Scientific
Research

Effect of Glass Composition on the Thermal Expansion of Relict Crystals of RuO$_2$ in Doped Lead-Silicate Glasses (Thick Film Resistors)

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Received January 8, 2011; *revised March* 6, 2011; *accepted March* 17, 2011

Abstract

The thermal expansion coefficients (TEC) of RuO$_2$ crystallits in thick film resistor (TFR) composites, consisting of RuO$_2$ dispersed in lead-silicate glass of various compositions, were evaluated from X-ray diffraction patterns at temperatures 298; 773; 973 and 1123 K corresponding to characteristic temperatures of resistivity and thermopower anomalies of the TFRs. It has been found that TEC of free RuO$_2$ powder along *a*-axis has an anomaly at T > 973 K (expansion is replaced by constriction), whereas constriction along *c*-axes remains for all temperatures. This anomaly disappears in doped glass of simplest composition (2SiO$_2$·PbO) but occurs in glasses of some complex compositions. Symmetry of unit cell of RuO$_2$ is not changed in the temperature range investigated.

Keywords: Ruthenium Dioxide, Anomalous Thermal Expansion, High Temperature X-Ray Diffraction, Anomalies of Resistivity and Thermopowe

1. Introduction

The structure of TFRs consisting of glass frit mixed with conducting powders (CP) of ruthenium oxide or metal ruthenates (namely, RuO$_2$, Pb$_2$Ru$_2$O$_6$ and Bi$_2$Ru$_2$O$_7$) was investigated to explain their conduction mechanism [1-4]. One of their peculiar behaviors is the fact that major portion of CP crystals remain in TFRs after firing. This is why many authors conclude that electrical conduction in TFR takes place due to infinite cluster(s) formed by linked CP particles.

This point of view and anomalies of the resistivity $\rho(T)$ and thermopower $S(T)$ of TFR at T > 700 K [5] as well as effect of CP content on sign and value of dρ/dT of the TFRs contradict one another.

Based on previous studies [6-8] and investigations of properties of RuO$_2$ at T < 500 K, it is assumed that RuO$_2$ does not exhibit the same anomalies.

The thermal expansion coefficient (TEC, α) of RuO$_2$ is anisotropic [6,7]—the unit cell is expanded in the *a* direction (α_a=100·10^{-7} K^{-1}), while in the *c* direction it is constricted (α_c= −23·10^{-7} K^{-1}). Lead-silicate glasses used in experiments have α ≈ 70·10^{-7} K^{-1}. So particles of RuO$_2$ in TFR are deformed {anisotropically} because of

temperature variations.

But, to our knowlwgde, this problem has not been investigated anywhere.

In addition, conduction of the RuO$_2$ powders we used is semiconductor-like [9], due to nonstoichiometry of its composition, which may affect their thermal expansion as well. In this connection, we have investigated thermal expansion of RuO$_2$ as free powder and in TFR, *i.e.* crystallites dispersed in glass, at 298; 773; 973 and 1123 K.

The samples we have investigated are free powders as well (*i.e.* without the substrate) and are prepared by standard technology without substrate (fired at 850°C in 10 min—see, for example, [5]).

Temperature points mentioned above are characteristic for anomalies in the $\rho(T)$ and $S(T)$ of TFR [5]. The glasses examined have the following composition (weight %):

1) SiO$_2$ 33; PbO 67;
2) SiO$_2$ 33; PbO 63; Al$_2$O$_3$ 4;
3) SiO$_2$ 27; PbO 67; BaO 4; MgO 2.

Content of CP was 16 mass % in all cases.

Using HTK-10 Anton PAAR high-temperature powder camera and CuKα radiation from Siemens D500 X-ray unit powder diffraction patterns were taken at

temperatures 298; 773; 973 and 1123 K at the Institute of Catalysis of Siberian Branch of the Russian Academy of Sciences (Novosibirsk).

2. Experimental Results

Table 1 shows the unit cell parameters at 298 K (accuracy of measurement is ±0.001 Å) of RuO_2 free powder and crystallits in TFRs made with glasses of various compositions (see above). The sequence of main reflexes of RuO_2 on X-ray patterns remains unchanged in all cases, indicating the symmetry of the unit cell is remained. Changes of unit cell parameters of free RuO_2 powder are shown in **Figure 1(a)** in the temperature range 298 - 1123 K. Thermal expansion coefficients (TEC) α_a and α_c of free powder and crystallites in TFRs, evaluated in the temperature range 298 - 1123 K, are listed in **Table 2**, together with average values of TEC from [11,12]. It is characteristic that values of α_a and α_c we evaluated in temperature range 298 - 773 K are nearly 50 % higher than that of single crystal of RuO_2 [11,12]. Partial substitution of PbO by Al_2O_3 in glass 1 does not change the variation of $\alpha_a(T)$ characteristic for TFR based on glass 1 (**Figure 1(b)**) but changes the $\alpha_c(T)$ (**Figure 1(c)**) —crystallites expand up to 973 K in the c direction instead of contraction, indicating that strengthening of the glass network by Al_2O_3 tends to force the RuO_2 particles to extend in concordance with the glass. This conclusion is confirmed by **Figure 1(d)** showing $a(T)$ and $c(T)$ of TFR based on glass 3. Part of the SiO_2 is replaced by BaO and MgO in this glass. BaO and MgO are not glass network formers in silicate glass and do not change usual properties of glass [10]. But partial depolymerisation of the glass network in this case allows RuO_2 crystallites to extend more freely in comparison with TFR based on glass 2. This effect appears as nonmonotonic behavior of $a(T)$ and $c(T)$.

The values of a and c we obtained are significantly higher than those of [11-13], and indicate that our samples have the most defective structure and non-stoichiometric composition caused by oxygen enrichment. This might be a possible reason for the appearence of the semiconductor properties in these powders [9].

Changes of unit cell parameters of free powder of the RuO_2 are shown in **Figure 1(a)** in the temperature range 298 - 1123 K. Temperature dependence of $c(T)$ is monotonic and is in agreement with the results of other authors

[11,12] while the minimum of $a(T)$ occurs at 973 K in contrast to the results of [11,12].

The TEC α_a and α_c of the tree powder and relicts of RuO_2 in TFR were evaluated in 298 - 1123 K temperature range and are listed in **Table 2** where mean values of TEC from [11,12] in same temperature interval are listed for comparison as well.

It is characteristic that values of α_a and α_c we evaluated in temperature range 298 - 773 K are nearly 50 % larger than that for the single crystal of RuO_2 [11,12].

The anomaly of α_a disappears in the TFR made of the simplest lead-silicate glass 1 and its value decreases up to the half of the original value. Shape of the $\alpha_c(T)$ is deformed slightly althought the module of α_c is increased nearly fourfold.

Substitution of the part of PbO by Al_2O_3 in glass 1 does not change the characteristic variation of $\alpha_a(T)$ of TFR based on the glass 1 (**Figure 1(b)**) but changes the $\alpha_c(T)$ (**Figure 1(c)**)—relicts of RuO_2 in c direction expand up to 973 K instead of constriction. So strengthening of the glass frame due to substitute Al_2O_3 leads to the bond strengthening between RuO_2 particles and glass so last forces their to extend in concord.

3. Conclusions

X-ray diffraction patterns of TFR at high temperature

Table 2. TEC of RuO_2 (10^{-7} K^{-1}).

		α_a	α_c
	RuO_2	144	-33.8
Our samples	RuO_2+gl.1	69.8	-127
	RuO_2+gl.2	74.2	+47.3
	RuO_2+gl.3	144	-20.3
[9]	RuO_2	103	-23.2
[10]	RuO_2	101	-28.3

(a)

(b)

Table 1. Parameters of the unit cell of RuO2 (Å) at 298 K.

		a	c
	RuO_2	4.523	3.113
Our samples	RuO_2+gl.1	4.523	3,144
	RuO_2+gl.2	4.538	3,113
	RuO_2+gl.3	4.523	3,118
[9]	RuO_2	4.4904	3.1064
[10]	RuO_2	4.4909	3.1064
[11]	RuO_2	4.51	3.11
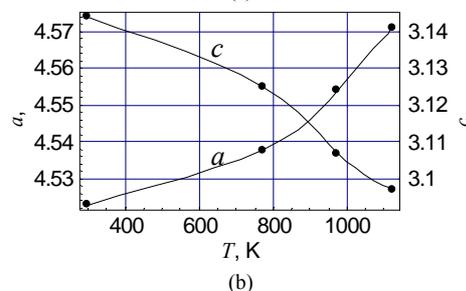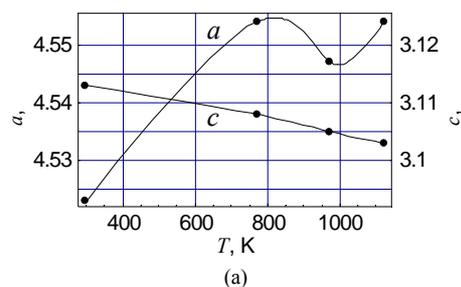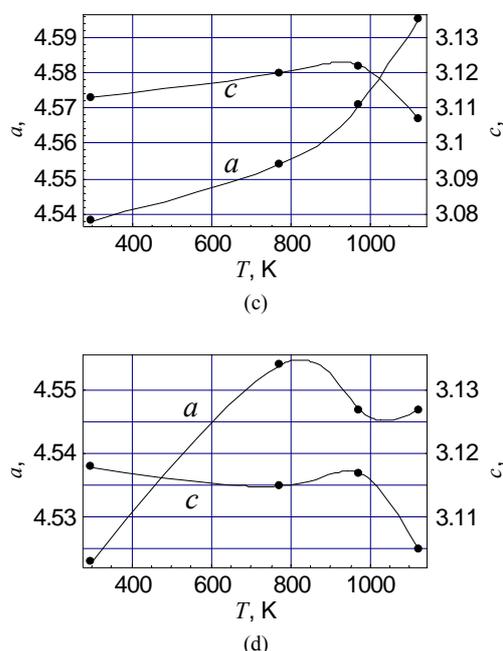
Figure 1. Temperature dependence of unit cell parameters of RuO2: (a) free powder; (b) with glass 1; (c) with glass 2; (d) with glass 3.

show that embedded RuO_2 crystallites are stressed due to mismatch of TEC of glass and RuO_2 crystals. $\alpha_a(T)$ of the latter is positive and almost twice as large as TEC of glass while $\alpha_c(T)$ is negative with absolute value being half that of glass TEC. Composition of glasses used in TFR strongly affects TEC of RuO_2 crystallites up to change of its sign. It is possible that enigmatic behavior of TFR, e.g. quadratic temperature dependence of resistance, is caused by thermal deformation of RuO_2 crystallites.

4. Acknowledgements

5. References

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