B. BLOMBERG, *Acta Chem. Scand.* **5**, 585 (1951); A. BIELAŃSKI, K. DYREK, J. POŻNICZEK, AND E. WENDA, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.* **19**, 507 (1971).
3. T. BAŁK AND J. ZIÓŁKOWSKI, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **20**, 821 (1972); J. HABER AND J. ZIÓŁKOWSKI, in "Proceedings, 7th Int. Symp. on Reactivity of Solids, Bristol, 1972," p. 782.
4. G. M. CLARK AND A. N. PICK, *J. Thermal Anal.* **7**, 289 (1975).
5. J. ZIÓŁKOWSKI AND P. COURTINE, *Ann. Chim.* **8**, 303 (1973).