

## Phase Diagram and Infrared-Spectral Investigation of the $2\text{TeO}_2 \cdot \text{V}_2\text{O}_5 - \text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{TeO}_2$ System

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The phase diagram of the  $2\text{TeO}_2 \cdot \text{V}_2\text{O}_5 - \text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{TeO}_2$  system is studied by X-ray diffraction, ir spectroscopy, and DTA. A new compound with a composition of  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 6\text{TeO}_2$  is established. The ir spectra of the alkaline trivanadates are interpreted. They are considered as structural analogs of the new phase. As a result of this comparison, the postulate is made that the main structural units in the  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 6\text{TeO}_2$  compound are  $\text{V}_2\text{O}_8$  groups, while tellurium is present both in the  $\text{TeO}_3$  and  $\text{TeO}_4$  groups. Contrary to the crystal phases, in glasses the transition from  $\text{VO}_5$  toward  $\text{VO}_4$  does not proceed through the formation of new structural units of vanadium; but rather a gradual transition of the structure is observed with a change in the composition from  $2\text{TeO}_2 \cdot \text{V}_2\text{O}_5$  to  $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{TeO}_2$ .

### Introduction

The crystal phases and glasses of the  $\text{TeO}_2 \cdot \text{V}_2\text{O}_5$  system were studied in earlier works, using infrared (ir) spectra (1) and X-ray analysis (2). The ir spectra were interpreted on the basis of the structure for the  $2\text{TeO}_2 \cdot \text{V}_2\text{O}_5$  ( $T_2V$ ) compound as previously suggested (3). Likewise, with the aid of ir spectra (4), the crystallographic investigations were confirmed (5), according to which the introduction of 50 mole% of  $\text{Na}_2\text{O}$  to a composition of  $T_2V$  led to the formation of the  $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{TeO}_2$  ( $NVT$ ) phase, whereby new structural units of vanadium and tellurium (the  $\text{VO}_4$  and  $\text{TeO}_4$  groups) were formed.

In the present investigation the  $2\text{TeO}_2 \cdot \text{V}_2\text{O}_5 - \text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{TeO}_2$  phase diagram is examined with the aim of checking the transformation of the  $\text{VO}_5$  polyhedra into  $\text{VO}_4$ , and also of  $\text{TeO}_3$  into  $\text{TeO}_4$  with a gradual increase in the  $\text{Na}_2\text{O}$  concen-

tration, in both the crystal phases and the glasses. The system studied is a quasi-binary section of the  $\text{Na}_2\text{O} - \text{V}_2\text{O}_5 - \text{TeO}_2$  three-component system.

The interest in the study of similar systems is continuously growing due to the possibilities they offer for use as lumino-phors and as catalysts in the synthesis of semiconductor glasses the metallurgy of vanadium, etc. (6-9).

### Experimental

The phase diagram is constructed as a result of investigations carried out with DTA, X-ray phase analysis and ir spectroscopy, using two types of specimens: (1) products of a solid-state synthesis of the  $T_2V$  with  $NVT_2$  compounds, taken in corresponding proportions (Fig. 1a), and (2) samples obtained after crystallization of glasses (Fig. 1b).

The pure glasses were obtained by melt-

ing mixtures of  $\text{TeO}_2$  (Merck, 99%),  $\text{V}_2\text{O}_5$  (Reanal, 99.5%) and  $\text{Na}_2\text{CO}_3$  (p.a.) in quartz crucibles at 700–800°C for half an hour. The melts were cooled on a copper plate. Crystallization of the glasses continued for 40–60 hr up to full crystallization at a temperature corresponding to the maximum crystallization rate (380–400°C).

The X-ray data were obtained with an URS 50 IM diffractometer ( $\text{CuK}\alpha$  radiation, Ni filter) on powdered samples, after their thermal treatment. DTA was carried out in quartz crucibles with a Paulik, Paulik, Erday derivatograph at a heating rate of 10°C/min. The ir spectra of the glasses and the crystal phases were taken on a double-beam UR-10 (Karl Zeiss-Jena) spectrophotometer in the range 1400–400  $\text{cm}^{-1}$  (range 1400–700  $\text{cm}^{-1}$ , NaCl prism, and range 700–400  $\text{cm}^{-1}$ , KBr prism). The precision of the location of the absorption peaks was  $\pm 1.5 \text{ cm}^{-1}$  for the crystal samples and  $\pm 3 \text{ cm}^{-1}$  for the glasses. The

samples were photometered as suspensions in Nujol.

## Results and Discussion

### Phase Diagram of the $2\text{TeO}_2 \cdot \text{V}_2\text{O}_5\text{--Na}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 2\text{TeO}_2$ System

A solid-state reaction between  $T_2V$  and  $NVT_2$  is shown with the aid of an X-ray phase analysis and an ir-spectral analysis. X-Ray diffractograms and ir spectra for compositions of the system discussed, thermally treated at 380°C for 15 hr, are presented in Figs. 1a and 2a. The formation of a new phase is established by the peaks at 7.05, 3.41, and 2.99 Å (Fig. 1a) as well as by the absorption mode at 995  $\text{cm}^{-1}$  (Fig. 2a). These characteristics are absent in the diffractograms (Nos. (1) and (8), Fig. 1a) and in the spectra (Nos. (1) and (8), Fig. 2a) of the initial compounds. A single phase is obtained by solid-state reaction only after



FIG. 1. X-Ray diffraction data on compositions in the  $T_2V\text{--}NVT_2$  system. (a) Products prepared by solid-state reaction: (1)  $T_2V$ ; (2)  $90T_2V \cdot 10NVT_2$ ; (3)  $70T_2V \cdot 30NVT_2$ ; (4)  $66.6T_2V \cdot 33.3NVT_2$ ; (5)  $50T_2V \cdot 50NVT_2$ ; (6)  $40T_2V \cdot 60NVT_2$ ; (7)  $20T_2V \cdot 80NVT_2$ ; (8)  $NVT_2$ . (b) Products prepared by crystallization of glasses: (1)  $33.3V_2O_5 \cdot 66.6TeO_2$ ; (2)  $2.5 Na_2O \cdot 32.5V_2O_5 \cdot 65TeO_2$ ; (3)  $7.5Na_2O \cdot 30.8V_2O_5 \cdot 61.7TeO_2$ ; (4)  $10Na_2O \cdot 30V_2O_5 \cdot 60TeO_2$ ; (5)  $12.5Na_2O \cdot 29.2V_2O_5 \cdot 58.3TeO_2$ ; (6)  $15Na_2O \cdot 28.3V_2O_5 \cdot 56.7TeO_2$ ; (7)  $20Na_2O \cdot 26.7V_2O_5 \cdot 53.3TeO_2$ ; (8)  $25Na_2O \cdot 25V_2O_5 \cdot 50TeO_2$ .

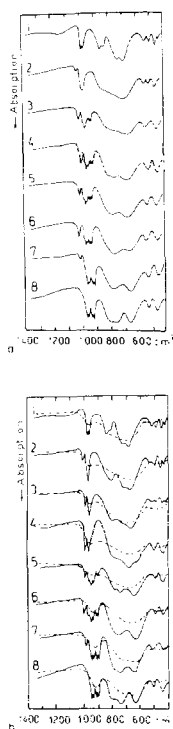


FIG. 2. Infrared spectra of compositions in the  $T_2V-NVT_2$  system: (a) products obtained by a solid-state reaction (the ratio of the components is stated in Fig. 1a). (b) Glasses (---), and their crystal products (—) (the ratio of the components is stated in Fig. 1b).

long-time heat treatment at higher temperature (Table I).

Data on the new phase may be even more distinctly illustrated by X-ray data (Fig. 1b) and ir spectra (Fig. 2b) of samples of the same compositions obtained by crystallization of pure glasses, because the reaction proceeds to completion more rapidly in this case.

To plot the liquidus curve of the system and the area of primary crystallization, DTA data are used (Fig. 3). In this investigation, preference is given to the results from DTA heating runs of previously crystallized glasses. In accordance with the results obtained, two eutectic temperatures at 430 and 445°C, having eutectic composi-

TABLE I  
INTERPLANAR  
SPACINGS  $d$  AND  
RELATIVE INTENSITIES  
OF  
 $Na_2O \cdot 3V_2O_5 \cdot 6TeO_2$   
( $NV_3T_6$ )

$d_{obs}$ (Å)	$I/I_0$
7,05	50
3,52	72
3,41	75
3,11	90
2,99	100
2,41	30
2,35	25
1,87	50

tions 30 mole% of  $NVT_2$  and 60 mole% of  $NVT_2$  are present in the phase diagram (Fig. 4). The distecticum between them ( $450 \pm 5^\circ C$ ) determines the most possible composition of the newly obtained congruent melting compound which possesses a molar ratio  $Na_2O : V_2O_5 : TeO_2 = 1 : 3 : 6$ , i.e.,  $Na_2O \cdot 3V_2O_5 \cdot 6TeO_2$  ( $NV_3T_6$ ).

In accordance with the conventional concepts of the physicochemical analysis (10), the flattened distecticum is an indication

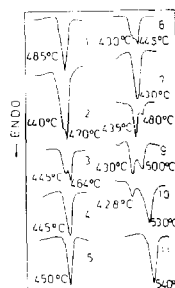


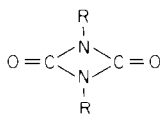
FIG. 3. DTA of crystallized glasses, having the following compositions: (1)  $33.3V_2O_5 \cdot 66.6TeO_2$ ; (2)  $2.5Na_2O \cdot 32.5V_2O_5 \cdot 65TeO_2$ ; (3)  $5Na_2O \cdot 31.7V_2O_5 \cdot 63.3TeO_2$ ; (4)  $7.5Na_2O \cdot 30.8V_2O_5 \cdot 61.7TeO_2$ ; (5)  $10Na_2O \cdot 30V_2O_5 \cdot 60TeO_2$ ; (6)  $12.5Na_2O \cdot 29.2V_2O_5 \cdot 58.3TeO_2$ ; (7)  $15Na_2O \cdot 28.3V_2O_5 \cdot 56.7TeO_2$ ; (8)  $17.5Na_2O \cdot 27.5V_2O_5 \cdot 55TeO_2$ ; (9)  $20Na_2O \cdot 26.7V_2O_5 \cdot 53.3TeO_2$ ; (10)  $22.5Na_2O \cdot 25.8V_2O_5 \cdot 51.7TeO_2$ ; (11)  $25Na_2O \cdot 25V_2O_5 \cdot 50TeO_2$ .



TABLE II  
LENGTH OF THE NONBRIDGING V-O BONDS (12)  
AND THE CHARACTERISTIC IR FREQUENCIES IN THE  
RANGE 1015-970 cm<sup>-1</sup> IN ALKALINE TRIVANADATES

Compound	Length of the V-O nonbridging bonds (Å)		V-O Stretching mode (cm <sup>-1</sup> )	
	in V <sub>2</sub> O <sub>8</sub> group	in VO <sub>5</sub> group		
KV <sub>3</sub> O <sub>8</sub>	2 × 1.58	1.58	975	1015
RbV <sub>3</sub> O <sub>8</sub>	—	—	975	1007
CsV <sub>3</sub> O <sub>8</sub>	2 × 1.58	1.62	970	1003

tated in opposite directions (Fig. 6b). In such a case, an interaction among their stretching modes should be expected and the high-frequency one ( $\nu_s$ ) would be inactive in an ir spectrum. A similar situation is observed, for example, in the case of dimer isocyanates of the



type (13). On the basis of this treatment, the following empirical assignment is made of the bands in the spectra of alkaline trivanadates in the range 1020-900 cm<sup>-1</sup>. The ir active antisymmetrical stretching vibration ( $\nu_{as}$ ) of the interacting isolated V-O bonds of the V<sub>2</sub>O<sub>8</sub> groups determines the band at 975-900 cm<sup>-1</sup>, while the absorption band in the range 1015-1000 cm<sup>-1</sup> corresponds to the third nonbridging bond. The systematic decrease in the latter band in the K, Rb, and Cs trivanadates (Table II) corresponds to the bond lengthening in the same order from 1.55 to 1.63 Å. The interpretation suggested is the most probable one since it is the only one with which the ir spectrum of KV<sub>3</sub>O<sub>8</sub> may be explained. The three nonbridging bonds in this compound have equal lengths, yet in spite of this, two bands are observed (Table II). Another

thing that is typical of the ir spectra of alkaline trivanadates is the fact that they do not possess a band at 830 cm<sup>-1</sup>, which corresponds to the antisymmetrical stretching vibrations of the V-O-V bond. This band is observed in vanadates with bonding of the vanadium-oxygen polyhedra by corners, i.e., in the formation of -V-O-V-chains as, for instance, in the alkaline metavanadates (14). The band discussed is found in the ir spectra of T<sub>2</sub>V (1) and is absent in the NVT<sub>2</sub> compound, which has V-O-Te bonds (4). It is also not seen in the spectrum of the NV<sub>3</sub>T<sub>6</sub> compound (Fig. 5.3). This signifies that there exist no oxygen bridges between the vanadate polyhedra in the new compound. Instead, a band at 790 cm<sup>-1</sup>, typical of the V-O-Te bonds (4) is present in NV<sub>3</sub>T<sub>6</sub> (Fig. 5.3). Comparison of these data shows that the introduction of Na<sub>2</sub>O into T<sub>2</sub>V leads to breaking of V-O chains, whereby the vanadium-oxygen polyhedra get such an orientation that they form V<sub>2</sub>O<sub>8</sub> complexes. This is also justified by the similarity in the spectra of NV<sub>3</sub>T<sub>6</sub> and of the alkaline trivanadates above 950 cm<sup>-1</sup>. However, in contrast to them, in this case the bonding of the V<sub>2</sub>O<sub>8</sub> groups is achieved through the Te-O-Te bridges. Hence, only one type of nonbridging V-O bond (of the V<sub>2</sub>O<sub>8</sub> groups) exists in NV<sub>3</sub>T<sub>6</sub>. The bands at 995 and 960 cm<sup>-1</sup> correspond to the symmetric and antisymmetric stretching modes of the interacting isolated bonds, respectively. The fact that in the NV<sub>3</sub>T<sub>6</sub> spectrum  $\nu_s$  and  $\nu_{as}$  are active may be explained by the lower symmetry of the V<sub>2</sub>O<sub>8</sub> complex. Moreover, the band for  $\nu_{as}$  at 960 cm<sup>-1</sup> is more intense.

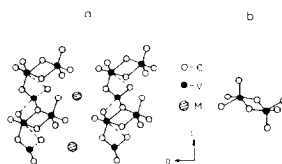


FIG. 6. Structure of MV<sub>3</sub>O<sub>8</sub> (12).

which is an additional indication for the ring-like nature of the  $V_2O_8$  groups. A similar behavior of the intensities of the two bands is typical for the cyclic anhydrides and imides (13), where the interacting carbonyl groups are found, also in a 1:3 position.

The structural analogy suggested is supported also by the similar stoichiometric ratio  $M_2O/V_2O_5$  in trivanadates and the  $Na_2O \cdot 3V_2O_5 \cdot 6TeO_2$ .

#### Infrared Spectra of Glasses

The discussion on glass structures is based on the comparison of their spectra (Fig. 2b) with those of the crystal phases. The vibration area of the isolated V–O groups is particularly sensitive to structural changes. The vitreous  $T_2V$  has in this interval a band at  $975\text{ cm}^{-1}$ —the stretching mode of the isolated V–O bond of the  $VO_5$  polyhedra (1). The  $VO_2$  group of  $NVT_2$  is characterized by a broad absorption band at  $920\text{ cm}^{-1}$  (4).

The ir spectra of the glasses in the system discussed possess a weak band near  $500\text{ cm}^{-1}$ , a broad band with a maximum between  $670$  and  $630\text{ cm}^{-1}$ , and a single band between  $975$ – $920\text{ cm}^{-1}$ , which shifts its position depending on the composition (Fig. 2b). The increase in the alkaline oxide content leads to a decrease in the intensity of the mode in the area  $850$ – $800\text{ cm}^{-1}$ .

The comparison of the spectra of the glasses with those of the two end-member crystalline phases in the system indicates that the vitreous state is achieved by a continuous transition from a structure typical of  $T_2V$  toward  $NVT_2$ .

The spectrum of a glass corresponding to the  $NV_3T_6$  stoichiometric composition differs from that of the corresponding crystal phase (No. (4), Fig. 2b). The bands at  $995$  and  $965\text{ cm}^{-1}$  are absent, while another band appears at  $950\text{ cm}^{-1}$ . This indicates that there exists a difference in the short-range order in the two phases, which is

confirmed also by the rounded course of the liquidus line near the compound (Fig. 4).

#### Conclusions

The ir spectra of the crystalline phases in the  $2TeO_2 \cdot V_2O_5$ – $Na_2O \cdot V_2O_5 \cdot 2TeO_2$  system show that  $Na_2O$  gives rise to a transformation of the  $VO_5$  groups ( $T_2V$ ) into  $VO_4$  polyhedra ( $NVT_2$ ) by the formation of  $V_2O_8$  complexes, typical of the new  $NV_3T_6$  phase. This transition requires the destruction of the V–O–V chains in  $T_2V$  (Fig. 7a), whereby new transverse chains are formed by bonding of the Te–O–Te bridges with the aid of V–O–Te bonds (Fig. 7b). What is typical of this case is the fact that the influence of the alkaline ions is reduced to a breaking of the relatively shorter V–O bridge bonds ( $1.95\text{ \AA}$ ), while the Te–O–Te transverse bridges ( $3.84\text{ \AA}$ ) are preserved. Moreover, the  $VO_5 \rightarrow VO_4$  transition is achieved in a complicated manner (through  $V_2O_8$  groups). A similar situation is observed in the transition  $V_2O_5 \rightarrow$  alkaline metavanadates. In this case the intermediate  $V_2O_8$  complexes are formed at the trivanadates.

The increase in the amount of the alkaline oxide in the  $T_2V$ – $NVT_2$  system causes a gradual transition of  $TeO_3$  into  $TeO_4$  complexes. This is established by the decrease in the intensity of the band at  $670\text{ cm}^{-1}$  and the appearance of a new band at  $630\text{ cm}^{-1}$  in the spectrum of  $NV_3T_6$  (Fig. 5.3). The first of these absorption peaks is characteristic of the  $T_2V$  compound (Fig. 5.1), where Te is

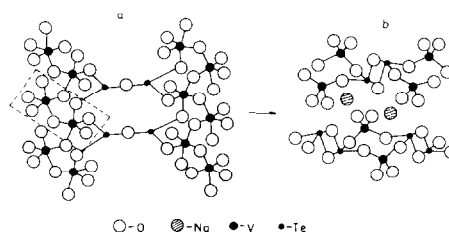


FIG. 7. Scheme of the  $T_2V$ – $NVT_2$  structural transition.

essentially three-coordinated in relation to oxygen (3), and the second of  $NVT_2$  (Fig. 5.2), where Te is four-coordinated (5). It is clear from these results that a part of the TeO<sub>3</sub> groups have been transformed into TeO<sub>4</sub> polyhedra in the new phase.

In contrast to the crystals, the VO<sub>5</sub> → VO<sub>4</sub> transition is achieved without the formation of complex vanadate units in the glasses. Due to the irregular distribution of the atoms in the glass structure, the Na ions can take positions that are more symmetrical among the other structural units. It follows from the ir spectra that with the increase in Na<sub>2</sub>O the isolated V-O bonds gradually become longer, the V-O-V bridges disappear, and the VO polyhedra become more symmetrical and, as a result, are transformed into VO<sub>4</sub> groups.

The existence of V<sub>2</sub>O<sub>8</sub> groups in the new phase has been suggested on the basis of the existing analogy with the ir spectra of the polyvanadates, whose structure is known. It is obvious that this indirect conclusion is under discussion and can finally be confirmed only by crystallographic investigation. However, the more generally accepted claim that the  $T_2V \rightarrow NVT_2$  transition passes through the formation of intermediate new groups of vanadium is beyond any doubt, because only in such a manner can the higher vibration modes observed in  $NV_3T_6$  as well as the shorter nonbridging V-O bonds, in comparison with the initial compounds, be explained. If it is assumed that sodium ions only break up bonds or electrostatically affect them without forming new complexes, this would mean that the V-O bonds gradually become longer

and the corresponding stretching vibrations should gradually decrease with the increase in the amount of Na<sub>2</sub>O. As has already been stated above, a similar transformation of the vanadium polyhedra is observed in the glasses of the system examined.

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