



# Neutron diffraction study of the crystal structure and structural phase transition of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{CrO}_3$ ( $0 \leq x \leq 0.3$ )

## The relationship between thermodynamic behavior and crystal structure changes at the phase transition

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### ABSTRACT

The crystal structure of the  $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{CrO}_3$  series, including the compositional and temperature dependence of the structural parameters, has been studied by variable temperature neutron diffraction measurements. The extent of the distortions from the ideal cubic perovskite structure has been evaluated quantitatively using the average bond lengths and the mean volumes of the  $[\text{CrO}_6]$  octahedron and  $[(\text{La}/\text{Ca}/\text{Sr})\text{O}_{12}]$  polyhedron, and has been shown to decrease with increase of Sr content or temperature. At the structural phase transition from the orthorhombic ( $Pnma$ ) structure to the rhombohedral ( $R\bar{3}c$ ) one, the volume of the  $[\text{CrO}_6]$  octahedron decreases whereas that of the  $[(\text{La}/\text{Ca}/\text{Sr})\text{O}_{12}]$  polyhedron shows little difference, resulting in an overall decrease in the level of distortion. The change in the degree of distortion at the phase transition decreases with increase of Sr content, in agreement with the smaller variation of the enthalpy and volume for the specimens with higher Sr content.

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## 1. Introduction

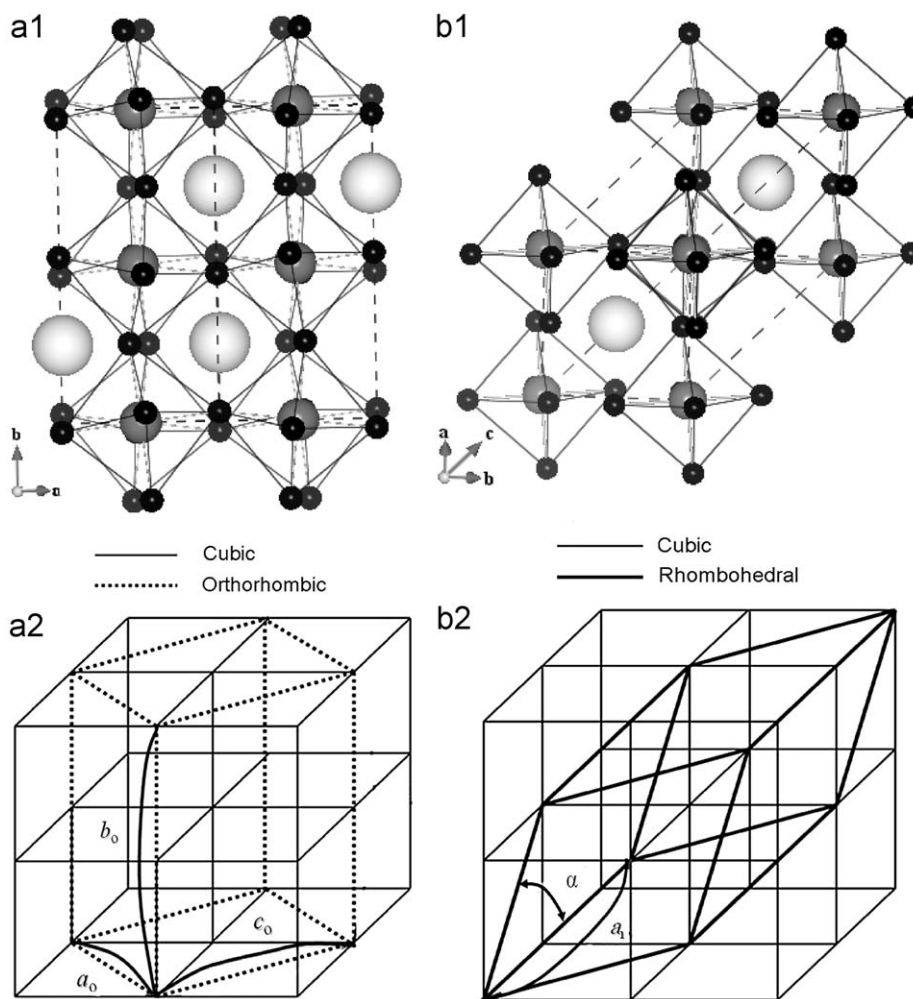
Electronically conducting oxides have been extensively examined at high temperatures for technological applications within various energy generation devices. One of the most promising energy conversion technologies is the solid oxide fuel cell (SOFC), which possesses very high energy conversion efficiency. In order to generate high voltages from an SOFC it is necessary to employ an interconnector to connect individual SOFCs in series. The material chosen for the interconnector must be stable at the typical SOFC operating temperature (1000–1300 K) under both oxidizing and reducing gas atmospheres. In this context, compounds in the series  $\text{La}_{1-x}\text{A}_x\text{CrO}_3$  ( $A=\text{Ca}, \text{Sr}$ ) have been investigated, since they possess a high electrical conductivity and high chemical stability at elevated temperatures under reductive atmospheres [1]. However, several problems have been raised for the application of  $\text{La}_{1-x}\text{A}_x\text{CrO}_3$ , including its poor sinterability. It was reported that partial Sr substitution onto the La site improves the sintering properties, though it has proved

difficult to obtain specimens with high enough sintering density for applications as an interconnector [2]. It has also been reported that partial Ca substitution or the addition of excess Ca is an effective approach to improve the sintering properties [2–5], with liquid phase sintering resulting in the preparation of specimens with sintering densities of over 95% synthesized by the addition of excess Ca. However, an additional serious problem is the presence of a structural phase transition between room temperature and the SOFC operating temperatures, which remains in the Ca substituted  $\text{LaCrO}_3$  system.

At room temperature, the crystal structure of  $\text{LaCrO}_3$  can be described as an orthorhombic distortion of the cubic perovskite structure in space group  $Pnma$  (no. 62). At 533 K a structural phase transition to a rhombohedrally distorted perovskite with space group  $R\bar{3}c$  (no. 167) is observed [6–10]. Fig. 1 shows a schematic drawing of (a1) the orthorhombic distorted perovskite and (b1) the rhombohedrally distorted one, prepared with program VENUS [11]. The tilt and rotation of the  $[\text{CrO}_6]$  octahedron can be described as  $a^+b^-b^-$  and  $a^-a^-a^-$  for orthorhombic phase and rhombohedral one, respectively, by using Glazer notation [12,13]. The relationship between the ideal cubic perovskite unit cell and (a2) the orthorhombic distorted one and (b2) the rhombohedrally distorted one are

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**Fig. 1.** Crystal structure drawing of (a1) the orthonormal distorted perovskite (space group:  $Pnma$ ) and (b1) the rhombohedrally distorted one (space group:  $R\bar{3}c$ ) prepared with program VENUS [11]. Small black sphere and large white one represent  $O^{2-}$  and  $La^{3+}/Ca^{2+}/Sr^{2+}$ , respectively. Cr ion is shown as light black sphere. The relationship between the ideal cubic perovskite unit cell and (a2) the orthonormal distorted perovskite unit cell and (b2) the rhombohedrally distorted one is also shown. For an ideal cubic perovskite structure,  $a/\sqrt{2}$ ,  $b/2$  and  $c/\sqrt{2}$  of the orthonormal lattice are the same and  $\alpha$  the angle of the rhombohedrally distorted phase is equal to  $60^\circ$ .

also depicted in Fig. 1. As this is a first order phase transition, it is accompanied by latent heat and discrete change in the volume, resulting in deterioration of the mechanical toughness and reliability of the SOFC [4]. Thus, for applications of  $LaCrO_3$  based compounds as interconnectors within an SOFC, no structural phase transition should occur between room temperature and the SOFC operating temperature. However, the phase transition temperature in  $La_{1-x}Ca_xCrO_3$  is observed to increase with increase of the Ca content [14,15]. Conversely, the phase transition temperature decreases with increase of Sr content in  $La_{1-x}Sr_xCrO_3$ , resulting in materials free from the phase transition over the temperature range of interest for  $x$  larger than 0.10 [16–18]. As a consequence, it might be expected that ceramic specimens possessing good sintering properties and an absence of the phase transition might be prepared by simultaneous substitution of Ca and Sr onto the La site.

In our preceding papers [19,20], excellent sintering properties of  $La_{0.70}Ca_{0.3-x}Sr_xCrO_3$  ceramic specimens were reported, with a sintering density in excess of 93% for specimens with  $x=0.10$ – $0.25$ . In addition, the phase transition temperature was observed to decrease with increase of the Sr content, resulting in an absence of the phase transition between room temperature and SOFC operating temperature for  $x$  larger than 0.20. Furthermore, differential scanning calorimetry (DSC), dilatometry and variable temperature X-ray diffraction studies indicated that the variation

of the enthalpy and volume at the phase transition,  $\Delta H$  and  $\Delta V$ , decrease with increase of Sr content. However, the origin of the decreases in the phase transition temperature,  $\Delta H$  and  $\Delta V$ , which can be regarded as important information for the control of the phase transition behavior, has not been clarified.

It might be expected that the variation of the phase transition behavior is related to changes in the crystal structure with temperature and substitution, including variations in the volume of the  $[CrO_6]$  octahedra, tilt angle, Cr–O–Cr angle and so on. Since the positions and thermal parameters of the oxide ions within metal oxides cannot be evaluated accurately using powder X-ray diffraction, such information was not presented in our previous paper [20]. However, whilst we could not clarify the origin of the smaller  $\Delta H$  and  $\Delta V$  with increase of Sr content, it was speculated that the variation of the distortion from the ideal cubic perovskite arrangement inferred from variations of the lattice parameters might be related to the variation of  $\Delta H$  and  $\Delta V$ . Subtle changes in the crystal structure can be more accurately evaluated using neutron diffraction, especially in the case of the positional and thermal parameters of the oxide ions. However, there have been few reports of neutron diffraction measurements of  $LaCrO_3$  based compounds. Sakai and co-workers reported the temperature variation of the crystal structure of the  $La_{1-x}Ca_xCrO_3$  system using neutron diffraction and observed an increase of the phase transition temperature and decrease of  $\Delta V$  with increase of Ca

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