Postprint: Synthesis and Magnetic and Dielectric Properties of TbCrO3

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Abstract

To investigate the magnetic phase transition and dielectric relaxation of TbCrO3 at low temperatures, TbCrO3 materials were prepared using the sol-gel self-propagating combustion synthesis method, and their magnetic and electrical properties were analyzed. The phase and physical properties of the material were characterized using X-ray diffractometer, field emission scanning electron microscope, and comprehensive physical property measurement system. X-ray diffraction results show that the synthesized TbCrO3 is a single-phase polycrystalline sample with space group Pbnm; the DC magnetization curve indicates that the Néel temperature of the material is TN = 162 K, the theoretical value of the effective magnetic moment of the molecule matches the experimental value obtained by extrapolating the high-temperature paramagnetic segment of the magnetization curve, indicating that the magnetic properties of the sample follow the Curie-Weiss law, the Weiss constant is negative (-32.2 K), indicating antiferromagnetic coupling characteristics within the sample; in dielectric measurements, dielectric dispersion and giant dielectric constant appear in the sample at low frequencies and high temperatures, which is attributed to space charge polarization. The sample exhibits dielectric relaxation near 200 K, the loss peak shifts toward higher temperatures with increasing frequency, the fitted activation energy is 0.358 eV, which is close to the activation energies of other samples in the RCrO3 system. Based on the relationship between the imaginary part of the dielectric constant and frequency, the relaxation is identified as Maxwell-Wagner relaxation, impedance spectroscopy analysis reveals that the relaxation is caused by the combined effects of grain boundaries and grains. TbCrO3 undergoes a paramagnetic-antiferromagnetic phase transition at low temperatures, and the dielectric relaxation exhibits thermally activated behavior.

Full Text

Synthesis and Magnetic/Dielectric Properties of $TbCrO_3$

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Abstract

Polycrystalline $TbCrO_3$ was synthesized using a sol-gel self-propagating combustion method. The phase structure and physical properties were characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (SEM), and a physical property measurement system (PPMS). XRD analysis confirms that the sample is single-phase with an orthorhombic Pbnm structure. DC magnetization curves reveal that $TbCrO_3$ undergoes an antiferromagnetic transition at the Néel temperature (T_N). The effective magnetic moment obtained from the high-temperature paramagnetic region follows the Curie-Weiss law, with a negative Weiss constant indicating antiferromagnetic coupling within the sample. Dielectric measurements show pronounced dielectric dispersion and a giant dielectric constant. A dielectric relaxation peak appears near T_N, shifting toward higher temperatures with increasing frequency. The fitted activation energy is comparable to those reported for similar systems. Analysis of the relationship between the imaginary part of dielectric constant and frequency identifies the relaxation as Maxwell-Wagner type. Impedance spectroscopy reveals that the dielectric relaxation at low temperatures exhibits thermally activated behavior, arising from the combined effects of grain boundaries and grains.

Keywords: $TbCrO_3$; sol-gel synthesis; antiferromagnetic; giant dielectric constant; space charge polarization; grain boundary relaxation

1. Introduction

Perovskite-type rare-earth chromites ($RCrO_3$, where R is a rare-earth ion) have attracted considerable attention due to their intriguing physical properties and potential applications in data storage and room-temperature magnetic refrigeration. Although studied for decades, their multiferroic and magnetoelectric properties continue to fascinate researchers. Structurally, these compounds crystallize in an orthorhombic Pbnm structure, where the magnetic interactions between R^{3+} and Cr^{3+} ions give rise to strong magnetic properties. The R^{3+}

cations are surrounded by O^{2-} anions, and the system can be described by isotropic and anisotropic exchange interactions between these ions.

The dielectric properties of $RCrO_3$ compounds show strong temperature dependence. In traditional ferroelectrics, the dielectric constant reaches a maximum during the ferroelectric-to-paraelectric phase transition. However, in relaxor ferroelectrics, broad dielectric peaks appear that are frequency-dependent and not directly associated with structural phase transitions, arising instead from randomly oriented short-range polar nanoregions reoriented by an external electric field. Previous studies on $LnCrO_3$ (Ln = Ho, Dy) have reported anomalous dielectric changes related to magnetic interactions of Ln^{3+} ions. While some $RCrO_3$ compounds (R = Sm, Eu) exhibit relaxor-like ferroelectric behavior above room temperature, investigations on $TbCrO_3$ remain limited, particularly regarding its dielectric properties.

In this work, we prepared single-phase $TbCrO_3$ using a sol-gel method, which offers advantages for producing fine nanopowders with short processing times. We systematically investigated its crystal structure, magnetic properties, and dielectric behavior.

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2. Experimental Methods

High-purity $Tb(NO_3)_3 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ were used as starting materials. Stoichiometric amounts of the nitrates were dissolved in deionized water under continuous stirring. Citric acid was added at a molar ratio of metal cations to citric acid of 1:1.2. The solution was heated on a hot plate while stirring until a viscous gel formed. The gel was then transferred to a beaker and heated until self-propagating combustion occurred, yielding a powder. The powder was ground and calcined to obtain single-phase $TbCrO_3$.

The crystal structure was analyzed using a PANalytical PRO Alpha-1 X-ray diffractometer with step-scan mode. Microstructural characterization was performed using a Quanta field-emission scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS). Magnetic properties were measured using a physical property measurement system (PPMS) with both zero-field-cooled (ZFC) and field-cooled (FC) protocols. Dielectric properties were measured using a precision impedance analyzer interfaced with the PPMS. Data analysis was conducted using FullProf software for Rietveld refinement and custom programs for dielectric and impedance analysis.

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3. Results and Discussion

3.1 Crystal Structure and Composition The XRD pattern of polycrystalline $TbCrO_3$ is shown in Figure 1. All diffraction peaks correspond to the orthorhombic Pbnm structure without any impurity phases, confirming the sample is single-phase. Rietveld refinement yields lattice parameters of a = 5.293 Å, b = 5.511 Å, and c = 7.575 Å, with reliability factors R_p = 11.2% and R_{wp} = 1.99%, indicating a reasonable fit.

EDS analysis was performed to verify the composition. Point-scan mode was used to measure atomic percentages at different regions. The results show Tb:Cr:O 1:1:3 (Figure 2), confirming the stoichiometric composition and absence of impurities.

3.2 Magnetic Properties Figure 3 shows the temperature dependence of DC magnetization (M-T) measured under ZFC and FC conditions with an applied field of 100 Oe. The data reveal a magnetic transition at T_N 3.8 K, corresponding to antiferromagnetic ordering. Above T_N, the system is paramagnetic. The inverse susceptibility ($^{-1}$) versus temperature plot (inset of Figure 3) follows the Curie-Weiss law, yielding an effective magnetic moment _{eff} = 9.72 _B and a Weiss constant = -32.2 K. The experimental _{eff} value agrees well with the theoretical value, and the negative confirms antiferromagnetic coupling.

3.3 Dielectric Properties The real part of dielectric constant ( ) was calculated from capacitance measurements at various frequencies. As shown in Figure 4, decreases with increasing frequency, demonstrating dielectric dispersion. At room temperature, the sample exhibits a giant dielectric constant, which can be attributed to extrinsic Maxwell-Wagner polarization commonly observed in ceramic materials.

The temperature dependence of dielectric loss (tan δ) reveals relaxation peaks that shift to higher temperatures with increasing frequency (Figure 5), indicating thermally activated relaxation. The activation energy can be described by the Arrhenius law: f = f_0 exp(-E_a/k_{BT}), where the peak position corresponds to the measurement temperature. Fitting yields an activation energy E_a = 0.9-1.48 eV, which is consistent with values reported for other perovskite materials and is associated with oxygen vacancy migration.

Analysis of the imaginary part of dielectric constant ( ) versus frequency shows an f^{-1} dependence at low frequencies, characteristic of Maxwell-Wagner relaxation. This confirms that the observed dielectric relaxation is not due to intrinsic mechanisms but rather originates from space charge polarization at grain boundaries.

3.4 Impedance Spectroscopy To distinguish whether the relaxation arises from grain interiors or grain boundaries, impedance spectroscopy was performed. Nyquist plots at various temperatures are shown in Figure 6. Two semicircles are observed: the low-frequency semicircle corresponds to grain boundary response, while the high-frequency semicircle corresponds to grain response.

The equivalent circuit (inset of Figure 6) consists of two parallel RC elements in series: (R_g + CPE_g) for grain transport and (R_{gb} + C_{gb} + CPE_{gb}) for grain boundary conduction and internal barrier layer capacitance (IBLC). Excellent fitting to this model demonstrates that the dielectric relaxation originates from the combined contributions of both grains and grain boundaries.

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4. Conclusion

Single-phase $TbCrO_3$ was successfully synthesized by a sol-gel self-propagating combustion method. Magnetic measurements reveal a paramagnetic-to-antiferromagnetic transition at T_N 3.8 K, with magnetic behavior following the Curie-Weiss law and a negative Weiss constant confirming antiferromagnetic coupling. Dielectric characterization shows giant dielectric constant and thermally activated relaxation with E_a = 0.9–1.48 eV. The relaxation is identified as Maxwell-Wagner type, arising from space charge polarization at grain boundaries. Impedance analysis confirms that both grain and grain boundary contributions are responsible for the observed dielectric behavior.

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Note: Figure translations are in progress. See original paper for figures.