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# COMPOSITION DEPENDENT SEMICONDUCTOR–METAL TRANSITION IN NEW MIXED VALENT TI-OXIDES†

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**Abstract**—A composition dependent semiconductor–metal transition is observed in a new series of Ti oxides of the type $LnBa_2Ti_3Oy$ (Ln = La, Gd and Y) in which Ti is in lower and/or mixed valent state. The new phases have been synthesised by the dc arc melting technique and characterised by powder X-ray diffraction, thermal analysis, electrical and magnetic measurements. Single phase compounds are found to form only when the nominal (average) Ti valence ($V_{Ti}$) is between 3.67 to 2.33. The crystal structure is simple cubic in which Ln/Ba and various Ti ions occupy respectively the A- and B-sites of a disordered $ABO_3$ perovskite type lattice. The semiconductor–metal transition is also found to depend on the $V_{Ti}$. The compounds show semiconducting behaviour for $3.67 < V_{Ti} > 2.67$ and are metallic when $V_{Ti} = 2.33$ which is the lowest possible value of $V_{Ti}$ in the system. No evidence for superconductivity has been observed in any of the metallic compositions down to 15 K. © 1997 Elsevier Science Ltd.

*Keywords:* A. oxides, D. electrical properties, D. superconductivity, D. phase transitions

## 1. INTRODUCTION

Mixed valent binary and ternary transition metal oxides have been a main subject of numerous studies in the physics and chemistry of solids because of their very interesting properties [1–4]. Many of them, especially in the proximity of the semiconductor–metal phase boundary have been found to exhibit many fascinating physical properties. It is well known that semiconductor–metal transitions in oxides can be brought about by changing the temperature, pressure or composition [5, 6]. One of the early interests was to study the temperature/pressure dependent semiconductor–metal transition in binary 3d transition oxides like $V_2O_3$, $Ti_2O_3$ and $VO_2$ [7]. This was followed by the discovery of superconductivity in mixed valent Ti-spinel oxide system $LiTi_2O_4$ in which a $T_c$ of 13.7 K was observed [8]. The discovery of high temperature superconductivity in mixed valent layered Cu oxides shifted the interest to copper based compounds [9]. The latest interest is in the observation of semiconductor–metal transition and the so called 'colossal' magnetoresistance (CMR) in mixed valent Mn-oxides [10–12]. In all the above systems, the importance of formal mixed valence towards the realisation of interesting properties have been demonstrated. Moreover, these systems exhibit a continuous variation from semiconductor to metallic (or *vice versa*) behaviour as a function of composition. In fact, these two criteria *viz.* the introduction of mixed valence (or valence fluctuations or disprortinations) in the lattice and realisation of a marginally metallic composition near semiconductor–metal phase boundary have been suggested as an empirical guide line for the search for new superconducting oxide systems [12, 13]. There have been some recent investigations in this direction on the early transition metal oxides [14, 15].

Composition dependent semiconductor to metal transitions in Ti-based oxides systems are known in the literature. For example, in $Ln_{1-x}A_xTiO_3$ (Ln = rare earth or Y, A = alkaline earth) such a transition is found to occur as the system goes from $d^0$ state ($ATiO_3$) to a $d^1$ state ($LnTiO_3$) [16–18]. Similar observations have been found also in the Ti-oxide spinel systems $Li_{1+x}Ti_{2-x}O_4$ [19] and $Li(Ti_{1-x}, V_x)_2O_4$ [20] and recently in perovskite related $La(Ti_{1-x}, V_x)O_3$ [21].

In our search for superconductivity in marginally metallic compositions near semiconductor–metal phase boundary in mixed valent Ti based systems, we have investigated the Ln–Ba–Ti–O system in which Ti is incorporated in a lower and/or mixed valent state. Similar to the high $T_c$ cuprates with the possible $Cu^{1+}$, $Cu^{2+}$ and $Cu^{3+}$ valence states, the present system provide the availability of three consecutive valence states, a prerequisite for charge disproportinaton. Further more, comparing with high $T_c$ cuprates, which formally contain $Cu^{2+}/Cu^{3+}$ ($d^9/d^8$ system), a $Ti^{3+}/Ti^{2+}$ ($d^1/d^2$ system) containing compounds can be promising considering their electronic equivalence in terms of hole formalism. This paper reports the synthesis and characterisation of a new series of mixed valent Ti-oxides in which a

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composition dependent semiconductor–metal transition is observed as a function of the average Ti valence ($V_{Ti}$) in the lattice. The results indicate that while semiconducting, semimetallic or metallic behaviour can be induced in compounds of the type $LnBa_2Ti_3O_y$, no evidence for superconductivity is observed above 15 K.

## 2. EXPERIMENTAL

Arc melting is a very versatile technique for the synthesis of a variety of compounds including lower and/or mixed valent transition metal oxides [22]. This synthesis route has been very successful in the synthesis of many Ti-based oxide systems [17, 20, 23]. All the compositions studied in the present investigation were synthesised by the dc arc melting technique (TRI-ARC Series 5, Centorr, USA) in Ti-gettered Ar- atmosphere starting from high purity $Ln_2O_3$, $BaCO_3$ and $Ti_xO_y$ (e.g. TiO, $Ti_2O_3$ and $TiO_2$). $Ln_2O_3$ and $TiO_2$ were preheated at 1200°C for 24 h prior to use. TiO and $Ti_2O_3$ were also prepared by arc melting technique starting from pure Ti-metal and $TiO_2$ in appropriate stoichiometry. A few select $LaBa_2Ti_3O_y$ compositions were also synthesised by the high temperature solid state reaction in evacuated and sealed quartz tubes starting from $La_2O_3$, BaO (prepared by the decomposition of $BaCO_3$) and $Ti_xO_y$ at 1200°C with repeated grindings and heatings. All the phases including the starting TiO and $Ti_2O_3$ were characterised by powder X-ray diffraction (XRD, Philips PW1140) using Ni-filtered $CuK_\alpha$ radiation. Thermogravimetric analyses (TGA, Perkin-Elmer, Model 3600) were carried out on select samples in pure oxygen atmosphere up to 900°C in an attempt to estimate the oxygen value (*y*) in the compounds. Low temperature (300–77 K) four probe dc electrical resistivity on as-cast samples were carried out on a closed cycle He-refrigerator (CTI Cryogenics, Model 21C). ac magnetic susceptibility (300–15 K) studies on powdered samples, mainly to check for any transition indicative of superconductivity, were carried out on a Sumitomo superconductivity measurement system (Model SCR-204T) in fields of the order of 0.30–0.35 Oe. Prior to resistivity and susceptibility studies the arc melted buttons were annealed at 1000°C in evacuated and sealed quartz tubes in order to homogenise the phases.

## 3. RESULTS AND DISCUSSION

Compounds of the type $LnBa_2Ti_3O_y$, Ln = La, Gd and Y presently synthesised and characterised are listed in Table 1. The shiny black and fragile arc-melted buttons were found to be reasonably stable under ordinary conditions. However, evidence for slow degradation was noticed upon powdering and prolonged exposure. All the samples were hence stored as as-cast in vacuum desiccator. The X-ray powder patterns (Figs 1 and 2) showed a close similarity to that of the many cubic perovskites known in the literature and hence the indexing was carried on accordingly. Moreover, the intensity ratio matched well with that of a theoretically generated XRD pattern using the Lazy-Pulverix computer programme [24] assuming a cubic perovskite lattice (Sp. Group Pm3m). The arc melted samples showed better purity and crystalinity compared to the samples synthesised by the solid state reaction route. The least square fitted cubic lattice parameters are given in Table 1. One of the compositions namely $LaBa_2(Ti_2^{4+}, Ti^{3+})O_{9.0}$ has been reported in the literature during the study of $LaTiO_3$–$BaTiO_3$ solid solution system by Johnston and Sestrich [25] and our lattice parameter is in good agreement with the reported value. No superstructure reflections corresponding to the ordering of either La and Ba ions at the A-sites or between the various Ti ions at the B-sites of the perovskite lattice where observed indicating only

Table 1. Structural and electrical data on the various $LnBa_2Ti_3O_y$ (Ln = La, Gd, Y) compositions

| No. | Composition* | $V_{Ti}$† | Lattice parameter (Å) | $\rho_{300\,K}$ (Ω cm) | $\rho_{77\,K}$ (Ω cm) | Remarks |
|---|---|---|---|---|---|---|
| 1 | $LaBa_2(Ti_2^{2+}, Ti^{3+})O_{7.0}$ | 2.33 | 4.031 | $1.48 \times 10^{-3}$ | $0.75 \times 10^{-3}$ | Metallic |
| 2 | $LaBa_2(Ti_2^{2+}, Ti^{4+})O_{7.5}$ | 2.67 | 4.001 | $6.31 \times 10^{-1}$ | $20.98 \times 10^{-1}$ | Semiconducting |
| 3 | $LaBa_2(Ti_2^{3+}, Ti^{2+})O_{7.5}$ | 2.67 | 4.050 | $1.71 \times 10^{-1}$ | $1.71 \times 10^{-1}$ | Semimetallic |
| 4 | $LaBa_2(Ti_3^{3+})O^{8.0}$ | 3.00 | 3.990 | 2.05 | 28.09 | Semiconducting |
| 5 | $LaBa_2(Ti_2^{4+}, Ti^{2+})O_{8.5}$ | 3.33 | 4.003 | 6.90 | 75.62 | Semiconducting |
| 6 | $LaBa_2(Ti_2^{3+}, Ti^{4+})O_{8.5}$ | 3.33 | 3.904 | 8.24 | 97.62 | Semiconducting |
| 7 | $LaBa_2(Ti_2^{4+}, Ti^{3+})O_{9.0}$ | 3.67 | 3.950<br>(3.98)‡ | 8.76 | 101.14 | Semiconducting |
| 8 | $GdBa_2(Ti_2^{2+}, Ti^{3+})O_{7.0}$ | 2.33 | 4.020 | $5.37 \times 10^{-3}$ | $4.61 \times 10^{-3}$ | Metallic |
| 9 | $GdBa_2(Ti_2^{3+}, Ti^{2+})O_{7.5}$ | 2.67 | 4.010 | $2.73 \times 10^{-1}$ | $14.95 \times 10^{-1}$ | Semiconducting |
| 10 | $YBa_2(Ti_2^{2+}, Ti^{3+})O_{7.0}$ | 2.33 | 3.959 | $5.99 \times 10^{-3}$ | $4.66 \times 10^{-3}$ | Metallic |
| 11 | $YBa_2(Ti_2^{2+}, Ti^{3+})O_{7.5}$ | 2.67 | 4.001 | $3.62 \times 10^{-3}$ | $4.18 \times 10^{-3}$ | Semiconducting |

*The oxygen value, '*y*' has not been determined. Only nominal values based on starting oxides are given.
†Average Ti valence calculated from the nominal starting compositions.
‡From Ref. [25].

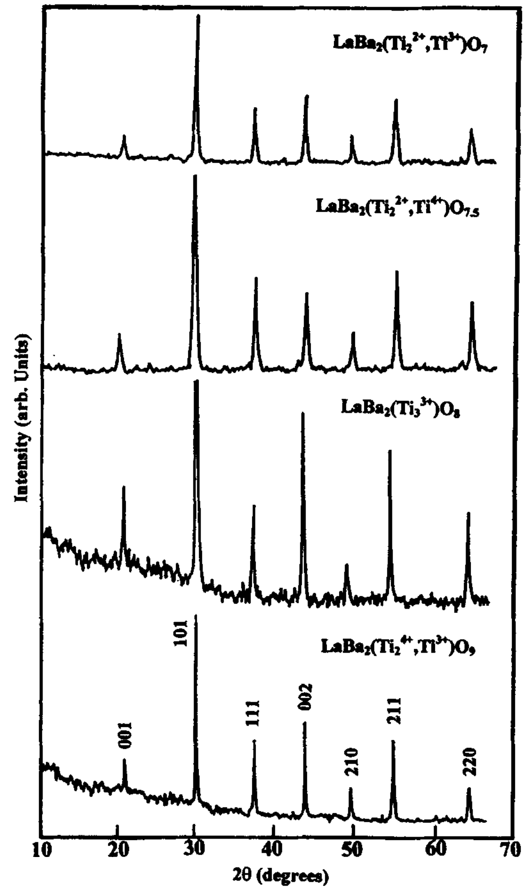

Fig. 1. X-ray powder patterns for various $\mathrm{LaBa_2Ti_3O_y}$ compositions.

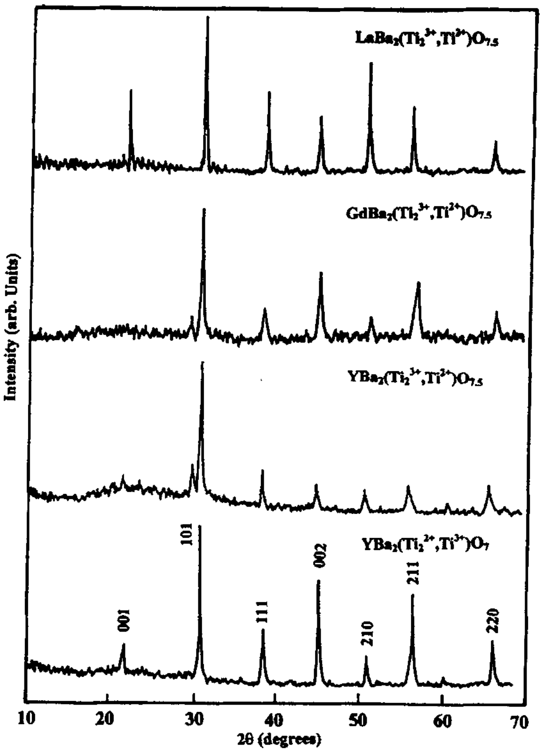

Fig. 2. X-ray powder patterns for $\mathrm{LnBa_2Ti_3O_y}$ (Ln = La, Gd, Y) compositions.

random occupancy for these ions in their respective crystallographic sites unlike in the case of many ordered perovskites of the type $\mathrm{A_3B_3O_9}$. The only exceptions were that of $\mathrm{LnBa_2(Ti_2^{3+}, Ti^{2+})O_{7.5}}$ (Ln = Y, Gd) were slight splitting of the lines has been noted, probably indicating a possible tetragonal distortion from the cubic perovskite structure for these compositions. This could be due to an ordering of Gd/Y and Ba ions in the lattice arising from their larger ionic radii difference compared to that between La and Ba. Presence of some low intensity impurity lines in the case of Ln = Gd indicates the lower limit for the ionic radii for the Ln-ions which can be accommodated in this type of phase. Due to the fact that oxygen content is not a constant for the series under investigation, the observed lattice parameters were not found to follow the expected trend from the ionic radii considerations of the various ions involved. However, among the various rare earth's (Ln) and with fixed Ti ratio and oxygen content, a systematic variation in accordance with the ionic radii of Ln was noticed. Our exploratory attempts to make a composition containing only $\mathrm{Ti^{4+}}$ or $\mathrm{Ti^{2+}}$ resulted only in multiphase samples indicating that single phase compounds could exist only in a narrow composition range where the average Ti valence is between 2+ and 4+.

TGA studies in oxygen atmosphere up to 900°C indicate that the samples start gaining oxygen around 400°C. The weight gain can be accounted due to the oxidation of lower valent Ti present in the samples to $\mathrm{Ti^{4+}}$. However, the oxygen uptake did not saturate up to 900°C (the upper limit of our TGA system) and hence the accurate estimation of the oxygen content was not possible in the present study. We also noted that the black colour of the starting materials change to white after the TGA run indicating oxidation of the sample. An X-ray examination of the white TGA end product showed that it is no longer a single phase (mainly $\mathrm{La_2Ti_2O_7}$ and $\mathrm{BaTiO_3}$). This observation further substantiates our failure to synthesise a compound with a nominal average Ti valence ($V_{Ti}$) greater than 3.67.

Four probe dc electrical resistivity has been measured on various $\mathrm{LnBa_2Ti_3O_y}$ compositions in the range 300–77 K. Since we were not successful to produce well sintered pellets after grinding, compacting and heating in evacuated and sealed quartz tubes even up to 1200°C, the measurements were done mainly on the cut pieces of the arc melted (and annealed) buttons using soldered indium contacts. The resistivity data are presented in Table 1 and the $\rho - T$ data is plotted in Figs 3 and 4. In the La–Ba–Ti–O system a continuous semconducting through semi-metallic to metallic transition was observed

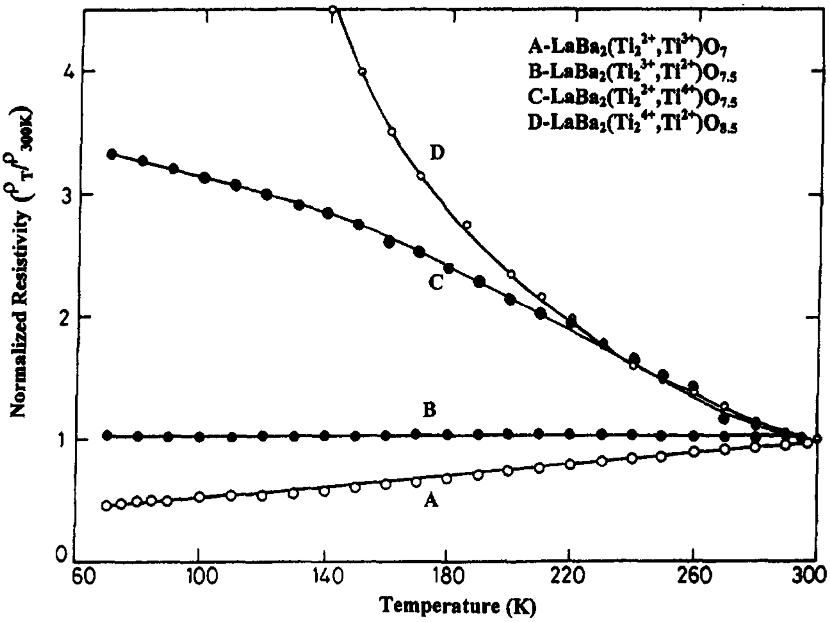

Fig. 3. Normalised resistivity *versus* temperature plots for various $LaBa_2Ti_3O_y$ compositions.

as $V_{Ti}$ changed from 3.67 to 2.33 (Fig. 3). The $LnBa_2(Ti_2^{2+}, Ti^{3+})O_{7.0}$ (Ln = La, Gd, Y) phases showed metallic behaviour with low room temperature resistivity values (Fig. 4). For a $V_{Ti}$ of 2.67 a semimetallic behaviour is noted in the La based system, whereas a semiconducting behaviour was observed for Ln = Gd, Y. Semiconducting behaviour was evident in all other cases including $YBa_2(Ti_2^{3+}Ti^{2+})O_{7.5}$. The compositions in the proximity of semiconductor–metal transitions were further tested for superconductivity down to 15 K using ac susceptibility. They all showed temperature independent paramagnetic behaviour (Fig. 5) and no transition indicative of the onset of superconductivity is noticed.

Based only on the X-ray data presented earlier, it is difficult to conclude that the compounds synthesised in the present investigation are new single phase materials. This is based on the fact that both $LaTiO_3$ and $BaTiO_3$ can exists in cubic perovskite structures (JCPDS file No.s 34–598, 31–174) with very close lattice parameters found in the present study. However, with the support of structural, electrical and magnetic data on single crystals of $LaTiO_3$ such a possibility can be ruled out.

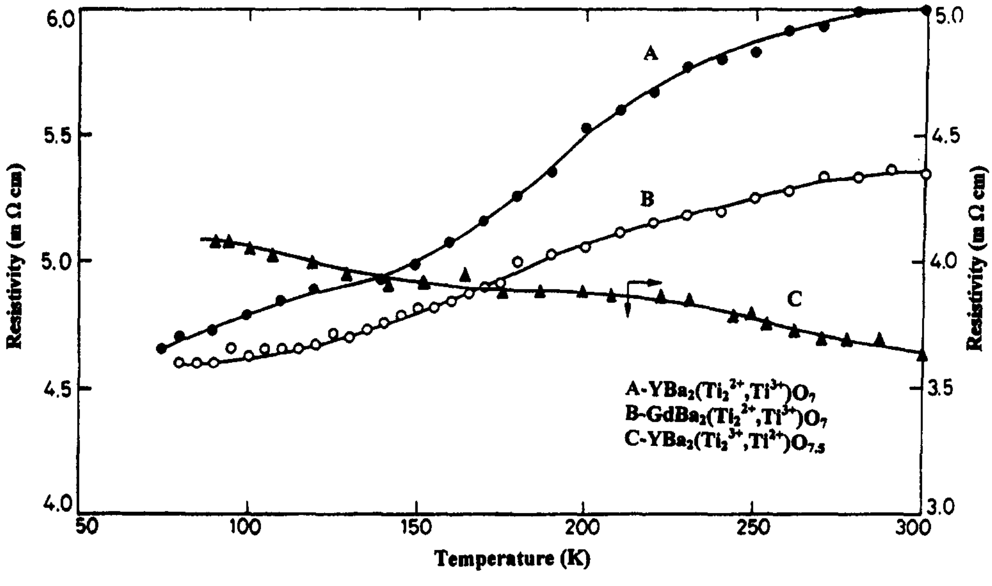

Fig. 4. Resistivity *versus* temperature plots for $LnBa_2Ti_3O_y$ (Ln = Gd, Y) compositions.

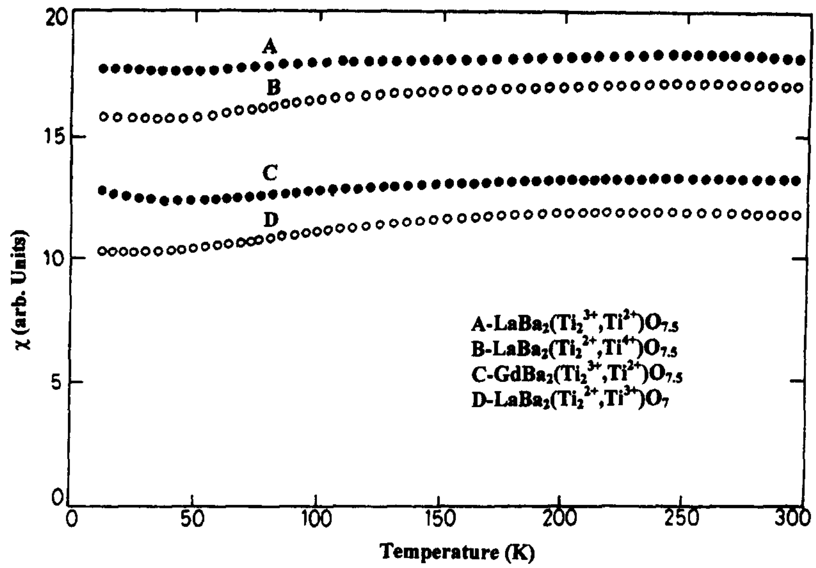

Fig. 5. Magnetic susceptibility *versus* temperature plots for some of the $LnBa_2Ti_3O_y$ (Ln = La, Gd) compositions near semiconductor–metal transition boundary.

Single crystal work on $LaTiO_3$ has shown that it adopts an orthorhombic $GdFeO_3$ type (Sp. Group Pbnm) structure, and it undergoes a metal to semiconductor transition at 125 K associated with an anti-ferromagnetic ordering with no structural changes occurring at or below this temperature [26]. No indication of such a transition were ever observed in any of the compositions in the La–Ba–Ti–O system which was found to undergo only a composition dependent metal to semiconductor transition.

It is well known that, whenever the average valence of Ti ($V_{Ti}$) is less than 3 in a ternary compound, delocalization of the electrons predominates and metallic behaviour is expected. On the other hand, when $V_{Ti}$ is greater than or equal to 3, electron localisation can be expected and results in a semiconductor behaviour due to the hopping type conduction. However, we note that there are some exceptions (Table 1). Detailed studies are necessary to clarify these observations.

## 4. CONCLUSIONS

Studies on phases of the type $LnBa_2Ti_3O_y$ (Ln = La, Gd, Y) show that the compounds can crystallise in a perovskite structure only if the average Ti valence is less than 4+. Both metallic and semiconducting behaviour has been realised in the system by changing the average electronic configuration of Ti. Even though a composition dependent semiconductor–metal transition was observed, no transition indicative of superconductivity is observed down to 15 K.

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