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Study of the metal-insulator transition in $Y_{1-x}A_xTiO_3$ (A=Ca, Sr and Ba)

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Abstract

The systematic variation of the transport properties of $Y_{1-x}A_x \text{TiO}_3$ (A=Ca, Sr and Ba) was explored as a function of 3d band filling n(=1-x) by measurement of X-ray diffraction, resistivity and thermopower. The end compound YTiO₃ is a Mott–Hubbard insulator with 3d¹ configuration for Ti and is converted into strongly correlated metallic state by substituting Y^{3+} by A^{2+} ions. The X-ray diffraction data reveal that $Y_{1-x}Ca_xTiO_3$ and low doped $Y_{1-x}Sr_xTiO_3$ are orthorhombic and high doped $Y_{1-x}Sr_xTiO_3$ are pseudo tetragonal whereas the compounds of the $Y_{1-x}Ba_xTiO_3$ series are cubic. The resistance measurement shows that in the tolerance factor range $0.93 \le t \le 1.02$, the $Y_{1-x}A_xTiO_3$ are metallic but beyond the range they are insulating. The normalised resistance of the correlated metallic samples is proportional to T^2 similar to the behavior of a Fermi liquid. In the insulating phase the activated type hopping mechanism is observed in the high temperature region. For all the samples the thermopower (*S*) follows a relation $S = S_0 + BT$ in the linear region where the *T*-linear term corresponds to Mott's relation for metals. The thermopower results indicate that the metal–insulator transition occurs due to the enhancement of the effective mass.

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1. Introduction

Recently the 3d transition metal oxides with a strong electron correlation effect have attracted much attention because they exhibit a variety of interesting electrical and magnetic properties [1,2] such as metal-insulator (MI) transition [3], charge ordering phenomenon [4], colossal magnetoresistance [5,6], antiferromagnetism [7], ferromagnetism, high temperature superconductivity, etc. [8-10]. In these oxides the conduction electron often becomes localized by the strong electron-electron interaction and the system tends to be an insulator (a Mott insulator). For some transition metal oxides a slight change of some parameters may introduce a transition between an insulator and a metal (a Mott transition). According to the Zaanen-Sawatzky–Allen scheme [11,12], the correlated insulator in transition metal oxides can be classified as the Mott insulator and the charge transfer insulator. In the case of the Mott insulator, a metal-insulator (MI) transfer takes place due to transition between the lower and upper Hubbard band (d-electron band) whereas for the charge transfer insulator the insulating gap is formed between the

occupied oxygen O2p band and the upper Hubbard band [2]. A Mott-Hubbard insulator can be transformed into a correlated metal by enhancing the one electron transfer interaction, i.e. reducing the relative strength of the electron correlation effect by application of external pressure or internal pressure by varying the chemical composition. In addition to such a band controlled MI transition at a fixed band filling, an MI transition can be introduced by hole doping (filling controlled MI transition). In the case of carrier doping it often becomes very difficult to tune the band filling without introducing any random potential for the electrons and up to a critical doping concentration the system behaves like an insulator which can be attributed to the localization due to the combined effect of the random potential and the correlation enhanced effective mass.

With the 3d¹ configuration for Ti, the parent compound RTiO₃ (R=rare-earth) represents a very suitable candidate for studying MI transition. RTiO₃ behaves like a Mott insulator where the insulating charge gap appears between the correlated states. The physical properties of the RTiO₃ series depend on the ionic radius of the R³⁺ ions or in other words vary as a continuous function of the tolerance factor of the compound [13,14]. The crystal structure of the RTiO₃ system belongs to the orthorhombically dis-

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torted perovskite structure (GdFeO₃-type) [15]. The TiO₆ octahedron tilts along the orthogonal direction with $a \approx$ $b \approx \sqrt{2}a_{\rm c}$ and $c = 2a_{\rm c}$ where $a_{\rm c}$ corresponds to the simple cubic perovskite dimension similar to that of SrTiO₃ with Ti^{4+} . As the ionic radius of R decreases, the lattice structure becomes more distorted and the Ti-O-Ti bond angle suffers a greater departure from 180° [15]. As a result the conduction band of the titanate is formed by the Ti 3d t_{2p} and O2p orbitals and the decrease of the bond angle causes a decrease of the one electron band width of the conduction band. YTiO₃ is a ferromagnetic insulator with Mott-Hubbard gap of 1 eV [16]. Now the hole doping may be carried out by the partial substitution of Y^{3+} by the divalent alkali earth metal A (=Ba, Ca and Sr) ion and in the $Y_{1-x}A_xTiO_3$ system the doping concentration (x) represents a nominal hole concentration per Ti site or the 3d band filling given by n = 1 - x. Here doping changes the Ti valence from 3^+ (x = 0) to 4^+ (x = 1) and transforms the Mott insulator (YTiO₃) with one 3d electron to a band insulator (ATiO₃) with no 3d electron. Thermoelectric power (TEP, S) measurement is a powerful tool to study the transport properties of a system. Though the titanates were probed by various experimental tools, the TEP information is still lacking. We have studied the doping induced MI transition in Mott-Hubbard system $Y_{1-x}A_xTiO_3$ as a function of band filling with X-ray diffraction, resistivity and thermoelectric power measurements and tried to correlate the different properties with the existing theories.

2. Experimental

TiO₂ powder was prefired at 1000 °C for 24 h. Polycrystalline ATiO₃ (A=Ca, Sr and Ba) was prepared by heating the mixture of TiO₂ and ACO₃ (A=Ca, Sr and Ba) in air at 1000–1200 °C for 48 h with intermediate grindings and pelletization. The structure of ATiO₃ was confirmed by X-ray diffraction. Yttrium oxide (Y₂O₃) was heated at 1000 °C in air for 12 h prior to use. The stoichiometric mixture of prefired ATiO₃, prefired Y₂O₃ and Ti₂O₃ was mixed homogeneously and pressed into pellets. The pelletized mixture was then melted in an arc furnace in argon atmosphere with repetitive turnings. To obtain a single phase the samples were remelted several times with intermediate grindings. The final samples were preserved in a dessicator purged with argon gas to avoid oxidation.

The crystal structure and the phase purity of the samples were checked by powder X-ray diffraction with Cu K α radiation using a Philips APD 1877 X-ray diffractometer. Temperature dependence of the electrical resistance and thermopower were measured using methods as described elsewhere [17]. The dc electrical resistivity measurements were performed following the four-probe technique. The thermopower of the samples was measured using a differential technique where a temperature gradient is created across the sample and the voltage developed between the hot and cold ends of the thermocouple formed by the sample and Cu wires is measured. The details of the set-up and measurement technique have been reported earlier [17].

3. Results and discussions

Fig. 1 depicts a representative X-ray diffraction pattern of Sr doped YTiO₃. Analysis of the X-ray data of the compounds shows that the samples studied are of single phase. The Ca doped YTiO₂ shows a perovskite crystal structure with orthorhombic distortion (GdFeO₃-type) throughout the concentration range studied. The unit cell parameters of $Y_{1-x}Ca_xTiO_3$ are plotted as a function of x in Fig. 2a. The nature of the curves indicates the formation of a continuous solid solution over the whole concentration region from x=0.3 to x=0.9. Fig. 2b presents the concentration dependence of the lattice constants of $Y_{1-x}Sr_xTiO_3$. This figure shows that up to x=0.5 the compounds have the orthorhombic structure whereas from x = 0.6 to x = 0.9 they adopt a pseudo tetragonal structure. In between x = 0.5 and x = 0.6, a structural phase transition occurs. The X-ray pattern of $Y_{1-x}Ba_xTiO_3$ can be well fitted with cubic symmetry and Fig. 2c shows the cubic cell parameter versus doping concentration. Thus it is found that the incorporation of the small size Ca^{2+} (r_{Ca} = 1.48 Å) ion produces an orthorhombic distortion throughout the whole concentration range. Comparatively the large size Sr^{2+} ion ($r_{\text{Sr}} = 1.58$ Å) produces an orthorhombic distortion for low doping and tetragonal distortion for higher doping whereas the largest Ba ion $(r_{Ba} = 1.75 \text{ \AA})$ produces cubic symmetry.

Fig. 3a presents the variation of the normalized resistance R_n (= R/R_{300}) of $Y_{1-x}Ca_xTiO_3$ with temperature.



Fig. 1. X-ray diffraction pattern for Y_{0.1}Sr_{0.9}TiO₃ sample.



Fig. 2. (a) Lattice parameters of $Y_{1-x}Ca_xTiO_3$ as a function of *x*. (b) Unit cell parameters of $Y_{1-x}Sr_xTiO_3$ versus doping concentrations (*x*). (c) Plot of cubic lattice constant of $Y_{1-x}Ba_xTiO_3$.

The x=0.3 sample shows a semiconductor-like nature since the resistance increases monotonically as the temperature decreases. For the samples with $x > 0.4 R_n(T)$ displays a metallic behavior where R_n increases rapidly



Fig. 3. (a) The temperature dependence of the normalized resistance $(R/R_{300} = R_n)$ for $Y_{1-x}Ca_x TiO_3$ with different *x*. (b) Thermal variation of R_n of $Y_{1-x}Sr_x TiO_3$ for various doping concentrations. (c) The normalized resistance (R/R_{300}) of $Y_{1-x}Ba_x TiO_3$ is plotted as a function of temperature for different *x*.

with T. For the x = 0.4 sample, R_n reaches a maximum and then decreases thereby making a metal $(dR_n/dT > 0)$ to insulator $(dR_n/dT < 0)$ transition at the peak. Fig. 3b shows the T dependence of R_n for $Y_{1-x}Sr_xTiO_3$ with different doping concentrations, which are similar to Ca doped YTiO₃. For x=0.3 and x=0.35 the samples are insulators whereas they are metallic for $x \ge 0.4$. The temperature at which a temperature induced MI transition occurs is difficult to detect for the Sr doped YTiO₃. A similar behavior was also found for $Y_{1-x}Ba_xTiO_3$ which is presented in Fig. 3c. In the metallic region R_n shows a quadratic dependence on T following the relation $R_n =$ $R_{n0} + AT^2$, where R_{n0} is the residual normalized resistance and A is a constant. In Fig. 4a we have plotted R_n of $Y_{1-x}Sr_xTiO_3$ as a function of T^2 . The curves are linear in nature. This behavior is reminiscent of the electron-elec-



Fig. 4. (a) T^2 -dependence of the normalised resistance (R_n) of $Y_{1-x}Sr_xTiO_3$. (b) Variation of $\ln R_n$ as a function of reciprocal temperature (1000/T) for $Y_{0.7}Ca_{0.3}TiO_3$, $Y_{0.7}Sr_{0.3}TiO_3$ and $Y_{0.1}Ba_{0.9}TiO_3$.

tron scattering process in a strongly correlated metal and is one of the characteristic features of a Fermi liquid [18,19]. As Y is replaced by Ca, R_n of the insulating YTiO₃ decreases with the MI transition at x = 0.4. The lowest R_n is observed at x = 0.6 then R_n again increases as the doping drives the samples gradually towards the band insulator CaTiO₃. But in the case of Sr doping R_n decreases as the band insulator SrTiO₃ is approached. For Ba doping, single phase compounds are not obtained for x < 0.6. Metallic behavior is obtained for x < 0.8 while for x > 0.8the semiconducting nature is found. In the insulating or semiconducting phase R_n follows an activated type hopping mechanism in the high temperature region. The thermally activated type hopping model offers the expression $R_{\rm n} = R_{\rm n0} \exp(E_{\rm g}/k_{\rm B}T)$ where $R_{\rm n0}$ is a constant and the activation energy $E_{\rm g}$ may be obtained from the gradient of $\ln R_{\rm n}$ versus 1000/T curves (Fig. 4b). The values of $E_{\rm s}$ along with the temperature range of validity are given in Table 1.

In order to separate the metallic phase from the insulating one as a function of dopant concentration we have calculated the tolerance factor 't' (defined as $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$) where r_B and r_A represent the six coordination B site Ti³⁺/Ti⁴⁺ radius and the average 12 coordination A site radius, respectively, and r_O is the effective oxygen radius) using the ionic radii given in the table of Shanon [20]. In Fig. 5 we have plotted t as a function of x for $Y_{1-x}A_xTiO_3$ (A=Ca, Sr and Ba) with a marking to separate the metallic phase from the insulating one. It is found that the metallic behavior is observed when t lies in the range $0.93 \le t \le 1.02$, while on either side of this range semiconducting nature is observed.

The thermal variation of the thermoelectric power (*S*) of $Y_{1-x}Ca_xTiO_3$ is presented in Fig. 6a for different *x* values. For x = 0.3 and x = 0.4 as *T* decreases *S* remains positive up to a certain temperature and then becomes negative. For x > 0.4 the observed negative values of *S* throughout the whole temperature range, suggest an electron carrier. It is worth mentioning here that in this region of *x*, the resistivity shows a correlated metallic behavior. At low temperatures *S* approaches zero. The *S*(*T*) dependence of $Y_{1-x}Sr_xTiO_3$ and $Y_{1-x}Ba_xTiO_3$ are plotted in Fig. 6b and 6c, respectively, for different band filling. The curves are similar in nature to those in Fig. 6a. For metals, Mott has

Table 1									
Values of the a	nctivation	energy	$(E_{\rm g})$	along	with	the	temperature	range	of
validity			-						

Sample	Activated type hopping					
	Values of E_g (eV)	Temperature range (K)				
$Y_{0.7}Ca_{0.3}TiO_3$	0.08	142-222				
Y _{0.7} Sr _{0.3} TiO ₃	0.03	170-300				
$Y_{0.65}Sr_{0.35}TiO_3$	0.02	173-300				
$Y_{0.2}Ba_{0.8}TiO_3$	0.03	183-300				



Fig. 5. The plot of the tolerance factor (*t*) as a function of *x* in $Y_{1-x}A_x$ TiO₃ (A=Ca, Sr and Ba) indicating the metallic and semiconduct-ing-insulating regions.

given an expression [21,22] for the diffusion thermopower as

$$S(T) = -\left(\pi^2 k_{\rm B}^2 T/3e\right) \left[\delta \ln \rho(E)/\delta E\right]_{E=E_{\rm F}}$$
(1)

Assuming that the conductivity is proportional to the energy and that there is a T-independent mean free path of carriers, expression (1) becomes

$$S(T) \approx -\pi^2 k_{\rm B}^2 T / 3eE_{\rm F} \tag{2}$$

where $E_{\rm F}$ is the Fermi energy. From the above relation S is linear with T. Experimental data for the linear region of S(T) curve fits well with an expression $S(T) = S_0 + BT$, where S_0 and B are constants. The T-linear term corresponds to Mott's relation for metals for which the coefficient B is identical with $\pi^2 k_{\rm B}^2/3eE_{\rm F}$. According to the free electron theory $E_{\rm F}$ is given by $E_{\rm F} = \hbar^2 / 2m^* (3\pi^2 n_{\rm f})^{2/3}$ where $\hbar = h/2\pi$, h being Planck's constant, m^* the effective mass and $n_{\rm f}$ the free electron density. We have estimated $n_{\rm f}$ using values of the mass density obtained from X-ray diffraction data under the assumption of four formula units per cell [15]. For $Y_{1-x}Sr_xTiO_3$, n_f is taken as $1.665.10^{22}(1-x)$. In Fig. 7 we have plotted *B* as a function of the doping concentration x. It is observed that the calculated curve with $m^* = 2m_0$ (where m_0 is the free electron mass) agrees satisfactorily with the experimental curve. The fitted values of m^* are in consonance with the value predicted by the band calculation for $SrTiO_3$ [23]. Such an enhancement $(m^*/m \sim 2)$ was also observed in the case of $Sr_{1-x}La_xTiO_3$ [24,25]. From the thermoelectric power measurement Onoda and Kohno [26] found that the effective mass m^* is twice the free electron mass for $La_{1-x}Sr_xTiO_3$. Tokura et al. [27] observed an increase of the T-linear term in the low temperature specific heat with band filling near the MI transition of $La_{1-x}Sr_xTiO_3$



Fig. 6. (a) Variation of the thermopower (S) in $Y_{1-x}Ca_xTiO_3$ with temperature for different x. (b) The temperature dependence of thermopower (S) in $Y_{1-x}Sr_xTiO_3$ for different compositions. (c) Thermopower versus temperature for $Y_{1-x}Ba_xTiO_3$ (x=0.6, 0.7, 0.75, 0.8 and 0.9).



Fig. 7. The filling (*x*) dependence of the coefficient *B* of the temperaturelinear term of the thermopower for $Y_{1-x}Sr_xTiO_3$.

indicating an enhancement of the effective mass. Thus the occurrence of the observed MI transition is associated with an enhancement of the effective mass of the carriers caused by the strong correlation effects. In our case a very simplified model for the thermopower also indicates a mass enhancement though the factor of enhancement obtained by other experimental techniques is higher. It is felt that for the analysis of the thermopower data a very precise expression is needed on the basis of the actual band structure.

4. Conclusions

In conclusion we can summarize the results as follows. In the case of small size Ca ion doping, YTiO₃ maintains the orthorhombic phase throughout the entire range of doping. As the ionic radius of the substituted A-ion increases, $Y_{1-r}A_rTiO_3$ shows phase transitions from orthorhombic to pseudo tetragonal phase and finally for the large ionic size Ba-ion doping, the system becomes cubic. Metallic behavior is observed in the range $0.93 \le t \le 1.02$, while on the outskirts of this range and beyond, the semiconducting behavior becomes prominent. The normalised resistance R_n is proportional to T^2 which is reminiscent of electron-electron correlation effects. In the insulating region the compounds follow the activated type hopping mechanism of charge transport. Thus the Mott insulator YTiO₃ can be transformed to correlated metals by doping with Ca, Sr and Ba and the electrical conduction behavior corresponds to the characteristics of a Fermi liquid. Analysis of the linear part of the S(T) data suggests that the occurrence of the MI transition is due to the enhancement of the effective mass of the carriers. However, it is felt that in the absence of a true expression based on the proper electronic structure an actual explanation of the TEP behavior is not possible.

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