

## Optimization of a Novel Composite Cathode for Intermediate Temperature SOFCs Applications

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### Abstract

$\text{Ba}_{0.95}\text{FeY}_{0.05}\text{O}_{2.81}$  was prepared by solid state reaction method to study its structure, conductivity and thermal expansion coefficients. X-ray powder diffraction at elevated temperatures showed the pure phase at 100 - 600 °C, then the phase changed at 700 - 800 °C. Electrical conductivity measurements at different temperatures showed that the conductivity increased with an increasing amount of  $\text{Co}_2\text{O}_3$ . The highest conductivity was observed for 10 wt%  $\text{Ba}_{0.95}\text{FeY}_{0.05}\text{O}_{2.81}$  + 90 wt%  $\text{Co}_2\text{O}_3$ . Thermal expansion coefficients were measured for different compositions to determine the compatibility with  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  electrolyte. Results showed that the conductivity and thermal expansion coefficient were sensitive to the composition. The optimum composition was 10 wt% BFY532 + 90 wt%  $\text{Co}_2\text{O}_3$ , which gave the highest conductivity at 600 - 800 °C. The thermal expansion coefficient was  $12.79 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  at 40 - 800 °C, which is compatible with the  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  electrolyte.

**Keywords:** Cathode, electrical conductivity, thermal expansion, crystallization, X-Ray diffraction

### Introduction

The performance of the cathode material is crucial for intermediate temperature solid oxide fuel cells (IT-SOFCs). Previous papers, studied the use of gold nano-particles are occasionally used to reduce the operating temperature. Mixed ionic-electronic conducting (MIEC) composite oxides are of increasing interest as electrode materials for SOFCs.  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (BSCF5582) was prepared by 50 % substitution of  $\text{Sr}^{2+}$  in  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  with a large size cation of  $\text{Ba}^{2+}$ . This composition showed high oxygen permeation flux at intermediate temperature SOFCs [1-6].

However, BSCF cathode material showed high thermal expansion and low electrical conductivity in comparison to common electrolytes. To improve the thermal expansion coefficient and electrical properties,  $\text{Co}_2\text{O}_3$  composite was added varying percentages and laminated with different electrolytes to observe its potential as a cathode [7-10].

A-site and B-site doped perovskites with  $\text{A}_{1-x}\text{A}'_x\text{B}_{1-y}\text{B}'_y\text{O}_{3-\delta}$  general formula and various chemical compositions are well known as excellent cathode materials [11-20]. Many reports evaluated the physicochemical properties of BSCF by changing elements such as Sr to La, Nb, Pr, Ni, or La, and Fe to La or Ti. These changes affected the crystal structure, electrical properties, and changes of oxygen stoichiometry.

$\text{YBaCo}_4\text{O}_7$  showed relatively low thermal expansion. Its mixed conductivity and electrochemical activity was significantly increased when in contact with doped  $\text{LaGaO}_3$  solid electrolyte. These properties are favorable for IT-SOFCs. Moderate doping of yttrium-barium cobaltate with iron showed a slight decrease in the total conductivity with predominantly a p-type electronic [21].

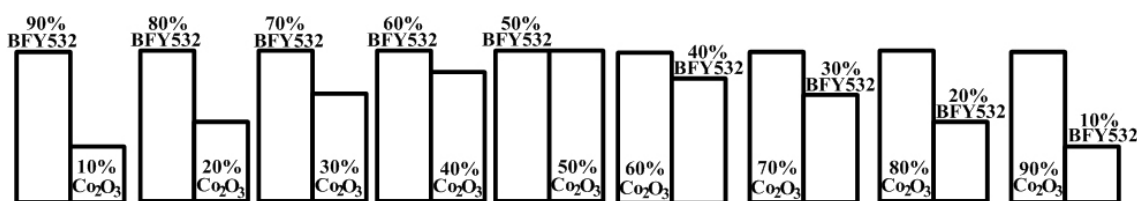
In this study, the composites  $\text{Ba}_{0.95}\text{FeY}_{0.05}\text{O}_{2.81}$  (BFY532) and  $\text{Co}_2\text{O}_3$  are optimized by investigating their conductivity, thermal expansion and crystal structure at intermediate temperatures (IT). The

electrical conductivity surprisingly increased, even though  $\text{Co}_2\text{O}_3$  is a semiconductor with negligible conductivity at temperatures lower than 800 °C [10]. The 10 wt%BFY532 + 90 wt% $\text{Co}_2\text{O}_3$  material showed great promise for use as a new composite electrode for IT-SOFCs.

## Materials and methods

### Sample preparation

Commercial powders BaO (99 %),  $\text{Y}_2\text{O}_3$  (99 %),  $\text{Co}_2\text{O}_3$  (99 %), and  $\text{Fe}_2\text{O}_3$  (99 %) were obtained from Sigma Aldrich GmbH, Germany. Stoichiometric amounts were mixed together to get the appropriate composition. The electrical conductivity of BFY532 (50 %BaO + 30 % $\text{Fe}_2\text{O}_3$  + 20 % $\text{Y}_2\text{O}_3$ ) was studied with different ratios of  $\text{Co}_2\text{O}_3$  added. The total weight % of the mixtures (e.g. BFY532 and  $\text{Co}_2\text{O}_3$ ) was kept constant. Nine composite powders were prepared, covering the composition range between 10 and 90 % of  $\text{Co}_2\text{O}_3$ , as shown in **Figure 1**.



**Figure 1** Ratios of BFY532 +  $\text{Co}_2\text{O}_3$ .

The powder mixtures were ground for 1 h and mixed with distilled water containing 10 % PVA (Polyvinyl alcohol) by weight. The mixtures were milled, with cylindrical alumina balls using a horizontal rotary ball mill for 24 h and then dried in an oven at 150 °C. They were then reground for 4 h in an in-house made grinding machine, and sieved at 150 mesh. The fine powders with some residual moisture content were then pressed into 13 mm diameter, 2 mm thick pellets using a uniaxial press under a pressure of 4000 psi. Finally, the pellets of BFY532 +  $\text{Co}_2\text{O}_3$  were sintered at 1100 °C, with a heating rate of 30 °C/min, for 5 h.

### X-ray powder diffraction analysis

Both the crystalline nature and phase purity were examined using powder X-ray diffraction (XRD) techniques (SHIMADSU XRD-7000 X-ray diffractometer, Japan) with Cu  $\text{K}\alpha$  radiation. The measurements were performed at room temperature, and at 100 °C intervals from 100 to 800 °C. A sample heating module (HT 1500 °C) was used for high temperature diffraction. Each composition was loaded in an alumina sample holder and inserted into the heating module. The module was heated from 40 °C to 800 °C at a heating rate of 10 °C/min. The 2 $\theta$  scanned diffraction data was recorded at a rate of 1.0 s/step with a step size of 0.02° from 10 to 60°. After the measurements were taken, the temperature was reduced to 40 °C at a cooling rate of 10 °C/min.

### Conductivity measurement

The conductivity of the pellets was measured with 4 probe dc technique (Scientific Equipment & Services Model DFP-02, India). Platinum (Pt) electrodes were used as the probes. Pt paste was printed in-between the Pt electrode and the pellet. All electrodes were pressed on the pellets to ensure good contact between them. Then the pellet with Pt electrode was placed in an in-house made furnace and heated up from 40 to 800 °C at a heating rate of 10 °C/min. The conductivity was measured at every 20 °C step.

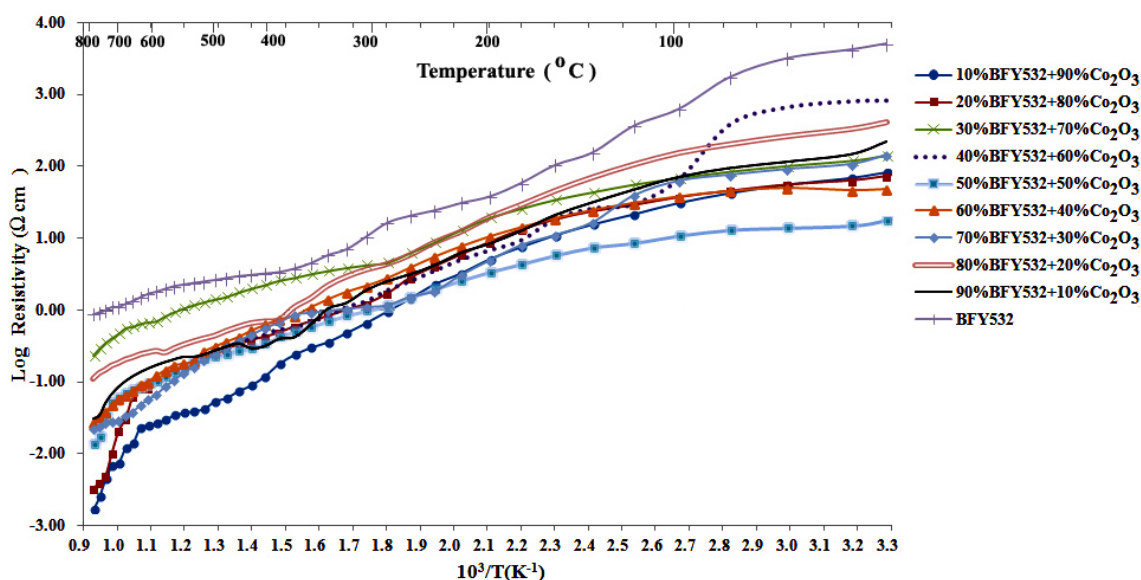
### Thermal expansion analysis

To check compatibility with the other materials of the cells, the thermal expansion coefficient (TEC) of BFY532 + Co<sub>2</sub>O<sub>3</sub> was studied. A large TEC mismatch between cathode and electrode may cause delamination and cracking. The TEC of BFY532 + Co<sub>2</sub>O<sub>3</sub> was compared to the most common electrolyte Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub>. Pellets were prepared from commercial Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> powder obtained from Fuel Cell Materials USA. The thermal expansion was measured in air at room temperature to 850 °C using SETARAM TMA, France. The heating rate used was 5 °C/min and the cooling rate was 10 °C/min.

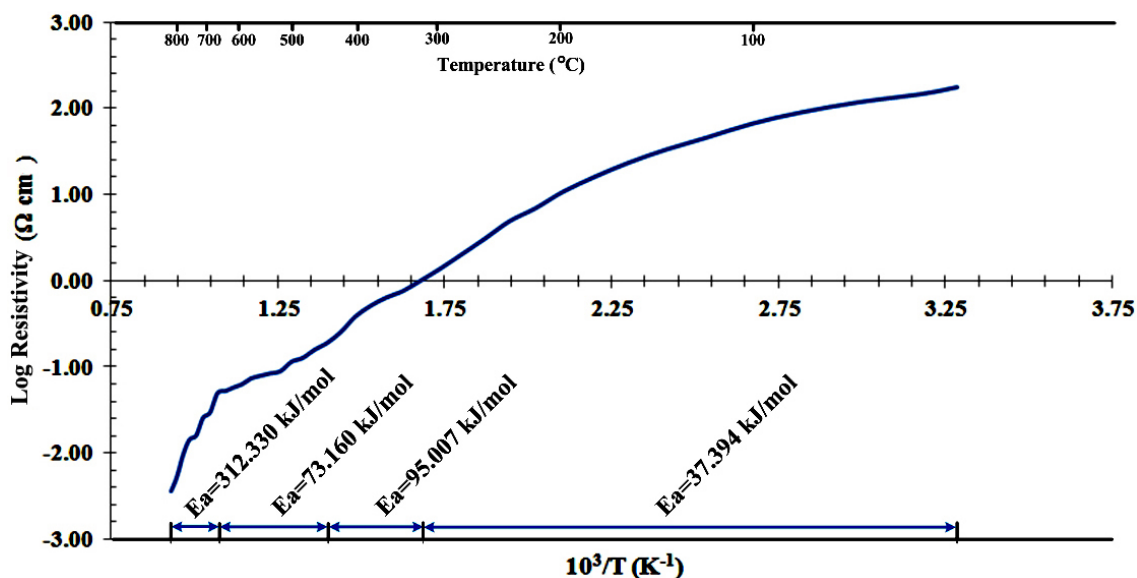
## Results and discussion

### DC conductivity

The temperature dependence of electrical conductivity for the samples is shown in **Figure 2**. The conductivity of BFY532 without Co<sub>2</sub>O<sub>3</sub> was very low. There was a significant increase in conductivity by incorporating Co<sub>2</sub>O<sub>3</sub>. The conductivity of 10 %BFY532 + 90 %Co<sub>2</sub>O<sub>3</sub> was the highest at intermediate temperatures. It increased slightly up to 660 °C and then rapidly to 588.55 Scm<sup>-1</sup> at 800 °C. The sudden increase may be due to the phase transition of Ba<sub>2</sub>Co<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> observed in **Figure 4**. The conductivity of different Co<sub>2</sub>O<sub>3</sub> ratios is non-linear. The composition with 70 % Co<sub>2</sub>O<sub>3</sub> had the lowest conductivity.



**Figure 2** The temperature dependence of electrical conductivity of BFY532 with different ratio % of Co<sub>2</sub>O<sub>3</sub> under atmospheric pressure.



**Figure 3** Different activation energy at different temperatures of 10 %BFY532 + 90 %Co<sub>2</sub>O<sub>3</sub>.

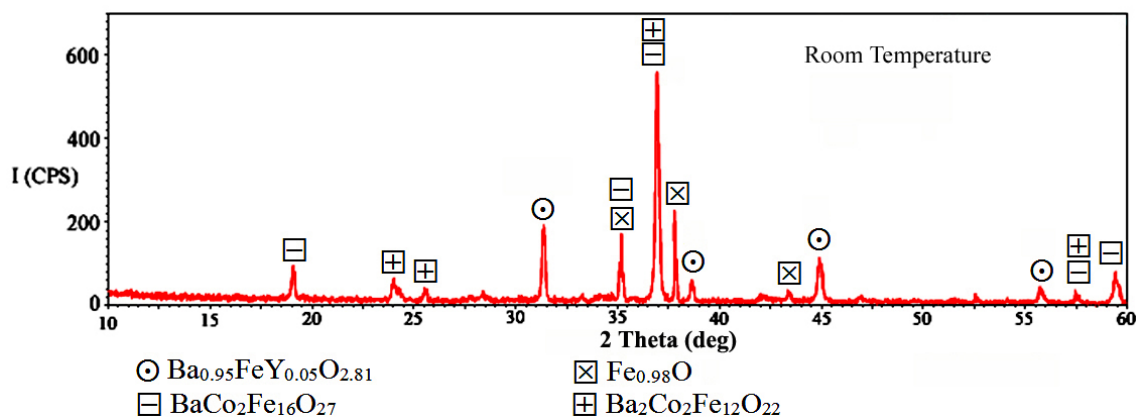
The activation energy increased from 37.394 kJ/mol at 40 - 300 °C to 95.007 kJ/mol at 300 - 450 °C. Then it decreased to 73.160 kJ/mol between 450 and 660 °C. The activation energy increased sharply to 312.330 kJ/mol at 660 - 800 °C as shown in **Figure 3**. The related activation energies indicate different oxygen permeation kinetics [22,23]. The activation energy from 450 - 660 °C is smaller than that from 300 - 450 °C. The lower activation energy from 450 - 660 °C could be caused by lower reactivity and a better thermal expansion close to Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> related in **Figure 6**. At 450 - 660 °C the mixture exhibited higher mobility of oxygen vacancy concentration, compared to values at 300 - 450 °C and 660 - 800 °C.

### Crystallography

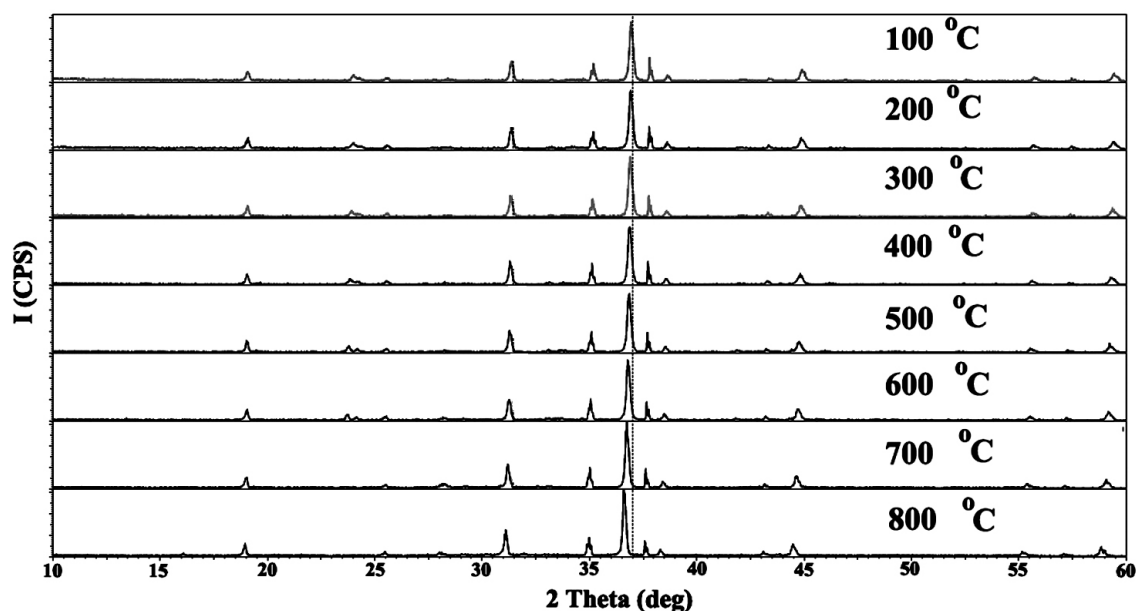
The X-ray diffraction patterns of the highest conductivity mixture, 10 %BFY532 + 90 %Co<sub>2</sub>O<sub>3</sub>, are shown in **Figure 4**. Peak matching was performed with XRD-6000/7000 version 5.21 software and International Center for Diffraction Data (ICDD 2010). There are peaks corresponding to Ba<sub>0.95</sub>FeY<sub>0.05</sub>O<sub>2.81</sub> (barium iron yttrium oxide), Fe<sub>0.98</sub>O, (iron oxide), BaCo<sub>2</sub>Fe<sub>16</sub>O<sub>27</sub> (barium cobalt iron oxide) and Ba<sub>2</sub>Co<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> (barium cobalt iron oxide). These are the four major composites that can be decomposed to form perovskite phase.

**Figure 5** shows the XRD patterns of the composite at elevated temperatures. The XRD patterns reveal a very strong cobalt oxalate which was the major phase, attributed to BaCo<sub>2</sub>Fe<sub>16</sub>O<sub>27</sub> and Ba<sub>2</sub>Co<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub>. At 700 - 800 °C, a crystallization of the Ba<sub>2</sub>Co<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> phase in the range 20 - 30° of 2 theta (deg) disappeared from the crystallographic.

From XRD analysis, Ba<sub>0.95</sub>FeY<sub>0.05</sub>O<sub>2.81</sub> compound exhibited a cubic crystal system. As reported in [24] BaFeO<sub>3-δ</sub> doped Y is a cubic system which contributed to an increase in both electrical and oxygen conductivity. The transition from high to low spin of Fe 3d electrons generated overlap between Fe 3d and O 2p electrons, which narrowed the energy gap allowing the composition to exhibit the high electrical conductivity behaviour of metallic materials. This suggests that the electrical conductivity was mainly the results of the Ba<sub>0.95</sub>FeY<sub>0.05</sub>O<sub>2.81</sub> composition.



**Figure 4** XRD pattern for 10 %BFY532 + 90 %Co<sub>2</sub>O<sub>3</sub> at room temperature.

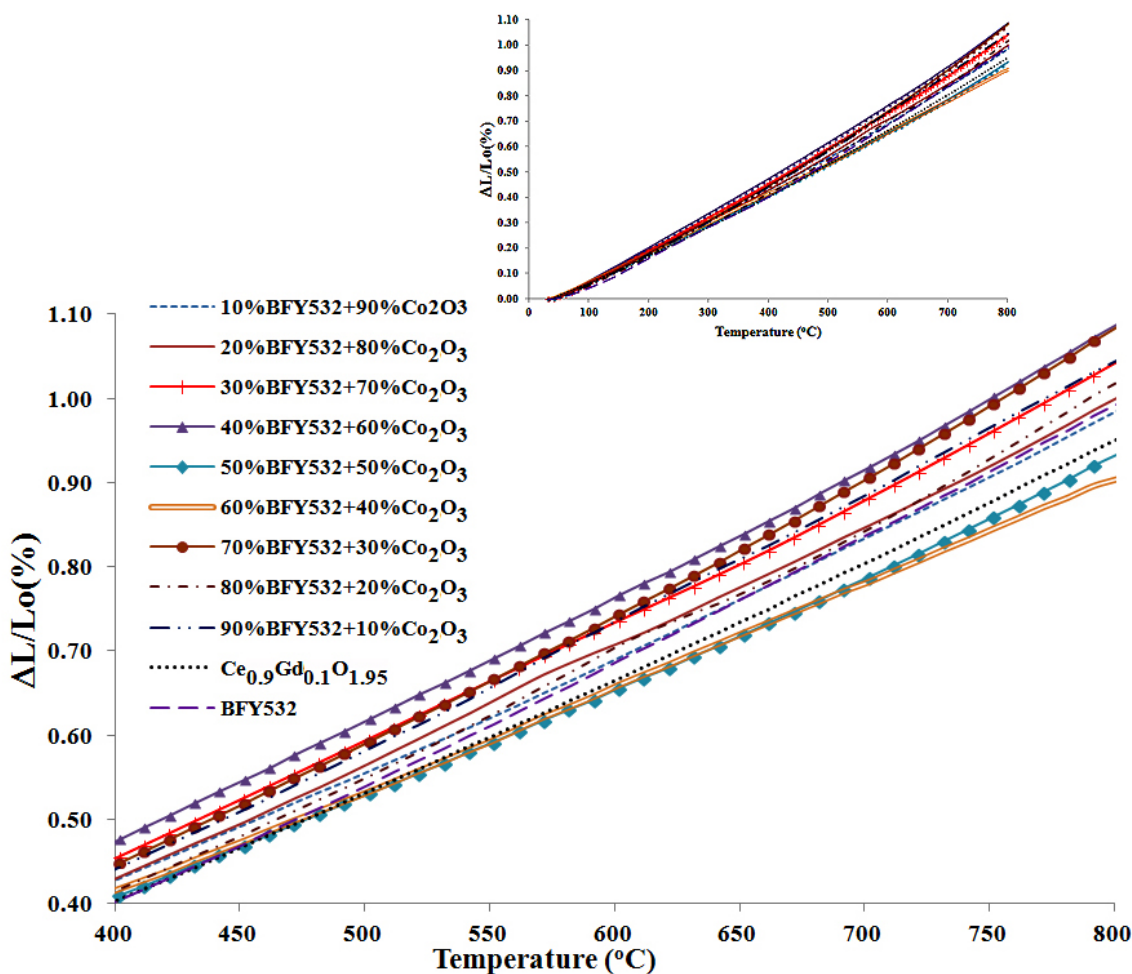


**Figure 5** XRD patterns of 10 %BFY532 + 90 %Co<sub>2</sub>O<sub>3</sub> at elevated temperature.

Fe<sub>0.98</sub>O and BaCo<sub>2</sub>Fe<sub>16</sub>O<sub>27</sub> have hexagonal crystal systems. Murakami *et al.* [25] explained that metallization of Fe<sub>0.98</sub>O could be inferred from resistance measurements and principles calculated by Sherman and Jansen (1995) which suggested the incorporation of FeO into iron metal which resulted in minimum ionicity. However, this idea still controversial as the relationship between ionicity and solubility is not well understood.

BaCo<sub>2</sub>Fe<sub>16</sub>O<sub>27</sub> is W-type hexagonal ferrites with low conductivity and high magnetic anisotropy. It is therefore easy to magnetize [26]. Ba<sub>2</sub>Co<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub> is Y-type ferrites with a rhombohedral crystal system. The electrical conductivity of ferrite results from 2 possible conduction mechanisms, n-type electron conduction and p-type hole conduction. In low conductance materials, p-type conduction occurs if one cation is replaced by another, resulting in a lower valency level, n-type conduction produces a higher

valency level. The oxygen deficiency of ferrites at high temperature promotes  $\text{Fe}^{+2}$  formation and also the n-type conduction. The p-type conduction is very low in ferrites [27].



**Figure 6** Linear thermal expansion curves for BFY532 +  $\text{Co}_2\text{O}_3$  under atmosphere pressure.

In general, the electronic conductivity value is much higher than the ionic conductivity for the materials. In this study the measured conductivities indicated a major electronic contribution associated with the tetravalent and trivalent state of the Fe and Co ions [4]. Increase in  $\text{Co}_2\text{O}_3$  content leads to a vast increase in electrical conductivity at room temperature.  $\text{Co}_2\text{O}_3$  rich samples show conductivity in excess of  $500 \text{ Scm}^{-1}$  at  $800^\circ\text{C}$ . However, the (Co,Fe)-O-(Co,Fe) double mechanism also decreases the average oxidation state of the Co and Fe cations. With high electrical conductivity the degree of delocalization of electrons near the Fermi level is also high and these holes may be associated with  $\text{Fe}^{3+}$  and  $\text{Co}^{3+}$  cations [28,29]. Therefore, 10 %BFY532 + 90 % $\text{Co}_2\text{O}_3$  composite may generate the (Co,Fe)-O-(Co,Fe) double mechanism when the temperature increases from 660 to  $800^\circ\text{C}$ .

### Thermal expansion

**Figure 6** shows the thermal expansions as a function of temperature. The TEC of the compositions were divided into temperature ranges of 40 - 200 °C, 200 - 400 °C, 600 - 800 °C and 40 - 800 °C, in a TEC range of  $11.75 - 13.84 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ . The TECs varied between 0.8 and 1.0 % of  $\Delta L/L_0$  and layer delamination was not observed. The TEC deviated from  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  as Co was introduced into the compositions. The Co content in perovskite oxide gave a high thermal expansion coefficient which resulted in changes in valence state from  $\text{Co}^{4+}$  to  $\text{Co}^{3+}$ , and  $\text{Co}^{3+}$  to  $\text{Co}^{2+}$ , respectively. The high TEC is generated by the spin state transition of Co from low to intermediate or high spin with elevating temperature [30].

As observed from the conductivity measurements, the 10 %BFY532 + 90 % $\text{Co}_2\text{O}_3$  composite had the highest conductivity and TEC value of  $12.79 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  at 40 - 800 °C. The TEC was similar to  $\text{YBaFe}_2\text{O}_{5+\delta}$  at  $14.60 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ . The composition of Y-O ionic bonds indicated that a decrease in TEC increased the binding energy between the ions in the crystal structure as they moved closer together [30]. The low thermal expansion of  $\text{YBaCo}_4\text{O}_7$  was related to the hexagonal crystal system as reported in [21]. From XRD analysis the compositions showed mainly hexagonal and cubic crystal systems. Therefore, 10 %BYF532 + 90 % $\text{Co}_2\text{O}_3$  may show a marked reduction in the ionic character of the Y-O bonds. The low TEC is affected by the changes in valence state of cobalt. It is possible that the high spin-state transition with increasing temperature causes the high TEC values.

The electrochemical properties of 10 %BYF532 + 90 % $\text{Co}_2\text{O}_3$  can be used as the cathode for the  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  composite electrolyte as SOFCs. They show high electrical and oxygen conductivity. The low thermal expansion at  $12.79 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  is close to that of the  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  composite electrolyte for compatibility between the layers of the fuel cells.

### Conclusions

Increasing  $\text{Co}_2\text{O}_3$  by wt% with 532BFY changes the electrical conductivity which also increases with temperature. The 10 %BFY532 + 90 % $\text{Co}_2\text{O}_3$  composite showed the highest electrical conductivity  $33.901 - 588.55 \text{ Scm}^{-1}$  at temperatures 600 - 800 °C, respectively. This is related to the perovskite phase of the composite as confirmed by the XRD pattern. Both hexagonal and cubic crystal systems existed in the composition but the rhombohedral disappeared at 600 - 800 °C. This phase transition may cause non-linear electrical conductivity with increasing activation energy at 600 - 800 °C. The phase transition of  $\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$  crystallite phase has shown an increase in conductivity. The thermal expansion coefficient was  $12.79 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ , close to that of the  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  electrolyte at 40 - 800 °C. The character of the Y-O bonds in the 10 %BFY532 + 90 % $\text{Co}_2\text{O}_3$  composition may reduce the thermal expansion. Therefore, the 10 %BFY532 + 90 % $\text{Co}_2\text{O}_3$  composition could be a potential cathode material for IT-SOFCs.

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