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Synthesis, characterization and thermal expansion of $Cr_{2-x}Ti_xO_{3+\delta}$

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ABSTRACT

$Cr_{2-x}Ti_xO_{3+\delta}$, where x varies from 0.1, 0.2 and 0.3 has been prepared by glycerol route and characterized by powder X-ray diffraction, dynamic light scattering, BET surface area and scanning electron microscopy. The thermal expansion coefficient of the powder samples was studied using a high-temperature X-ray diffractometer. The bulk thermal expansion was studied by dilatometry. An anomaly in the '*c*' direction was found initially in the Ti doped samples which manifested in '*a*' direction as well at high dopant concentration. The anomalies shown by these compounds could not be manifested in the bulk thermal expansion because of the polycrystalline nature of the samples as revealed by dilatometry.

1. Introduction

In the recent years, there has been an increased demand to develop newer sensor materials for applications in electronic and other industries. Ternary transition metal oxides have been investigated extensively for sensing reactive gases, since they exhibit both high selectivity and sensitivity [1]. Titanium-substituted chromium oxides (CTO) have been developed successfully as gas-sensitive resistors at elevated temperatures for the detection of combustible and toxic gases [2–6]. In recent years the study of Cr_2O_3 thin films has become a topic of great interest because of their practical applications in fields like the detection of hazardous gases [7–9]. When the films are deposited at substrate temperature $Ts < 550\,^{\circ}C$ they grow with an amorphous structure, and those deposited at $Ts \geq 550\,^{\circ}C$ grow in a crystalline structure that depends on the x-values in $Cr_{2-x}Ti_xO_{3+\delta}$. There are great differences in the electrical and optical properties of the crystalline and amorphous films. While the crystalline ones are insulators with an optical band gap that depends on the titanium concentration, the amorphous are semiconductors, with an electrical conduction that strongly depends on the x-value and with a little change in the optical band gap. Therefore, we consider that it is important to study the different physical properties of the $Cr_{2-x}Ti_xO_{3+\delta}$ in order to have a well characterized material that has potential practical applications.

The technique generally used for the preparation of titanium-substituted chromium oxides consists of a solid-state reaction between chromium and titanium oxide [1,10]. The Cr_2O_3 and TiO_2 powders are mixed, milled and calcined to achieve the solid-state reaction. The potential disadvantages of this method are poor chemical homogeneity, introduction of chemical impurities during the milling stage and poor control of the microstructure during sintering. Sintering, microstructure, impurities and non-homogeneity are known to have an influence on the gas sensor response. The development of powders with tailored properties is of major importance for the improvement of the selectivity, sensitivity and reproducibility of the gas sensors. Solution-based technique has proven to be an excellent means to control particle size, shape and the degree of impurity in material synthesis [11–19]. Solution-based technique has proven to be an excellent means to control particle size, shape and the degree of impurity in material synthesis [11–19]. Although much of the reported work have focused on the synthesis of ceramics by plasma spray coating, solution-based synthesis on chromium titanium oxide is very much limited [17–22].

The compound $Cr_{2-x}Ti_xO_{3+\delta}$ (where $x = 0$, 0.1, 0.2 and 0.3) has been prepared by us using HMTA as fuel and reported earlier [23]. In this paper, we describe the synthesis of $Cr_{2-x}Ti_xO_{3+\delta}$ (where $x = 0–0.3$ with an interval 0.01) by glycerol route [24]. The technique is useful in obtaining homogeneous precursor powder of multi component system, which on suitable heat treatment forms phase-pure powder at low temperature. The thermal expansion of the compound was studied by high-temperature XRD. The bulk expansion of the compounds was studied by dilatometry.

2. Experimental

2.1. Sample preparation and characterization by room temperature and high-temperature XRD

Titanium(IV) nitrate solution was prepared by precipitating titanium trichloride into titanium hydroxide by addition of liquor ammonia and then redissolving

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hydroxide in concentrated nitric acid over an ice-bath. The titanium nitrate solution was stored in the refrigerator. The chromium(III) nitrate solution was prepared by dissolving the A.R. grade chromium nitrate crystals in distilled water. Both the nitrate stock solutions were analyzed for their metal contents by gravimetric method. Suitable volumes of the metal nitrate solutions were mixed to achieve the required compositions mentioned above. To this mixture of nitrate solution, glycerol was added and the mixture was heated on a hot plate with continuous stirring until a green fine powder (precursor) was formed. The precursor powders were calcined at 1023 K for 4 h to get crystalline phases. The formation of the compounds was examined by X-ray powder diffraction (XRD) method. High-temperature XRD patterns of these compounds were recorded under reduced pressure (10^{-5} mbar) in a STOE diffractometer from 298 to 1273 K. The patterns were taken at an interval of 100 K with Cu Kα radiation ($\lambda = 1.5406$ Å) in the range $2\theta = 10–65°$ using HDK-2.4 Buhler high-temperature attachment. In the high-temperature chamber, the well ground samples, mixed with a drop of collodine were mounted on a platinum–rhodium sample carrier which is spot welded at the bottom with a Pt/Pt–13%Rh thermocouple and was resistively heated at a programmed rate. The sample temperature was controlled by a PID temperature controller within ±1 K. The sample was kept isothermal for about 60 min at each temperature step in order to ensure thermal equilibrium. The unit cell parameters at each temperature were determined using least-squares method using a computer program LATPAR [25] with an accuracy of ±0.001 Å.

The average particle size of the powder was measured by X-ray line-broadening technique using Sherrer formula [26].

$$D = \frac{0.9\lambda}{\beta \cos\theta},$$

where D is the crystallite size and λ, the Cu Kα radiation wavelength; the corrected FWHM, β, of the diffraction peak is $\beta^2 = B^2_{\mathrm{obs}} - b^2$, where B_{obs} and b are the observed line width at half-peak intensity of crystalline $Cr_{2-x}Ti_xO_{3+\delta}$ and coarse quartz, respectively. TG-DTA analyses of the samples were carried out by a thermal analyzer, Model 92-16.18, Setaram, France, to study the thermal stability of the compound.

2.2. Thermal expansion studies using dilatometer

The bulk expansion of the materials was studied by Netszch make dilatometer in O_2 atmosphere. The apparatus used for thermal expansion measurement was a pushrod type dilatometer (DIL 402). The sample temperature was measured by a B type thermocouple (Pt30%Rh–Pt6%Rh) mounted in the sample holder. The temperature calibration of the dilatometer was carried out in the present study by the phase transition temperature of National Institute of Standards and Technology (NIST) reference materials (indium: $T_{\mathrm{fus}} = 429.748$ K; tin $T_{\mathrm{fus}} = 505.078$ K; zinc: $T_{\mathrm{fus}} = 692.750$ K; gold $T_{\mathrm{fus}} = 1337.35$ K). The calibrated thermocouple was placed directly below the sample. Selection of temperature program was controlled by a computer via data acquisition system.

The sample supporter measuring unit and displaceable furnace of the dilatometer were mounted horizontally. The expansion was measured in the axial direction. The sample holder and push rod were made of recrystallized alumina. The expansion of the pellet under negligible load is measured as a function of temperature while subjected to the controlled temperature program. The change in length of the sample due to heating resulted in the movement in the pushrod which was detected by the linear variable displacement transducer (LVDT) giving rise to an electrical signal and transmitted to the analog to digital converter. The expansion signal and the e.m.f. of the thermocouple in the form of digitized experimental data are collected at periodic time intervals and are stored for the evaluation in the computer. The reference sample used was a single crystal of alumina of 25 mm length and 5 mm in diameter. The measurement of the thermal expansion was performed in the temperature range from 300 to 1273 K. The whole experiment was carried out in high purity flowing argon gas atmosphere (flow rate 6 l/h) the experiments were carried out using a heating rate of 8 K/min. The sample was cooled to room temperature using argon gas.

3. Results and discussions

CTO (hexagonal structure and S.G.: $R3C$) could be prepared by solution combustion (SC) synthesis method in the presence of glycerol. Glycerol is a source of C and H, which on combustion form CO_2 and H_2O and liberates heat. Glycerol seems to decompose to form, among other products, carboxylic acids, which in turn, form complexes with metal ions, thereby preventing the precipitation of chromium at lower pH. This is probably the reason for simultaneous precipitation of chromium and titanium at a higher pH of around 7. The high viscosity of glycerol may also be playing a role in preventing the segregation of chromium and titanium during precipitation. The exothermicity (adiabatic temperature, T_{ad}) of the redox reaction is very high. Though these aspects are not fully understood, the usefulness of the 'glycerol route' for obtaining good-quality chromium titanium oxide (CTO) powder has been established. Fig. 1 gives the TG-DTA pattern of the gel heated up to 800 °C in air. The two initial weight losses at around 120 and 230 °C are due to the removal of loose water and bound water in the gel. At around 365 °C weight loss along with a large exotherm was observed. At this temperature the gel ignites, with high exothermicity liberating a large volume of gases and converts into a precursor compound. Further small weight loss at around 600 °C may be due to loss of residual carbon present in the precursor. Potential advantages of this wet chemical route over the conventional solid-state reaction method include better homogeneity, better compositional control and lower processing temperatures. The room temperature XRD patterns of calcined CTO powders at 1273 K shown in Fig. 2. XRD patterns of all samples incorporated with Ti were compared with Cr_2O_3 as well as TiO_2. All the patterns were similar to the XRD pattern of Cr_2O_3. Since Ti^{4+} and Cr^{3+} possess identical ionic radius (0.061 nm), this behaviour is expected. The absence of individual TiO_2 peaks showed that a true solid solution has been formed rather than a mechanical mixture of TiO_2 with Cr_2O_3. The pellets obtained were having porosities in the range 40–50% in these pellets determined by gas pycnometry. The room temperature resistance of pure Cr_2O_3 was nearly two orders smaller than that of Ti-substituted samples. By incorporation of Ti the resistance found to increase. Table 1 shows the pellet characteristics of the various samples. Although Negai et al. [27] observed a change from p- to n-type conductivity when TiO_2 was above 1.85 mol% in Cr_2O_3 for the measurements around 1473 K, our studies in the temperature regions of RT–1273 K, all samples exhibited p-type behaviour only. EDAX analysis of the different samples confirmed a close correlation between the achieved average bulk compositions and the nominal compositions. No impurity was detected by EDAX analysis. The binding energy positions of the Cr $2p_{3/2}$, Ti $2p_{3/2}$ and O 1s levels of these powder samples are given in Table 2. No significant variation in the positions of the Cr $2p_{3/2}$

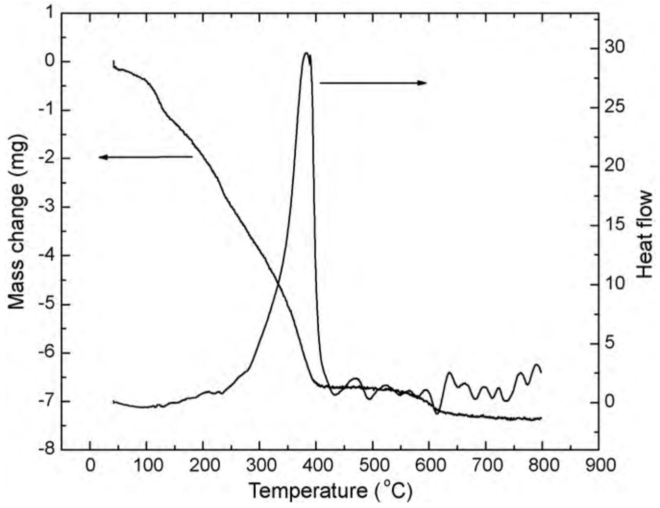

Fig. 1. TG-DTA pattern of CTO gel in air.

Table 1
Pellet characteristics of the $Cr_{2-x}Ti_xO_{3+\delta}$ sintered at 1273 K.

Sr. No.	Sample	Porosity (%)	Typical room temperature resistance (MΩ)
1	Cr_2O_3	50	0.74–0.76
2	$Cr_{1.9}Ti_{0.1}O_{3+\delta}$	42	3.8–4.7
3	$Cr_{1.8}Ti_{0.2}O_{3+\delta}$	40	20.4–23.5
4	$Cr_{1.7}Ti_{0.3}O_{3+\delta}$	44	36–38.7

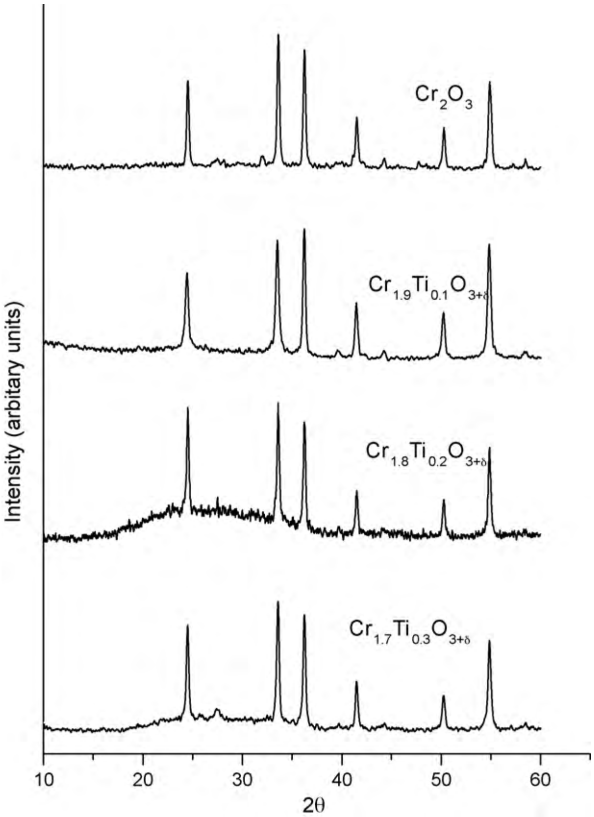

Fig. 2. Room temperature XRD of $Cr_{2-x}Ti_xO_{3+\delta}$, where x varies from 0.1, 0.2 and 0.3 calcined at 1073 K.

and Ti $2p_{3/2}$ levels is observed between the different compositions. The binding energy positions of the Cr $2p_{3/2}$, Ti $2p_{3/2}$ and O 1s levels are in good agreement with literatures values [28]. Also these studies showed that Ti^{3+} is in below detectable limits in these samples. By this analysis the compositions Ti incorporated samples were found to be $Cr_{1.72}Ti_{0.28}O_{3.14}$ (for the nominal composition $Cr_{1.7}Ti_{0.3}O_{3+\delta}$) assuming all the Ti is in 4+. For the nominal compositions $Cr_{1.8}Ti_{0.2}O_{3+\delta}$ and $Cr_{1.9}Ti_{0.1}O_{3+\delta}$, the compositions determined were $Cr_{1.81}Ti_{0.19}O_{3.095}$ and $Cr_{1.87}Ti_{0.13}O_{3.065}$, respectively. So rough estimation of "δ" value is 0.14, 0.095 and 0.065 for $Cr_{1.7}Ti_{0.3}O_{3+\delta}$, $Cr_{1.8}Ti_{0.2}O_{3+\delta}$ and $Cr_{1.9}Ti_{0.1}O_{3+\delta}$, respectively.

3.1. Thermal expansion behavior

Fig. 3 gives the thermogram of CTO powder calcined at 1273 K studied by simultaneous TG-DTA. The thermogram did not show any major weight changes occurring in the sample. DTA peak did not show any exotherm indicating the absence of any structural changes taking place in the sample. The HT-XRD patterns of $Cr_{2-x}Ti_xO_{3+\delta}$, where x varies from 0, 0.1, 0.2 and 0.3 recorded at different temperatures up to 1273 K did not show any phase changes. The lattice parameters were obtained within an accuracy of ±0.001 Å using least-squares refinement method. The variation of lattice parameters a, c and volume as a function of temperature from 298 to 1273 K for Cr_2O_3, $Cr_{1.9}Ti_{0.1}O_{3+\delta}$, $Cr_{1.8}Ti_{0.2}O_{3+\delta}$, $Cr_{1.7}Ti_{0.3}O_{3+\delta}$, respectively, are shown in Figs. 4–7. As seen from Fig. 4, Cr_2O_3 show increase of lattice parameters and cell volume with increase in temperature through out. Percentage expansion of lattice parameters and cell volume was calculated using the formula:

Table 2
XPS binding energies for $Cr_{2-x}Ti_xO_{3+\delta}$ samples (x = 0.1, 0.2 and 0.3).

Nominal composition	Cr $2p_{3/2}$	Ti $2p_{3/2}$	O 1s
$Cr_{1.9}Ti_{0.1}O_{3+\delta}$	577.1	458.2	530.4
$Cr_{1.8}Ti_{0.2}O_{3+\delta}$	577.3	458.4	530.5
$Cr_{1.8}Ti_{0.2}O_{3+\delta}$	577.1	458	530.2

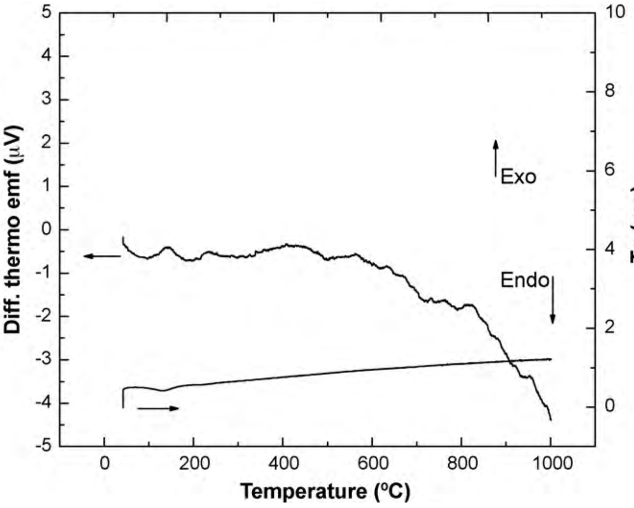

Fig. 3. TG-DTA plot of $Cr_{1.8}Ti_{0.2}O_{3+\delta}$.

$$\text{Expansion}(\%) = \left\{ \frac{(a_t - a_{298})}{a_{298}} \right\} \times 100$$

where a_t represents the lattice parameter or volume at any temperature T and a_{298}, at room temperature.

The percentage expansion values of variation of lattice parameters a and c of Cr_2O_3 were fitted into a third order polynomial equations of the form $A + B_1T + B_2T^2 + B_3T^3$, where A, B_1, B_2 and B_3 are constants and T denotes the absolute temperature. The equa-

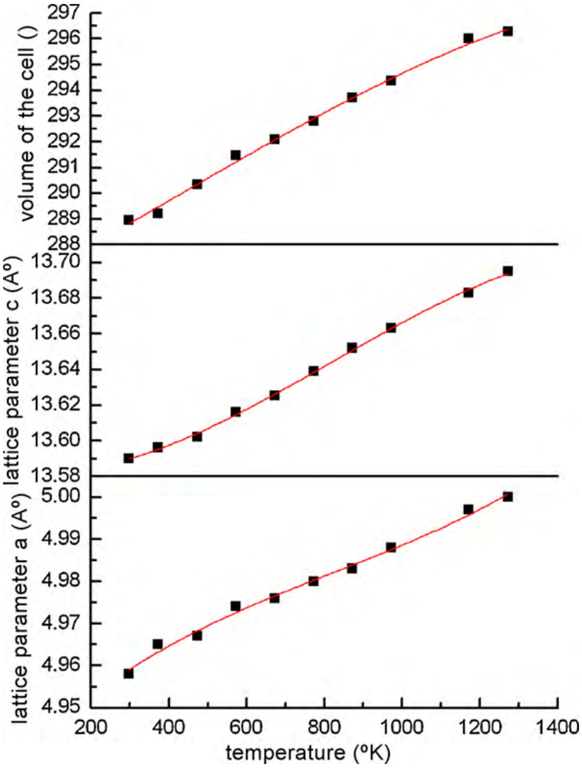

Fig. 4. Variation of lattice parameters and cell volume with temperature for Cr_2O_3.

Table 3
The coefficient of average linear and volume thermal expansion of Cr_2O_3, $Cr_{1.9}Ti_{0.1}O_{3+\delta}$, $Cr_{1.8}Ti_{0.2}O_{3+\delta}$ and $Cr_{1.7}Ti_{0.3}O_{3+\delta}$.

Compound	Temperature range (K)	Average thermal expansion coefficient (linear)		Volume (K^{-1})
		α_a (K^{-1})	α_c (K^{-1})	
Cr_2O_3	298–1273	9.95×10^{-6}	7.47×10^{-6}	$2.84.14 \times 10^{-5}$
$Cr_{1.9}Ti_{0.1}O_{3+\delta}$	298–1073	10.9×10^{-6}	7.03×10^{-6}	2.64×10^{-5}
$Cr_{1.8}Ti_{0.2}O_{3+\delta}$	298–873	11.72×10^{-6}	5.26×10^{-6}	2.59×10^{-5}
$Cr_{1.7}Ti_{0.3}O_{3+\delta}$	298–873	8.04×10^{-6}	3.30×10^{-6}	2.04×10^{-5}

tions for a, c and cell volume for Cr_2O_3 in the temperature range 298–1273 K is given below:

$$a(\text{Å}) = 4.9366 + 9.3306 \times 10^{-5}\,T - 6.9092 \times 10^{-8}\,T^2 + 2.7794 \times 10^{-11}\,T^3 \quad (1)$$

$$c(\text{Å}) = 13.5830 - 2.4747 \times 10^{-5}\,T + 1.8164 \times 10^{-7}\,T^2 - 7.3694 \times 10^{-11}\,T^3 \quad (2)$$

$$\text{Vol.}(\text{Å})^3 = 286.3210 + 0.0079\,T + 1.9854 \times 10^{-6}\,T^2 - 1.5742 \times 10^{-9}\,T^3 \quad (3)$$

where as when Cr is substituted with Ti, the c axis shows anomaly in the expansion. In the case of $Cr_{1.9}Ti_{0.1}O_{3+\delta}$, the c axis of the unit cell does not increase with the temperature through out the temperature range. Even though the thermal expansion along the c axis of the unit cell was continuously increasing up to 850 K, beyond 850 K an anomaly in the expansion along the axis could be seen. Where as in the case of pure chromia, unit cell continuously showed an expansion along direction a. However, the cell volume of this compound showed a continuous increase with increase in temperature. The equations for a, c and cell volume for $Cr_{1.9}Ti_{0.1}O_{3+\delta}$ is given below:

$$a(\text{Å}) = 4.9273 + 5.8713 \times 10^{-5}\,T - 8.3584 \times 10^{-9}\,T^2 + 8.0944 \times 10^{-12}T^3 \quad (4)$$

$$c(\text{Å}) = 13.5889 - 8.6699 \times 10^{-6}\,T + 1.5797 \times 10^{-7}\,T^2 - 7.5496 \times 10^{-11}\,T^3 \quad (\text{up to } 870\,\text{K}) \quad (5)$$

$$\text{Vol.}(\text{Å})^3 = 285.3316 + 0.0098\,T - 5.0666 \times 10^{-6}\,T^2 + 3.2875 \times 10^{-9}\,T^3 \quad (6)$$

In 10 and 15 mole% Ti-substituted samples, the anomaly in the expansion along the c axis is extensively seen from Figs. 6 and 7. The anomaly was even observed in lattice parameter a beyond temperature 873 K when plotted with the temperature.

The equations for both $Cr_{1.8}Ti_{0.2}O_{3+\delta}$ and $Cr_{1.7}Ti_{0.3}O_{3+\delta}$ for lattice parameter a (up to 870 K) and unit cell volume is given as:

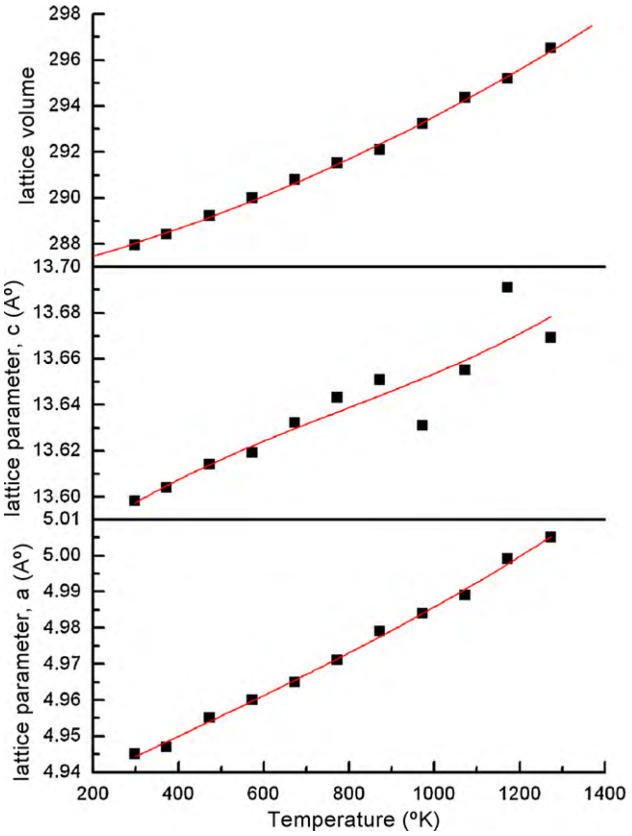

Fig. 5. Variation of lattice parameters and cell volume with temperature for $Cr_{1.9}Ti_{0.1}O_{3+\delta}$.

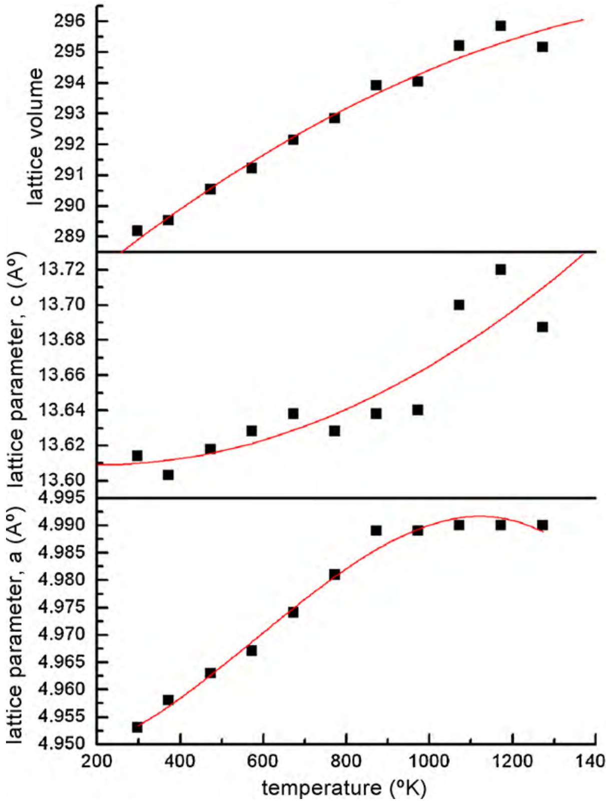

Fig. 6. Variation of lattice parameters and cell volume with temperature for $Cr_{1.8}Ti_{0.2}O_{3+\delta}$.

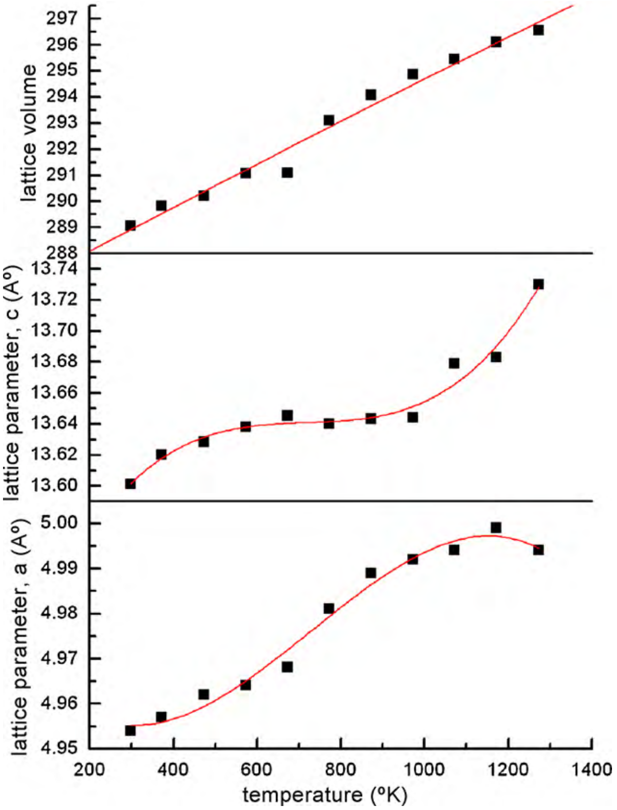

Fig. 7. Variation of lattice parameters and cell volume with temperature for $Cr_{1.7}Ti_{0.3}O_{3+\delta}$.

$Cr_{1.8}Ti_{0.2}O_{3+\delta}$

$$a(\text{Å}) = 4.9294 + 1.0957 \times 10^{-4}\,T - 1.2520 \times 10^{-7}\,T^2 + 8.0944 \times 10^{-11}\,T^3 \quad (\text{up to } 870\,\text{K}) \tag{7}$$

$$\text{Vol.}(\text{Å})^3 = 286.8427 + 0.0071\,T + 1.5986 \times 10^{-6}\,T^2 - 1.017 \times 10^{-9}\,T^3 \tag{8}$$

$Cr_{1.7}Ti_{0.3}O_{3+\delta}$

$$a(\text{Å}) = 4.9758 - 1.4717 \times 10^{-4}\,T + 3.0363 \times 10^{-7}\,T^2 - 1.3862 \times 10^{-10}\,T^3 \quad (\text{up to } 870\,\text{K}) \tag{9}$$

$$\text{Vol.}(\text{Å})^3 = 290.3209 - 0.0103T + 2.62785986 \times 10^{-5}\,T^2 - 1.260 \times 10^{-8}\,T^3 \tag{10}$$

The thermal expansion coefficient of a for these compounds, i.e., α_a was obtained by using the relation:

$$\alpha_a = \left(\frac{\delta a_T}{\delta_T}\right)\left(\frac{1}{a_{298}}\right) \tag{11}$$

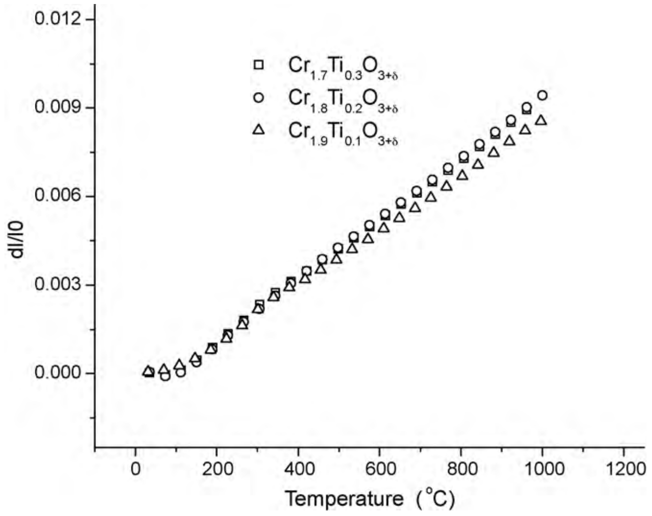

Fig. 8. Bulk thermal expansion of CTO powders studied by dilatometry.

where $(\delta a_T/\delta_T)$ is the temperature derivative of the lattice parameter a and a_{298} is room temperature lattice parameter. Similarly, α_c and volume expansion coefficient α_v were calculated by differentiating respective equations using the formula given in Eq. (11). The values of average coefficients of thermal expansion of lattice parameters and cell volume of Cr_2O_3 and $Cr_{1.9}Ti_{0.1}O_{3+\delta}$ in the temperature range 298–1273 K and of $Cr_{1.8}Ti_{0.2}O_{3+\delta}$ and $Cr_{1.7}Ti_{0.3}O_{3+\delta}$ for temperature range of 298–873 K are given in Table 3. The α_c and volume expansion coefficient α_v was found to be decreasing continuously with addition of Ti in the lattice. The Ti substitution incorporates defects in the Cr_2O_3 lattice which is found to orient only along the c lattice initially. With increasing Ti concentrations it was observed that defects are uniformly distributed. The bulk thermal expansion of these compounds was also studied using a dilatometer. Fig. 8 shows the dilatogram showing the thermal expansion of $Cr_{1.9}Ti_{0.1}O_{3+\delta}$, $Cr_{1.8}Ti_{0.2}O_{3+\delta}$ and $Cr_{1.7}Ti_{0.3}O_{3+\delta}$. A continuous increase in the expansion with increase in temperature for all compounds was observed in this study. As expected, the expansion studied by a dilatometer would be an average expansion occurring in the sample. Even if they possessed to non-cubic geometry, since these compounds were polycrystalline in nature, the thermal expansion studied by this method would be the average thermal expansion occurring in the samples in all possible directions, as these crystals are oriented in all possible directions. The bulk thermal expansion values of these compounds were determined using the equation:

$$\alpha = \left(\frac{\Delta l}{lo}\right)\left(\frac{1}{\Delta T}\right) \tag{12}$$

where $\Delta l/lo$ is the fractional change in length and ΔT being the change in the temperature. The bulk thermal expansion values of these compounds were plotted as a function of temperature is presented in Fig. 9. The bulk thermal expansion was found to linearly increase up to 550 K then reaches a plateau. The average thermal expansion in the temperature range 600–1273 K is given in Table 4. The average thermal expansion values studied by dilatometry were found to be lesser compared to the values determined by HT-XRD as all the samples possessed high porosity. Since the material is polycrystalline in nature, the anomalies existing in the compounds do not affect the bulk thermal expansion and these compounds can be used as chemical sensor materials in the form of thin films successfully [8].

Table 4
The bulk thermal expansion coefficients studied by dilatometry.

Compound	Temperature range (K)	Alpha (volume) (K^{-1})
$Cr_{1.7}Ti_{0.3}O_{3+\delta}$	600–1273	9.31×10^{-6}
$Cr_{1.8}Ti_{0.2}O_{3+\delta}$	600–1273	8.54×10^{-6}
$Cr_{1.9}Ti_{0.1}O_{3+\delta}$	600–1273	8.61×10^{-6}

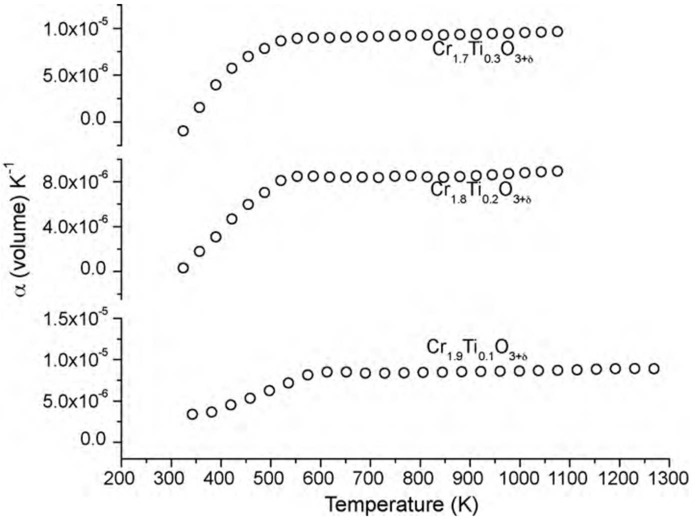

Fig. 9. Variation of bulk thermal expansion with temperature.

4. Conclusions

The linear thermal expansion value of Cr_2O_3 is affected by incorporation of Ti right from the dopant concentration 5 mole%. The defects confined only to c direction initially at 5 mole% of Ti in Cr_2O_3 where as it manifested in a direction also at higher concentrations. The bulk thermal expansion values studied by dilatometry showed abescence of any such anomaly in the compounds as the bulk expansion is represented by the polycrystalline nature of these compounds.

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