

Crystallographic Evolution of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ ($0 \leq x \leq 0.09$) and Its Implications for Magnetocaloric Materials

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Abstract – Magnetic refrigeration utilizing the magnetocaloric effect (MCE) is becoming a sustainable option compared to conventional gas-compression cooling technologies. In this study, the structural properties of potassium-doped $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ ($x = 0.01, 0.03, 0.05, 0.07$, and 0.09) polycrystalline materials were investigated to assess their potential for magnetocaloric applications. The samples were synthesized via wet mechanical milling followed by sintering at 1000°C , using high-purity La_2O_3 , CaCO_3 , K_2CO_3 , and MnCO_3 . X-ray diffraction (XRD) served as a technique for structure analysis, and the Rietveld method played a role in the refinement process. The results showed that single-phase perovskite structures with orthorhombic symmetry (Pnma space group) were successfully formed for all compositions up to $x = 0.07$, whereas the $x = 0.09$ sample exhibited a secondary CaO phase. The increase in K^+ levels caused the unit cell volume to grow, mainly due to the lengthening of the a -axis, while the b and c dimensions saw a reduction. Crystallinity also improved with increasing K content up to $x = 0.07$. These crystallographic modifications suggest potential implications for magnetocaloric behavior, although direct measurements were not performed.

Keywords: Magnetocaloric applications; magnetocaloric effect; wet mechanical milling; perovskite; X-ray diffraction.

1. Introduction

The demand for environmentally friendly refrigeration has stimulated interest in magnetic refrigeration, which operates based on the magnetocaloric effect (MCE) a phenomenon in which the temperature of a material changes upon application or removal of a magnetic field [1, 2]. Compared to conventional vapor-compression cooling, magnetic refrigeration eliminates harmful refrigerants, making it more sustainable [3].

Although giant MCE was first demonstrated in rare-earth-based systems such as $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$ [4], their reliance on expensive rare-earth elements limits scalability [5]. Perovskite manganites (ABO_3 systems) offer a promising alternative due to their lower cost, structural tunability, and potential room-temperature MCE [6, 7]. Substitution at the A-site, e.g., with Ca^{2+} , Sr^{2+} , or K^+ , alters lattice distortion, bond angles, and magnetic exchange interactions, directly influencing MCE behavior [8–10].

Among manganites, $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ (LCKMO) is attractive because K^+ substitution modifies structural and electronic interactions. Previous work [11] reported an enhanced Curie temperature at higher K doping ($x = 0.15$). However, excessive substitution often induces secondary phases such as CaO [12, 13]. Moreover, many earlier studies used wide doping intervals or solid-state synthesis, limiting resolution of subtle structural changes [14, 15].

Recent advances in perovskite manganites highlight their promising magnetocaloric response and structural tunability [16]. This study systematically investigates $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ with fine doping steps ($\Delta x = 0.02$, $0 \leq x \leq 0.09$) using wet mechanical milling, a method that ensures better homogeneity. We focus on crystallographic analysis via Rietveld refinement of XRD data to determine phase stability, lattice parameter evolution, and bond distortions. The goal is to link structural changes to possible magnetocaloric

implications, providing a clearer understanding of the phase boundary and structural–property correlations in potassium-doped perovskite manganites.

2. Material and Methods

The LCKMO compound was synthesized using pro analysis grade materials obtained from Sigma-Aldrich ($\geq 99.9\%$ purity), including lanthanum oxide (La_2O_3), calcium carbonate (CaCO_3), potassium carbonate (K_2CO_3), and manganese carbonate (MnCO_3). Every precursor was weighed in accordance with stoichiometric calculations derived from the following reaction equation:



Powders were mixed with ethanol and milled in a PW 1000 Mill/Mixer at a 2:1 ball-to-powder ratio for 5 h. Ethanol minimized agglomeration and improved homogeneity [17]. After drying, powders were sintered at 1000°C for 5 h. No pre-calcination was performed. The choice of milling duration and sintering temperature follows previous studies [18, 19].

XRD measurements were performed using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with a step size of 0.01° . Structural refinement employed GSAS software [20, 21] with AMCSD CIF entry 96-152-1155 as reference.

3. Result

XRD patterns of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ samples (Fig. 1) show that the main diffraction reflections are consistent with an orthorhombic perovskite structure with the Pnma space group. For compositions with $x = 0 - 0.07$, the observed reflections can be indexed to the perovskite phase, indicating the formation of a single-phase perovskite structure. At $x = 0.09$, additional weak reflections attributable to CaO are observed, indicating the formation of a secondary phase. This identification is further supported by the Rietveld refinement, which gives a CaO phase fraction of approximately 1.31% for $x = 0.09$. Thus, under the present synthesis conditions, the incorporation of K at $x = 0.09$ is accompanied by the onset of CaO secondary-phase formation [12, 13].

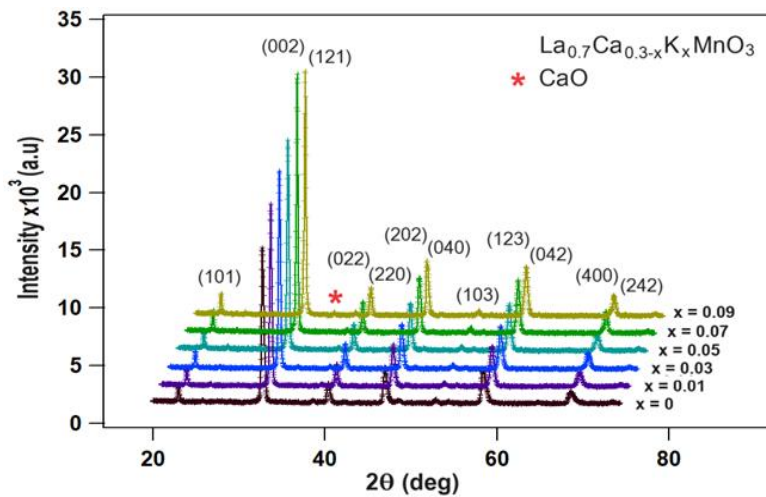


Figure 1. XRD profile of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ ($x = 0, 0.01, 0.03, 0.05, 0.07$, and 0.09).

4. Discussion

The refinement reliability factors were within acceptable limits ($R_{wp} = 6.73\text{--}8.54\%$, $\chi^2 < 2$), demonstrating good agreement between observed and calculated patterns. These values validate the structural model used for refinement [20, 21]. The representative refinement profiles are shown in Fig. 2.

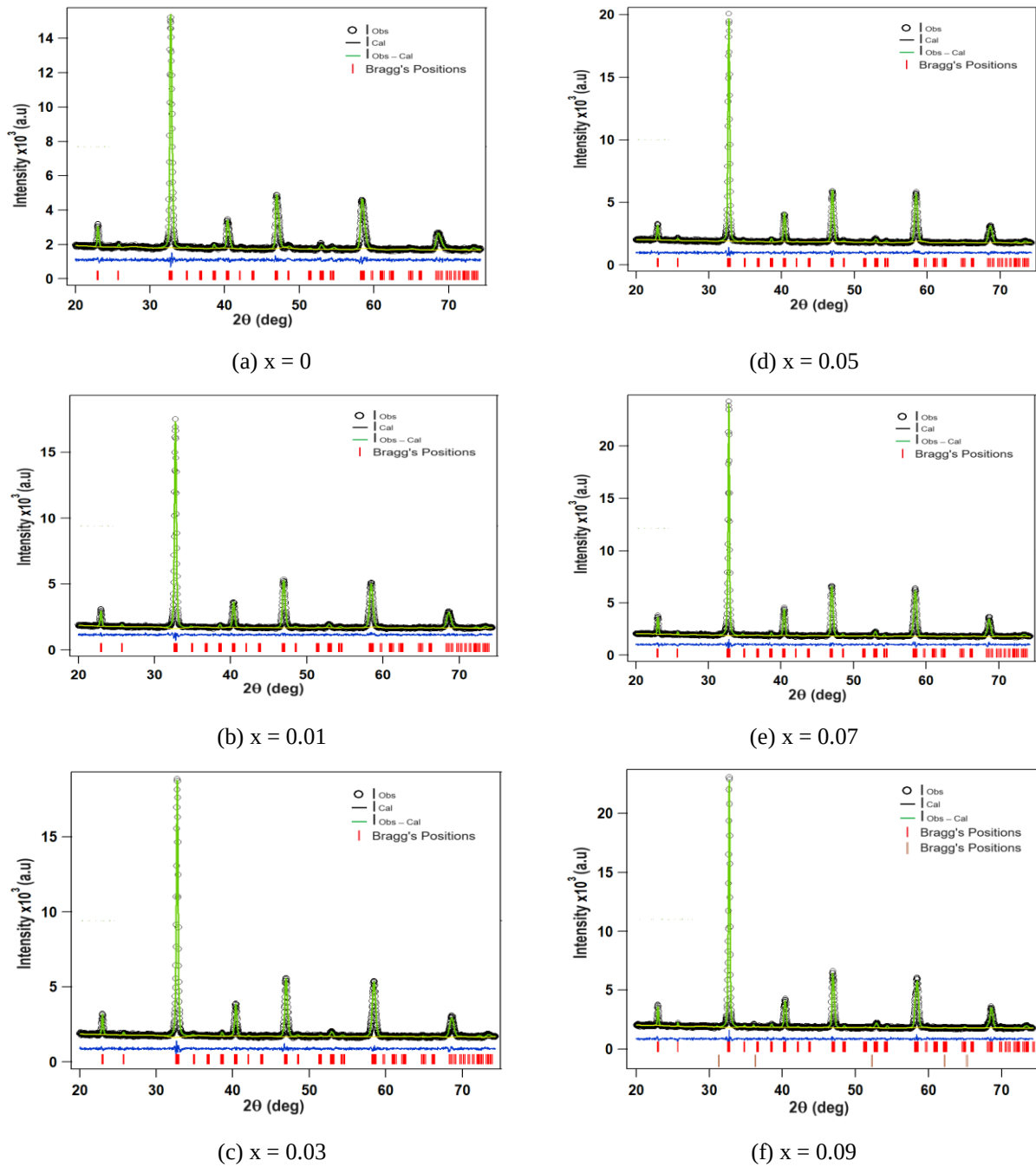


Figure 2. XRD refinement of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ ($x = 0\text{--}0.09$) compositions.

The qualitative analysis of the XRD patterns (Fig. 3a and 3b) reveals systematic peak shifts toward lower 2θ values with increasing K doping, suggesting lattice expansion. These peak shifts are attributed to the larger ionic radius of K^+ (1.38 Å) compared to Ca^{2+} (1.12 Å). The refined lattice parameters obtained from the Rietveld analysis (Table 1) show a systematic increase in the a -axis from 5.4430(3) Å at $x = 0$ to 5.4978(2) Å at $x = 0.07$. In contrast, the b -axis decreases from 7.7604(4) to 7.7287(3) Å, while the c -axis decreases slightly from 5.4776(3) to 5.4705(2) Å. These changes demonstrate an anisotropic modification of the orthorhombic lattice upon K^+ substitution. Because the $x = 0.09$ sample contains a secondary CaO phase, only $x = 0\text{--}0.07$ was used to discuss the systematic evolution of the single-phase perovskite lattice.

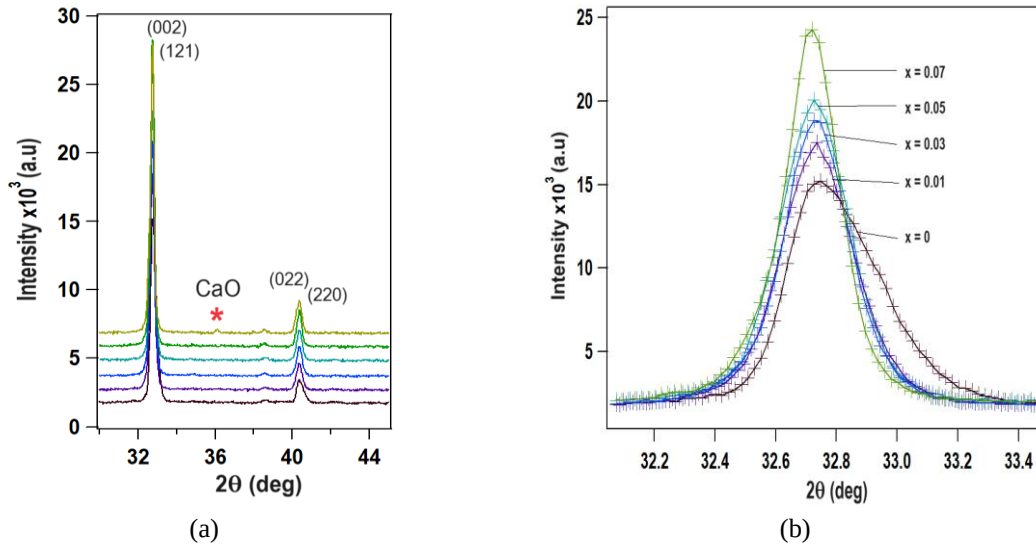


Figure 3. Qualitative analysis of the XRD pattern for $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ samples.

The $x = 0.09$ composition was excluded from the lattice-parameter trend analysis because its XRD pattern revealed a secondary CaO phase. The refined lattice parameters for $x = 0$ – 0.07 were therefore used to describe the evolution of the single-phase perovskite lattice. The $x = 0.09$ sample remains included in the phase-identification analysis because the additional CaO reflections provide evidence of the onset of secondary-phase formation under the present synthesis conditions. This observation is consistent with prior reports showing that A-site substitution by larger cations induces structural strain and modifies phase stability [11–13]. The crystal structure evolution is illustrated in Fig. 4a and 4b.

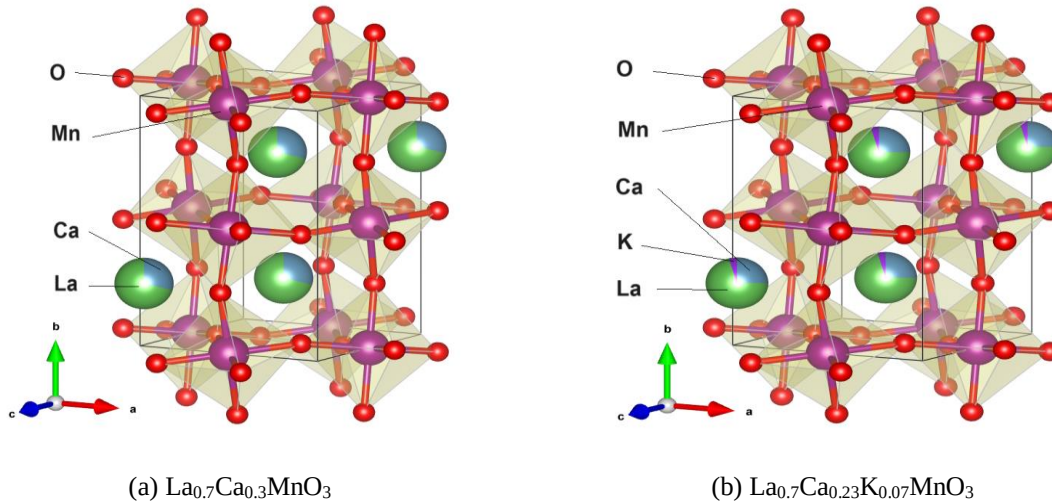


Figure 4. Crystal structures of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$.

The refined lattice parameters clearly show that the unit-cell volume expands from $234.55 \text{ \AA}^3$ ($x = 0.00$) to $236.12 \text{ \AA}^3$ ($x = 0.07$). The trend reflects the substitution effect of K^+ and its impact on the perovskite framework. Such lattice expansion influences Mn–O bond distances and Mn–O–Mn bond angles, parameters strongly correlated with double-exchange interactions and magnetic transition temperatures [8–10, 22].

The variation of lattice parameters with doping is summarized in Table 1, while the unit-cell volume trend is highlighted in Figure 3b. These results emphasize that small structural changes, induced by chemical substitution, can drive significant physical property modifications.

Table 1. Structural data for $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ series.

Composition	x = 0	x = 0.01	x = 0.03	x = 0.05	x = 0.07
Chemical Formula	$\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$	$\text{La}_{0.7}\text{Ca}_{0.29}\text{K}_{0.01}\text{MnO}_3$	$\text{La}_{0.7}\text{Ca}_{0.27}\text{K}_{0.03}\text{MnO}_3$	$\text{La}_{0.7}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$	$\text{La}_{0.7}\text{Ca}_{0.23}\text{K}_{0.07}\text{MnO}_3$
Molecule weight, Mr (g mol ⁻¹)	212.1949	212.1851	212.1656	212.1456	212.1264
Temperature (K)	300 K	300 K	300 K	300 K	300 K
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pnma	Pnma	Pnma	Pnma	Pnma
Unit cell dimension a (Å)	5.4430(3)	5.4589(6)	5.4698(7)	5.4834(5)	5.4978(2)
Unit cell dimension b (Å)	7.7604(4)	7.7502(5)	7.7482(4)	7.7392(5)	7.7287(3)
Unit cell dimension c (Å)	5.4776(3)	5.4720(5)	5.4702(5)	5.4708(4)	5.4705(2)
Unit-cell volume, V (Å ³)	231.37(3)	231.51(2)	231.83(2)	232.17(2)	232.45(2)
Atomic density, (gr.cm ⁻³)	6.0800	6.0800	6.0820	6.0840	6.0890
Strain (%)	0.6810	0.6819	0.6841	0.6874	0.6886
Crystallite size (nm)	120.16	120.01	117.85	111.66	104.83
Mn – O Bond length (Å)	1.9742	1.9717	1.9715	1.9698	1.9662
Mn – O – Mn Bond Angle (deg)	158.6631	158.7022	158.6929	158.6804	158.6378
Rad. wavelength, λ (Å)	1.5406	1.5406	1.5406	1.5406	1.5406
Crystal form	Powder	Powder	Powder	Powder	Powder
Goodness-of-fit, χ ²	1.38	1.32	1.33	1.31	1.34
R _{wp}	0.0263	0.0252	0.0259	0.0250	0.0269

Peak broadening analysis indicates that the full width at half maximum (FWHM) of the (002) diffraction peaks decreases with increasing K content up to $x = 0.07$. This suggests improved crystallinity and grain growth. Crystallite sizes estimated using the Scherrer equation increased from ~105 nm ($x = 0.00$) to ~120 nm ($x = 0.07$), with ± 5 nm uncertainty. The corresponding microstrain decreased slightly, suggesting a reduction in lattice distortion and structural disorder [23].

However, for $x = 0.09$, FWHM values increased again, and secondary phase formation was confirmed, leading to deterioration in structural quality. Figure 2 shows the Rietveld refinement profiles for the different K-doping compositions, demonstrating the agreement between the observed and calculated XRD patterns. These results align with previous findings on manganites synthesized via milling and sintering, where optimal doping enhances crystallinity while overdoping introduces defects [17–19].

Refinement analysis revealed slight reductions in Mn–O bond lengths and Mn–O–Mn bond angles ($\sim 0.02^\circ$) as K doping increased. Although small, these distortions significantly affect the electron bandwidth, influencing magnetic interactions. The Goldschmidt tolerance factor decreased from 0.928 ($x = 0.00$) to 0.923 ($x = 0.07$), reflecting enhanced lattice strain and distortion.

Such structural distortions are crucial since they directly correlate with double-exchange efficiency and magnetic entropy change in manganites [22, 24, 25]. Figure 4b illustrates the crystal structure of the $x = 0.07$ composition, while the calculated tolerance factor values indicate a change in lattice distortion with increasing K doping.

Although this study did not perform direct magnetocaloric effect (MCE) measurements, the observed structural modifications lattice expansion, bond angle reduction, and crystallinity improvement are well known to influence magnetocaloric performance. Recent studies confirm that structural distortions correlate with entropy change in La-based manganites [16, 25]. Furthermore, chemically pressured manganites show similar behavior, strengthening this interpretation [26].

Therefore, compositions up to $x = 0.07$ exhibit structural characteristics favorable for enhanced MCE, while $x = 0.09$ shows limitations due to phase separation. Future studies should integrate magnetic and caloric measurements to validate these predictions and quantify the actual MCE performance.

5. Conclusion

$\text{La}_{0.7}\text{Ca}_{0.3-x}\text{K}_x\text{MnO}_3$ samples synthesized via wet mechanical milling exhibited single-phase orthorhombic perovskite structures with the Pnma space group for compositions up to $x = 0.07$. At $x = 0.09$, additional CaO reflections were detected in the XRD pattern, with a refined CaO phase fraction of approximately 1.31%, indicating the onset of secondary-phase formation under the present synthesis conditions. Increasing K content resulted in an increase in the a-axis and slight decreases in the b- and c-axes for the single-phase compositions ($x = 0-0.07$), accompanied by changes in the Mn–O–Mn bond geometry. These crystallographic modifications may influence the magnetic interactions and magnetocaloric behavior of the material. However, because direct magnetic and magnetocaloric measurements were not performed in this study, the actual magnetocaloric performance cannot be confirmed from the present structural data alone. Further magnetic and caloric measurements are therefore required to establish the relationship between K substitution, structural evolution, and magnetocaloric properties.

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