Asian Journal of Chemistry Vol. 15, No. 2 (2003), 1085–1090

Electrical Conductivity and Electronic Absorption Spectra of $CaTiO_3$ Doped with Ga_2O_3

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The temperature dependence of the electrical conductivity of pure $CaTiO_3$ and that containing Ga_2O_3 dopant with different concentration was investigated between 291 and 773°C. The conductivity in this temperature range varied widely with the percentage change in the concentration of dopant.

In the lower temperature range, no variation of conductivity was observed. This was interpreted as impurity controlled conduction.

In the higher temperature range, all doped investigated samples, as well as pure $CaTiO_3$ exhibited nearly the same shape and the same value of activation energy. This behaviour was attributed to ionization energy present and/or change from cubic to orthorhombic modification. The optical absorption spectra indicate two absorption maxima (ΔE_1 and ΔE_2). The values of ΔE_1 depend on the lattice defects present; ΔE_2 represents the gap width of $CaTiO_3$. It was observed that change of Δe_2 due to additives is very slight; these changes may be attributed to the variation in the volume of unit cell of the doped samples.

INTRODUCTION

Perovskite structure such as $CaTiO_3$, $BaTiO_3$ and $SrTiO_3$ have interesting behaviour as they are widely used in electrical capacitors and condensers. Doping this insulator compound with different ions results in the formation of defects leading to a change of these properties to conducting materials. $BaTiO_3$ as well as $SrTiO_3$ have been studied[1, 2]. Calcium titanate did not attract the attention of research workers.

Leonov[3] added MgO and excess CaO in order to prevent change in dielectric properties of CaTiO3 as a function of heating. Gubken[4] and Tochenaya[5] have studied the effect of addition of Cr^{3+} and Y^{3+} ions on the dielectric properties of $CaTiO_3$. They found that addition of Cr^{3+} has no effect on its crystal structure, while it increases the dielectric constant, specific conductivity and dielectric loss. Y^{3+} has no effect on its properties. As far as the author is aware no work is listed in literature concerning addition of trivalent Ga^{3+} ions as dopant to $CaTiO_3$.

The present work was done in order to correlate the effect of incorporation of Ga_2O_3 with the electrical conductivity and the band gap values and effect of dopant on this value.

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EXPERIMENTAL

The $CaTiO_3$ used in this work was prepared as the usual ceramic of mixing $CaCO_3$ with TiO_2 according to Valeev and others[6–8]. Samples with additives were prepared by weighing the appropriate proportions of $CaTiO_3$ and Ga_2O_3 to attain the chemical formula $Cu_xCa_{1-x}TiO_3$ with $x = 0.00$ (pure), 0.5, 1, 3 and 5 mole fractions.

All samples were then calcined on an open platinum crucible at 1373 K for 3 h and cooled gradually in the furnace at room temperature. All samples were sieved through a 0.2 mesh and palletized at a pressure of 5000 kg/cm^2 and fired at 1523 K for 3 h, then cooled as mentioned to obtain a higher degree of homogenization.

The electrical resistivity measurements were carried out at 20 kHz in the temperature range 308–780 K. The conductivity cell used was the same as that reported before[9]. The optical measurements were carried out using a Shimadzu double beam monochromater recording spectrophotometer mode 204–23300, with an integration sphere attachment special for powder samples. The spectrum was recorded from 200–1400 nm against a reference path of USP MgO. The experimental conditions were kept constant for all the investigated samples.

RESULTS AND DISCUSSION

The variation of log σ *vs.* 1000/T for pure and Ga_2O_3 doped $CaTiO_3$ is shown in Fig. 1. All samples show semiconducting behaviour in the investigated range of temperature (300–775 K). All curves show nearly the same behaviour having a lower temperature and a higher temperature region. In the lower temperature range, no variation of conductivity was observed. This behaviour may be interpreted as impurity controlled conduction[10] and defects are independent of temperature[11]. Sample containing 0.5% Ga_2O_3 shows a higher conductivity value at room temperature which decreases by increasing temperature. This may be due to the fact that this sample absorbs water which is released by temperature effect.

The formation of high resistance barrier in ceramic material may be interpreted by the constancy of conduction with variation of temperature in the lower range[12, 13]. Also in this range it is observed that the pure sample does not show stability of values. The stability in conduction increases with per cent of doped material. This is in accordance with that previously postulated[9].

Another feature, which can be observed in the curves, is the presence of a knee between the two mentioned regions (that is, between the extrinsic or low temperature and the intrinsic or high temperature regions). This knee temperature ranges from 172–242°C.

Table-1 shows the knee's temperature and activation energy values as a function of dopant concentration. It is observed that this knee temperature increases with per cent of doping indicating increase of impurity content.

The intrinsic conduction range is shown in all tested samples where the activation energy for conduction was calculated using Arrhenius equation:

$$\sigma = \sigma^0 e^{-\Delta E/2KT}$$

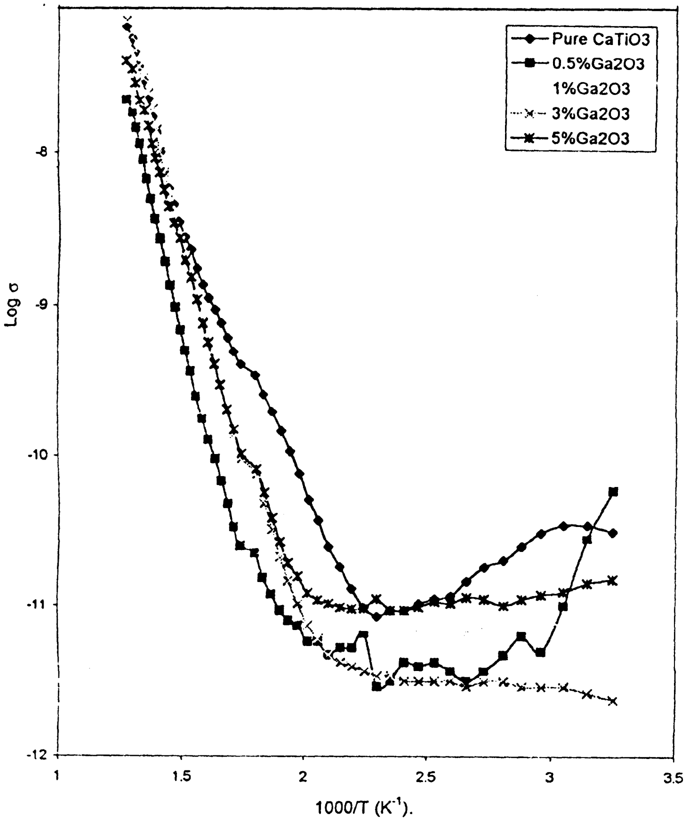

Fig. 1. The variation of dc-conductivity with temperature for $CaTiO_3$ doped with different concentrations of Ga_2O_3

where σ is the conductivity, σ^0 is a pre-exponential factor, ΔE is the activation energy for conduction (forbidden energy gap), K is Boltzmann constant and T is the absolute temperature. This intrinsic range is generally reproducible and is characterized for the material under test.

TABLE-1
KNEE'S TEMPERATURE AND ACTIVATION ENERGY VALUES AS A FUNCTION OF DOPANT CONCENTRATION

Concentration	Knee	ΔE_1	ΔE_2
Pure	172	1.360	2.40
0.5	202	0.650	2.57
1.0	222	0.520	1.86
3.0	232	0.720	2.16
3.0	242	0.195	1.95

It can be seen from Table-1 that a change in slopes in the intrinsic range appears. Such changes are interpreted as a result of phase transition[14] in pure $CaTiO_3$.

It can be observed that the samples containing 0.5% Ga_2O_3 show higher activation energy value and lower conductivity. This means that Ga_2O_3 in this concentration dissolves it with least distortion in the lattice of the host material and hence least strain induced energy levels are added in the energy gap.

Increasing the concentration of Ga_2O_3 leads to more reduction of Ti^{4+} to Ti^{3+} and more strain induced energy states and decreasing of the energy gap width. The higher conductivity values with lower activation energy ones suppose that the electronic band model is valid as a conduction mechanism.

TABLE-2
DIFFUSE REFLECTING VALUES OF $CaTiO_3$ AS FUNCTION OF DOPANT CONCENTRATION

No.	Pure	0.5%	1.0%	3.0%	5.0%
1	0.534	0.534	—	0.540	0.534
2	0.554	0.552	—	—	0.554
3	0.566	0.568	—	—	0.566
	—	—	—	—	0.614
4	0.630	0.638	0.632	0.631	0.631
	—	—	—	0.638	0.636
5	0.690	0.681	0.681	0.703	0.681
6	0.716	0.734	0.742	0.765	0.756
	—	0.765	—	0.783	0.666
7	0.855	0.866	0.866	0.854	0.855
8	0.996	1.056	1.060	—	1.612
1st optical absorption ΔE_1	1.450	1.470	1.470	1.590	1.470
2nd optical absorption ΔE_2	2.704	2.883	2.883	2.883	2.883

The value of ΔE obtained from conductivity cannot be valid as gap width value as its value is not constant. For this reason the value of gap width must be obtained optically. The reflectivity data for pure $CaTiO_3$ and that doped with different concentration of Ga_2O_3 are presented in Fig. 2. An examination of this curve shows many absorption bands in the near infrared region. These bands are tabulated in Table-2. Two absorption edges ΔE_1 and ΔE_2 are observed. Calculation of their values is carried out at the mid point of the linear part of maximum absorption[15].

Discussing the presence of different absorption peaks, this may arise from excitation of electrons from valence band to one of higher energy state created within the energy gap. This is in conformity with the finding of these bands[15, 16] and their energy states can be divided into:

(a) Temperature levels either added deliberately or on manufacturing.

(b) Strain induced in the lattice, which is associated with the insertion of the foreign atoms due to differences in atomic size, valence and electrongativity.

The values of ΔE_1 and ΔE_2 are nearly constant for all samples. This may be due to one of the following:

1. The concentration and type of defects created from the introduction of dopant.
2. Movement of the carriers in the disordered regions of the grain boundaries.
3. Existence of phase transformations.

The ionic radii of Ga^{2+}, Ca^{2+} and Ti^{4+} are 0.62, 1.06 and 0.69 Å respectively[17]. As a result of formation of solid solution for $CaTiO_3$ doped with Ga_2O_3, electrons will be produced. The existence of this electron in the disorder regions of the grain boundaries represents an impurity level in the energy gap of $CaTiO_3$ which may cause the optical absorption of the value of ΔE_1. The position of the second absorption edge ΔE_2 corresponds to the gap width that amounts to 2.88 eV. This value is in good agreement with the value obtained by different authors. This value is more or less constant and any slight change may be attributed to the volume of unit cell of doped samples. This absorption edge is generally expected as a measure of the forbidden energy gap width where the electrons are excited from the valence band to the conduction band. This intrinsic absorption edge ΔE_2 of this sample depends on the variations of the structure as cubic phase has a value 3.83 eV for the gap width.

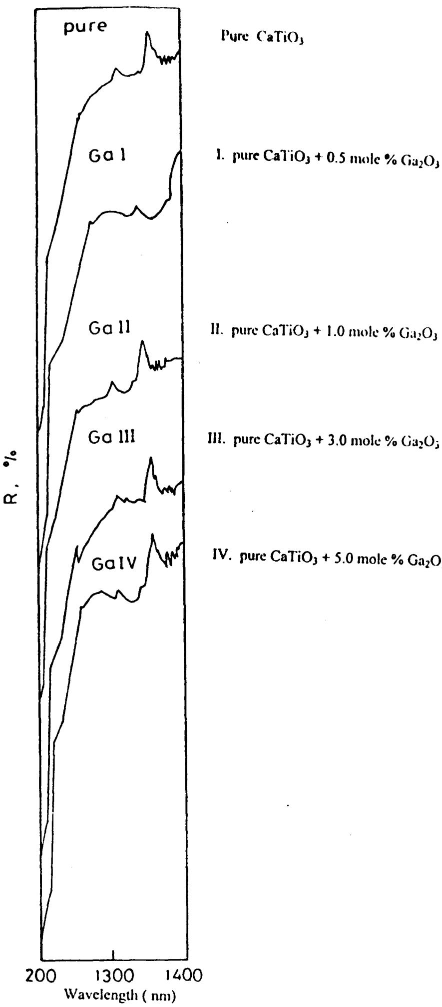

Fig. 2. Diffuse reflectance of $CaTiO_3$ with different Ga_2O_3 additions

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(*Received*: 19 November 2002; *Accepted*: 22 January 2003) AJC-2983