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RESEARCHES CONCERNING PHASE TRANSITION OF ZIRCONIUM TITANATE PREPARED BY ELECTROLYTIC METHOD

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ABSTRACT

Powder zirconium titanate ceramics obtained by an electrolytic method has been investigated. Continuous phase transition were found to occur in powder zirconium titanate above and below a major discontinuity at 1120^{o}C±10^{o}C. The phase transition is characterised by a decrease in the length of the longest unit-cell dimension, on conversion of the high-temperature form to the low-temperature structure. The unit-cell volume decreases continuously and linearly with decreasing temperature.

KEYWORDS: zirconium titanate, electrodeposition, phase transition, structure

1. Introduction

Zirconium titanate is a ceramic material that is used not only in the refractory industry but has application in electronic industry. Zirconium titanate is well known for the stability of some properties, namely those dielectrics, as well as for the small electric leakage. All these properties lead to its using in fabrication of condensers and resonant components at filters and oscillators with stable frequency in microwaves field.

Zirconium titanate is one of the most important ferroelectric materials used in manufacturing of ceramic transducers [4, 5]. Along with extension of using domain of zirconium titanate, the interest for preparation crystalline structure, phase transformation and for factors that influence the dielectric properties has been amplified.

Currently, is known that solid solution of $ZrTiO_4$-$Zr_5Ti_7O_{27}$, over temperature of 1200^{o}C, has an orthorhombic structure of α-PbO_2 type where zirconium and titanium atoms are random distributed into octahedral holes that are equivalents point of view of symmetry, such as presented in figure 1. Below 1200^{o}C, all compositions suffer a continuum phase transformation characterised by an increased arrangement of zirconium and titanium atoms.

For compositions that are similarly with $ZrTi_2O_6$ (e.g. $Zr_5Ti_7O_{24}$) ordinate structure has zirconium atoms segregated in each the third octahedral layer along of axis a, as in figure 1 (b) [1]. The passing from the form that is typical for the high temperature to the form that is specific at low temperature is characterised by a decreasing of the dimension of the higher elementary cell. The dimensions of the elemental cell are dependent of the thermal treatment history. In technical literature there are papers that present data concerning solid solutions of zirconium titanate obtained at high temperatures starting from titanium oxide and zirconium oxide.

2. Experimental

Present study has main aim the monitoring the structure of zirconium titanate at high and low temperature prepared by electrolytic method [3].

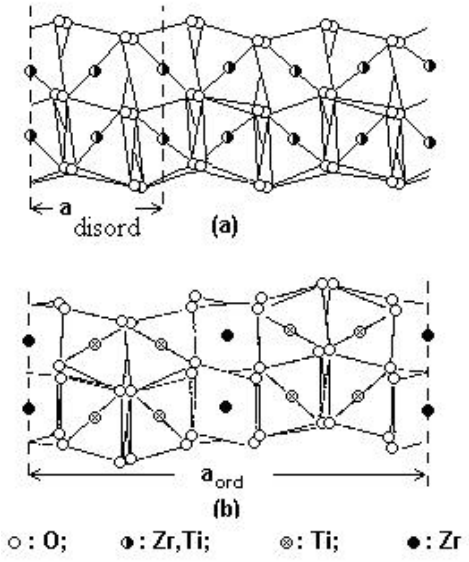

Fig. 1. *Projection of zirconium titanate on (010) plane.*

As opposed to classical methods where temperatures around of 1500^{O}C are necessary, in this case zirconium titanate is obtained at temperature of 600^{O}C-800^{O}C. After thermal treatment accomplished in air, powder, initially being in amorphous state, becomes crystalline.

This aspect has been carried out by X-ray diffraction method on DRON-3 equipment in CuKα radiation with U=32kV and I= 22mA.

It is worthy of note that powder didn't contain one of individual components of zirconium or titanium oxides and the analysis performed with electronic probe sowed a ratio Zr/Ti in the 0,97-1,02 range.

Hereby, obtained powder has been subjected to certain thermal treatments into chamber of high temperature of type UDV-1800 that is an annex of X-ray diffractometer.

The temperature was measured by a Pt-PtRh (10%) thermocouple having an accuracy of ±1^{o}C and electronic controlled.

The heating was done up to 1400^{o}C, monitoring the phase modification and evolution of lattice parameters by using a computerised technique on base of diffraction data [2].

3. Results and discussions

Different samples of zirconium titanate have been subjected to thermal treatment at various temperatures in range of 800^{o}C-1400^{o}C. The heating was performed with a rate of 1^{o}C/min.

Before recording the diffraction spectrum, the sample has kept a hour at treatment temperature. The experiments were performed in two manners.

A first mode consisted in monitoring of the same sample at diverse temperatures of thermal treatment, both heating and cooling.

The second mode consisted in heating of sample at each temperature of chosen thermal treatment, thus the X-ray diffraction spectrum was recorded.

The performed calculus didn't evinced significant differences in order to be taken in discussion.

In figure 2 the variation of lattice parameters versus thermal treatment temperature. The lattice parameter was estimated by measuring the angular position of X-ray diffraction lines appeared at high angles. In this way a good the accuracy of lattice parameter is obtained.

It was ascertain that the lattice parameter having the higher value, namely **c**, presents an accentuate variation in temperature range of 1100-1200^{o}C.

This result is in accordance with measurements of electric conductivity In range of temperatures corresponding to transition phase, that is approximate to 1200^{o}C, a significant variation of electric conductivity was carried out that can be connected to a modification of the electric charge type.

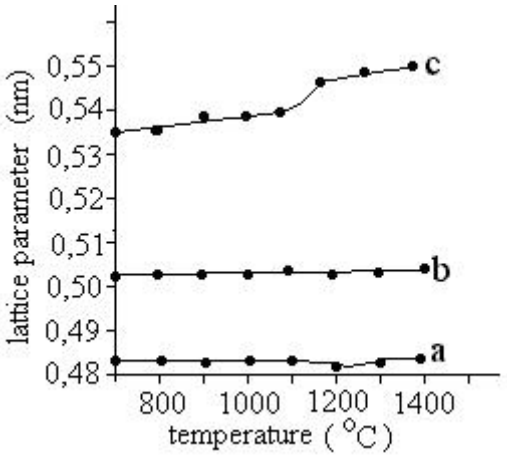

Fig. 2. *Variation of dimension of elemental cell on thermal treatment temperature.*

These results were interpreted as indicating a structural transition that occurs in this temperature range and that is accompanied of a deficiency of oxygen at high temperature and an excess of oxygen at low temperature [6].

Beside the accentuate variation of lattice parameter **c** which occurs at transition temperature between phase present at high temperature and phase from low temperature, a weak linear variation both above and bellow transition temperature.

The dimensions in direction of axis **a** and **b** remain unchanged after phase transition. In vicinity of transition temperature order-disorder a small variation of parameter **a** ascertained, but it can be considered as minor in regard to spread of experimental data. In studied temperature range, parameter **b** didn't present important changes.

The volume of elemental lattice presents a weak variation in regard to temperature. It continually and linearly decreases in proportion as thermal treatment temperature decreases both for phase from low temperature and the phase from high temperature.

The transition from the form that is present at high temperature to the form that is present at low temperature difficult occurs and demand a long time, it depending, probably, of cooling rate and thermal treatment temperature. Hereby, the cooling from 1400^{o}C at temperature around 700^{o}C having a rate of 1^{o}C/h is not accompanied of a complete transformation.

If the cooling occurs from temperature of 1200^{o}C at 700^{o}C, having the same rate, it is possible to obtain a complete passing at structure from low temperature. The difficult kinetic of transformation is an index of a structural changes that requests a

rearrangement on long distance of cations from lattice.

The continuously decreasing of volume of elemental lattice can correspond to a "modulation" of packing of anions as a response to ordering of cations. This fact can change the coordination of zirconium from six to seven or eight as is in other structures where zirconium is present.

The "modulation" of anions packing doesn't lead to a modification of crystal symmetry, fact that is proved by X-ray diffraction spectrum.

Continuously phase transition can be connected to continuously thermodynamic changes concerning to order-disorder characteristic of zirconium and titanium ions. The diffraction studies with neutron and electrons, as well as electronic microscopy can bring further information hereto.

4. Conclusions

1. Zirconium titanate powder prepared by electrolytic method has been subjected to thermal treatment and by XRD technique the lattice parameters were estimated at various temperatures.
2. During thermal treatment the lattice parameters **a,** and **b** remain unchanged, while the lattice parameter **c** presents an accentuate variation in temperature range of 1100-1200^{o}C.
3. The changes of lattice parameter **c** can be connected with significant variation of electric conductivity, indicating a structural transition accompanied of a deficiency of oxygen at high temperature.
4. At the same heating or cooling rate, the transition of lattice cell between the same two temperatures occur with different transformation kinetics due to further requested time for rearrangement on long distance of cations from lattice.
5. The continuously decreasing of volume of elemental lattice can correspond to a "modulation" of packing of anions as a response to ordering of cations.

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