# SYNTHESIS AND PROPERTIES OF FeNb<sub>11</sub>O<sub>29</sub>

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Using the XRD method a comparative study was performed on the synthesis reaction course for the FeNb<sub>11</sub>O<sub>29</sub> phase taking as reactants the mixtures of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and T-Nb<sub>2</sub>O<sub>5</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and H-Nb<sub>2</sub>O<sub>5</sub>, FeNbO<sub>4</sub> and T-Nb<sub>2</sub>O<sub>5</sub> or FeNb<sub>49</sub>O<sub>124</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The above synthesis was also carried out by a solution method with the use of Fe(NO<sub>3</sub>)<sub>3</sub> and ammonium niobium(V) oxalate solutions. It has been shown that independently of the kind of the used reacting substances an intermediate product of reaction or a product of a parallel reaction is FeNbO<sub>4</sub>. The optimal method of synthesis with the use of solid reactants relies on the calcination of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/T-Nb<sub>2</sub>O<sub>5</sub> mixture at 1000°C. The synthesis of FeNb11O<sub>29</sub> by the solution method enables preparation of the pure product at 950°C. Independently of the starting substances, the monoclinic modification of FeNb<sub>11</sub>O<sub>29</sub> is formed which at 1250°C undergoes a polymorphic transformation into the orthorhombic modification. The IR spectra recorded for both polymorphs of FeNb<sub>11</sub>O<sub>29</sub> and H-Nb<sub>2</sub>O<sub>5</sub>, belonging to block-structure phases, in comparison to the spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and FeNbO<sub>4</sub> contain additional absorption bands in the wavenumber range 1100-850 cm<sup>-1</sup>. They are most probably due to stretching vibrations within octahedra containing very short M-O bonds, characteristic for the block-structure phases.

### INTRODUCTION

Phases of crystallographic double shear are formed in multicomponent systems comprising the oxides of niobium, vanadium, molybdenum and tungsten [1-14]. The occurrence in their crystal structures of ReO<sub>3</sub>-type blocks built from corner-sharing octahedra of the dimensions  $n \times m \times \infty$ , limited in two dimensions  $(n \times m)$ as a result of the presence of shear planes and unlimited in the third dimension, can cause a distinctly marked anisotropy of physical properties. The few hitherto performed investigations dealing with this subject and concerning the thermal expansion of these phases seem to fully corroborate this supposition [1,2]. A special attention is deserved by the fact that in the case of the compounds Nb<sub>14</sub>Mo<sub>3</sub>O<sub>44</sub> and Nb<sub>12</sub>MoO<sub>33</sub> [2] the determined coefficients of thermal expansion in the direction concordant with the direction in which the blocks  $n \times m \times$  $\times \infty$  spread to infinity possessed seldom occurring negative values. This makes the phases of block structures an especially interesting subject of research.

The literature review has shown that in the systems  $MO - Nb_2O_5$  (M=Mg, Ni, Zn),  $M_2O_3 - Nb_2O_5$  (M=Al, Ga, Cr, Fe) and  $MO_2 - Nb_2O_5$  (M=Ti, Nb) some phases of the general formula  $M_xNb_{12-x}O_{29}$  are formed [3-14]. Their characteristic feature is dimorphism, the known polymorphs being monoclinic ones isostructural with monoclinic modification of  $Nb_{12}O_{29}$  [3] as well as orthorhombic ones isostructural with orthorhombic modification of  $Nb_{12}O_{29}$  [4].

Both the phases of monoclinic and orthorhombic structure belong to the double shear type. In their structures the ReO<sub>3</sub>-type blocks occur, with their dimensions of  $n \times m \times \infty$ . The blocks neighbouring with each other share common edges, half of them at the level y = 0 and the other half at the level y = 0.5. The monoclinic phases (figure 1) differ from the orthorhombic phases (figure 2) by the manner of linking the  $n \times m \times \infty$  blocks at the individual levels.

The  $M_xNb_{12-x}O_{29}$  phases are most frequently obtained by chemical transport or solid-state reactions between the corresponding oxides  $M_xO_y$  and  $Nb_2O_5$  in the temperature range 1200-1450°C [3-14].

The aim of the presented work was searching for some alternative synthesis methods for double shear phases that would allow their preparation at significantly lower temperatures and during much shorter time as well as learning the mechanism of their formation. As a model the synthesis reaction of FeNb<sub>11</sub>O<sub>29</sub> was selected. This compound was obtained by performing the reactions between FeNbO<sub>4</sub> and T-Nb<sub>2</sub>O<sub>5</sub> as well as between FeNb<sub>49</sub>O<sub>124</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The synthesis of FeNb<sub>11</sub>O<sub>29</sub> was carried out also by the solution method using solutions of Fe(NO<sub>3</sub>)<sub>3</sub> and ammonium niobium(V) oxalate. For the exemplary synthesis reaction of FeNb<sub>11</sub>O<sub>29</sub> a comparison was also made as to the reactivity of T-Nb<sub>2</sub>O<sub>5</sub> and H-Nb<sub>2</sub>O<sub>5</sub> towards  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Considering the fact that

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the block-structure phases have not been so far a subject of thorough IR investigations, it has been recorded in the frames of this work the IR spectra of the monoclinic and the orthorhombic polymorph of  $FeNb_{11}O_{29}$ . and undertaken an attempt to interpret them.

### **EXPERIMENTAL**

The reactants used for the synthesis of the phases FeNb<sub>11</sub>O<sub>29</sub>, FeNbO<sub>4</sub> and FeNb<sub>49</sub>O<sub>124</sub> were  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> a.p. (POCH, Gliwice, Poland) and T-Nb<sub>2</sub>O<sub>5</sub> (the orthorhombic polymorph) 99.9% (Aldrich, Germany), and in the case of FeNb<sub>11</sub>O<sub>29</sub> also H-Nb<sub>2</sub>O<sub>5</sub> (monoclinic polymorph) obtained from T-Nb<sub>2</sub>O<sub>5</sub> by calcination at 1300°C for 1 hour. In the solution method the reactants were Fe(NO<sub>3</sub>)<sub>3</sub> 9H<sub>2</sub>O a.p. (POCH Gliwce, Poland) and ammonium niobium(V) oxalate 99.99% (Aldrich, Germany). In the case of solid-state reactions the components weighed in appropriate proportions were ground in an agate mortar and next calcined under preset conditions in the atmosphere of air in a resistance furnace. After each calcination cycle the contents of the preparations were determined by XRD method. FeNbO4 was obtained by calcination of the mixture of oxides at 1200°C for 4 hours and FeNb<sub>49</sub>O<sub>124</sub> at 1100°C for 12 hours, at 1200°C for 4 hours and next at 1300°C for 16 hours and at 1350°C for 4 hours. The investigations aimed at comparing the reactivity of T-Nb<sub>2</sub>O<sub>5</sub> and H-Nb<sub>2</sub>O<sub>5</sub> towards  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as well as at learning the reaction mechanism were conducted by calcination of the mixtures of appropriate reactants at 600, 650, 700, 750, 800, 850, 900 and 1000°C for 24 hours, at 1100°C for 12 hours, whereas at 1200, 1250 and 1300°C in cycles lasting 1 or 4 hours.

For the preparation of FeNb<sub>11</sub>O<sub>29</sub> by the solution method two solutions were prepared. In 100 cm<sup>3</sup> of distilled water 6.7176 g of ammonium niobium(V) oxalate were dissolved and in 50 cm<sup>3</sup> of water - 0.5243 g Fe(NO<sub>3</sub>)<sub>3</sub> \* 9H<sub>2</sub>O. Next into the solution of ammonium niobium(V) oxalate the solution of Fe(NO<sub>3</sub>)<sub>3</sub> was slowly poured at energetic stirring. Such obtained clear solution of a greenish colour and pH = 1 was evaporated to dryness at 60°C on an electric heating plate. The yellow precipitate obtained after evaporation was calcined at 400°C and 600°C in 30-min cycles and next at 600, 650, 700, 750, 800, 850, 900, and 950°C in 24-hour cycles.

The IR spectra were recorded in the wave-number range of 1500-250 cm<sup>-1</sup> by Specord M80 (Carl Zeiss, Jena, Germany). A technique of pressing pellets with KBr at a mass ratio of 1:300 was applied.



Figure 1. Projection of the monoclinic polymorph of  $Nb_{12}O_{29}$  structure onto XZ plane [3].



Figure 2. Projection of the orthorhombic polymorph of  $Nb_{12}O_{29}$  structure onto XZ plane [4].

For the TG measurements between 20 and 1000°C, a Paulik-Erdey derivatograph (MOM, Budapest, Hungary) was used. 500 mg samples were placed in quartz crucible and heated in air at a rate of 10°C/min.

The powder diffraction patterns of obtained samples were registered with the aid of the diffractometer DRON-3 (Bourevestnik, Sankt Petersburg, using the radiation CoK $\alpha$ /Fe.

### **RESULTS AND DISCUSSION**

The research was begun by comparing the reactivity of T-Nb<sub>2</sub>O<sub>5</sub> and H-Nb<sub>2</sub>O<sub>5</sub> towards  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Such a comparison seems to be very interesting because of the fact that both these polymorphs of niobium(V) oxide differ significantly by their structure. The modification H-Nb<sub>2</sub>O<sub>5</sub> belongs to the double shear type of phases and contains in its structure the ReO<sub>3</sub>-type blocks of the dimensions  $3\times4\times\infty$  and  $3\times5\times\infty$ [15]. On the other hand, T-Nb<sub>2</sub>O<sub>5</sub> does not belong to the block-structure phases. It is built up from corner-sharing and edge-sharing octahedra of NbO<sub>6</sub> and pentagonal bipyramids of NbO<sub>7</sub>. In structural voids occurring among such connected polyhedra the remaining niobium ions are randomly distributed having 9 oxygen ions in their direct environment. [16].

In the case of the FeNb<sub>11</sub>O<sub>29</sub> phase synthesis with the use of H-Nb<sub>2</sub>O<sub>5</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> the analysis of diffraction patterns recorded on subsequent stages of synthesis showed that only after the calcination at 850°C the diffractogram revealed beside the reflections due to initial oxides also some new reflections of weak intensity, characteristic for FeNbO<sub>4</sub>. After the calcination stage at 900°C their intensity significantly increased, which was accompanied however by an appearance of low-intensity reflections characteristic for FeNb<sub>11</sub>O<sub>29</sub> as well as by a distinct decrease in intensity of the reflections characteristic for H-Nb<sub>2</sub>O<sub>5</sub>. After subsequent calcination stages at 950 and 1000°C the intensity of the reflections characteristic for H-Nb<sub>2</sub>O<sub>5</sub> and FeNbO<sub>4</sub> gradually decreased, while that of FeNb<sub>11</sub>O<sub>29</sub> distinctly increased. The diffractogram of the preparation obtained after calcination for 12 hours at 1100°C revealed a set of diffraction lines characteristic only for the monoclinic polymorph of FeNb<sub>11</sub>O<sub>29</sub>. This diffraction pattern was indexed by means of the program REFINEMENT. The parameters of its monoclinic unit cell of A type are the following: a = 31.183(3) A, b = 3.8280(7) A, c = 20.614(3) A,  $\beta = 113.04(2)^{\circ}$ . Two subsequent stages of heating at 1200°C for 4 hours did not cause any significant change of the diffraction pattern. However, as a result of heating the preparation at 1250°C for 4 hours the orthorhombic polymorph of FeNb<sub>11</sub>O<sub>29</sub> was obtained. Further heating at 1250 and 1300°C did not cause any change of the diffraction pattern. This diffractogram was indexed and the parameters of the orthorhombic A-centered unit cell are the following: a = 28.684(4) Å, b = 3.8240(9) Å and c = 20.607(3) Å. Heating such obtained orthorhombic polymorph of FeNb<sub>11</sub>O<sub>29</sub> at 1200°C and 1000°C did not change the diffraction pattern of the preparation. Thus it can be said that the polymorphic transformation of the monoclinic modification into the orthorhombic one is irreversible. Figure 3 presents a selected angular range of the powder diffractograms of the monoclinic (curve a) and orthorhombic polymorph (curve b). A comparative analysis of these diffractograms indicates their very close similarity resulting from an undoubted structural similarity of the two phases. The occurrence of the polymorphic transformation is accompanied by an appearance in the diffractogram of the reflections (104), (111), (106) and (711) (curve b) the presence of which allows an unambiguous identification of the orthorhombic polymorph.

Analysis of the diffraction patterns of the reaction mixture containing T-Nb<sub>2</sub>O<sub>5</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> taken after subsequent heating stages showed that already after heating at 800°C the intensity of the reflections characteristic for the initial oxides decreased a little, which was accompanied by an appearance of very low-intensity reflections characteristic for FeNb<sub>11</sub>O<sub>29</sub> and FeNbO<sub>4</sub>. In turn, after heating at 850°C the intensity of the reflections characteristic for T-Nb<sub>2</sub>O<sub>5</sub> and α-Fe<sub>2</sub>O<sub>3</sub> significantly decreased, while that of FeNb<sub>11</sub>O<sub>29</sub> and FeNbO<sub>4</sub> increased. The intensity of the reflections characteristic for FeNb<sub>11</sub>O<sub>29</sub> was much bigger than that of FeNbO<sub>4</sub>. After the subsequent heating stages at 900 and 950°C the intensity of the FeNb<sub>11</sub>O<sub>29</sub> reflections distinctly increased, while that of FeNbO4 decreased. A pure monoclinic phase of FeNb<sub>11</sub>O<sub>29</sub> was obtained after heating at 1000°C. The next heating stages at 1100 and 1200°C did not cause a significant change of the diffraction pattern. In turn, after heating at 1250°C for 4 hours the pure orthorhombic FeNb<sub>11</sub>O<sub>29</sub> was obtained. The diffraction patterns of the monoclinic and orthorhombic



Figure 3. 3. Powder diffraction patterns of monoclinic polymorph of  $FeNb_{11}O_{29}$  (curve a) and orthorhombic (curve b).

FeNb<sub>11</sub>O<sub>29</sub> obtained with the use of T-Nb<sub>2</sub>O<sub>5</sub> were identical with those recorded after the synthesis using H-Nb<sub>2</sub>O<sub>5</sub>. The conducted comparative research on the reactivity of H-Nb<sub>2</sub>O<sub>5</sub> and T-Nb<sub>2</sub>O<sub>5</sub> towards  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has shown that the synthesis of monoclinic FeNb<sub>11</sub>O<sub>29</sub> is possible with the use of T-Nb<sub>2</sub>O<sub>5</sub> already at 1000°C, while with the use of H-Nb<sub>2</sub>O<sub>5</sub> it requires a temperature by 100°C higher. At the same time, this temperature is by 150°C lower than that given in literature concerning the synthesis of this phase [13]. Moreover, independently of the kind of the used reactants the intermediate product of the reaction is FeNbO<sub>4</sub> and the monoclinicto-orthorhombic transformation begins at 1250°C.

During the attempts to optimise the synthesis conditions for monoclinic FeNb<sub>11</sub>O<sub>29</sub> a mixture of T-Nb<sub>2</sub>O<sub>5</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> weighed at appropriate proportions was heated at 1000°C in 4-hour cycles, it being shown in previous experiments that at this temperature a completion of the reaction was achieved. The conducted investigations showed that the pure monoclinic FeNb<sub>11</sub>O<sub>29</sub> can be obtained already after the second heating cycle at 1000°C. In order to optimise in turn the preparation conditions for orthorhombic FeNb<sub>11</sub>O<sub>29</sub>, a previously obtained at 1000°C preparation of monoclinic FeNb<sub>11</sub>O<sub>29</sub> was next heated in 4-hour cycles at 1050, 1100, 1150, 1200 and 1250°C. A preparation containing the orthorhombic FeNb<sub>11</sub>O<sub>29</sub> was obtained only after the heating stage at 1250°C, which additionally corroborates the correctness of the earlier determined temperature of the monoclinic-to-orthorhombic transformation. Because an intermediate product in the synthesis reaction of FeNb<sub>11</sub>O<sub>29</sub> is FeNbO<sub>4</sub>, an attempt was undertaken to synthesize FeNb<sub>11</sub>O<sub>29</sub> with the use of FeNbO<sub>4</sub> and T-Nb<sub>2</sub>O<sub>5</sub> according to the total equation:

## $FeNbO_4 + 5 Nb_2O_5 = FeNb_{11}O_{29}$

The performed investigations showed that the diffraction pattern of the reacting mixture underwent a distinct change at 850°C. At this temperature a polymorphic transformation begins as a result of which T-Nb<sub>2</sub>O<sub>5</sub> transforms initially into a mixture of M-Nb<sub>2</sub>O<sub>5</sub> and H- $Nb_2O_5[17,18]$ , whereas the amount of FeNbO<sub>4</sub> does not change. Only after the heating cycle at 900°C the diffractogram reveals the presence of very low-intensity reflections characteristic for FeNb<sub>11</sub>O<sub>29</sub>, which is accompanied by an increase in intensity of the reflections belonging to the H-Nb<sub>2</sub>O<sub>5</sub> set and only a slight decrease of reflections intesities ascribed to M-Nb<sub>2</sub>O<sub>5</sub> and FeNbO<sub>4</sub>. This tendency continues until the heating at 1100°C inclusive after which the diffractogram contains the reflections characteristic for FeNb<sub>11</sub>O<sub>29</sub>, FeNbO<sub>4</sub> and H-Nb<sub>2</sub>O<sub>5</sub>. The pure monoclinic FeNb<sub>11</sub>O<sub>29</sub> was obtained only after 16 hours of calcination at 1200°C.

The carried out investigations have thus shown that the synthesis process with the use of  $FeNbO_4$  occurs much more slowly and has a much more complex course than in the previous cases. Most probably this is due to the presence of a large amount of FeNbO<sub>4</sub> in the reacting mixture. A slow course of the reaction between FeNbO<sub>4</sub> and Nb<sub>2</sub>O<sub>5</sub> also suggests that in the reacting mixtures containing the oxides at temperatures of 800-900C order of magnitude some parallel reactions occur leading to FeNbO<sub>4</sub> and FeNb<sub>11</sub>O<sub>29</sub>. The application of T-Nb<sub>2</sub>O<sub>5</sub> creates more advantageous conditions for the reaction course towards the formation of FeNb<sub>11</sub>O<sub>29</sub>. Thanks to a smaller amount of FeNbO<sub>4</sub> being formed in the initial reaction stage, the reaction between T-Nb<sub>2</sub>O<sub>5</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>+</sub> leads much more quickly to obtaining a monophase preparation of FeNb<sub>11</sub>O<sub>29</sub>.

In the reacting mixtures of none of the hitherto described reactions after any stage the phase FeNb<sub>49</sub>O<sub>124</sub>  $(M_xNb_{25-x}O_{62})$  was ever identified, the phase that beside  $FeNbO_4$  and  $FeNb_{11}O_{29}$  is formed in the system  $Fe_2O_3$  -- Nb<sub>2</sub>O<sub>5</sub>. Certain light is shed upon this fact by the course of the synthesis process of FeNb<sub>49</sub>O<sub>124</sub>. This phase was obtained within the frames of this work by using FeNb<sub>11</sub>O<sub>29</sub> and T-Nb<sub>2</sub>O<sub>5</sub> as the reactants. The phase FeNb<sub>49</sub>O<sub>124</sub> appeared in the reacting mixture only after heating at 1200°C and in a pure state it was obtained at 1350°C. Thus its obtaining requires applying much higher temperatures of synthesis. However, there exists a possibility that the compound FeNb<sub>49</sub>O<sub>124</sub> being formed in the reacting mixtures enters into a quick reaction forming FeNbO<sub>4</sub> or FeNb<sub>11</sub>O<sub>29</sub>. In order to verify this opinion an attempt was undertaken to synthesize the phase FeNb<sub>11</sub>O<sub>29</sub> with the use of FeNb<sub>49</sub>O<sub>124</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as reactants, according to the overall reaction:

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$$\text{FeNb}_{49}\text{O}_{124} + 19\text{Fe}_2\text{O}_3 = 49 \text{ FeNb}_{11}\text{O}_{29}$$

Analysis of the diffraction patterns obtained after subsequent stages of synthesis showed that the reaction between FeNb<sub>49</sub>O<sub>124</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> starts already at 850°C, however its rate is in these conditions very small. In the diffractogram after this calcination stage a set of low-intensity diffraction reflections was recorded, characteristic for FeNbO4, as well as a set of high-intensity reflections belonging to the non-reacted FeNb<sub>49</sub>O<sub>124</sub>. Small amounts of  $FeNb_{11}O_{29}$  appeared in the reacting mixture only after the calcination stage at 900°C, which was accompanied by a slight decrease of intensities of the diffraction reflections characteristic for  $FeNbO_4$  and FeNb<sub>49</sub>O<sub>124</sub>. After subsequent calcination stages the intensities of the reflections characteristic for FeNbO<sub>4</sub> and FeNb49O124 gradually decreased, while those of FeNb<sub>11</sub>O<sub>29</sub> increased. The pure monoclinic FeNb<sub>11</sub>O<sub>29</sub> was obtained after the calcination stage at 1200°C. The conducted research seems to indicate that the stage at which the FeNb<sub>49</sub>O<sub>124</sub> phase as intermediate is formed does not occur in the synthesis process of  $FeNb_{11}O_{29}$ .

The synthesis of  $FeNb_{11}O_{29}$  was performed also by the solution method with the use of  $Fe(NO_3)_3$  and ammonium niobium(V) oxalate solutions. In order to determine the calcination conditions, the solid yellow product obtained after water evaporation to dryness was

subjected to TG investigation. The TG curve has a complex shape. A series of processes quickly following one another, accompanied by a considerable mass loss, begins at 80°C and ends at 400°C. This stage is most probably due to the decomposition of organic precursor [10,18]. In the diffractogram of the calcination product obtained at 400°C after 30 minutes (figure 4, curve a) no diffraction reflections were recorded, which is an evidence of its amorphous state. At 550°C a subsequent process begins, associated with a mass loss, that ends at 620°C. In the TG curve above 620°C no further measurable mass losses were recorded. In the diffractogram of preparation heated at 600°C for 30 minutes a set of diffraction reflections was recorded corresponding to the polymorph TT-Nb<sub>2</sub>O<sub>5</sub> [18-20] (figure 5, curve b). Thus it can be supposed that at this stage of the process a solid solution of Fe<sup>3+</sup> in TT-Nb<sub>2</sub>O<sub>5</sub> is formed. One can not exclude however that iron ions may initially be present in the form of amorphous solid not detectable by XRD. Subsequent stages of calcination at 600, 650 and



Figure 4. Powder diffraction patterns of products obtained after selected stages of the  $FeNb_{11}O_{29}$  synthesis using solution method: a - amorphous product after heating at 400°C (1 h; b - solid solutions of  $Fe^{3+}$  ions in the TT-Nb<sub>2</sub>O<sub>5</sub> after additional heating at 600°C (30 min.); c - solid solutions of Fe<sub>3</sub> in the T-Nb<sub>2</sub>O<sub>5</sub> after heating at 700°C (24 h); d - mixture of T-Nb<sub>2</sub>O<sub>5</sub>, FeNbO<sub>4</sub> (filled circle) and monoclinic  $FeNb_{11}O_{29}$  after heating at 950°C (24h).

700°C cause a slow polymorphic transformation into T-Nb<sub>2</sub>O<sub>5</sub>. The powder diffraction pattern recorded after the calcination stage at 700°C contains a set of reflections characteristic for T-Nb<sub>2</sub>O<sub>5</sub> [16,18] (figure 4, curve c), which in turn is most probably an evidence of a solid solution formation of Fe<sup>3+</sup> in T-Nb<sub>2</sub>O<sub>5</sub>. After calcination at 750°C in the powder diffractogram some low-intensity reflections appeared, beside those characteristic for T-Nb<sub>2</sub>O<sub>5</sub>, that can be ascribed to FeNbO<sub>4</sub> and FeNb<sub>11</sub>O<sub>29</sub> (figure 4, curve d). In the diffractograms recorded after subsequent heating stages at 800 and 850°C the intensities of the diffraction reflections characteristic for T-Nb<sub>2</sub>O<sub>5</sub> and FeNbO<sub>4</sub> gradually decreased, while those of FeNb<sub>11</sub>O<sub>29</sub> gradually increased. The pure monoclinic FeNb<sub>11</sub>O<sub>29</sub> was obtained after the calcination stage at 950°C (figure 4, curve e).

Summarizing the performed experiments aimed at obtaining  $FeNb_{11}O_{29}$ , attention should be paid to the complexity of its synthesis process. Independently of the kind of the used reactants, in the reacting mixtures the phase  $FeNbO_4$  appeared. In the case of the reaction in which the reactants were  $FeNbO_4$  and  $T-Nb_2O_5$  a distinctly slower course of the synthesis was observed and the pure phase  $FeNb_{11}O_{29}$  was obtained at a much higher temperature. The research results also indicate that the application of  $T-Nb_2O_5$  to a greater extent than  $H-Nb_2O_5$  favours the formation of  $FeNb_{11}O_{29}$  and gene-



Figure 5. IR spectra of: a-  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; b - FeNbO<sub>4</sub>; c - monoclinic polymorph of FeNb<sub>11</sub>O<sub>29</sub>; d - orthorhombic polymorph of FeNb<sub>11</sub>O<sub>29</sub>; e - H-Nb<sub>2</sub>O<sub>5</sub>.

rally quickens its synthesis process. On the base of a comparison between the temperatures at which the pure phase  $FeNb_{11}O_{29}$  was obtained, it seems to be most advantageous to perform the synthesis by the solution method that allows obtaining the pure monoclinic polymorph already at 950°C. Independently of the applied preparation method the orthorhombic polymorph of  $FeNb_{11}O_{29}$  can be obtained only at 1250°C.

The monoclinic and the orthorhombic modifications of the phase FeNb<sub>11</sub>O<sub>29</sub> were subjected to an investigation with the use of infra-red spectroscopy. Figure 5 presents the IR spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (curve a), the monoclinic FeNbO<sub>4</sub> of wolframite structure (curve b), the monoclinic  $\text{FeNb}_{11}\text{O}_{29}$  (curve c), the orthorhombic FeNb<sub>11</sub>O<sub>29</sub> (curve d) and H-Nb<sub>2</sub>O<sub>5</sub> (curve e). A comparative analysis of the location and intensities of their absorption bands indicates a very close similarity among the IR spectra of monoclinic FeNb<sub>11</sub>O<sub>29</sub> (curve c), orthorhombic FeNb<sub>11</sub>O<sub>29</sub> (curve d) and H-Nb<sub>2</sub>O<sub>5</sub> (curve e) which belong to block-structure phases, as well as some distinct differences in their comparison to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (curve a) and FeNbO<sub>4</sub> (curve b). The essential difference relies on an appearance of additional absorption bands in the IR spectra of the block-structure phases, occurring in the wavenumber range 1100-850 cm<sup>-1</sup> and absent in the spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and FeNbO<sub>4</sub>. In the structures of all the five investigated compounds the MO<sub>6</sub> octahedra occur, connected to one another in various ways. A common feature of the block-structure phases, differentiating them from  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and FeNbO<sub>4</sub>, is the presence of shear planes. Analysis of the structural data of the monoclinic and orthorhombic polymorphs of  $Ti_2Nb_{10}O_{29}$  and  $Nb_{12}O_{29}$  [3-5] showed that the octahedra occurring within the shear planes are very strongly distorted and the interatomic distances M-O cover the range 1.7-2.9 A. It seems that the very short bonds M-O are responsible for the occurrence of the additional absorption bands in the range 1100-850 cm<sup>-1</sup>. In the structure of both the monoclinic and the orthorhombic polymorph the metal ions occupy 6 independent crystallographic positions that can be filled by iron and niobium in a mixed manner. The occurrence of the 1100-850 cm<sup>-1</sup> absorption band also in the IR spectrum of H-Nb<sub>2</sub>O<sub>5</sub> indicates that the very strongly distorted positions in octahedral coordination containing the very short M-O bonds may be preferentially occupied by niobium which is much heavier than iron.

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#### SYNTÉZA A VLASTNOSTI FeNb<sub>11</sub>O<sub>29</sub>

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S použitím rtg difrakce jsme provedli srovnávací studii syntetické reakce vedoucí k FeNb<sub>11</sub>O<sub>29</sub> ze směsi α-Fe<sub>2</sub>O<sub>3</sub> a T-Nb<sub>2</sub>O<sub>5</sub>, α-Fe<sub>2</sub>O<sub>3</sub> a H-Nb<sub>2</sub>O<sub>5</sub>, FeNbO<sub>4</sub> a T-Nb<sub>2</sub>O<sub>5</sub> a konečně FeNb<sub>49</sub>O<sub>124</sub> a  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Syntéza byla provedena rovněž z roztoku Fe(NO<sub>3</sub>)<sub>3</sub> a šťavelanu niobičnoamonného. Zjistili jsme, že bez ohledu na výchozí látky byl reakčním meziproduktem nebo vedlejším produktem FeNbO4. Nejlepší metodou byla v případě tuhých výchozích látek směs α-Fe2O3 a T-Nb2O5 a teplota 1000°C. Příprava FeNb<sub>11</sub>O<sub>29</sub> z roztoku umožňuje přípravu čistého produktu při 950°C. Nezávisle na výchozích látkách vzniká the monoklinická modifikace FeNb11O29, která při 1250°C podléhá polymorfní transformaci orthorhombickou modifikaci. IČ spektra změřená pro obě modifikace FeNb<sub>11</sub>O<sub>29</sub> a H-Nb<sub>2</sub>O<sub>5</sub>, patřící k fázím s blokovou strukturou, ve srovnání se spektry α-Fe<sub>2</sub>O<sub>3</sub> a FeNbO<sub>4</sub> obsahují nové absorpční pásy při vlnočtech v rozmezí 1100-850 cm<sup>-1</sup>. Jde pravděpodobně o valenční vibrace (stretching) v oktaedrech s velmi krátkými vazbami M-O, typickými pro fáze s blokovou strukturou.