



Temperature-dependent electron paramagnetic resonance detect oxygen vacancy defects and Cr valence of tetragonal $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ceramics

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ABSTRACT

Temperature-dependent electron paramagnetic resonance (EPR) study was employed to detect oxygen vacancy defects in the tetragonal $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x = 5\%$) ceramic for the first time. In the rhombohedral phase below -150°C , an EPR signal at $g = 1.955$ appeared in the insulating $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x = 5\%$) ceramic with an electrical resistivity of $10^8 \Omega \text{cm}$ and was assigned to ionized oxygen vacancy defects. $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ceramics exhibited a tetragonal structure except $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x = 10\%$) with a tetragonal-hexagonal mixed phase and a first-order phase transition dielectric behavior ($\epsilon'_m > 11,000$). Mixed valence Cr ions could coexist in ceramics, form $\text{Cr}_{\text{Ti}'}-\text{V}_\text{O}$ or $\text{Cr}_{\text{Ti}}-\text{Ti}_{\text{Ti}'}$ defect complexes and make no contribution to a dielectric peak shift towards low temperature.

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Introduction

Barium titanate (BaTiO_3) ceramics represents a material system of fundamental importance for a wide range of technical applications. Defects, particularly acceptor-type 3d transition elements, change the physical properties of BaTiO_3 ceramics and the technical application is supported by purposeful incorporation into BaTiO_3 . During the past several years, electron paramagnetic resonance (EPR), a technique for probing the electronic structure of paramagnetic defects in polycrystalline, have provided a catalogue of the microscopic properties of 3d ions incorporated in BaTiO_3 [1–5]. For doped BaTiO_3 ceramics, two EPR signals at $g = 2.004$ and 1.974 have been confirmed to be associated with ionized Ti vacancies and Ba vacancies [6], respectively. In addition, EPR was employed to detect oxygen vacancy defects (V_O) of tetragonal $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ($x = 3\%$) ceramics [7], an EPR signal at $g = 1.955$ appeared below -100°C and was assigned to ionized V_O . Oxygen vacancies are often accompanied by transition metal ions occupying Ti sites, such as, Co [1,2], Cr [1,3], Mn [1,4], and Fe [1,5]. However, it is also difficult to detect V_O -related EPR signals because of the strong EPR responses from transition metal ions.

To our knowledge, most EPR investigations are focused on ion valence for Cr-doped BaTiO_3 ceramics [1,3], whereas temperature-dependent EPR research of V_O has yet to make similar reports. In this work, we first discovered oxygen vacancy defects of Cr-doped BaTiO_3 ceramics and determine Cr dopant charge states.

Experimental section

$\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ (Cr_2O_3 , $x = 0.05\%$, 0.5% , 5% , and 10%) ceramics were prepared using a conventional cold-pressing ceramic technique described elsewhere [7]. The final sintering conditions were chosen as 1400°C for 12 h in air. The structure, microstructure and dielectric properties were carried out using DX-2700 X-ray diffraction (XRD), LabRAM XploRA Raman spectrometer (RS), EVOMA 10 scanning electron microscope (SEM), A300-10/12 X-band spectrometer (EPR) and Concept 41 dielectric/impedance spectrometer (NOVOCONTROL GmbH).

Results and discussion

XRD pattern of $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ceramics are shown in Fig. 1. All samples exhibited a tetragonal perovskite structure except $x = 10\%$ with tetragonal-hexagonal mixed phases denoted by an asterisk and a circle in Fig. 2, respectively. The results are similar to

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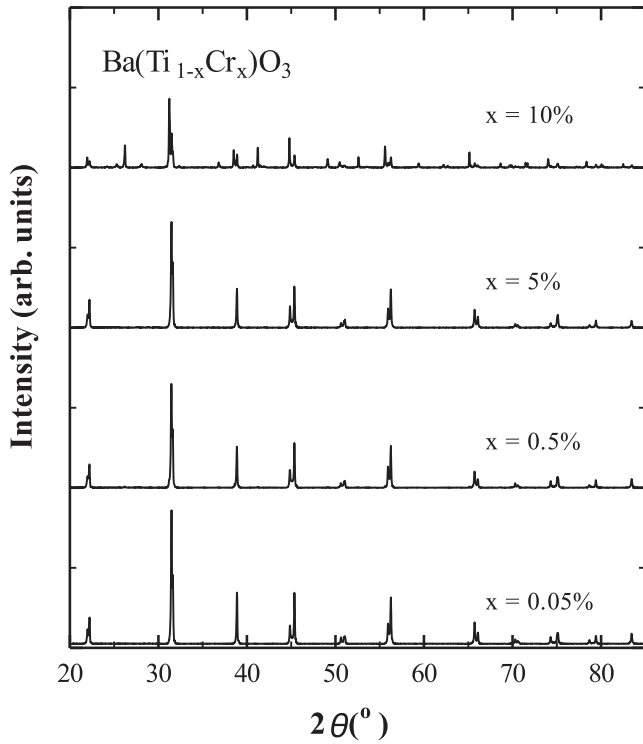


Fig. 1. XRD pattern of Ba(Ti_{1-x}Cr_x)O₃ ceramics.

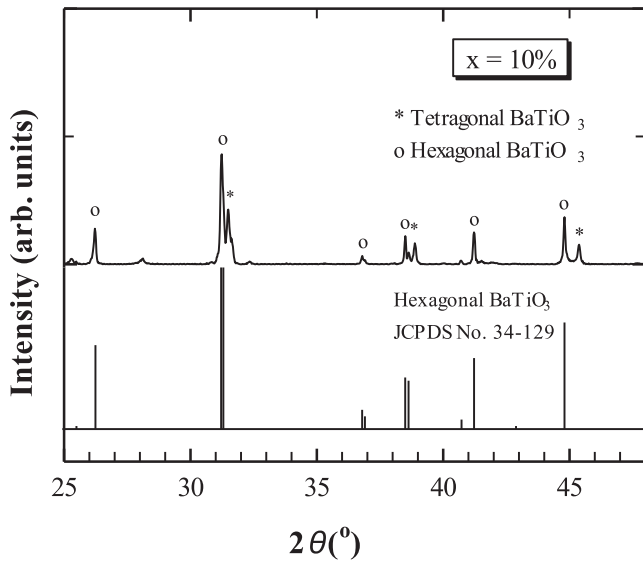


Fig. 2. XRD pattern of x = 10% ceramic, the data of the hexagonal BaTiO₃ (JCPDS Cards No. 34-129) is given for comparison.

reference for Cr concentrations ≥ 1.0 mol% the samples are completely hexagonal [8].

The unit cell volumes (V_0) of Ba(Ti_{1-x}Cr_x)O₃ [64.47 Å³ ($x = 0.05\%$), 64.5 Å³ ($x = 0.5\%$) and 64.42 Å³ ($x = 5\%$)] are shown in Fig. 3 and the V_0 value of Ba(Ti_{1-x}Cr_x)O₃ have the tendency of increasing first and then decreasing with increasing x . This is an abnormal phenomenon because Cr³⁺ (0.615 Å) ion is greater than Ti⁴⁺ (0.605 Å) ion [9]. Cr is known to be substituted for Ti site due to its ionic size [Cr³⁺, Cr⁴⁺ (0.55 Å), Cr⁵⁺ (0.49 Å), Cr⁶⁺ (0.44 Å)] approaching to Ti⁴⁺ and far smaller than Ba²⁺ (1.61 Å). It has been reported [2,3] that in air-sintered ceramics chromium is

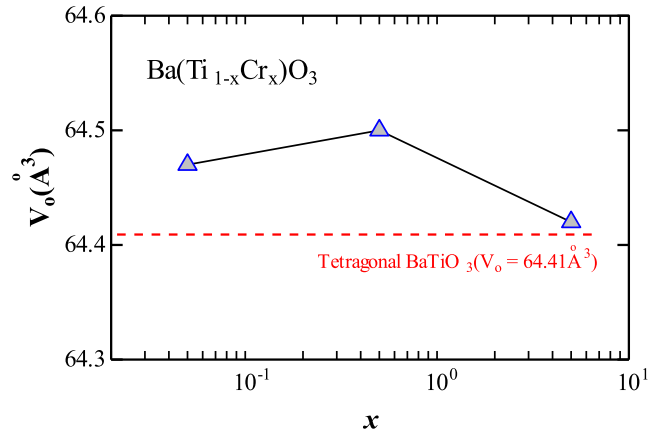


Fig. 3. Plot of the unit cell volume (V_0) as functions of x for Ba(Ti_{1-x}Cr_x)O₃. The data of the tetragonal (JCPDS Cards No. 5-626) is given for comparison.

incorporated with valence states 3+ and +4 when Cr₂O₃ is chosen as dopant. Muzur indicated that Cr⁶⁺ are reduced into Cr⁴⁺ and Cr⁵⁺ for oxidized sample when Cr⁶⁺ ions doped in BaTiO₃ [8]. Qi indicated that when the acceptor-doped samples were prepared under air condition, due to enough oxygen existence and on the basis of charge balance, the Cr³⁺ (3d³) can be partly oxidized to form Cr⁵⁺ (3d¹) [10]. So, in our samples we speculate Cr³⁺ can not entirely exist in the perovskite lattice or surface owing to valence mismatching, this change of V_0 gives direct evidence for the existence of mixed valence Cr ions in Ti⁴⁺ sites. Mixed valence states of Cr can together exist and form the defect complexes Cr_{Ti}-V_O or Cr_{Ti}-Ti_{Ti'}, the evidence substantially explains why acceptor-doped Ba(Ti_{1-x}Cr_x)O₃ ceramics prepared in air are approximately insulating ceramics below 100 °C (Fig. 6).

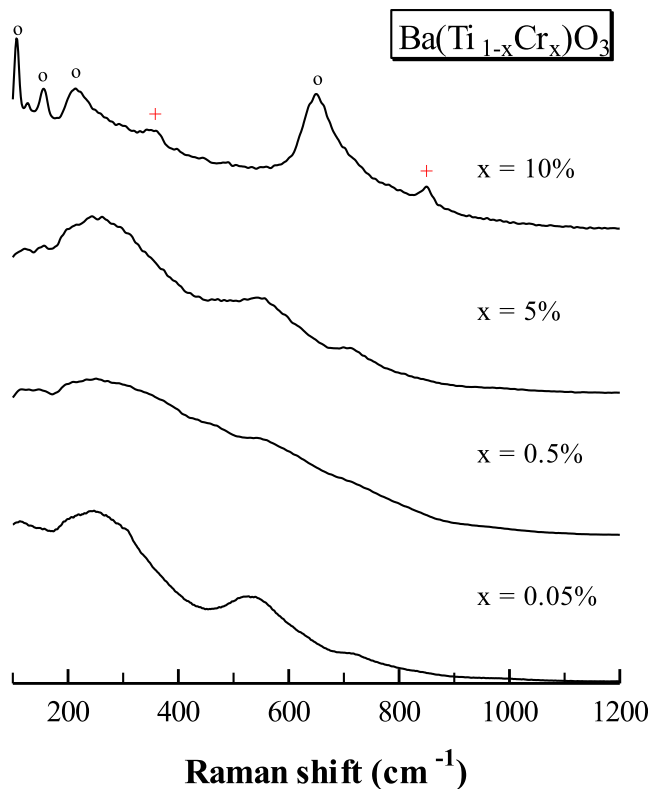


Fig. 4. Raman spectra of Ba(Ti_{1-x}Cr_x)O₃ ceramics.

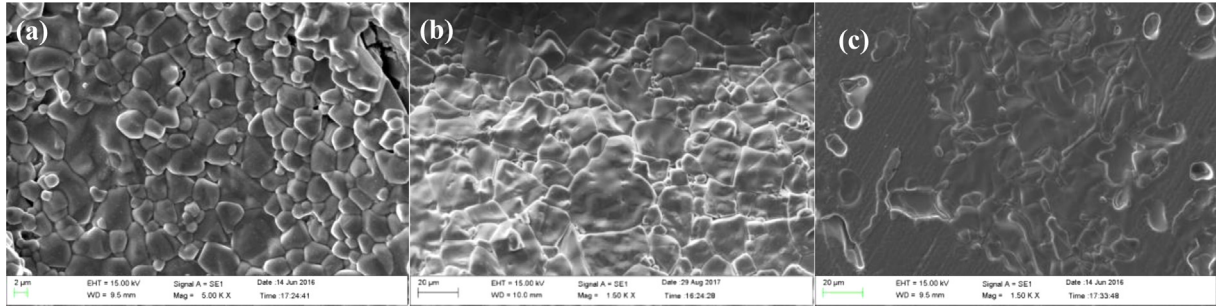


Fig. 5. SEM images of $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ceramics (a) $x = 0.05\%$, (b) $x = 5\%$ and (c) $x = 10\%$.

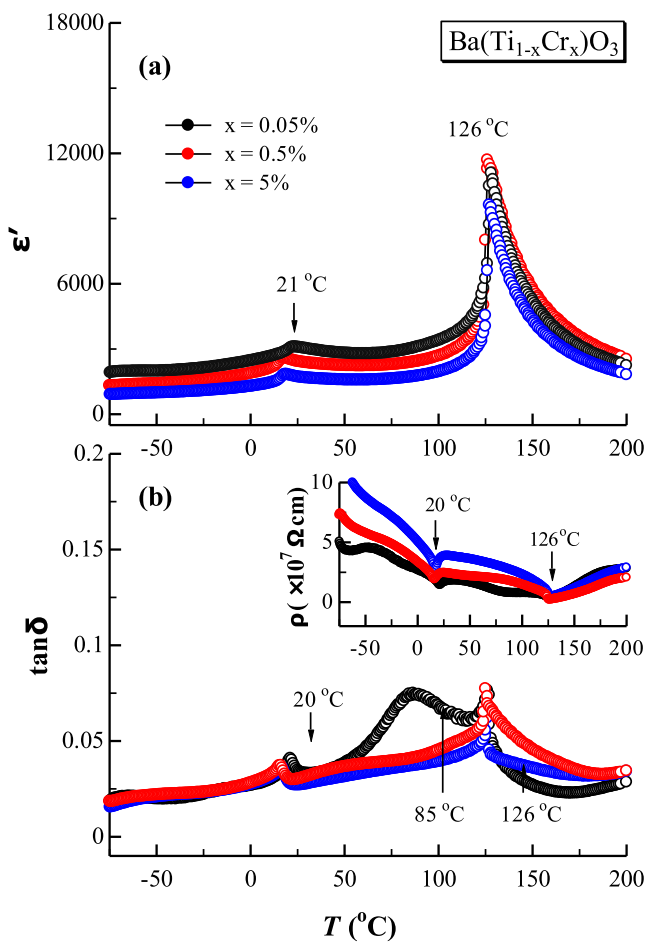


Fig. 6. Temperature-dependencies of dielectric permittivity (ϵ') (a), loss ($\tan \delta$) (b), and resistivity (ρ) (inset) for $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x \leq 5\%$) ceramics.

Raman spectra of $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ceramics are shown in Fig. 4. The tetragonal BaTiO_3 in the low-wavenumber region of 100–1200 cm^{-1} shows four phonon modes peaking at approximately 260, 520, 720, and 305 cm^{-1} [11]. The first three modes appear in all of the $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ceramics. When $x = 10\%$, a series of bands denoted by a circle are attributed to the hexagonal. Two bands at $\sim 823 \text{ cm}^{-1}$ and $\sim 365 \text{ cm}^{-1}$ are speculated from the tetragonal phase. It is reported that aliovalent substitution of Nb^{5+} [12] or Ca^{2+} [13] at Ti site in BaTiO_3 can cause a $\sim 840 \text{ cm}^{-1}$ band, which may be attributed to an internal deformation of the BO_6 octahedron in BaTiO_3 , which is known as the Raman charge effect [11]. In addition, the main Raman peak of Cr_2O_3 (not given here) appears at 531 cm^{-1} and its intensity is one-tenth with

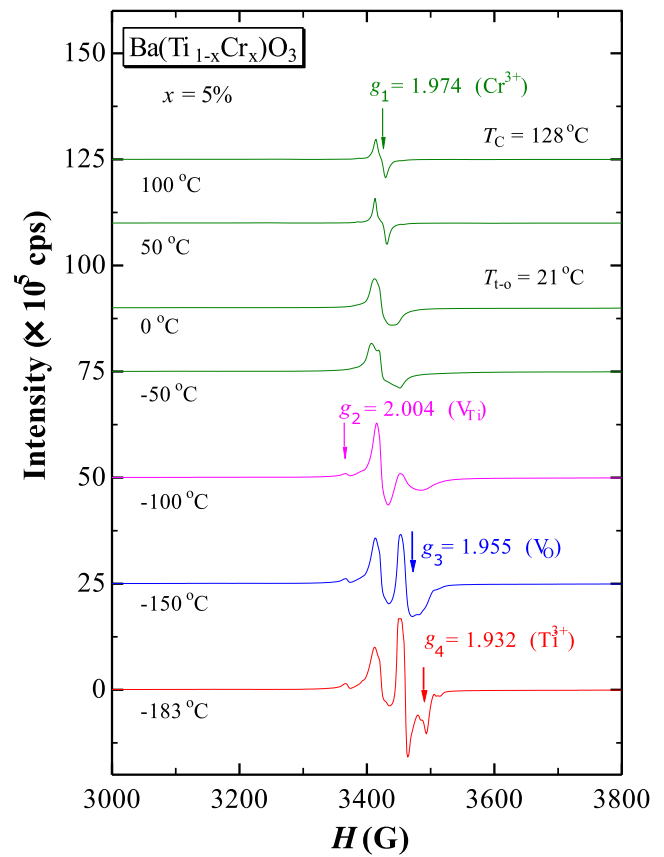


Fig. 7. Temperature-dependent EPR spectra for $x = 5\%$.

respect to the perovskite phase. Based on these results, the $\sim 823 \text{ cm}^{-1}$ band is attributed to a vibrating mode caused by a certain amount of Cr^{3+} or Cr^{5+} ions incorporated into the perovskite grains. But no band or a very weak peaking at $\sim 823 \text{ cm}^{-1}$ was observed when $x \leq 5\%$. That may be because that the same concentrations of Cr^{3+} and V_O or Cr^{5+} and Ti^{3+} defect complexes formed in the BaTiO_3 host lattice are charge self-balanced and equivalent to $\text{Ba}^{2+}\text{-Ti}^{4+}$, showing no Raman charge effect, whereas the extra Cr^{3+} ions that exceeded $\text{Cr}_{\text{Ti}'}\text{-V}_\text{O}$ or $\text{Cr}_{\text{Ti}}\text{-Ti}'$ complexes still exhibited Raman charge effect for $x = 10\%$. Thus, the evolution in the 823 cm^{-1} band could also explain the existence of mixed valence Cr ions in Ti^{4+} sites and the formation of $\text{Cr}_{\text{Ti}'}\text{-V}_\text{O}$ or $\text{Cr}_{\text{Ti}}\text{-Ti}'$ defect complexes.

SEM images of $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x = 0.05\%$, 5% and 10%) ceramics are shown in Fig. 5(a–c). At very low Cr concentrations of 0.05%, the microstructure exhibited a homogeneous and denser microstructure with globular grains of about $\sim 2 \mu\text{m}$ in size. The

average grain size increases with increasing Cr content and reaches more than 15 μm at a nominal concentration of 5%. The microstructure of $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x = 10\%$) becomes bimodal. One fraction of grains corresponds to these small globular grains ($\sim 10 \mu\text{m}$). The other fraction exhibits exaggerated growth, plate-like shaped grains of which this grain fraction is typical for hexagonal BaTiO_3 [2,14]. The obviously liquid phase-assisted, exaggerated grain growth is probably caused by a Cr-containing eutectic with unknown composition.

The temperature-dependence of the dielectric permittivity (ϵ'), dissipation factor ($\tan \delta$), and resistivity (ρ) for $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x \leq 5\%$) ceramics are shown in Fig. 6. BaTiO_3 showed a first-order phase transition and a sharp-peak feature at its Curie point ($T_C \approx 126^\circ\text{C}$) [15]. Similar to BaTiO_3 , Curie temperature (T_C) for $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ceramics occurred at 126°C , leading to a first-order phase transition with high- k sharp-peak behavior ($\epsilon'_m > 11,000$). This fact indicates that the mixed valence states of Cr ions make no contribution to a peak shift towards low temperature. The $\epsilon'-T$ curves for $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ceramics showed the presence of two phase transitions from cubic to tetragonal and from tetragonal to orthorhombic, and the temperatures of which correspond to $T_C = 126^\circ\text{C}$ and $T_{t-o} = 21^\circ\text{C}$, respectively. $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ceramics (except $x = 0.05\%$) shows a lower $\tan \delta$ (< 0.048) below 100°C , and is approximately insulating at -100°C , with an order of magnitude of $10^8 \Omega \text{ cm}$.

The temperature-dependent EPR spectra of $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x = 5\%$) are shown in Fig. 7. A stronger signal at $g_1 = 1.974$ was observed in the sample at about room-temperature, which is associated with Cr^{3+} ion incorporated into BaTiO_3 . This signal corresponds very well to measure results of Muller et al. [2]. Their Cr^{3+} causing a frequency-independent line width of 240 G. Additional evidence supporting the view that the resonance at $g = 1.974$ is due to Cr^{3+} is provided by Schwartz et al. [1].

A signal at $g_2 = 2.004$ was observed below -100°C and associated with ionized Ti vacancies [6]. When $T \leq -150^\circ\text{C}$, a new signal at $g_3 = 1.955$ appears and we attributed this signal to ionized oxygen vacancies [7]. The intensity of this signal increases with decreasing T , and a slight signal splitting occurs at $T = -183^\circ\text{C}$. Detailed explanations can be found in the reference 7. As T decreases to -183°C , this signal at $g_4 = 1.932$ was also observed in $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x = 5\%$) and attributed to Ti^{3+} -related defects. Kolodiaznyi indicated that Ti^{3+} -related defects could be observed only at low temperatures owing to the short spin-lattice relaxation time (τ) [6].

Conclusions

Cr-doped BaTiO_3 ceramics were prepared using a solid state reaction method. All samples exhibited tetragonal perovskite structure except $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x = 10\%$) with tetragonal-

hexagonal mixed phases. The abnormal phenomenon of V_0 change and the evolution of the 823 cm^{-1} band for Cr-doped BaTiO_3 ceramics give direct evidence for the existence of mixed valence Cr ions in Ti^{4+} sites and the formation of $\text{Cr}_{\text{Ti}'}-\text{V}_\text{O}$ or $\text{Cr}_{\text{Ti}'}-\text{Ti}_{\text{Ti}'}$ defect complexes. Mixed valence states of Cr ions make no contribution to a peak shift towards low temperature, Curie temperature for $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x \leq 5\%$) ceramics occurred at 126°C , leading to a first-order phase transition. The signal of Cr^{3+} ($g_1 = 1.974$), Ti vacancies ($g_2 = 2.004$), oxygen vacancies ($g_3 = 1.955$) and Ti^{3+} ($g_4 = 1.932$) were observed as T decreases to -183°C in temperature-dependent EPR spectra of $\text{Ba}(\text{Ti}_{1-x}\text{Cr}_x)\text{O}_3$ ($x = 5\%$) ceramic.

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