SYNTHESIS AND PROPERTIES OF FeNb$_{11}$O$_{29}$

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Using the XRD method a comparative study was performed on the synthesis reaction course for the FeNb$_{11}$O$_{29}$ phase taking as reactants the mixtures of $\alpha$-Fe$_2$O$_3$ and T-Nb$_2$O$_5$, $\alpha$-Fe$_2$O$_3$ and H-Nb$_2$O$_5$, FeNbO$_4$ and T-Nb$_2$O$_5$ or FeNb$_{49}$O$_{124}$ and $\alpha$-Fe$_2$O$_3$. The above synthesis was also carried out by a solution method with the use of Fe(NO$_3$)$_3$ 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$_4$. The optimal method of synthesis with the use of solid reactants relies on the calcination of the $\alpha$-Fe$_2$O$_3$/T-Nb$_2$O$_5$ mixture at 1000°C. The synthesis of FeNb$_{11}$O$_{29}$ by the solution method enables preparation of the pure product at 950°C. Independently of the starting substances, the monoclinic modification of FeNb$_{11}$O$_{29}$ is formed which at 1250°C undergoes a polymorphic transformation into the orthorhombic modification. The IR spectra recorded for both polymorphs of FeNb$_{11}$O$_{29}$ and H-Nb$_2$O$_5$, belonging to block-structure phases, in comparison to the spectra of $\alpha$-Fe$_2$O$_3$ and FeNbO$_4$ contain additional absorption bands in the wavenumber range 1100-850 cm$^{-1}$. 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$_3$-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$_x$Mo$_9$O$_{24}$ and Nb$_{12}$MoO$_{33}$ [2] the determined coefficients of thermal expansion in the direction concordant with the direction containing the blocks $n \times m \times \infty$ 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$_2$O$_5$ (M=Mg, Ni, Zn), M$_2$O$_3$ - Nb$_2$O$_5$ (M=Al, Ga, Cr, Fe) and MO$_2$ - Nb$_2$O$_5$ (M=Ti, Nb) some phases of the general formula M$_x$Nb$_{12-x}$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$_3$-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$_x$Nb$_{12-x}$O$_{29}$ phases are most frequently obtained by chemical transport or solid-state reactions between the corresponding oxides M$_x$O$_y$ and Nb$_2$O$_5$ 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$_{11}$O$_{29}$ was selected. This compound was obtained by performing the reactions between FeNbO$_4$ and T-Nb$_2$O$_5$ as well as between FeNb$_{49}$O$_{124}$ and $\alpha$-Fe$_2$O$_3$. The synthesis of FeNb$_{11}$O$_{29}$ was carried out also by the solution method using solutions of Fe(NO$_3$)$_3$ and ammonium niobium(V) oxalate. For the exemplary synthesis reaction of FeNb$_{11}$O$_{29}$ a comparison was also made as to the reactivity of T-Nb$_2$O$_5$ and H-Nb$_2$O$_5$ towards $\alpha$-Fe$_2$O$_3$. Considering the fact that
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$_{11}$O$_{29}$, FeNbO$_4$ and FeNb$_{58}$O$_{124}$ were α-Fe$_2$O$_3$ a.p. (POCH, Gliwice, Poland) and T-Nb$_2$O$_5$ (the orthorhombic polymorph) 99.9% (Aldrich, Germany), and in the case of FeNb$_{11}$O$_{29}$ also H-Nb$_2$O$_5$ (monoclinic polymorph) obtained from T-Nb$_2$O$_5$ by calcination at 1300°C for 1 hour. In the solution method the reactants were Fe(NO$_3$)$_3$ 9H$_2$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. FeNbO$_4$ was obtained by calcination of the mixture of oxides at 1200°C for 4 hours and FeNb$_{58}$O$_{124}$ 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$_2$O$_5$ and H-Nb$_2$O$_5$ towards α-Fe$_2$O$_3$ 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$_{11}$O$_{29}$ by the solution method two solutions were prepared. In 100 cm$^3$ of distilled water 6.7176 g of ammonium niobium(V) oxalate were dissolved and in 50 cm$^3$ of water - 0.5243 g Fe(NO$_3$)$_3$ * 9H$_2$O. Next into the solution of ammonium niobium(V) oxalate the solution of Fe(NO$_3$)$_3$ 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$^{-1}$ 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].](image1)

![Figure 2. Projection of the orthorhombic polymorph of Nb$_{12}$O$_{29}$ structure onto XZ plane [4].](image2)
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, Russia) using the radiation CoKα/Fe.

RESULTS AND DISCUSSION

The research was begun by comparing the reactivity of T-Nb2O5 and H-Nb2O5 towards α-Fe2O3. 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-Nb2O5 belongs to the double shear type of phases and contains in its structure the ReO3-type blocks of the dimensions 3×4×∞ and 3×5×∞ [15]. On the other hand, T-Nb2O5 does not belong to the block-structure phases. It is built up from corner-sharing and edge-sharing octahedra of NbO6 and pentagonal bipyramids of NbO7. In structural voids occurring among such connected polyhedra the remaining niobium ions are randomly distributed having 9 oxygen ions in their direct environment.

In the case of the FeNb11O29 syntheses with the use of H-Nb2O5 and α-Fe2O3, 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 FeNbO4. After the calcination stage at 900°C their intensity significantly increased, which was accompanied by an appearance of new reflections characteristic for FeNb11O29 as well as by a distinct decrease in intensity of the reflections characteristic for H-Nb2O5. After subsequent calcination stages at 950 and 1000°C the intensity of the reflections characteristic for H-Nb2O5 and α-Fe2O3 significantly decreased, while that of FeNb11O29 and FeNbO4 increased. The intensity of the reflections characteristic for FeNb11O29 was much bigger than that of FeNbO4. After the subsequent heating stages at 900 and 950°C the intensity of the FeNb11O29 reflections distinctly increased, while that of FeNbO4 decreased. A pure monoclinic phase of FeNb11O29 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 FeNb5O29 was obtained. The diffraction patterns of the monoclinic and orthorhombic

![Figure 3. Powder diffraction patterns of monoclinic polymorph of FeNb5O29 (curve a) and orthorhombic (curve b).](image-url)
FeNb$_4$O$_{124}$ obtained with the use of T-Nb$_2$O$_5$ were identical with those recorded after the synthesis using H-Nb$_2$O$_5$. The conducted comparative research on the reactivity of H-Nb$_2$O$_5$ and T-Nb$_2$O$_5$ towards $\alpha$-Fe$_2$O$_3$ has shown that the synthesis of monoclinic FeNb$_{11}$O$_{29}$ is possible with the use of T-Nb$_2$O$_5$ already at 1000°C, while with the use of H-Nb$_2$O$_5$ 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$_4$ and the monoclinic-to-orthorhombic transformation begins at 1250°C.

During the attempts to optimise the synthesis conditions for monoclinic FeNb$_{11}$O$_{29}$ a mixture of T-Nb$_2$O$_5$ and $\alpha$-Fe$_2$O$_3$ 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$_{11}$O$_{29}$ can be obtained already after the second heating cycle at 1000°C. In order to optimise in turn the preparation conditions for orthorhombic FeNb$_{11}$O$_{29}$, a previously obtained at 1000°C preparation of monoclinic FeNb$_{11}$O$_{29}$ was next heated in 4-hour cycles at 1050, 1100, 1150, 1200 and 1250°C. A preparation containing the orthorhombic FeNb$_{11}$O$_{29}$ 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$_{11}$O$_{29}$ is FeNbO$_4$, an attempt was undertaken to synthesize FeNb$_{11}$O$_{29}$ with the use of FeNbO$_4$ and T-Nb$_2$O$_5$ according to the total equation:

$$\text{FeNbO}_4 + 5 \text{Nb}_2\text{O}_5 = \text{FeNb}_{11}\text{O}_{29}$$

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$_2$O$_5$ transforms initially into a mixture of M-Nb$_2$O$_5$ and H-Nb$_2$O$_5$[17,18], whereas the amount of FeNbO$_4$ does not change. Only after the heating cycle at 900°C the diffractogram reveals the presence of very low-intensity reflections characteristic for FeNb$_{11}$O$_{29}$, which is accompanied by an increase in intensity of the reflections belonging to the H-Nb$_2$O$_5$ set and only a slight decrease of reflections intensities ascribed to M-Nb$_2$O$_5$ and FeNbO$_4$. This tendency continues until the heating at 1100°C inclusive after which the diffractogram contains the reflections characteristic for FeNb$_{11}$O$_{29}$, FeNbO$_4$ and H-Nb$_2$O$_5$. The pure monoclinic FeNb$_{11}$O$_{29}$ 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$_4$ in the reacting mixture. A slow course of the reaction between FeNbO$_4$ and Nb$_2$O$_5$ also suggests that in the reacting mixtures containing the oxides at temperatures of 800-900°C order of magnitude some parallel reactions occur leading to FeNbO$_4$ and FeNb$_{11}$O$_{29}$. The application of T-Nb$_2$O$_5$ creates more advantageous conditions for the reaction course towards the formation of FeNb$_{11}$O$_{29}$. Thanks to a smaller amount of FeNbO$_4$ being formed in the initial reaction stage, the reaction between T-Nb$_2$O$_5$ and $\alpha$-Fe$_2$O$_3$ leads much more quickly to obtaining a monophase preparation of FeNb$_{11}$O$_{29}$.

In the reacting mixtures of none of the hitherto described reactions after any stage the phase FeNb$_{49}$O$_{124}$ (M,Nb$_{25.4}$O$_{63.4}$) was ever identified, the phase that beside FeNbO$_4$ and FeNb$_{11}$O$_{29}$ is formed in the system Fe$_2$O$_3$ - Nb$_2$O$_5$. Certain light is shed upon this fact by the course of the synthesis process of FeNb$_{49}$O$_{124}$. This phase was obtained within the frames of this work by using FeNb$_{11}$O$_{29}$ and T-Nb$_2$O$_5$ as the reactants. The phase FeNb$_{11}$O$_{29}$ 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$_{49}$O$_{124}$, being formed in the reacting mixtures enters into a quick reaction forming FeNbO$_4$ or FeNb$_{11}$O$_{29}$. In order to verify this opinion an attempt was undertaken to synthesize the phase FeNb$_{11}$O$_{29}$ with the use of FeNb$_{49}$O$_{124}$ and $\alpha$-Fe$_2$O$_3$ as reactants, according to the overall reaction:

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

Analysis of the diffraction patterns obtained after subsequent stages of synthesis showed that the reaction between FeNb$_{49}$O$_{124}$ and $\alpha$-Fe$_2$O$_3$ 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 FeNbO$_4$, as well as a set of high-intensity reflections belonging to the non-reacted FeNb$_{49}$O$_{124}$. 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$_{49}$O$_{124}$. After subsequent calcination stages the intensities of the reflections characteristic for FeNbO$_4$ and FeNb$_{49}$O$_{124}$ gradually decreased, while those of FeNb$_{11}$O$_{29}$ increased. The pure monoclinic FeNb$_{11}$O$_{29}$ was obtained after the calcination stage at 1200°C. The conducted research seems to indicate that the stage at which the FeNb$_{49}$O$_{124}$ 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-Nb₂O₅ [18-20] (figure 4, curve b). Thus it can be supposed that at this stage of the process a solid solution of Fe⁺³ in TT-Nb₂O₅ 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 700°C cause a slow polymorphic transformation into T-Nb₂O₅. The powder diffraction pattern recorded after the calcination stage at 700°C contains a set of reflections characteristic for T-Nb₂O₅ [16,18] (figure 4, curve c), which in turn is most probably an evidence of a solid solution formation of Fe⁺² in T-Nb₂O₅. After calcination at 750°C in the powder diffractogram some low-intensity reflections appeared, beside those characteristic for T-Nb₂O₅, that can be ascribed to FeNbO₄ and FeNb₁₁O₂₉ (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-Nb₂O₅ and FeNbO₄ gradually decreased, while those of FeNb₁₁O₂₉ gradually increased. The pure monoclinic FeNb₁₁O₂₉ was obtained after the calcination stage at 950°C (figure 4, curve e).

Summarizing the performed experiments aimed at obtaining FeNb₁₁O₂₉, 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 FeNbO₄ appeared. In the case of the reaction in which the reactants were FeNbO₄ and T-Nb₂O₅ a distinctly slower course of the synthesis was observed and the pure phase FeNb₁₁O₂₉ was obtained at a much higher temperature. The research results also indicate that the application of T-Nb₂O₅ to a greater extent than H-Nb₂O₅ favours the formation of FeNb₁₁O₂₉ and gene-

Figure 4. Powder diffraction patterns of products obtained after selected stages of the FeNb₁₁O₂₉ synthesis using solution method: a - amorphous product after heating at 400°C (1 h); b - solid solutions of Fe⁺³ ions in the TT-Nb₂O₅ after additional heating at 600°C (30 min.); c - solid solutions of Fe⁺³ in the T-Nb₂O₅, after heating at 700°C (24 h); d - mixture of T-Nb₂O₅, FeNbO₄ (filled circle) and monoclinic FeNb₁₁O₂₉ (filled squares); e - pure sample of monoclinic FeNb₁₁O₂₉ after heating at 950°C (24 h).

Figure 5. IR spectra of: a - α-Fe₂O₃; b - FeNbO₄; c - monoclinic polymorph of FeNb₁₁O₂₉; d - orthorhombic polymorph of FeNb₁₁O₂₉; e - H-Nb₂O₅.
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$_{11}$O$_{29}$ were subjected to an investigation with the use of infra-red spectroscopy. Figure 5 presents the IR spectra of $\alpha$-Fe$_2$O$_3$ (curve a), the monoclinic FeNbO$_4$ of wolframite structure (curve b), the monoclinic FeNb$_{11}$O$_{29}$ (curve c), the orthorhombic FeNb$_{11}$O$_{29}$ (curve d) and H-Nb$_2$O$_5$ (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$_{11}$O$_{29}$ (curve c), 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 MO$_6$ octahedra occurring in the wavenumber range 1100-850 cm$^{-1}$.

MO$_6$ octahedra occur, connected to one another in various ways. A common feature of the block-structure phases, differentiating them from $\alpha$-Fe$_2$O$_3$ and FeNbO$_4$ is the presence of shear planes. Analysis of the structural data of the monoclinic and orthorhombic polymorphs of Ti$_x$Nb$_{1-x}$O$_4$ and Nb$_x$O$_{2y}$ [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 Å. It seems that the very short M-O bonds are responsible for the occurrence of the absorption bands in the range 1100-850 cm$^{-1}$.

References