The effect of high-temperature annealing on the phase transformations of the perovskite $\text{YTiO}_{3-x}$ system

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DOI:10.29317/ejpfm.2019030308
Received: 26.07.2019 - after revision

This paper presents the results of a study of the structural characteristics of perovskite systems based on $\text{YTiO}_x$. These samples were subjected to heat treatment in the process of solid-phase synthesis. The change in physicochemical properties was investigated by scanning electron microscopy, X-ray structural and energy dispersive analysis. In the course of the work, it was found that the synthesized samples are a mixture of three phases characteristic of yttrium compounds with titanium. A quantitative change in the phases during the heat treatment indicates phase transformations and a change in the basic crystallographic characteristics. The results of these studies indicate that during thermal annealing, the density of perovskites changes, indicating phase transformations due to the mobility of impurity defects and distortion of the crystal lattice.

Keywords: perovskites, oxides, crystal structure, thermal annealing.

Introduction

The relevance of research in the field of condensed matter physics is based on the study of small displacements and translational movements of ions and atoms inside the crystal lattice of metals. The inconsistency of the results obtained may
require a more detailed and in-depth study of the behavior of materials. New information on the synthesis of compounds with improved characteristics opens up applications in various fields of science and technology. By analyzing and predicting the conduct of these processes in working devices that were created on the basis of the studied perovskite-like samples, it is possible to solve various kinds of problems that generally determine the progress of technical industries. The developed methods of complex analysis, including the analysis of X-ray diffraction patterns, are able to reveal various structural changes in the process of synthesis or modification [1-3].

The structure of many solids is usually thought to be more crystalline and symmetrical, where groups of atoms are an integral part. This method of perception is convenient for representing the symmetry and antisymmetry of modifications [4, 5]. Octahedra are traditionally distinguished in a perovskite-type structure. Since each atom belongs to two octahedra, the rotation of one part leads to a change in the system of other lattices, thereby it is possible to obtain a new structure with different interatomic distances [6, 7]. All solid-state electrical and electrochemical devices are characterized by such properties as high mechanical strength and a sufficiently small size. This conclusion simplifies the search for new materials with desired properties, since a change in the crystal lattice parameters and ion mobility largely determines the material properties [8].

The presence of elements (cations) of different crystallochemical characteristics in perovskite systems allows controlling and changing the chemical and phase composition over a wide range [9, 10]. The authors of this article [11] revealed the relationship between ionic mobility and the thermodynamic characteristic, as the formation of defects in a crystal. It follows that the preparation and study of new materials with desired properties largely depends on the analysis of the internal behavior of the crystal lattice in a convenient temperature range. Currently, the urgent task is the synthesis and study of perovskite-like materials with the necessary properties for further use for scientific purposes [12, 13].

Based on the foregoing, it is of interest to synthesize perovskite systems based on YTiOx by solid-phase synthesis followed by heat treatment and study their physicochemical and magnetic properties.

**Experimental part**

The studied samples were obtained by the mechanochemical method by mixing microstructure powders of salts of yttrium nitrate hexahydrate (YN₃O₉ · 6H₂O) and titanium oxide (Sigma Aldrich) in an agate mortar to obtain a substrate of uniform consistency. The mixing ratio of the elements was selected in the following weight ratios of YN₃O₉ and TiO₂ 1:1. Then, the obtained substrate was annealed in a muffle furnace in an oxygen-containing medium at temperatures of 600 °C, 800 °C, and 1000 °C for 5 hours.

The morphology of the obtained samples was studied using a JEOL 7500F scanning electron microscope at an accelerating voltage of 5 kV in SEI mode. The effect of various component ratios on the elemental ratio in the synthesized
samples was studied using a Hitachi TM3030 scanning electron microscope with an attachment for energy dispersive analysis of Oxford Instruments at an accelerating voltage of 15 kV.

The phase composition and changes in the crystallographic parameters were studied on a D8 ADVANCE ECO (Bruker) X-ray diffractometer in the geometry of the Bragg-Brentano survey in the angular range of 20 - 75°, with a step of 0.01°, the set time at 5 sec. To analyze the obtained diffraction patterns and the phase composition of the studied samples, the PDF2 database (2016) was used. The parameters and contribution of each phase were evaluated using the Rietveld method and TOPAS v.4.2 software.

1. The study of morphology and elemental composition

Figure 1 shows SEM images of perovskite-like structures after high-temperature annealing.

According to these micrographs, we can conclude that with increasing annealing temperature, the formation of massive sphere-like particles with a size of 150 - 200 nm is observed, but it should also be noted that at a temperature of 800 °C, a new transition phase of the YTiO₃ system is formed. It can be concluded that, after the formation of the transition phase and the increase in the annealing temperature, fragmentation of the sample is observed, followed by the formation of diamond-shaped particles.

To assess the influence of synthesis conditions on the elemental composition and stoichiometric ratio of components, the method of energy dispersive analysis was applied. Table 1 presents data on changes in the elemental composition of the studied samples.

| Annealing temperature | Elemental content, at% |
|-----------------------|------------------------|
|                       | Oxygen (O) | Titanium (Ti) | Yttrium (Y) |
| Initial               | 66.4±6.3   | 31.3±1.6      | 2.2±0.3      |
| 600°C                 | 65.1±6.6   | 28.1±1.5      | 6.9±0.9      |
| 800°C                 | 73.9±7.1   | 21.2±1.3      | 5.0±0.8      |
| 1000°C                | 72.4±6.0   | 16.6±0.9      | 11.3±1.5     |

According to the data obtained, it can be concluded that with increasing annealing temperature, the content of yttrium increases, while the atomic ratio of titanium decreases. For samples subjected to thermal annealing in air, an increase in the oxygen content with increasing temperature is characteristic. The presence of a sharp decrease and increase in the atomic contents of titanium and yttrium, respectively, at temperatures of 800 °C – 1000 °C, may indicate the formation of a new transition phase with a significant distortion of the structure.

Figure 2 shows a graph of the dependence of the atomic content on the annealing temperature for a visual assessment of the effect on the elemental composition of the samples. Thanks to these data, it is possible to visualize the behavior of the components that make up the system with increasing annealing temperature.
Figure 1. SEM images of perovskite-like structures.

1.1 Phase analysis of synthesized structures

To assess the phase composition, the Rietveld method was used, based on the analysis of the shape of diffraction maxima. Table 2 presents the results of the evaluation of the phase composition.
Table 2.
Phase composition data.

| Temperature | Phase          | Structure type | Space group   | Phase content, % |
|-------------|----------------|----------------|---------------|------------------|
| 1000°C      | TiO₂ Titanium Oxide | Orthorhombic  | Fm-3m(225)   | 33,7             |
|             | Ti₉O₁₇ Titanium Oxide | Triclinic      | I-1(2)        | 21,1             |
|             | YN Yttrium Oxide  | Hexagonal      | P63mc(186)   | 32,7             |
|             | Ti₂N Titanium Nitride | Tetragonal    | P42/mnm(136) | 12,5             |
| 800°C       | TiO₂ Titanium Oxide | Orthorhombic  | Fm-3m(225)   | 24,8             |
|             | Ti₉O₁₇ Titanium Oxide | Triclinic      | I-1(2)        | 13,9             |
|             | YN Yttrium Oxide  | Hexagonal      | P63mc(186)   | 53,4             |
|             | Ti₂N Titanium Nitride | Tetragonal    | P42/mnm(136) | 7,8              |
| 600°C       | TiO₂ Titanium Oxide | Orthorhombic  | Fm-3m(225)   | 34,4             |
|             | Ti₉O₁₇ Titanium Oxide | Triclinic      | I-1(2)        | 38,7             |
|             | YN Yttrium Oxide  | Hexagonal      | P63mc(186)   | 23,2             |
|             | Ti₂N Titanium Nitride | Tetragonal    | P42/mnm(136) | 3,7              |
| Initial     | TiO₂ Titanium Oxide | Orthorhombic  | Fm-3m(225)   | 56,1             |
|             | Ti₉O₁₇ Titanium Oxide | Triclinic      | I-1(2)        | 30,6             |
|             | YN Yttrium Oxide  | Hexagonal      | P63mc(186)   | 7,1              |
|             | Ti₂N Titanium Nitride | Tetragonal    | P42/mnm(136) | 6,4              |

As can be seen from the data presented, in the case of initial samples that were not subjected to thermal annealing, the dominant phase in the structure is the phase of titanium oxide with an orthorhombic type of crystal lattice, spatial syngony Fm-3m (225). After heat treatment at 600 °C, the titanium oxide phase with a triclinic crystal lattice predominates. After increasing the temperature, the yttrium nitride phase gradually increases, reaching a maximum at 800 °C, and then decreases. Thus, after increasing the temperature to 1000 °C, the predominant phase in the composition of the samples is titanium oxide and yttrium nitride. The growth of oxygen ions also affects the mobility of linear defects and at the
same time significantly changes the crystalline characteristics. The data on the parameters of the crystal lattices with temperature are presented in Table 3.

Table 3.
Data of crystallographic characteristics (crystal lattice parameter).

| Temperature | Phase     | Crystal lattice parameter, Å |
|-------------|-----------|-----------------------------|
|             |           | a   | b   | c   |
| **TiO₂** Titanium Oxide | 4.5563 | 5.5533 | 4.8857 |
| **Ti₉O₁₇** Titanium Oxide | 4.5563 | 5.5533 | 4.8857 |
| **YN Yttrium Oxide** | 3.7818 | | 6.0332 |
| **Ti₂N Titanium Nitride** | 4.9452 | | 3.0342 |
| 800°C       | **TiO₂** Titanium Oxide | 4.6934 | 5.5533 | 4.8791 |
|             | **Ti₉O₁₇** Titanium Oxide | 4.5563 | 5.5533 | 4.8857 |
|             | **YN Yttrium Oxide** | 3.7818 | | 6.0332 |
|             | **Ti₂N Titanium Nitride** | 4.9452 | | 3.0342 |
| 600°C       | **TiO₂** Titanium Oxide | 4.7017 | 5.5271 | 4.8857 |
|             | **Ti₉O₁₇** Titanium Oxide | 4.5563 | 5.5533 | 4.8857 |
|             | **YN Yttrium Oxide** | 3.7818 | | 6.0332 |
|             | **Ti₂N Titanium Nitride** | 4.9452 | | 3.0342 |
| Initial     | **TiO₂** Titanium Oxide | 4.3782 | 5.6262 | 4.9302 |
|             | **Ti₉O₁₇** Titanium Oxide | 4.5563 | 5.5533 | 4.8857 |
|             | **YN Yttrium Oxide** | 3.7818 | | 6.0332 |
|             | **Ti₂N Titanium Nitride** | 4.9452 | | 3.0342 |

A decrease in the content of the titanium oxide (TiO₂) phase leads to a change in the structural parameters of the crystal lattice, which leads to an increase in the density of dislocation defects and distortions in the structure [14]. In turn, the change in the crystal lattice parameters and their deviation from the reference values from the PDF2 database is due to the difference in the ionic radii of the components, as well as the processes of substitution and incorporation of yttrium.
and titanium ions into the nodes and interstices of the crystal lattice of both phases. The growth of oxygen ions also affects the mobility of linear defects and at the same time significantly changes the crystalline characteristics. Table 4 presents the results of density changes for each phase.

![Figure 2. Dependence of atomic content on annealing temperature.](image)

Table 4.
Data on changes in phase density.

| Temperature | Phase                | Density, g/cm³ | Reference value according to PDF 2 database |
|-------------|----------------------|----------------|---------------------------------------------|
| 1000°C      | TiO₂ Titanium Oxide  | 4.352 PDF-01-076-6065 | 4.292                                       |
|             | Ti₉O₁₇ Titanium Oxide | 4.266 PDF-00-050-0791   | 4.266                                       |
|             | YN Yttrium Oxide     | 4.627 PDF-01-083-3592   | 4.573                                       |
|             | Ti₂N Titanium Nitride | 4.915 PDF-00-017-0386   | 4.914                                       |
| 800°C       | TiO₂ Titanium Oxide  | 4.352 PDF-01-076-6065 | 4.168                                       |
|             | Ti₉O₁₇ Titanium Oxide | 4.266 PDF-00-050-0791   | 4.165                                       |
|             | YN Yttrium Oxide     | 4.627 PDF-01-083-3592   | 4.572                                       |
|             | Ti₂N Titanium Nitride | 4.915 PDF-00-017-0386   | 4.914                                       |
| 600°C       | TiO₂ Titanium Oxide  | 4.352 PDF-01-076-6065 | 4.179                                       |
|             | Ti₉O₁₇ Titanium Oxide | 4.266 PDF-00-050-0791   | 4.179                                       |
|             | YN Yttrium Oxide     | 4.627 PDF-01-083-3592   | 4.572                                       |
|             | Ti₂N Titanium Nitride | 4.915 PDF-00-017-0386   | 4.914                                       |
| Initial     | TiO₂ Titanium Oxide  | 4.352 PDF-01-076-6065 | 4.213                                       |
|             | Ti₉O₁₇ Titanium Oxide | 4.266 PDF-00-050-0791   | 4.265                                       |
|             | YN Yttrium Oxide     | 4.627 PDF-01-083-3592   | 4.572                                       |
|             | Ti₂N Titanium Nitride | 4.915 PDF-00-017-0386   | 4.914                                       |
A decrease in the phase of titanium oxide (TiO$_2$) and an increase in the phase of titanium nitride in the structure lead to an increase in distortions and the appearance of vacancy defects due to the motion of atoms in the crystal lattice under the influence of temperature. It is also known that the process of the disappearance of excess defects from the crystal that arose during mechanical grinding, by heat treatment, leads to an increase in the phase density. In this case, the occurrence of vacancy defects and the substitution of atoms in a solid solution of the introduction of the yttrium – titanium system have a significant effect on the magnetic properties of the samples under study [15, 16]. The results of changes in the porosity of the material of each phase are presented in Table 5. The integral porosity of the studied samples was found according to the formula (1):

$$P_{dil} = (1 - \frac{p}{p_0}) \cdot 100\%,$$  \hspace{1cm} (1)

where $p_0$ is the density of the reference sample.

Table 5.
Data on changes in phase porosity.

| Temperature | Phase            | Porosity, % |
|-------------|------------------|-------------|
| 1000°C      | TiO$_2$ Titanium Oxide | 1.374       |
|             | Ti$_{19}$O$_{17}$ Titanium Oxide | 0.021       |
|             | YN Yttrium Oxide | 1.178       |
|             | Ti$_2$N Titanium Nitride | 0.022       |
| 800°C       | TiO$_2$ Titanium Oxide | 4.256       |
|             | Ti$_{19}$O$_{17}$ Titanium Oxide | 0.021       |
|             | YN Yttrium Oxide | 1.178       |
|             | Ti$_2$N Titanium Nitride | 0.022       |
| 600°C       | TiO$_2$ Titanium Oxide | 3.969       |
|             | Ti$_{19}$O$_{17}$ Titanium Oxide | 0.021       |
|             | YN Yttrium Oxide | 1.178       |
|             | Ti$_2$N Titanium Nitride | 0.022       |
| Initial     | TiO$_2$ Titanium Oxide | 3.191       |
|             | Ti$_{19}$O$_{17}$ Titanium Oxide | 0.021       |
|             | YN Yttrium Oxide | 1.178       |
|             | Ti$_2$N Titanium Nitride | 0.022       |

According to the calculation of porosity, we can conclude that with an increase in the two predominant phases of titanium nitride and titanium oxide IV-valent, with increasing annealing temperature, the porosity of the crystalline phase increases.

**Conclusion**

In the course of the study, a methodology was developed for producing double perovskite systems based on YN$_3$O$_9$ and TiO$_2$ solid-phase synthesis and subsequent thermal annealing, as well as a study of structural and phase transformations as a result of thermal annealing. Salts YN$_3$O$_9$ and TiO$_2$ were
used as initial components for the synthesis of double perovskites. An increase in the annealing temperature leads to a change in the phase composition of the synthesized perovskites. It was found that an increase in the annealing temperature leads to a change in the density and porosity of the perovskite system, which indicates phase transformations caused by the incorporation and distortion of the crystal lattice as a result of migration of defects and impurity components. An increase in the concentration of oxygen ions in the crystalline structure, which is caused by thermal processes, leads to crystalline changes based on the movements of point and linear defects. Significant modifications of the crystal lattice may also affect the magnetic characteristics of this system.

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