

Lattice thermal expansion of $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$

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Abstract

Lattice thermal expansion studies on $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0, 0.02, 0.05, 0.1, 0.3$ and 0.5) were carried out by high temperature XRD from room temperature to 1173 K. A linear increase in lattice parameter was observed with increase in copper concentration indicating the substitution of copper in the lattice. The % volume thermal expansion ($\nabla V \cdot 100/V$) increases with temperature. As the copper concentration increases from 0.0 to 30 mol.%, the % volume thermal expansion decreases from 5.98 to 4.522. The lattice and volume thermal expansion coefficients (TEC), $\bar{\alpha}_a$, $\bar{\alpha}_c$, and $\bar{\alpha}_v$, averaged between 298 and 1023 K are calculated using the HTXRD data. $\bar{\alpha}_a$, $\bar{\alpha}_c$ and $\bar{\alpha}_v$ decreased from 26.78×10^{-6} to $18.27 \times 10^{-6} \text{ K}^{-1}$, 27.81×10^{-6} to $24.56 \times 10^{-6} \text{ K}^{-1}$ and 82.45×10^{-6} to $72.9 \times 10^{-6} \text{ K}^{-1}$, respectively, as the copper concentration increased from 0 to 30 mol.%. The decrease in TEC with copper loading is due to the introduction of the covalent character of the Cu–O bond in the otherwise ionic nature of the La–O bond in LaCoO_3 . The larger decrease in $\bar{\alpha}_a$ as compared to $\bar{\alpha}_c$ confirms the substitution of more copper in the a – b plane rather than in the c -axis.

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1. Introduction

Much research is being carried out to prepare materials for solid oxide fuel cells (SOFC) with highly efficient power generation. The thermal expansion coefficient of the material used in an SOFC must equal that of the electrolyte. Although perovskite oxides such as LaCoO_3 have been used as cathode materials due to their high electrical conductivity ($\sim 10^3 \text{ S cm}^{-1}$ at 1000°C), their thermal expansion is twice as large as that of yttria-stabilized zirconia. Many investigators have reported in the literature only on the synthesis and characterization of perovskite materials, i.e. LaCoO_3 , LaCrO_3 , LaMnO_3 , etc., and the substitution of both A and B cations by different cations and not on their thermal expansion behaviour. Recently Nagamoto et al. [1] reported that the thermal expansion coefficient of $\text{LaCo}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Ni, Fe}$) averaging between 25 and 1000°C revealed a linear decrease with the Fe content due to the formation of the enthalpy of the perovskite type oxide and the bond length between the B-cation and its nearest oxide ion. Mathews et al. [2] have reported the phase transition, bulk

and lattice expansion behaviour of $\text{LaM}_{1-x}\text{Cr}_x\text{O}_3$ ($M = \text{Sr, Nd}$) by dilatometry and HTXRD from room temperature to 1123 and 1023 K, respectively, in static air. The coefficients of average linear and volume thermal expansion (α_l and α_v) of LaCrO_3 showed a marginal increase on Sr^{2+} substitution to different extents whereas a reverse trend was observed for Nd^{3+} substitution. Partial substitution of Sr for La in LaMnO_3 increases the thermal expansion coefficient [3]. Gilbu et al. [4] reported the thermal expansion and structural transition of $\text{LaCo}_{1-t}\text{Cr}_t\text{O}_3$ in the temperature range 120–1200 K. The thermal expansion coefficients decrease with increasing t , the change being subtle for $t \leq 0.60$, and more pronounced for $t > 0.6$. There are no reports on the thermal properties of $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ so far in the literature. The objective of this work is to examine the effect of the partial substitution of the B-site cation, i.e. Co by copper in LaCoO_3 , on the thermal expansion behaviour of the material which is calcined at lower temperature (873 K) for application in oxidation reactions.

2. Experimental

Four samples of $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0, 0.02, 0.05$ and 0.1) were prepared by mixing the nitrates of La, Cu and Co.

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Table 1
TG-DTA data of $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$

Sample	% wt. loss	Temperature range	Exothermic	Endothermic
$\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.0$)	4.5	48.27–132.5	–	Y
	9.6	133.3–173.1	Y	–
	16.9	173.6–293.0	–	Y
	30.9	294.0–471.7	Y	–
	3.6	473.3–666.3	–	–
	Total = 65.51			
$\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.02$)	21.78	66.1–166.5	Y	–
	22.59	167.4–307.9	–	Y
	24.78	311.9–462.3	Y	–
	3.06	463.9–625.5	–	–
	Total = 73.21			
$\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.5$)	19.75	48.73–167.5	Y	–
	23.15	169.37–310.2	–	Y
	24.70	312.10–454.4	Y	–
	3.40	456.20–612.5	–	–
	Total = 71.00			
$\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.10$)	4.23	50.80–166.4	–	Y
	22.02	166.43–299.4	–	Y
	31.83	301.40–459.3	Y	–
	4.35	459.60–612.5	–	–
	Total = 62.42			

A stoichiometric amount of La_2O_3 was moistened with distilled water and a minimum amount of HNO_3 was added while slowly heating the mixture in a hot plate. After getting a clear transparent solution, stoichiometric amounts of

cobalt nitrate and copper nitrate were added and dissolved using a magnetic stirrer. Then a mole of citric acid corresponding to every mole of the metal atom was added to the dark pink/red transparent solution. The resulting solution

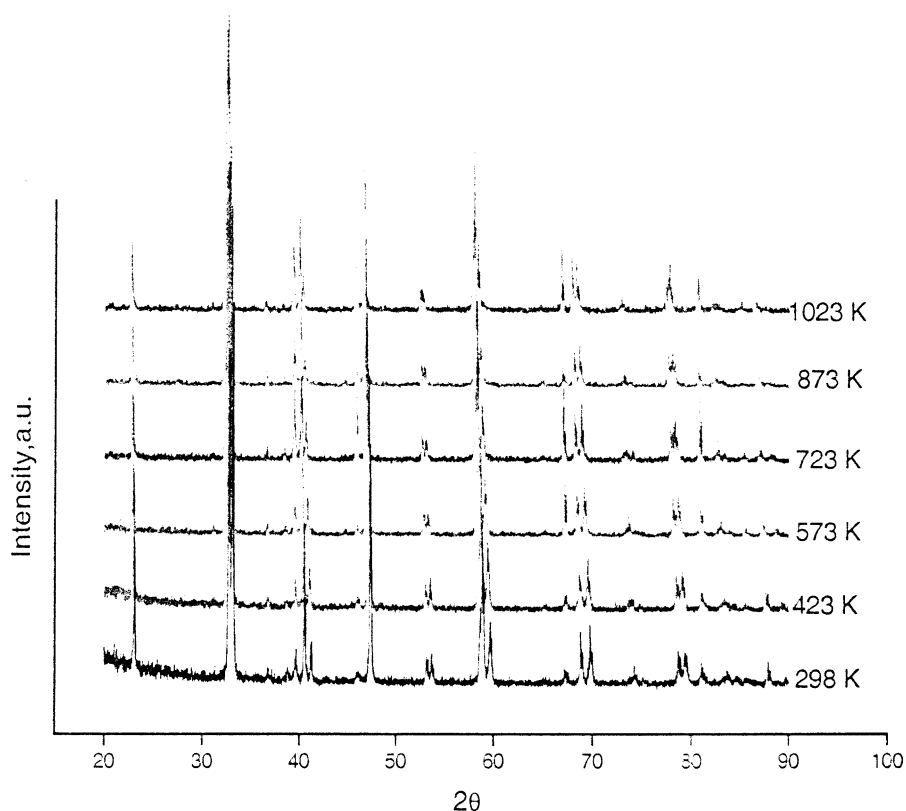


Fig. 1. Multiple high temperature powder X-ray diffraction patterns of a typical sample LaCoO_3 .

Table 2

Lattice parameters and unit cell volume, V , of LaCoO_3 and $\text{LaCo}_{0.98}\text{Cu}_{0.02}\text{O}_3$ obtained from HTXRD

Temp.	LaCoO_3			$\text{LaCo}_{0.98}\text{Cu}_{0.02}\text{O}_3$		
	a (nm)	c (nm)	V (nm ³)	a (nm)	c (nm)	V (nm ³)
298	0.5421(9)	1.3143(4)	0.3346(1)	0.5429(2)	1.3140(2)	0.3354(3)
423	0.5435(7)	1.3190(3)	0.3375(1)	0.5442(4)	1.3182(2)	0.3381(4)
573	0.5477(4)	1.3249(8)	0.3442(6)	0.5465(9)	1.3228(6)	0.3422(6)
723	0.5469(0)	1.3330(3)	0.3455(3)	0.5441(0)	1.3373(3)	0.3428(6)
873	0.5515(8)	1.3348(8)	0.3517(1)	0.5501(3)	1.3351(4)	0.3499(3)
1023	0.5526(5)	1.3408(2)	0.3546(5)	0.5517(9)	1.3401(7)	0.3533(7)

Table 3

Lattice parameters and unit cell volume, V , of $\text{LaCo}_{0.95}\text{Cu}_{0.05}\text{O}_3$ and $\text{LaCo}_{0.9}\text{Cu}_{0.1}\text{O}_3$ obtained from HTXRD

Temp.	$\text{LaCo}_{0.95}\text{Cu}_{0.05}\text{O}_3$			$\text{LaCo}_{0.9}\text{Cu}_{0.1}\text{O}_3$		
	a (nm)	c (nm)	V (nm ³)	a (nm)	c (nm)	V (nm ³)
298	0.5415(2)	1.3138(5)	0.3336(6)	0.5427(3)	1.3126(7)	0.3346(5)
423	0.5441(1)	1.3206(0)	0.3385(9)	0.5432(6)	1.3175(7)	0.3367(6)
573	0.5456(1)	1.3265(2)	0.3419(9)	0.5460(9)	1.3218(5)	0.3413(3)
723	0.5469(7)	1.3385(8)	0.3467(9)	0.5477(2)	1.3322(9)	0.3461(4)
873	0.5501(1)	1.3358(8)	0.3501(0)	0.5492(3)	1.3366(5)	0.3491(9)
1023	0.5501(2)	1.3387(4)	0.3508(6)	0.5498(5)	1.3372(9)	0.3500(6)

was heated slowly to dryness and then dehydrated at 383 K overnight (12 h) in a vacuum oven to yield an amorphous solid precursor. The samples were calcined for 12 h at 623 K, for 12 h at 773 K, and for another 15 h at 873 K using a programmable furnace.

2.1. Sample characterisation

The calcined material was analysed with a TG-DTA (Model 92, SETARAM, France) instrument. The thermograms of the samples were recorded at a heating rate of 10 K min⁻¹ from RT to 1273 K in a flow of air. The formation of the crystalline perovskite phase was monitored by powder XRD analyses of the calcined samples using a RIGAKU D-MAX III VC (Japan) instrument with Ni filtered Cu K α radiation (0.1542 nm) and a graphite crystal monochromator. The sample was rotated throughout the scan for better counting statistics and to minimize preferred orientation effect if present. The d values were indexed to a primitive rhombohedral cell (non-primitive hexagonal cell). In order to study the thermal expansion behaviour of these materials, their lattice thermal expansion was investigated using a high temperature X-ray diffractometer, using a Philips X'pert Pro XRD unit equipped with Anton Paar HTK attachment. Silicon was used as an external standard. A small amount of sample was mounted on a Pt stage-cum-heating element. A Pt/Pt-13% thermocouple spot-welded to the bottom of the stage was used for measuring the temperature. The XRD patterns were recorded in the 2θ range 20.01–79.99° from room temperature to 1173 K in static air. The Si and Pt were used to calibrate the instrument. The variation in lattice parameters a and c as a function of temperature for all four samples ($x = 0, 0.02, 0.05$ and 0.1 in $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$)

were calculated using a least square refinement program. Unit cell volume V and the average thermal expansion coefficients across a ($\alpha_a = \nabla a/a^* \nabla T$) and c ($\alpha_c = \nabla c/c^* \nabla T$) axes as well as volume thermal expansion coefficient ($\alpha_v = \nabla V/V^* \nabla T$) were also evaluated in the complete temperature range of investigation (298–1023 K). % Volume thermal expansion ($\nabla V^* 100/V$) was also calculated and plotted against temperature.

3. Results and discussion

Table 1 gives the TG-DTA data of the samples, which show that in this citrate route of synthesis a direct

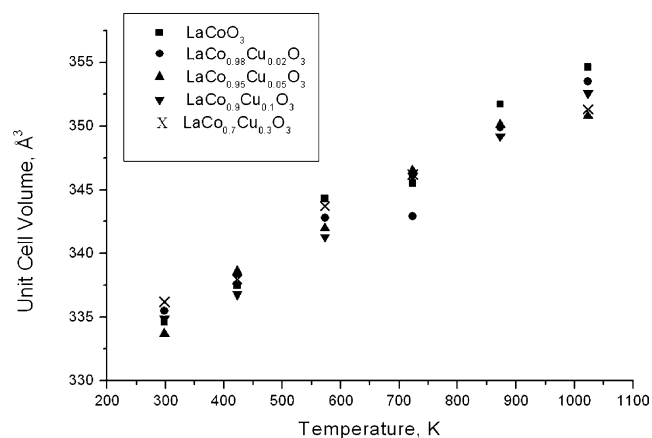


Fig. 2. Variation of unit cell volume with temperature: (a) LaCoO_3 , (b) $\text{LaCo}_{0.98}\text{Cu}_{0.02}\text{O}_3$, (c) $\text{LaCo}_{0.95}\text{Cu}_{0.05}\text{O}_3$, (d) $\text{LaCo}_{0.9}\text{Cu}_{0.1}\text{O}_3$ and (e) $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$.

transformation of the amorphous oxides to crystalline LaCoO_3 phase occurs without the presence of any intermediate oxides. The thermograms were similar for all precursors and the net weight loss was of the order of 60–70%. Fig. 1 shows the multiple plots of the HTXRD patterns (temperature range 298–1023 K) of a typical sample LaCoO_3 that shows the rhombohedral symmetry perovskite phase. Single-phase rhombohedral $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ in the temperature range 298–1023 K were detected for compositions in the range $0.0 < x < 0.1$. The variation in lattice parameters a and c and the unit cell volume V as a function

Table 4

Lattice parameters and unit cell volume, V , of $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$ obtained from HTXRD

Temp.	$\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$		
	a (nm)	c (nm)	V (nm^3)
298	0.5435(1)	1.3139(5)	0.3361(4)
423	0.5437(1)	1.3203(4)	0.3380(0)
573	0.5458(1)	1.3322(1)	0.3437(2)
723	0.5472(4)	1.3352(8)	0.3462(4)
873	—	—	—
1023	0.5507(2)	1.3377(3)	0.3513(8)

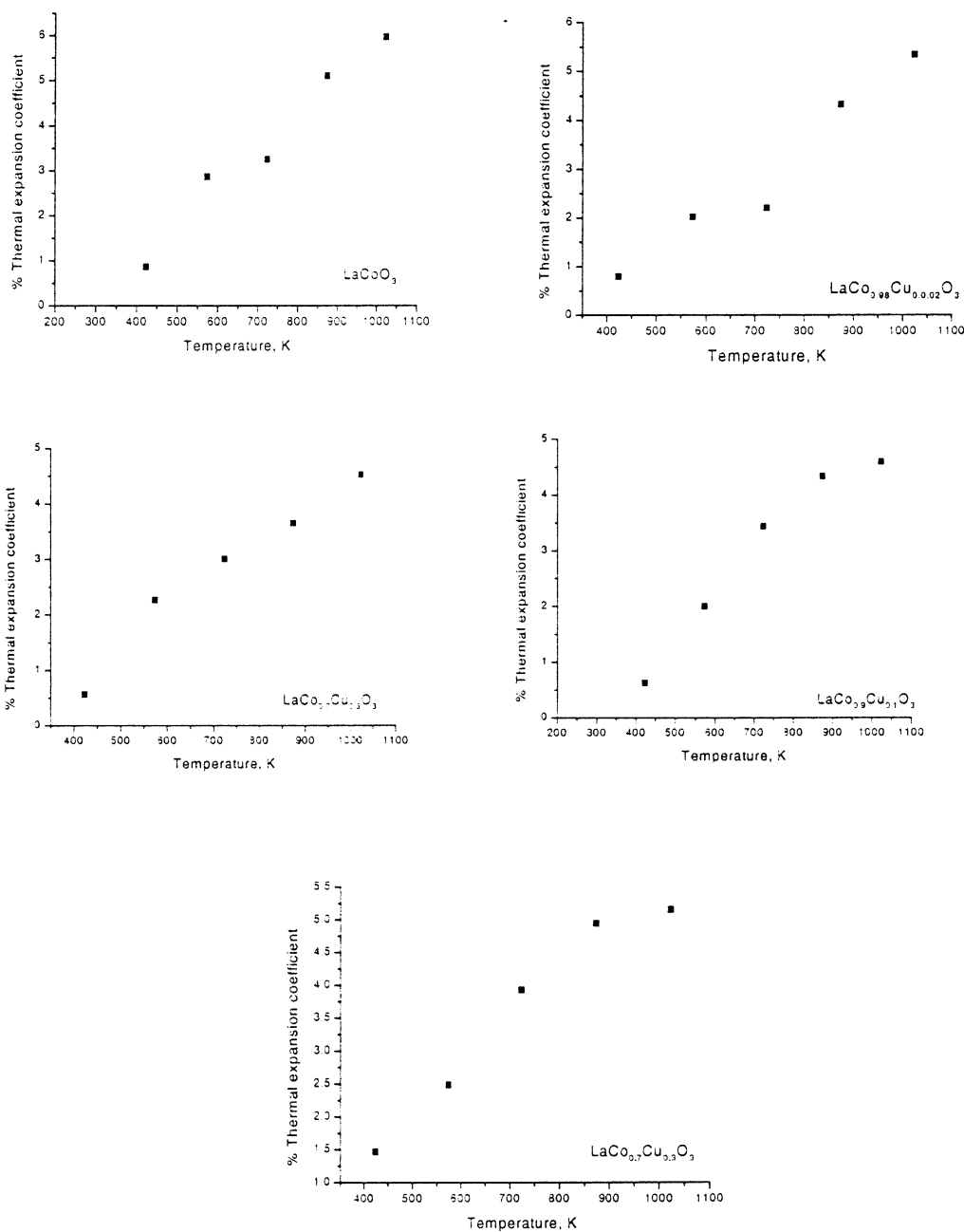


Fig. 3. Percentage volume thermal expansion of LaCoO_3 , $\text{LaCo}_{0.98}\text{Cu}_{0.02}\text{O}_3$, $\text{LaCo}_{0.95}\text{Cu}_{0.05}\text{O}_3$, $\text{LaCo}_{0.9}\text{Cu}_{0.1}\text{O}_3$ and $\text{LaCo}_{0.7}\text{Cu}_{0.3}\text{O}_3$ with increase in temperature.

of temperature for all four samples ($x = 0.0, 0.02, 0.05, 0.1$ and 0.3 in $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$) are given in Tables 2–4. There is a linear increase in the lattice parameters and volume with increase in copper concentration indicating the substitution of copper in cobalt site. Fig. 2 shows the increase in unit cell volume with increase in temperature for all samples under study. As the copper concentration increases to 30 mol.%, the variation is obeying Vegard's law.

The HTXRD patterns also do not show any phase transformation in the temperature range (298–1023 K) of the present investigation. A slow scanning of some of the samples to check the phase transformation also did not show any phase change. The resolution of doublets became poor at higher temperature, probably because they would have merged with

increase in temperature. The typical variation of % lattice thermal expansion ($\nabla V \times 100/V$) for the five samples under study as a function of temperature is shown in Fig. 3(a)–(d) which shows a linear increase with increase in temperature. The increase in thermal expansion relates to a decrease in melting point [5]. As the copper concentration increases from 0.0 to 30 mol.%, the % lattice/or volume thermal expansion decreases from 5.98 to 4.522. Fig. 4(a)–(b) shows the variation of average thermal expansion coefficients α_a , α_c and α_v with change in copper concentration, respectively. A very steep decreasing trend is seen for α_a and α_v , from 26.78×10^{-6} to $18.27 \times 10^{-6} \text{ K}^{-1}$ and 82.45×10^{-6} to $72.9 \times 10^{-6} \text{ K}^{-1}$, respectively, as the concentration of copper is increased to 10 mol.%, which then remains more or less constant with further increase in copper loading. In the c -direction the decrease in α_c is marginal from 27.81×10^{-6} to $24.56 \times 10^{-6} \text{ K}^{-1}$ as the copper concentration increases from 0 to 30 mol.%. The decrease in TEC with copper loading is due to the introduction of the covalent character of the Cu–O bond (which has considerable orbital overlap and in turn covalent character) in the otherwise ionic nature of the La–O bond (due to high electropositivity of La) in LaCoO_3 . It is well known that ionic solids have a higher thermal expansion coefficient compared to covalent solids. The larger decrease in $\bar{\alpha}_a$ with increase in copper loading, as compared to $\bar{\alpha}_c$, infers the substitution of Co by copper in the a – b plane rather than in the c -axis. From the trend it can be extrapolated that the sample with 20 mol.% copper would lie on the curves drawn in Fig. 4 as we lost the sample with 20 mol.% copper prepared in the same batch of experiments.

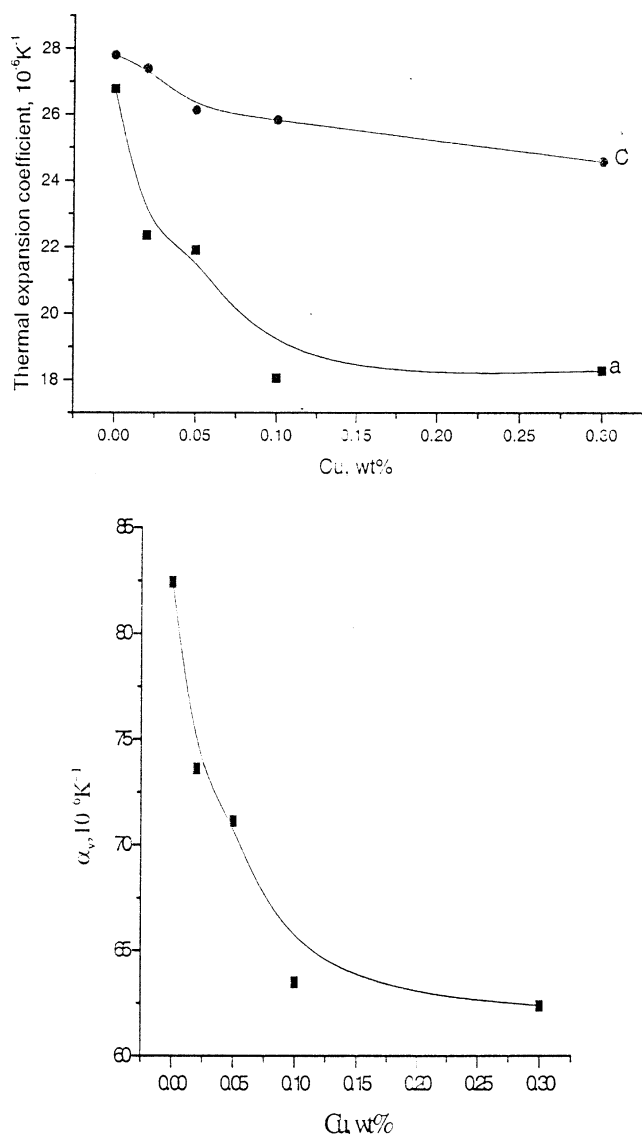


Fig. 4. Variation of average lattice (α_a and α_c) and volume thermal expansion (α_v) coefficient in the temperature range of 298–1023 K with increase in copper loading.

4. Conclusions

The HTXRD studies on the $\text{LaCo}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.0, 0.02, 0.05, 0.1$ and 0.3) in the temperature range 298–1023 K reveal that substitution of cobalt by copper in LaCoO_3 has a marked effect on the thermal expansion behaviour due to the considerable overlap of orbitals and in turn has covalent character. This induces a marked decrease in the average volume thermal expansion coefficient, in the temperature range 298–1023 K, with copper loading. The lattice and volume thermal expansion coefficients (TEC), $\bar{\alpha}_a$, $\bar{\alpha}_c$, and $\bar{\alpha}_v$ averaged between 298 and 1023 K calculated using the HTXRD data, decreased from 26.78×10^{-6} to $18.27 \times 10^{-6} \text{ K}^{-1}$, 27.81×10^{-6} to $24.56 \times 10^{-6} \text{ K}^{-1}$ and 82.45×10^{-6} to $72.9 \times 10^{-6} \text{ K}^{-1}$, respectively, as the copper concentration increased from 0 to 30 mol.%. The larger decrease in $\bar{\alpha}_a$ as compared to $\bar{\alpha}_c$ confirms the substitution of cobalt by copper in the a – b plane rather than in the c -axis which is supported by the trend in the variation observed in the unit cell parameters. This inference is being confirmed by neutron diffraction. The % lattice/or volume thermal expansion increases with temperature and decreases from 5.98 to 4.522 with increase in copper doping.

Acknowledgements

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