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SOL-GEL PREPARATION OF RUTILE TYPE SOLID SOLUTION IN TiO_2–RuO_2 SYSTEM

J. Málek[1]*, *A. Watanabe*[2] and *T. Mitsuhashi*[2]

[1]Joint Laboratory of Solid State Chemistry, Academy of Sciences of the Czech Republic and
University of Pardubice, Studentská 84, Pardubice 532 10, Czech Republic
[2]National Institute for Research in Inorganic Materials, Science and Technology Agency of Japan
Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Abstract

The preparation of rutile type solid solutions in $(TiO_2)_x$–$(RuO_2)_{1-x}$ system in the $0\leq x\leq 0.7$ concentration range is described. The single phase solid solutions are formed by controlled nanocrystallization of amorphous gels prepared by the sol-gel method. The kinetics of this crystallization process has been analyzed. It was found that the crystallization does not correspond to the Johnson-Mehl-Avrami model and it can be described by the two-parameter Šesták-Berggren kinetic model.

Keywords: crystallization kinetics, sol-gel, solid solutions, ruthenia, titania

Introduction

It is well known that $(TiO_2)_x$–$(RuO_2)_{1-x}$ system exhibits interesting photocatalytic properties [1–5]. Single crystals in this system were prepared by transport reaction at 1000°C [6]. It was found that there are the solubility limits for ruthenia rich phase ($x\leq 0.02$) and for titania rich phase ($x\geq 0.98$). These two phases coexist in $0.02<x<0.98$ concentration range. Polycrystalline solid solutions were prepared by pyrolysis of the mixture of $TiCl_4$ and $RuCl_3$ on the titania substrate [7]. In the range of 400–800°C solid solutions with a rutile structure are formed throughout the entire concentration range and they contain chlorine impurities of several at.%. In the temperature range above 800°C, the chlorine content becomes insignificant (~0.1 at.%) and the solid solutions decompose into two rutile phases, which are solid solutions based on RuO_2 and TiO_2 [7]. Another method of preparation is based on annealing of the mixture of TiO_2 and metallic Ru powder at 1300°C in the air [8]. A ceramic route of preparation of rutile type solid solutions at 1120°C was described also in [9]. It was found that there are the following solubility limits: $x\leq 0.2$ for ruthenia rich phase and $x\geq 0.9$ for titania rich phase. These two phases coexist in $0.2<x<0.9$ concentration range.

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[*] Author for correspondence: fax: +420-40-603-6011; e-mail: jiri.malek@upce.cz

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The sol-gel method allows a simple preparation of oxidic solid solutions with a continuous variation of the stoichiometry. It is frequently used for the synthesis of electrical and magnetic ceramic materials with optimized properties [10]. A high homogeneity of the amorphous oxide mixture prepared by this method causes that crystallization of metastable phases occurs without a long range diffusion at relatively low temperatures. The aim of this paper is to report the preparation of rutile type solid solutions in $(TiO_2)_x$–$(RuO_2)_{1-x}$ system by the nanocrystallization of amorphous gels synthesized by a sol-gel method.

Experimental

Solid solutions $(TiO_2)_x$–$(RuO_2)_{1-x}$ were prepared by crystalization of the amorphous gels. These gels were obtained by very slow adding of a dilute alkaline solution (2M ammonia) into the mixed solution of $TiCl_4$ and $RuCl_3$. Precipitated gels were filtered, washed several times and then partially dried at 120°C for 10 h in the air. Chlorine and other impurities were not detected by energy dispersive microanalysis (KEVEX, Delta 5) in dried powders.

Differential scanning calorimetry (DSC) measurements were performed by using a Perkin Elmer Model DSC-7 in an atmosphere of dry nitrogen (40 ml min^{-1}). Samples of about 10 mg were encapsulated in aluminum sample pans. The instrument was previously calibrated with In, Pb, and Zn standards. Non-isothermal DSC curves were obtained with selected heating rates of 2–20 K min^{-1} in the range 25–600°C. Thermogravimetric (TG) experiments were carried out using a Perkin Elmer Model TGA-7 in static air atmosphere.

Phase identification was performed by using a Rigaku Model RINT2000 X-ray diffractometer (XRD) equipped with horizontal goniometer and scintillation counter, utilizing Ni-filtered CuK_α radiation (40 kV, 30 mA). The scans were performed over the 2θ range of 20–100° at the slow scanning speed of 0.6 deg min^{-1}.

Results and discussion

X-ray diffraction revealed that partially dried gels were amorphous for $x \leq 0.7$. Titania rich powders ($x \geq 0.9$) were nanocrystalline materials having structure of anatase. These powders contain residual water which is continuously loosed on heating as shown in Fig. 1. The water content for powders containing ruthenia ($x<1$) is higher than 20%. Considerably lower water content (about 14%) was found for pure titania powder. This is not surprising because more water is retained usually in partially dried amorphous gels than in nanocrystalline powders prepared in the same way.

Solid solutions $(TiO_2)_x$–$(RuO_2)_{1-x}$ were prepared by continuous heating of partially dried amorphous gels at 10 K min^{-1} up to 600°C in dry nitrogen flow. Typical DSC crystallization curves obtained under these conditions are shown in Fig. 2. It is seen that pure ruthenia gel crystallizes at the lowest temperature. The crystallization temperature then increases with the titania content, reaching its maximum at x=0.6 and finally decreases.

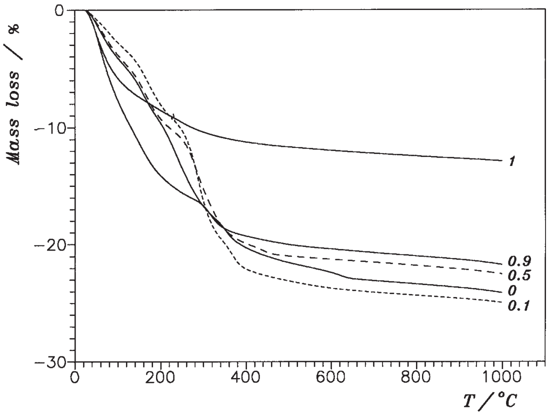

Fig. 1 TG curves of partially dried $(TiO_2)_x$–$(RuO_2)_{1-x}$ gels measured at 5 K min^{-1} in the static air atmosphere. The chemical composition x is shown next to the curves

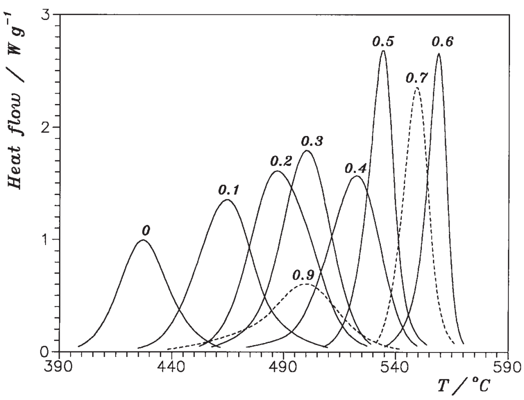

Fig. 2 DSC crystallization curves of partially dried $(TiO_2)_x$–$(RuO_2)_{1-x}$ gels measured with dry nitrogen flow at 10 K min^{-1}. The chemical composition x is shown next to the curves

The crystallization kinetics of pure ruthenia gel has recently been studied [11] and it was shown that the crystallization kinetics cannot be described by the one parameter Johnson-Mehl-Avrami nucleation growth model [12]. However, the two-parameter Šesták-Berggren model [13,14] provides a very good description of the experimental data both in isothermal and non-isothermal conditions. The same behavior was confirmed also for other compositions of $(TiO_2)_x$–$(RuO_2)_{1-x}$ system. The kinetic equation can be expressed in the following form:

$$\phi = \Delta H_c A \exp(-E_a/RT)\alpha^M(1-\alpha)^N \tag{1}$$

where ϕ is the measured heat flow, A is the preexponential factor, E_a is the apparent activation energy, α is the fractional conversion, and the two parameters of M and N are the kinetic exponents of the Šesták-Berggren model. The parameters of Eq. (1)

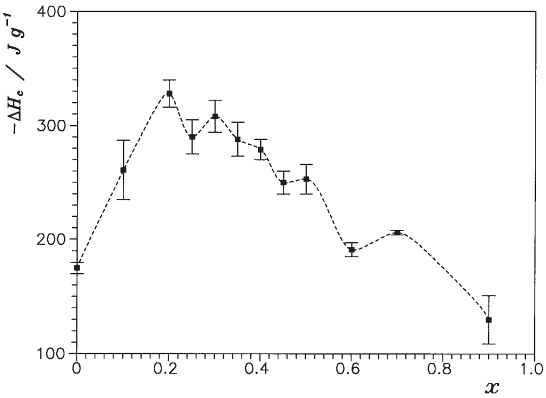

Fig. 3 Crystallization enthalpy as a function of chemical composition of partially dried $(TiO_2)_x$–$(RuO_2)_{1-x}$ gels

were calculated using the method described elsewhere [15] and they are summarized in Table 1. The crystallization enthalpy varies more than 100% having a maximum value for x=0.2 as shown in Fig. 3. On the other hand, the compositional dependence of the apparent activation energy exhibits more complex behavior (Fig. 4). There is a clear minimum for x=0.25 and maximum for x=0.6 composition.

Table 1 Parameters characterizing crystallization kinetics of amorphous gels of $(TiO_2)_x$ – $(RuO_2)_{1-x}$ composition

x	$-\Delta H_c$ /J g^{-1}	ln$A$/s^{-1}	E_a/kJ mol^{-1}	M	N
0	175±5	25.0±0.1	168±3	0.63±0.02	1.31±0.06
0.10	261±26	36.3±0.1	247±11	0.52±0.04	1.50±0.05
0.20	328±12	34.2±0.1	241±6	0.42±0.02	1.25±0.03
0.25	290±15	24.3±0.2	182±7	0.45±0.05	1.03±0.05
0.30	311±14	30.2±0.2	219±3	0.60±0.06	1.11±0.06
0.35	288±15	30.2±0.1	229±6	0.30±0.08	1.07±0.01
0.40	281±9	31.1±0.2	232±6	0.54±0.08	1.02±0.03
0.45	250±10	35.8±0.1	264±6	0.79±0.06	1.22±0.02
0.50	258±16	39.5±0.1	285±7	1.01±0.06	1.09±0.08
0.60	191±6	49.8±0.2	363±28	0.90±0.10	0.80±0.09
0.70	208±4	37.2±0.1	275±3	0.90±0.10	1.00±0.20
0.90	130±21	35.1±0.1	251±13	0.52±0.02	1.32±0.04

The crystallized $(TiO_2)_x$–$(RuO_2)_{1-x}$ powders are nanocrystalline materials and the average crystal size ranges between 15–30 nm. X-ray diffractograms of these powders are shown in Fig. 5. It is seen that pure titania powder (x=1) has the anatase type crystal structure. The lattice parameters were calculated: a=3.7878 Å, c=

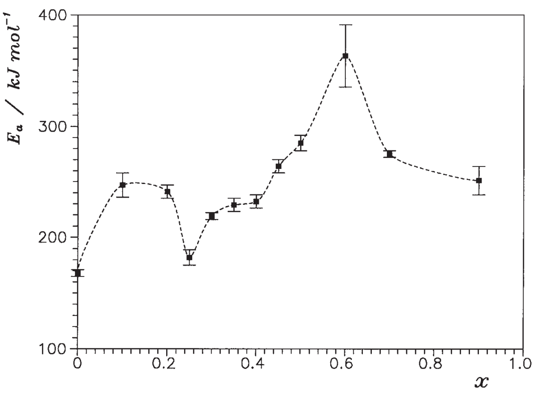

Fig. 4 Compositional dependence of apparent activation energy for the crystallization of partially dried $(TiO_2)_x$–$(RuO_2)_{1-x}$ gels

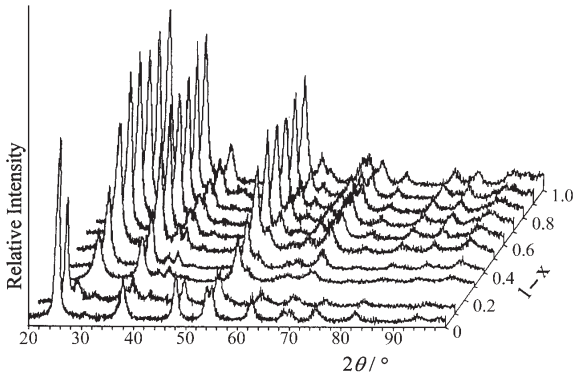

Fig. 5 X-ray diffraction patterns of crystallized $(TiO_2)_x$–$(RuO_2)_{1-x}$ gels

9.4971 Å. The x=0.9 powder is a mixture of anatase TiO_2 and rutile type solid solution. However, the crystallized $(TiO_2)_x$–$(RuO_2)_{1-x}$ powders for $0\leq x\leq 0.7$ are single phase of rutile type solid solutions. The lattice parameters of these phases were calculated by least square method from the 2θ values of 13 diffraction lines, after $K_{\alpha 2}$ separation. The calculated lattice parameters are summarized in Table 2. The parameter a increases and the parameter c decreases with TiO_2 content in the nearly monotonous way except the $0.25<x<0.35$ and $x>0.6$ ranges.

Figure 6 shows the compositional dependence of tetragonal ratio of lattice parameters shown in Table 2 for nanocrystalline $(TiO_2)_x$–$(RuO_2)_{1-x}$ powders. The broken line corresponds to linear Vegard's rule calculated for published lattice parameters of pure TiO_2 (JCPDS 21-1276) and pure RuO_2 (JCPDS 40-1290). It is clear that the Vegard's rule is closely approached for $0.35\leq x\leq 0.4$ samples. However, there are considerable departures in $0.1\leq x\leq 0.3$ and $0.45\leq x\leq 0.7$ ranges. These ranges are close

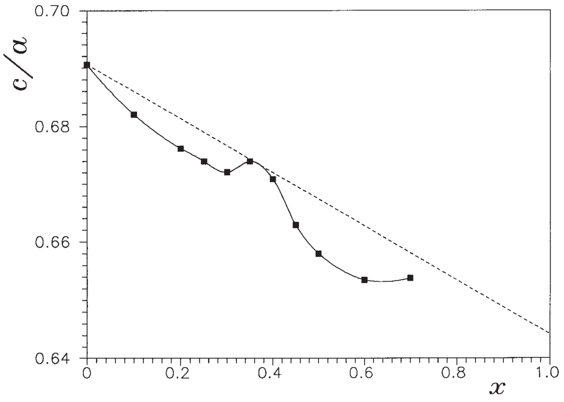

Fig. 6 Compositional dependence of tetragonal ratio of rutile type solid solutions in $(TiO_2)_x$–$(RuO_2)_{1-x}$ system. Points correspond to lattice parameters calculated from X-ray diffraction patterns shown in Fig. 5. Broken line represents linear dependence between lattice parameters of pure TiO_2 (JCPDS 21-1276) and pure RuO_2 (JCPDS 40-1290)

to those where unusual variations in the apparent activation energy were observed. The reason for such behavior is unknown.

Table 2 Lattice parameters of $(TiO_2)_x$–$(RuO_2)_{1-x}$ rutile type solid solution prepared by crystallization of amorphous gels

x	*a*/Ĺ	*c*/Ĺ
0	4.499±0.002	3.108±0.002
0.10	4.524±0.001	3.085±0.001
0.20	4.533±0.002	3.065±0.002
0.25	4.538±0.004	3.058±0.005
0.30	4.538±0.001	3.050±0.001
0.35	4.535±0.004	3.057±0.005
0.40	4.540±0.001	3.046±0.001
0.45	4.557±0.004	3.021±0.003
0.50	4.576±0.003	3.011±0.003
0.60	4.569±0.006	2.986±0.006
0.70	4.574±0.004	2.991±0.004

Conclusions

Single phase solid solutions in the $(TiO_2)_x$–$(RuO_2)_{1-x}$ system were prepared by controlled nanocrystallization of amorphous gels in the $0 \leq x \leq 0.7$ concentration range. The kinetics of this crystallization process does not correspond to the Johnson-Mehl-Avrami nucleation-growth model and it can be described by the two-parameter Šesták-Berggren model.

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