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Dielectric properties, ac conductivity and thermal behaviour of flux grown cadmium titanate crystals

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Abstract

The dependence of loss tangent (tan δ) and both real and imaginary parts of the dielectric constant (ε' and ε'') on temperature in the range 298–923 K and frequency in the range 10^3–10^6 Hz for flux grown $CdTiO_3$ single crystals is reported. The $\ln \sigma_{ac}$ versus T plots suggest the conduction mechanism to be ionic hopping conduction. From $\ln \sigma_{ac}$ versus frequency curves, it can be seen that the slope decreases with the rise in temperature, suggesting that the ionic hopping conduction diminishes with the rise in temperature. The activation energy at various fixed frequencies is calculated from the slope of the graph between $\ln \sigma_{ac}$ versus $1/T$ ($\times 10^3$ K^{-1}). Thermal behaviour of flux grown $CdTiO_3$ crystals using thermoanalytical techniques including TG, DTA and DTG is discussed. Thermal analysis suggests decomposition of $CdTiO_3$ in the temperature interval of 1386–1693 K leading to the formation of TiO_2 as the final product. Results obtained on application of TG based models viz. Horowitz–Metzger, Coats–Redfern and Piloyan–Novikova are reported. The results of kinetics of thermal decomposition suggest contracting cylinder model as the one that is relevant to the decomposition of $CdTiO_3$. The kinetic parameters viz. the order of reaction, activation energy, frequency factor, and entropy of activation using the above mentioned models are computed.

Keywords: $CdTiO_3$ crystals; Dielectric characteristics; ac conductivity; Thermal behaviour

1. Introduction

Cadmium titanate ($CdTiO_3$) belongs to a large family of the titanium-based oxides with perovskite structure of the form ABO_3, which have been intensively studied for their ferroelectric and electro-optical applications. Among the well-known ferroelectric perovskite type titanates, $CdTiO_3$ is unique in its structure. Its paraelectric phase has a deformed perovskite structure while the paraelectric phases of other titanates are cubic [1]. $CdTiO_3$ perovskite has been the object of several studies using X-ray diffraction [2–4], dielectric properties methods [4–6], infrared spectroscopy [7] and perturbed angular correction technique [8,9]. Shan et al. [10] established that single crystals of $CdTiO_3$ obtained by flux method showed the orthorhombic perovskite structure with the space group *Pnma* at room temperature and a dielectric anomaly appeared near 80 K. Phonons and specific features of the ferroelectric states in $CdTiO_3$ have been studied recently at cryogenic temperatures [11]. Raman characterization of $CdTiO_3$ prepared by sol–gel technique is reported [12]. Kabirov et al. [13] have studied the structure formation and phase transitions in cadmium titanate. First-principles study of the orthorhombic $CdTiO_3$ perovskite has been reported [14]. Angelo Montenero et al. [15] have studied the structural and electrical properties of sol–gel-processed $CdTiO_3$ powders and films.

Since the data on dielectric properties (except at cryogenic temperatures) and thermal behaviour of flux grown $CdTiO_3$ do not exist in the literature, we present in our paper our investigations based on measurements of the dependence of dielectric constant, loss tangent and conductivity on applied frequency and temperature over a wide range. The thermal behaviour of $CdTiO_3$ single crystals is studied using DTA, DTG and TG. The values of kinetic parameters, for example, order of reaction, activation energy, frequency factor and entropy of activation are worked out.

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2. Experiment

2.1. Crystal growth

Because of high melting point, crystals of $CdTiO_3$ are difficult to grow from pure melts. $CdTiO_3$ has been grown from KF flux by the technique reported by Watts et al. [16]. 1.65 g CdO, 1.05 g TiO_2 and 4.0 g KF are taken in 10 cm^3 platinum crucible. Since CdO has a tendency to dissociate to Cd when heated to high temperature which can result in damage to the platinum crucible, the soak temperature is, therefore, limited to 1393 K and the maximum heating rate is 50 K h^{-1}. The soak time is 1 h and the cooling rate is 4 K h^{-1}. The final temperature is 823 K at which good yield crystals of dark brown colour upto 2 mm × 2 mm × 1 mm are obtained.

2.2. Dielectric constant

The flux grown single crystal of $CdTiO_3$ of thickness of about 1.43 mm and 4.24 mm^2 area is used for undertaking dielectric and conductivity studies. The dielectric constant and loss tangent of $CdTiO_3$ single crystals are measured with the help of impedance analyzer (LF 4192 A model) manufactured by Hewlett Packard (USA) and further automated by using a computer for data recording, storage and analysis. The instrument directly provides the values of capacitance C and loss tangent $\tan\delta$. The dielectric constant is calculated using the formula $\varepsilon' = \frac{Ct}{\varepsilon_0 A}$, where C is the capacitance (F), t the thickness (m), A the cross-sectional area (m^2) of the sample and ε_0 is the absolute permittivity of the free space having a value of 8.854×10^{-12} F m^{-1}. The imaginary dielectric constant (ε'') of the capacitor is calculated using the relation $\varepsilon'' = \varepsilon' \tan\delta$ where $\tan\delta$ is the loss tangent. The alternating current conductivity σ_{ac} (Ω^{-1} m^{-1}) is calculated using the relation $\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon' \tan\delta$, where f is the frequency of the applied ac field (Hz). The activation energy of the crystal is calculated from an Arrehenius plot of $\ln\sigma_{ac}$ using the relation $\sigma_{ac} = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$, where σ_{ac} is the conductivity at temperature T, E_a the activation energy for the electrical process and k is the Boltzmann constant.

2.3. Thermal studies

Thermal behaviour is investigated using thermogravimetry (TG), differential thermal analysis (DTA) and derivative thermogravimetry (DTG) curves were recorded simultaneously on Perkin-Elmer (Pyris Diamond) using alumina powder as the reference material over the temperature range from 25 to 1450 °C. A sample of 12.93 mg of $CdTiO_3$ was taken in an alumina pan and the recordings were carried out in a nitrogen atmosphere at a constant heating rate of 10 °C min^{-1} and chart speed of 20 cm h^{-1} and flow rate of 300 ml min^{-1}.

3. Results and discussion

3.1. Dielectric characteristics

A dielectric characteristic study of the flux grown $CdTiO_3$ indicates its response to an applied electric field. Variations in the dielectric constant (ε') and loss tangent ($\tan\delta$) may be attributed to different types of polarization, which may come into play at different stages of its responses to varying temperature and frequency of the applied alternating field.

The dependence of the loss tangent ($\tan\delta$), dielectric constant (ε') and imaginary dielectric constant (ε'') on temperature and frequency of the applied ac field is studied in the temperature range of 298–923 K and frequency range of 10^3–10^6 Hz. The data so obtained are recorded in Table 1. Fig. 1 shows loss tangent ($\tan\delta$) as a function of temperature for $CdTiO_3$ at some frequencies in the range 10^3–10^6 Hz. From these plots it can be seen that the values of $\tan\delta$ are invariant with the rise in temperature upto 600 K. Above 600 K, $\tan\delta$ begins to increase with the rise in temperature upto 923 K. At higher temperatures, one observes that the rate of increase of $\tan\delta$ is higher for lower frequency as has also been reported for other materials by Das et al.

Table 1
Data on loss tangent ($\tan\delta$), dielectric constant (ε') and imaginary dielectric constant (ε'') of flux grown $CdTiO_3$ crystals at different temperatures and frequencies ($\nu = 10^3$–10^6 Hz)

T (K)	$\nu = 10^3$ Hz			$\nu = 10^4$ Hz			$\nu = 10^5$ Hz			$\nu = 10^6$ Hz		
	$\tan\delta$	ε'	ε''	$\tan\delta$	ε'	ε''	$\tan\delta$	ε'	ε''	$\tan\delta$	ε'	ε''
298	0.42	3700	1554	0.05	2600	130	<0.01	2400	21.60	<0.01	2400	16.80
323	0.43	3730	1603.9	0.06	2620	163.75	<0.01	2410	32.29	<0.01	2410	20.73
373	0.38	3800	1444	0.07	2711	180.55	<0.01	2474	36.12	<0.01	2474	23.01
423	0.43	4000	1720	0.07	2866	202.05	0.02	2600	40.56	<0.01	2611	26.89
473	0.48	4271	2050	0.11	2994	317.36	0.02	2710	43.90	<0.01	2675	33.97
523	0.48	4370	2097.6	0.11	3060	332.93	0.02	2748	47.54	<0.01	2729	36.02
573	0.59	4520	2666.8	0.12	3160	365.61	0.02	2830	63.67	<0.01	2784	39.25
623	1.18	4710	5557.8	0.20	3295	642.52	0.03	2894	99.26	0.02	2830	44.43
673	3.29	5060	16647.4	0.52	3480	1809.60	0.11	2970	332.64	0.03	2842	80.14
723	6.52	6040	39380.8	1.71	3683	6312.66	0.24	3010	735.64	0.04	2850	124.8
773	11.10	7240	80364	3.78	4120	15573.6	0.54	3020	1627.48	0.08	2783	214.2
823	16.30	9110	148493	8.86	4670	40488.9	1.45	3200	4640	0.20	2930	579.5
873	20.30	10540	213962	12.20	5160	62952	3.80	3360	12768	0.34	3030	1040
923	25.90	11600	300440	19.10	6070	108046	9.70	3730	36181	2.00	3240	6480