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An Ethylene Glycol-Based New Sol-gel Route to Multiferroic (1-x)LaCrO₃-xBiCrO₃ Solid Solution

Bahareh Abbasi,¹ Haiyan Guo,^{1,2*} Hua Wu,^{1,3} Hamel N. Tailor,¹ and Zuo-Guang Ye^{1*}

¹ *Department of Chemistry and 4D LABS, Simon Fraser University,
8888 University Drive, Burnaby, British Columbia, V5A 1S6, Canada*

² *Department of Electromechanical Engineering, Qingdao Huanghai University,
3111 Linghai Rd, Huangdao District, Qingdao 266427, China*

³ *Department of Applied Physics, Donghua University, 2999 Ren Min Road,
Songjiang District, 201620 Shanghai, China*

Abstract

Solid solution of multiferroic (1-x)LaCrO₃-xBiCrO₃ has been synthesized in the perovskite structure via a new sol-gel route using ethylene glycol as solvent. This synthetic process is proved to be superior to the solid state reaction method, with a lower formation temperature, improved reactivity and a higher solubility limit. The complex chemical reactions taking place in the sol and precursor powder upon heating are investigated by simultaneous thermal gravity and differential thermal analysis (TG/DTA). The substitution of BiCrO₃ for LaCrO₃ results in a higher density for the ceramics and an increased electric conductivity at high temperatures. The sol-gel synthesized La_{1-x}Bi_xCrO₃ solid solution (with x=0.3) exhibits a superparaelectric behaviour with a slim and non-linear polarization - electric field hysteresis loop, while a double hysteresis loop of antiferroelectric appearance is displayed in the compound with x = 0.4.

Keywords: Lanthanum-bismuth chromite solid solution La_{1-x}Bi_xCrO₃, sol-gel process, perovskite structure, superparaelectric behaviour, ferroelectricity, multiferroic.

* *Corresponding Authors.* Emails: zye@sfu.ca , happyhellen2001@hotmail.com

1. Introduction

Lanthanum chromite, LaCrO_3 , crystallizes in an orthorhombic perovskite structure at room temperature. Its high electronic conductivity, low ionic conductivity and good chemical stability in both oxidizing and reducing environments at high temperatures have made it one of the most promising candidates for use as an interconnect material in high-temperature solid oxide fuel cells and catalysis.^{1,2} In terms of magnetic properties, the localized magnetic moments on Cr^{3+} ($3d^3$) order antiferromagnetically below the Néel temperature (T_N) of 282 K, giving rise to a G_x -type magnetic structure, with the Cr^{3+} ions antiferromagnetically coupled to the six surrounding chromium ions.³ Because of the anti-symmetric Dzyaloshinsky-Moriya interaction, this ordering is accompanied with the spin canting of the Cr^{3+} moments.^{4,5} The magnetic properties of LaCrO_3 were found to be affected by the substitution of La^{3+} with different ions, e.g. $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$,³ $\text{La}_{1-x}\text{Sr}_x\text{CrO}_{3-\delta}$,⁶ and $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$,⁷ and $\text{La}_{0.95}\text{Nd}_{0.05}\text{CrO}_3$,⁸ with the appearance of weak ferromagnetism.

From a crystal structural point of view, LaCrO_3 belongs to the centro-symmetric space group $Pbnm$ with a phase transition from the orthorhombic to rhombohedral phase occurring at 260 °C upon heating.⁹ No ferroelectric properties have been found in pure LaCrO_3 . By substituting La^{3+} with Bi^{3+} , we have synthesized the solid solution of $(1-x)\text{LaCrO}_3-x\text{BiCrO}_3$, which adopts an orthorhombic structure of LaCrO_3 -type with a solubility limit of $x = 0.35$.¹⁰ Interestingly, ferroelectricity is revealed in $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ with $0.1 \leq x \leq 0.35$ by dielectric hysteresis loops displayed at 77 K, and the remanent polarization was found to be enhanced by the increase of Bi^{3+} concentration.^{10,11} The origin of the ferroelectricity is attributed to the structural distortion induced by the

stereochemically active Bi^{3+} ion on the A-site of the perovskite structure. On the other hand, magnetic hysteresis has been displayed in $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ ($0.1 \leq x \leq 0.3$) below the Néel temperature, T_N . With the increase of Bi^{3+} -content, T_N decreases, while the magnetization below T_N is enhanced, that is, a weakened antiferromagnetic coupling favours the canting of spins from the Dzyaloshinsky-Moriya interaction, giving rise to an enhanced “ferromagnetism”.¹² Therefore, the substitution of Bi^{3+} for La^{3+} was found to induce the ferroelectricity and enhance the ferromagnetic ordering, making the $(1-x)\text{LaCrO}_3-x\text{BiCrO}_3$ solid solution an interesting class of multiferroic materials with increased degrees of freedoms (magnetic and electric) and interactions (ferromagnetic, ferroelectric and magnetoelectric), useful for such applications as high-density memory and spintronic devices.^{13,14}

For the applications of LaCrO_3 -based materials in solid oxide fuel cells and magneto-electric devices, it is important to prepare highly densified ceramics. However, the poor sinterability and low density of pure lanthanum chromite pose a significant challenge to the processing of these materials. Many methods have been exploited to overcome this drawback, mostly with the substitution of alkaline earth or transition metal ions for La^{3+} , which was shown to be an effective solution.^{15,16} In the synthesis of $(1-x)\text{LaCrO}_3-x\text{BiCrO}_3$, it was found that the substitution of Bi^{3+} for La^{3+} can also enhance the density of the solid solution ceramics compared with the pure LaCrO_3 ceramics, with the relative density reaching 90% after sintering at 1200 °C.¹⁰ Such a significant improvement in the sinterability and densification of the LaCrO_3 -type ceramics by the substitution of Bi_2O_3 for La_2O_3 has pointed to a new route to the sintering of highly densified interconnect materials for solid oxide fuel cell applications. Subsequently, a

citrate-nitrate combustion route was developed for the synthesis of the $(1-x)\text{LaCrO}_3-x\text{BiCrO}_3$ solid solution and the sintering of the ceramics.¹⁷ This method has led to formation of pure $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ ($0.1 \leq x \leq 0.3$) perovskite phase at 800 °C, much lower than by solid state reaction method. In the present work, a new solution chemical process using ethylene glycol as solvent is developed to prepare the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ solid solution in the form of ceramics and the thermal stability and electric properties of the materials are characterized.

2. Materials Synthesis

The solid solution of $(1-x)\text{LaCrO}_3-x\text{BiCrO}_3$ ($\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$) (with nominal compositions of $0 \leq x \leq 0.5$) was prepared by a sol-gel method. The key to a successful sol-gel process is to find the right solvent that can readily dissolve all the starting ingredients without precipitation. In this work, ethylene glycol is chosen as the solvent because of its ability to dissolve all the starting reagents and to coordinate and crosslink the cations¹⁸. It has been proved to be an effective solvent for the synthesis of complex oxides such as $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$,¹⁹⁻²² and $\text{Sr}_2\text{Bi}_2\text{Ta}_2\text{O}_9$.²³ Furthermore, the fine precursor powder obtained after the pyrolysis process, which possesses a large specific surface area and high reactivity, is advantageous in producing high-density ceramics, which is also necessary for achieving enhanced properties.

The starting reagents of lanthanum acetate ($\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 1.5\text{H}_2\text{O}$), chromium nitrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), and bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) were dissolved in stoichiometric amounts in the ethylene glycol solvent to obtain a clear solution. The solution was then stirred, heated to 100 °C and kept for about 50 minutes. To remove the organic species

the solution was further heated to 500 °C for two hours until a green powder was produced. The powder was hand-ground in an agate mortar for 20 minutes and then pressed into pellets. The pellets were calcined and sintered at 1000 - 1200 °C in air to form the perovskite phase and to obtain densified ceramics. The flowchart of the synthetic process is displayed in Figure 1.

3. Characterization Techniques

The phase purity, crystal structure and average grain size of the solid solution synthesized were analyzed by means of powder X-ray diffraction (XRD) on the ceramic samples using Cu K α radiation (Rigaku Rapid-Axis Diffractometer, 42 mA, 45 kV, $2\theta = 15 - 80^\circ$). The pyrolysis process and thermal events were investigated by simultaneous thermal gravimetry / differential thermal analysis (TG/DTA) on a Seiko Exstar 6300 TG/DTA Thermal Analyzer. Gold layers were sputtered on the parallel surfaces of the ceramics for electrical characterization. The electric resistance/conductivity of the samples was measured using a Keithley electrometer (Model 6514). The polarization versus electric field measurements were performed at 77 K using a ferroelectric testing instrument (Radiant Technologies, RT66A, 10 Hz).

4. Results and Discussion

Figure 2 shows the powder XRD patterns of the La_{1-x}Bi_xCrO₃ samples with $x = 0, 0.1, 0.2, 0.3, 0.4$ and 0.5 prepared at 1000 °C. All the compositions with $x \leq 0.4$ show a pure perovskite structure of orthorhombic symmetry (of LaCrO₃-type phase). Some weak peaks of an impurity phase (which is yet to be identified) appear in the pattern of the $x = 0.50$ sample (as marked by "*" in Fig. 2), suggesting that the solubility limit is passed with this composition. These results indicate that the sol-gel process has led to the

formation of the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ solid solution at lower temperature (1000 vs. 1200 °C) with a higher solubility limit ($x = 0.40$ vs. 0.35), compared with the solid state reaction method which also requires more complex experimental conditions (e.g., in sealed Pt tube).¹⁰ The lower formation temperature and higher solubility limit can be attributed to the chemical characteristics of the sol-gel reactions (hydrolysis, pyrolysis, condensation and polymerization) that promote more homogenous mixing of the constituent species at nanometer scale and lead to more reactive intermediate (precursor) phases, consequently reducing the processing temperature and favouring the formation of the solid solution.^{24,25}

The lattice parameters of the solid solution were calculated from the XRD patterns using Powdercell software. Although the variations of the lattice parameters a , b and c do not exhibit systematic trends as a function of Bi-concentration, the unit cell volume of $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ ($0 \leq x \leq 0.4$), calculated from the lattice parameters, decreases monotonically from that of LaCrO_3 with the increasing concentration of BiCrO_3 , as shown in Fig. 3. This variation is consistent with that found for the ceramics prepared by solid state reaction,¹⁰ and it can be attributed to the a larger degree of covalency in the Bi-O bond due to a decreased electronegativity difference in Bi-O compared to La-O, while the ionic radii of La^{3+} and Bi^{3+} in coordination VIII are quite similar (1.30 and 1.31 Å, respectively²⁶). More systematic structural analysis based on high-resolution diffraction data needs to be performed in order to resolve the detailed crystal structure and phase symmetry of this solid solution.

The average grain size of the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ ceramics is estimated from the XRD peak broadening using the Scherrer equation. It is found to vary between 20 and 30 nm, as shown in Fig. 4. These values indicate the formation of nano-sized grains in the

ceramics, arising from the lower processing temperature and finer particles of the sol-gel process. Figure 5 presents the variation, as a function of Bi concentration (x), of the relative density of the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ ceramics sintered at 1200°C , which was determined by measuring the mass and volume of the samples. It shows that the substitution of BiCrO_3 for LaCrO_3 has improved the sinterability of the LaCrO_3 -based ceramics, as was in the case of solid state reaction,¹⁰ but this improvement is more significant in the present sol-gel processing since the density of the sol-gel prepared ceramics is much higher than those prepared by solid state reaction: e.g. 81.6% vs. 40% for the pure LaCrO_3 ceramics, and 98% vs. 80% for the $\text{La}_{0.7}\text{Bi}_{0.3}\text{CrO}_3$ ceramics. This reflects the above-mentioned advantages of the sol-gel preparation method in favouring phase formation and enhancing ceramic densification.

To monitor the chemical reactions that took place during the thermal treatments, simultaneous TG/DTA analyses were performed on both a sol sample and a green powder sample. Figure 6 shows the TG/DAT curves of the sol of " $\text{La}_{0.6}\text{Bi}_{0.4}\text{CrO}_3$ " (in the sol-gel process). The major weight loss that ended at 195°C upon heating on TG (Fig. 6(a)), accompanied by a huge endothermic event on DTA (Fig. 6(b)), likely results from the evaporation of ethylene glycol which has a boiling point of 197°C . The weak exothermic peak around 320°C (with a weak weight loss) may arise from the cross-linking and polymerization reactions, leading to the formation of the metal-organic framework (gel) accompanied by the loss of some organic species. Note that this thermal behaviour is different from the DTA curves of the gel of $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ obtained from the self-combustion method where only exothermic events were detected due to the nature of the combustion reactions.¹⁸ Figure 7 gives the TG(a)/DAT(b) curves of a pellet of the

precursor powder obtained after the heat treatment at 500 °C. It can be seen that three weight losses occurred at 640 °C, 740°C and 840 °C, respectively. The first two losses were more significant and were accompanied by broad endothermic peaks, indicating further decomposition of the metal-organic ligand frameworks, leading to the formation of the metal oxide complexes and eventual the perovskite solid solution phase. In solid state reaction,¹⁰ the endothermic peak in the starting oxide mixture results from an eutectic-like partial melting event that occurs in the ternary system of $\text{La}_2\text{O}_3\text{--Cr}_2\text{O}_3\text{--Bi}_2\text{O}_3$ due to the presence of the low-melting-point Bi_2O_3 (m.p.= 825 °C). The partial melting of the system gives rise to a liquid phase at the grain boundary, which favors the sintering of dense ceramics at a relatively low temperature. In the present sol-gel route, more complex reactions are expected to take place, leading to a lower crystallization temperature in consistence with the lower sintering temperature. However, more detailed investigations are needed to fully understand the mechanisms of those thermal reactions and the sol-gel process overall.

The electric resistance of the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ ($0 \leq x \leq 0.4$) ceramics was measured in the temperature range of 30 to 700 °C and the results are shown in Fig. 8. It can be seen that by Bi-substitution, the conductivity at low temperature is decreased significantly, from 0.316 S/m for LaCrO_3 to 0.001 S/m for $\text{La}_{0.60}\text{Bi}_{0.40}\text{CrO}_3$ at 345 K. This decrease of conductivity is beneficial to the improvement of dielectric, ferroelectric and multiferroic properties of the solid solution. On the other hand, the conductivity of $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ at 1000 K is increased by Bi-substitution, from 2.512 S/m for LaCrO_3 to 39.811 S/m for $\text{La}_{0.70}\text{Bi}_{0.30}\text{CrO}_3$. This increased conductivity at high temperatures suggests that the sol-gel prepared $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ ceramics are useful for applications as as interconnect

materials in solid oxide fuel cells. The polarization versus bipolar electric field relations, $P(E)$, could only be measured at low temperatures. Figure 9 shows the ferroelectric hysteresis loops for the compositions of $x = 0.3$ and 0.4 displayed at the liquid N_2 temperature. Compared with the measurements made on the samples prepared by solid state reaction,¹⁰ the $P(E)$ curve of the sol-gel prepared $La_{0.7}Bi_{0.3}CrO_3$ appears to be slimmer with a weak remanent polarization of $P_r = 0.1 \mu C/cm^2$, but it shows a better saturation. Such a slim and highly non-linear $P(E)$ loop is characteristic of superparaelectric behaviour which could arise from the nano-sized grains (Fig. 4) in the sol-gel prepared ceramics which could break the long-range polarization down to dipoles of nanometer scale.²⁷ In addition, the $P(E)$ curve of the $La_{0.6}Bi_{0.4}CrO_3$ ceramic displays a slim, nonlinear double hysteresis loop, which seems to suggest some kind of antiferroelectric behaviour. The ferroelectricity in $La_{1-x}Bi_xCrO_3$ is believed to have originated from the structural distortion induced by the stereochemically active lone pair electrons of Bi^{3+} ion on the A-site of the perovskite structure.¹⁰ The interesting and distinct polarization - electric field behaviours found in the sol-gel samples indicate that the macroscopic ferroelectric properties of the $La_{1-x}Bi_xCrO_3$ ceramics closely depend on their microstructures, such as nano-sized grains/particles vs. micron-sized grains/particles, that can be different depending on the various synthetic methods.

4. Conclusions

The solid solution of $(1-x)LaCrO_3-xBiCrO_3$ ($0 \leq x \leq 0.40$) has been synthesized in the perovskite structure in the forms of fine powders and ceramics by using a new sol-gel process. The substitution of $BiCrO_3$ for $LaCrO_3$ is found to reduce the unit cell volume, improve the density of the ceramics and increase the conductivity of the solid solution.

Simultaneous thermal gravity and differential thermal analysis (TG/DTA) was performed to monitor the complex chemical reactions taking place in the sol and precursor powder upon heating, giving rise to a preliminary picture about the reaction process. Compared with the solid state reaction method, the sol-gel process demonstrates some advantages: i) molecular level mixing and cross-linking polymerization lead to more reactive precursor phases and a better sinterability for the ceramics; ii) the solubility limit is extended to $x = 0.40$; iii) the process can be handled in air vs. in a Bi_2O_3 -rich environment or sealed Pt-tube; and iv) the pure perovskite phase can be synthesized at 1000°C instead of 1200°C . Moreover, the sol-gel synthesized $\text{La}_{(1-x)}\text{Bi}_x\text{CrO}_3$ ($x=0.3$) exhibits a superparaelectric behaviour with a slim and non-linear polarization - electric field hysteresis loop, while a double hysteresis loop of antiferroelectric appearance is displayed in $\text{La}_{(1-x)}\text{Bi}_x\text{CrO}_3$ (with $x=0.4$).

It would be interesting to investigate possible dielectric relaxation in the superparaelectric state of the $\text{La}_{(1-x)}\text{Bi}_x\text{CrO}_3$ solid solution, as is characteristic of relaxor ferroelectrics with the presence of polar nanoregions.^{28,29} It is also expected that an analogous superparamagnetic state could exist in these materials below their Néel temperature, leading to magneto-electric relaxation, as recently observed in the $\text{Pb}(\text{Fe}_{2/3}\text{W}_{1/3})\text{O}_3$ single crystals.³⁰

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Figure Captions:

Figure 1. Flowchart for the preparation of the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ solid solution ceramics by a sol-gel process using ethylene glycol as solvent.

Figure 2. X-ray diffraction patterns for the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ solid solution with different compositions, $x = 0, 0.1, 0.2, 0.3, 0.4$, and 0.5 , corresponding to LaCrO_3 , Bi_{10} , Bi_{20} , Bi_{30} , Bi_{40} and Bi_{50} , respectively.

Figure 3. Variation of the unit cell volume of the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ solid solution as a function of Bi concentration x .

Figure 4. Estimated average grain size for the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ solid solution ceramics of different compositions.

Figure 5. Variation of the relative density of the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ solid solution ceramics as a function of Bi concentration x .

Figure 6. Simultaneous TG(a)/DTA(b) curves of a sol sample of " $\text{La}_{0.6}\text{Bi}_{0.4}\text{CrO}_3$ " taken during the sol-gel process.

Figure 7. Simultaneous TG(a)/DTA(b) curves of a green pellet of the precursor powder of " $\text{La}_{0.6}\text{Bi}_{0.4}\text{CrO}_3$ " obtained after heat treatment at 500°C .

Figure 8. Variation of the conductivity as a function of reciprocal temperature for the $\text{La}_{1-x}\text{Bi}_x\text{CrO}_3$ compounds ($x = 0, 0.10, 0.20, 0.30$ and 0.40).

Figure 9. Polarization vs. electric field hysteresis loops displayed at 77 K for the $(1-x)\text{LaCrO}_3$ - $x\text{BiCrO}_3$ ceramics with $x = 0.3$ (a) and 0.4 (b).

Figures & Captions

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