Key Engineering Materials Vols. 132-136 (1997) pp. 1313-1316

THERMODYNAMIC AND EXPERIMENTAL INVESTIGATION OF THE EFFECT OF RARE-EARTH IONS (Ln^{3+}) NATURE ON THE POSISTOR PROPERTIES OF ($Ba_{1-x}Ln_x^{3+}$)TiO_3.

A.G.Belous, O.I.V'yunov, O.Z.Yanchevskii, L.L.Kovalenko
Department of Solid State Chemistry, Institute of General and Inorganic Chemistry
Palladin avenue 32/34, 252680 Kyiv-142, Ukraine
Phone/ fax: +38 (044) 444-2211; e-mail:postmaster@ionc.kiev.ua

Keywords: posistor, rare-earth ions, substitutions, grain size.

Abstract. Systems based on $BaTiO_3$ with aliovalent substitutions in A cation sublattice have been investigated. The effect of substitution on the microstructure and electrophysical properties of ceramic is shown. The results of thermodynamic consideration were shown to be in agreement with experimental data on the effect of rare-earth ions on the electrophysical properties of posistor materials.

Introduction

Semiconducting barium titanate, which is widely used for the preparation of posistor materials, is prepared by aliovalent substitution in one of cation sublattices. Rare-earth ions can be used as ions substituting for barium ions [1-4]. Ref.[1] showed that in the series from La^{3+} to Ho^{3+} rare-earth ions introduced into barium titanate act as donors and give rise to posistor properties. At the same time, when Ba^{2+} is substituted by Tm^{3+}, Yb^{3+} and Lu^{3+}, no posistor properties arise. This is accounted for by the fact that the above ions (Tm^{3+}, Yb^{3+}, Lu^{3+}) are part of titanium sublattice and act as acceptors. The Er^{3+} ion is a transitional one and can act as both donor (for A-to-B ratio less than unity) and acceptor (for A-to-B ratio greater than unity). At the same time, ref.[1] does not explain why some rare-earth ions are part of sublattice A and others are part of sublattice B. It does not report concentration ranges in which semiconductor properties are generated. There is also a discrepancy in describing the dependence of critical rare earth concentration: ref.[2] reports that the critical concentration decreases with Ln^{3+} radius, and ref.[1] shows it to be the same for all rare-earth elements except Er^{3+}. Therefore, this paper deals with the elucidation of the above questions.

2 Materials Preparation and Experimental Methods

All the samples for this investigation were prepared by a conventional solid-state reaction technique. Extra-pure $BaCO_3$, TiO_2, Sc_2O_3, Y_2O_3, La_2O_3, Nd_2O_3, Sm_2O_3, Dy_2O_3, Lu_2O_3, SiO_2 were used as starting reagents. Phase changes were studied by the thermogravimetric method using a Q-1000 OD-102 device. X-ray diffractometry (XRD) measurements were carried out on a DRON-3M diffractometer with Cu*K*α radiation. The lattice parameters were determined using the 224 and 422 reflections, the determination error being $5\cdot10^{-5}$ nm. Samples sintered at 1340-1360°C were used to study the electrophysical properties. Ohmic contacts were produced by burning aluminum paste applied to posistor surfaces. The granular structure of as-fired surfaces was examined using an electron-probe microanalyzer (EPMA, JEOL JCXA-733, Japan).

Results and Discussion

XRD data for barium titanate doped by rare-earth elements are shown in Fig.1. The reduced $(Ba_{1-X}Ln_X)TiO_3$ perovskite lattice parameters $\bar{a} = (a^2c)^{1/3}$ as a function of rare-earth ion concentration pass through a maximum. At low rare-earth ion concentrations, the increase in this parameter may be attributed to the appearance of Ti^{3+} ions, whose radius is larger than that of Ti^{4+} ions, in B sublattice. It should be noted that the increase in lattice parameter cannot be attributed either to the aliovalent substitution of barium by rare-earth ions (the ionic radius of all rare-earth elements is smaller than that of barium) or to the aliovalent substitution of titanium by rare-earth ions (this substitution prevents the arising of semiconductor properties). The reduced parameter maximum corresponds to the concentration at which a resistance minimum is observed. At high concentrations, this parameter decreases due to both a decrease in Ti^{3+} ion concentration and the aliovalent substitution of barium by elements with smaller ionic radius.

Comparison of the dependences of the lowest specific resistance at room temperature (ρ_{20^oC}) and average grain size (d_{av}) in the case of adding rare-earth elements (Fig.2) showed that when yttrium is added, the broadest concentration range in which semiconductor properties exist is observed.

It is known [5] that in the case of complicated perovskite compounds such as $(A_X', A_{X2}''... A_{XK}^{(K)})(B_Y', B_{Y2}''... B_{YL}^{(L)})X_3$, where $\sum_{i=1}^{k} x_i=1$ and $\sum_{j=1}^{l} y_j=1$ ($x_i>0$, $y_j>0$), the crystal electroneutrality requirement:

$$\sum_{i=1}^{k} x_i n_{A(i)} + \sum_{j=1}^{l} y_j n_{B(j)} + 3n_x = 0 \tag{1}$$

where $n_{A(i)}$, $n_{B(j)}$ and n_x are the valences of corresponding ion, and definite requirement to ion size:

$$t_1 < t = \frac{\overline{R}_A + R_O}{\sqrt{2}(\overline{R}_B + R_O)} < t_2; \quad a_1 < a = \frac{R_{Ai}}{R_O} < a_2; \quad b_1 < b = \frac{R_{Bi}}{R_O} < b_2 \tag{2}$$

where $\overline{R}_A = \sum_{i=1}^{k} x_i R_{A(i)}$ and $\overline{R}_B = \sum_{j=1}^{l} x_J R_{B(J)}$, must be met. These conditions limit the size of ions $A^{(i)}$ and $B^{(j)}$ and the average radii $\overline{R}_A$ and $\overline{R}_B$. Numerous experimental data show that usually t_1=0,76, t_2=1,03; a_1=0,73, a_2=1,13; b_1=0,41, b_2=0,74.

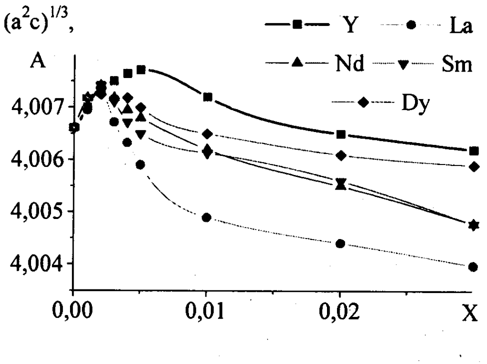


Fig.1 Reduced lattice parameters of the $(Ba_{1-X}Ln_X)TiO_3$ ceramic, where Ln = Y, La, Nd, Sm, Dy *vs.* the degree of aliovalent substitution (x).

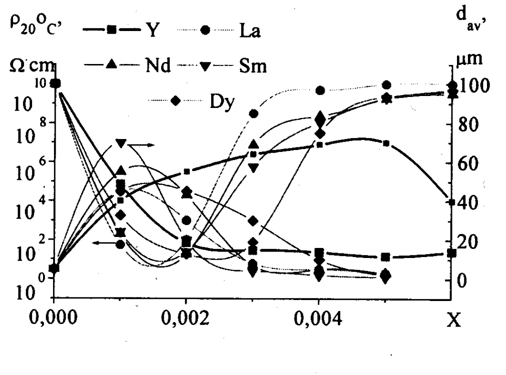


Fig.2 Specific resistance (ρ, 20°C) and average grain size (d_{av}) of the $(Ba_{1-X}Ln_X)TiO_3$ ceramic, where Ln = Y, La, Nd, Sm, Dy *vs.* the degree of aliovalent substitution (x).

The perovskites under investigation may be represented as $(Ba_{1-X}Ln_X)TiO_3$, where Ln = Sc, Y, Ln, Nd, Sm, Dy, Lu; $0 \leq X \leq 0.03$. The calculations of steric parameters for complex perovskites showed that the perovskite structure must be formed independent of the Ln^{3+} radius value in the aliovalent substitution concentration ranges studied. It should be also noted that we showed earlier for $La_{2/3-X}Li_{3X}TiO_3$ that the A sublattice of the complex (A'A")BX$_3$ perovskite can contain a small Li^+ ion if the second A sublattice ion meets all perovskite structure requirements [6,7]. The calculation of steric parameters carried out by us and the data of refs. [6,7] allow us to suggest that all rare-earth ions are in the A sublattice whatever Ln^{3+} radius. Ref.[8] reports that the arising of semiconductor properties in $(Ba_{1-X}^{2+}Ln_X^{3+})TiO_3$ perovskites is associated with the formation of solid solutions $(1-X)Ba^{2+}Ti^{4+}O_3$ - $xLn^{3+}Ti^{3+}O_3$. The calculation of steric parameters for $Ln^{3+}Ti^{3+}O_3$ carried out by us showed that the perovskite structure must form when Ln is Y and La-Ho and must not form when Ln is Tm, Yb and Lu. The ionic radius of erbium is close to the maximum radius, for which the existence of the $Ln^{3+}Ti^{3+}O_3$ perovskite structure is still possible. These results are in good agreement with both the results obtained by us and the data of ref.[1] and show that semiconductor properties will arise if the steric requirements for the formation of the $Ln^{3+}Ti^{3+}O_3$ perovskite are met. In this case, the doping process may by represented as redox reactions of formation of rare-earth titanates $LnTi^{3+}O_3$ and their dissolution in $BaTiO_3$ [9,10] on the one hand:

$$\begin{aligned}(1-X)BaCO_3 + \tfrac{x}{2}Ln_2O_3 + TiO_2 \rightarrow (Ba_{1-X}^{2+}Ln_X^{3+})(Ti_X^{3+}Ti_{1-X}^{4+})O_3 + \\ + (1-X)CO_2 \uparrow + \tfrac{x}{4}O_2 \uparrow\end{aligned} \qquad (3)$$

and oxidation of the semiconducting solid solution $(Ba_{1-X}Ln_X)(Ti_{1-X}^{4+}Ti_X^{3+})O_3$ followed by the formation of rare-earth dititanates [10] on the other hand:

$$\begin{aligned}&(Ba_{1-X}^{2+}Ln_X^{3+})(Ti_X^{3+}Ti_{1-X}^{4+})O_3 + \tfrac{X}{4}O_2 \equiv [Ba_{1-X}Ti_{1-X}O_{3(1-X)} + xLnTiO_3] + \tfrac{X}{4}O_2 \Leftrightarrow \\ &\Leftrightarrow (1-X)BaTiO_3 + \tfrac{X}{2}La_2Ti_2O_7\end{aligned} \qquad (4)$$

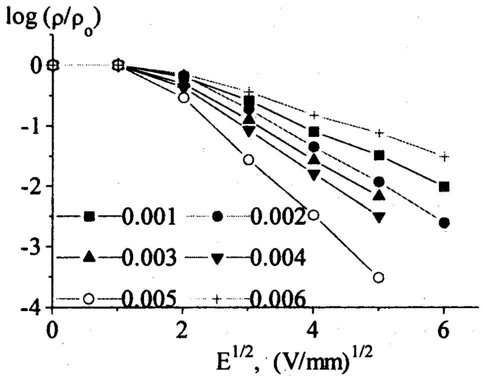
Equation (4) simplifies to:

$$xLn^{3+}Ti^{3+}O_3 + \tfrac{x}{4}O_2 \Leftrightarrow \tfrac{x}{2}Ln_2Ti_2^{4+}O_7 \qquad (5)$$

There are no thermodynamic data for these systems; however, ref.[8] reports a qualitative estimation of oxidation reaction energetics in accordance with eq. (5). The enthalpy of this reaction may be represented as follows:

$$\Delta H = x(\Delta H_{fTi^{4+}O_2}^{el} - \Delta H_{fTi^{3+}O_{1.5}}^{el}) + x(\Delta H_{fLnTi^{3+}O_{3.5}}^{ox} - \Delta H_{fLnTi^{3+}O_3}^{ox}) - \Delta H^{dis} \qquad (6)$$

where ΔH_f^{el} is the enthalpy of TiO_2 and $1/2Ti_2O_3$ formation from elements, ΔH^{ox} the enthalpy of $LnTiO_3$ and $1/2Ln_2Ti_2O_7$ formation from oxides and ΔH^{dis} the enthalpy of $LnTiO_3$ dissolution in $BaTiO_3$. On the basis of the analysis reported in ref.[8] it can be concluded that the lower the absolute value of difference in formation enthalpy between $Ln_2Ti_2O_7$ and $LnTiO_3$, the weaker the endothermic effect of solid solution formation, and hence at a lower temperature the formation of a semiconducting solid solution is possible, or at a fixed temperature a high degree of reduction of $BaTiO_3$ is attained. This indicates that the broadest concentration range of semiconductor properties must be observed when barium ions are substituted by yttrium ions, which agrees with experiment.



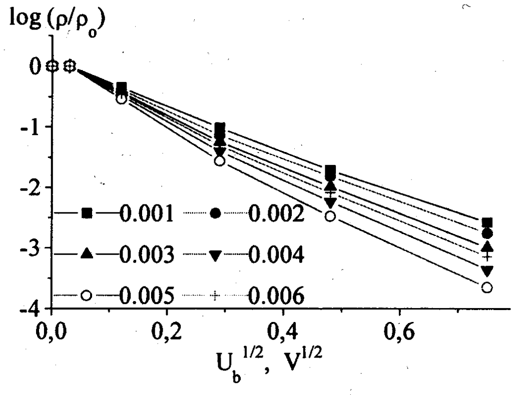


Fig.3 Logarithm of the normalized specific resistance (log ρ/ρ$_0$) of the $(Ba_{1-x}Y_x)TiO_3$ ceramic *vs.* field strength (T=300°C).

Fig.4 Logarithm of the normalized specific resistance (log ρ/ρ$_0$) of the $(Ba_{1-x}Y_x)TiO_3$ ceramic *vs.* voltage across an individual grain boundary (T=300°C).

Investigations of electrophysical properties showed that the strongest varistor effect is observed in ceramic at x=0.005 (yttrium) (fig.3). At the same concentrations, the grain size (d_{av}) is a maximum. Fig.4 shows plots of specific resistance normalized with respect to its value at zero voltage versus single-boundary voltage (U_b=E x d_{av}), which were made using grain size data. As can be seen from fig.4, these plots are linear when voltage is over 0.3 V. The dependences of the slope of the linear region of the curve $\lg(\rho/\rho_0)=f(U_b)^{1/2}$ on the yttrium concentration are essentially the same. It follows that the ceramic grain size influences mainly the varistor effect.

Conclusion

The investigations carried out allow us to conclude that when rare-earth elements are added to barium titanate, the arising of semiconductor properties is coupled with the formation of the solid solution $Ba^{2+}Ti^{4+}O_3$ - $Ln^{3+}Ti^{3+}O_3$. If the ionic radii of rare-earth ions do not meet the steric requirements, which are necessary for the formation of the $Ln^{3+}Ti^{3+}O_3$ perovskite, semiconductor properties will not arise. The concentration ranges in which semiconductor properties arise in $(Ba_{1-x}Ln_x)TiO_3$, where Ln = Y, La, Nd, Sm, Dy, have been established. It has been shown that the broadest concentration range of semiconductor properties is formed in the case of aliovalent substitution of barium by yttrium ions, which may be accounted for in terms of the thermodynamic conditions of $Ln^{3+}Ti^{3+}O_3$ formation.

References

[1] P.A.Xue, Y.Chen, R.J.Brook, Mater.Sci and Eng. v.B1 (1988) p.193-201.
[2] S.B.Desu, D.A.Payne, J.Am.Ceram.Soc. v.73, 11 (1990) p.3391-3421.
[3] O.I.Prokopalo, Y.I.Goltsov *et al*, Izv. AN SSSR, Ser.Fiz., v.33, 7 (1969) p.1157-1161.
[4] B.A.Rotenberg, Y.L.Danilyuk *et al*, Fizika Tvyordovo Tela, v.1, 10 (1965) p.3048-3053.
[5] G.A.Smolenskii, A.I.Agranovskaya, Zhurnal Teoreticheskoi Fiziki, v.28 (1958) p.1491.
[6] A.G.Belous, G.N.Novitskaya *et al*, Zhurnal Neorganicheskoi Khimii, v.32, 2 (1987) p.283-286
[7] A.G.Belous, Solid State Ionics, v.90 (1996) p.193-196.
[8] Y.P.Kostikov, B.B.Leikina, Neorganicheskie Materialy, v.21, 11 (1985) p.1915-1917.
[9] E.I.Gindin, M.A.Kvantov *et al*, Izv. AN SSSR, Neorg. Materialy, v.16, 11 (1983) p.2068.
[10] A.I.Leonov, M.A.Kvantov *et al*, Izv. AN SSSR, Neorg. Materialy, v.19 , 5 (1983) p.799.