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Colossal and relaxor-like dielectric behaviors in $SrCrO_4$ ceramics

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ABSTRACT

Ceramic $SrCrO_4$ samples were prepared via conventional solid state reaction route. Dielectric properties of $SrCrO_4$ were systematically investigated in the frequency range of 10^2–10^6 Hz and temperature range of 5–900 K. Colossal dielectric behavior near room temperature and relaxor-like dielectric behavior around 730 K with an extremely high dielectric constant up to 1.62×10^5 were found. Dual relaxation mechanism composed of a dipolar and a Maxwell-Wagner relaxations is found to be responsible for the colossal dielectric behavior. The dipolar relaxation (R1) is related the defect dipole pair of $OH_O^{\bullet}$-Cr^{3+} caused by chemically absorbed water. The Maxwell-Wagner relaxation (R2) results from grain boundaries. The relaxor-like dielectric behavior is associated with the hopping motion of oxygen vacancies which leads to a high-temperature relaxation (R3).

1. Introduction

The discovery of the so-called colossal dielectric constant (CDC, $\varepsilon_r' > 10^4$) in $CaCu_3Ti_4O_{12}$ (CCTO) has triggered a burst of research activities [1,2]. Nowadays, CDC behavior has been widely reported in non-ferroelectric oxides, such as Ti-, Co-, Mn-based oxides [3–5], and even in non-oxide materials like GaAs [6]. It is a salient and universal feature for CDC behavior in non-ferroelectric oxides that the CDC behavior is closely associated with mixed-valence structure and oxygen vacancies [7]. In most non-ferroelectric oxides, the relaxing entities are localized electrons, which are created by oxygen vacancies. The electrons hopping between transition metal ions with polyvalent states (e.g., Cu^+/Cu^{2+}, Ti^{3+}/Ti^{4+}, Fe^{2+}/Fe^{3+}, Mn^{3+}/Mn^{4+}, and so on) leads to reorientational polarization which underlies the CDC behavior [8]. Based on this point, the chromium-based compounds, such as perovskite chromites and monazite-type chromates, having the polyvalent Cr ions, they might be promising candidates for CDC materials. Truly, the recent results have revealed that the Cr-based materials and even the Cr-doped oxides show curious dielectric properties. For example, both CDC behavior and ferroelectricity had been reported in perovskite chromites $RCrO_3$ (R = La, Pr, Sm) [9–11]. Extremely high dielectric constants over 10^5 had been found in Cr-containing oxide Ca_2TiCrO_6 [12] and Cr-doped oxide $Ca_{1-x}Bi_xTi_{1-x}Cr_xO_3$ [13].

Recently, the monazite-type structured oxides with the formula $MeXO_4$ (Me = Pb, Cr) and a tetrahedral anion group XO_4 (X = P, As, Se, Cr, Si, …) have received extensive attention as they are important photocatalytic materials responding to ultraviolet and visible light. Among them, only $LaVO_4$, $PbCrO_4$, and $CaSeO_4$ have been thoroughly studied [14–18]. Whereas for the compounds like $SrCrO_4$, $PbSeO_4$, and $SrSeO_4$, their properties have been seldom measured so far. $SrCrO_4$ is a monazite-type structured compound (space group $p2_1/n$) which is a representative of disordered $MeXO_4$ oxides [19]. Existing research work concerning $SrCrO_4$ compound has been performed mainly on the properties of photo-catalysis [20] and solid lubricant [21]. The dielectric properties of $SrCrO_4$ has never been investigated before.

Herein, by means of various dielectric functions, the dielectric properties of $SrCrO_4$ were thoroughly investigated in a wide temperature range from 5 to 900 K and frequency range of 10^2 –10^6 Hz. Three relaxations leading to colossal dielectric constant and relaxor-like dielectric behaviors were observed and their mechanisms were discussed.

2. Experimental details

The samples were synthesized by a solid-state reaction method using the starting materials $SrCO_3$ (≥99.0%) and Cr_2O_3 (≥99.99%). The powders were weighed according to the stoichiometry of $SrCrO_4$ (SCO) and then thoroughly mixed for 4 h using an agate mortar. The mixture was first calcined at 1073 K for 12 h and then at 1273 K for 12 h with intermediate grinding. Finally the resultant powders were reground and uniaxially pressed into pellets with

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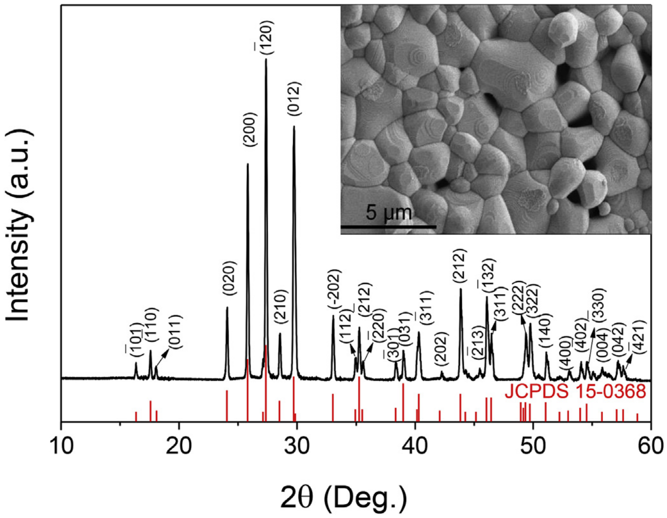

Fig. 1. XRD pattern of $SrCrO_4$ recorded at room temperature. The inset shows the SEM image of the fracture surface for an as-prepared pellet.

the dimension of 14 mm in diameter and 1–2 mm in thickness under a pressure of 20 MPa. Finally the pellets were sintered at 1373 K in O_2 for 12 h followed by slowly cooling down to room temperature to maintain the oxygen stoichiometry and avoid the generation of the second phase [22].

Phase purity of the sintered pellets was characterized by X-ray diffraction (XRD) on a Rigaku SmartLab diffractometer (Rigaku Smartlab Beijing Co, Beijing, China) with Cu *Kα* radiation. Microstructure was studied by a field-emission scanning electron microscope (SEM, Model S-4800, Hitachi Co., Tokyo, Japan). X-ray photo-electron spectroscopy (XPS, Thermo-Fisher ESCALAB 250Xi) was used to analyze the valence states of O and Cr elements. The experimental curves were fitted with a program XPSPEAK41 based on a combination of Gaussian-Lorentzian lines. The thermally stimulated depolarization current (TSDC) measurements were performed by an electrometer (6517 A, Keithley) connected to physical properties measurement system (PPMS, Quantum Design). The temperature-dependent dielectric properties in low temperature range of 5–300 K were measured using a Wayne Kerr 6500 B precise impedance analyzer (Wayne Kerr Electronic Instrument Co., Shenzhen, China) with the sample mounted in a holder placed inside a Janis SHI-4ST-1 close-loop refrigerator cryopump (Research CO., INC, USA). The frequency- and temperature-dependent dielectric properties in the high temperature range (300–890 K) were obtained using a Wayne Kerr 6500 B precise impedance analyzer with the sample mounted in a holder placed inside a PST-2000HL dielectric measuring system (Partulab Co., Wuhan, China). The temperature domain dielectric properties were measured at fixed frequencies by varying temperature with a heating ramp of 2 K/min. The frequency domain dielectric properties were measured at fixed temperatures by scanning frequency from 10^2 to 10^6 Hz. Electrodes were made by printing silver paste on both sides of the disk-type samples and then fired at 800 K for 2 h in order to remove the polymeric component before measuring. The ac measuring signal was 100 mV rms.

3. Results and discussion

The XRD of the as-prepared $SrCrO_4$ ceramic sample is shown in Fig. 1. The pattern was analyzed using Jade 6 power diffraction data analysis software [23]. It was found that the pattern can be indexed to a monazite structure (JCPDS file No. 15-0368) with the space group of P21/n (14). The average crystalline size and calculated lattice parameters are shown in Table 1. These parameters are fairly consistent with the reported values ($a = 7.065(4)$ nm, b = 7.375(4) nm, c = 6.741(4) nm, Z = 4, $\beta = 103.08(4)^o$) by Effenberger et al. [19].

A typical SEM photograph of the fracture surface of $SrCrO_4$ was shown in the inset of Fig. 1. It reveals that the grain size is non-uniform. The grains with an average size about 2–5 μm are densely packed together with some small pores (with the size less than 0.5 μm). The relative density is 90% of the theoretical density, as determined by the Archimedes method.

Fig. 2 and the inset present the temperature dependence of the dielectric constant (ε'_r) and the loss tangent ($\tan\delta = \varepsilon''_r/\varepsilon'_r$, where ε'' is the imaginary part of the complex permittivity ε^*_r) of $SrCrO_4$ measured under various frequencies, respectively. Similar to all CDC materials, the dielectric constant of $SrCrO_4$ shows a steep increase from a low-temperature plateau of ~33 to a high value over 10^4. This increase occurs at a temperature very close to room temperature accompanied by a loss tangent peak. The peak position shifts to high temperature with increasing measuring frequency indicative of thermally activated relaxation. Following the CDC behavior, there exists a pronounced relaxor-like dielectric constant peak around 730 K. The maximum dielectric constant reaches an extremely high value up to 1.62×10^5. At the beginning of the relaxor-like behavior (~500 K), the loss tangent remarkably increases and a hump at ~550 K can be seen in the curve recorded with 100 Hz. This finding indicates that the conductivity dominates the dielectric properties in the temperature range where the relaxor-like behavior occurs. The conductivity-related dielectric behavior usually behaves as increasing background, which shadows the information of dielectric relaxation.

To decipher to the nature of the relaxation, we performed detailed dielectric measurements in the frequency domain in the temperature range where CDC behavior occurs. Fig. 3(a) shows the frequency dependence of tan δ for $SrCrO_4$ at temperatures ranging from 313 to 573 K with a temperature step of $\Delta T = 20$ K. The curves, especially for those measured with lower temperatures, are found to be composed of two close peaks. This finding indicates that the CDC behavior is actually associated with two thermally activated relaxations. To separate the two peaks and to obtain their accurate peak positions, the curves of tan δ were fitted using two Gaussian peaks. As an illustration, Fig. 3(b) shows the fitting result to the experimental data of tan δ measured at 333 K. Perfect fitting result was achieved and the two peaks were well separated. For brevity, the two peaks are named as R1 and R2 in the order of ascending (descending) temperature (frequency). The measuring temperature and the peak position (f_P) for both relaxations deduced from the fittings were plotted according to the Arrhenius law [24]:

$$f_P = f_0 \exp(-E_a/k_B T) \tag{1}$$

where f_0 is the pre-exponential factor, E_a is the activation energy for

Table 1
Summaries of characteristic data of $SrCrO_4$.

Lattice Parameters (nm)			Average grain size (μm)	ε' (100 Hz&300 K)	tan δ (100 Hz & 300 K)	Activation energy (eV)	
a	b	c				grain	grain boundary
7.081	7.388	6.711	2–5	1596	1.095	0.32	0.34