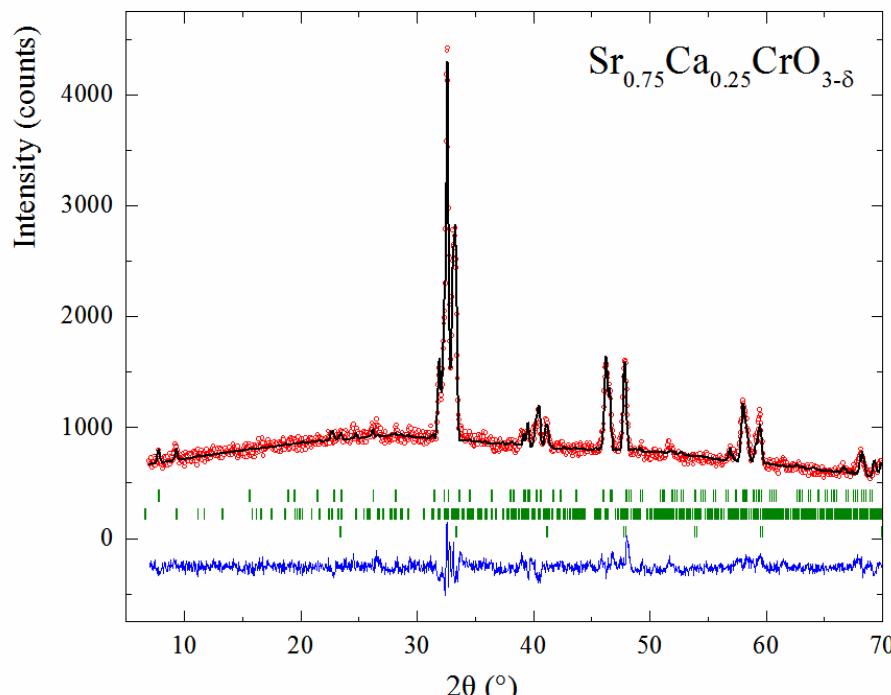


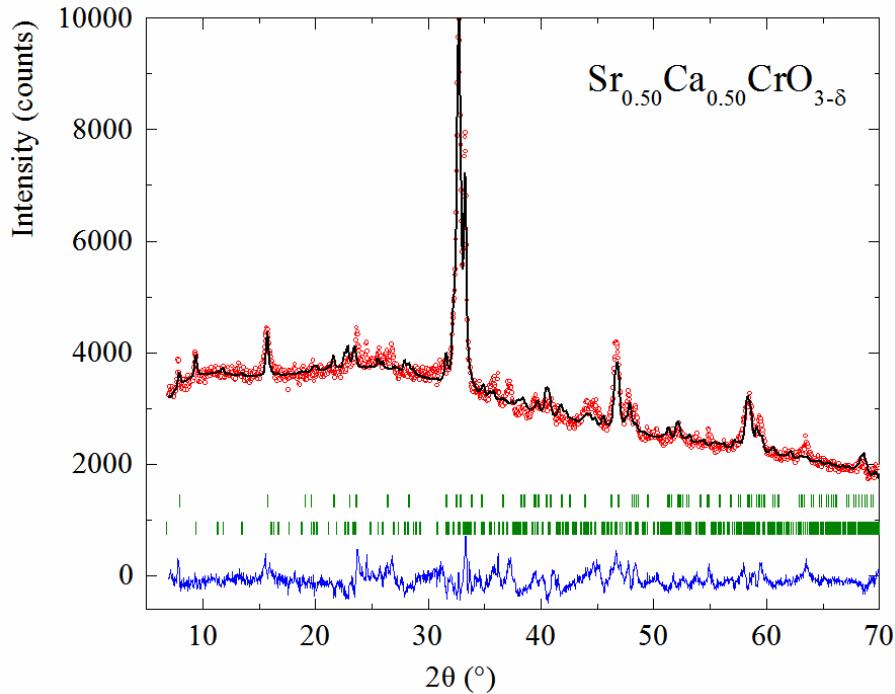
Supplementary Information: Rietveld Refinements for the 6H and 15R superstructure phases in the three $\text{Sr}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ samples are shown in Supp. Figures 1, 2 and 3. The space groups, agreement factors and lattice parameters are summarised in Supp. Tables 1, 2 and 3.



Supp. Figure 1: PXRD and 3-phase Rietveld refinement of $\text{Sr}_{0.75}\text{Ca}_{0.25}\text{CrO}_{3-\delta}$. Green vertical lines represent the $\text{Sr}_{0.75}\text{Ca}_{0.25}\text{CrO}_3$, 6H and 15R phases from top to the bottom respectively. The crystallographic information for the $\text{Sr}_{0.75}\text{Ca}_{0.25}\text{CrO}_3$, 6H and 15R phases were taken from published data.

Table 1: Space groups, agreement factors, lattice parameters, lattice volumes of $\text{Sr}_{0.75}\text{Ca}_{0.25}\text{CrO}_{3-\delta}$ phases.

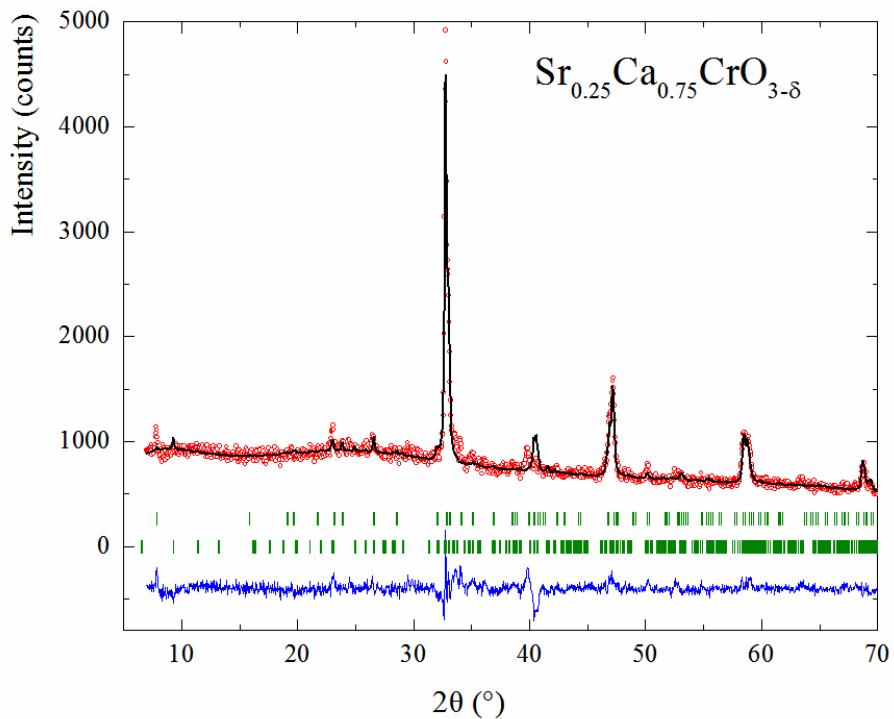
$\text{Sr}_{0.75}\text{Ca}_{0.25}\text{CrO}_{3-\delta}$							
Superstructure phase	15R		Superstructure phase	6H			
Space group	$R\bar{3}m$		Space group	$P2/m$			
Phase Composition	0.238(7)		Phase Composition	0.500(7)			
χ^2	2.153						
R_{wp}	0.050						
Lattice Parameters	Constants (Å)	Angles (°)	Lattice Parameters	Constants (Å)	Angles (°)		
	$a= 5.487(1)$	$\alpha=90$		$a=9.540(2)$	$\alpha=90$		
	$b= 5.487(1)$	$\beta=90$		$b= 5.500(1)$	$\beta=92.78(1)$		
	$c= 34.16(1)$	$\gamma=120$		$c= 13.423(2)$	$\gamma=90$		
Lattice Volume (Å ³)	890.7(4)		Lattice Volume (Å ³)	703.6(3)			



Supp. Figure 2: PXRD and 2-phase Rietveld refinement of $\text{Sr}_{0.50}\text{Ca}_{0.50}\text{CrO}_{3-\delta}$. The top green vertical lines represent the 6H phase and the bottom ones represent the 15R phase.

Table 3: Space groups, agreement factors, lattice parameters, lattice volumes of $\text{Sr}_{0.50}\text{Ca}_{0.50}\text{CrO}_{3-\delta}$ phases.

Sr _{0.50} Ca _{0.50} CrO _{3-δ}							
Superstructure phase	15R		Superstructure phase	6H			
Space Group	$R\bar{3}m$		Space Group	$P2/m$			
Phase Composition	0.21(1)		Phase Composition	0.79(1)			
χ^2	6.980						
R_{wp}	0.0480						
Lattice Parameters	Constants (Å)	Angles (°)	Lattice Parameters	Constants (Å)	Angles (°)		
	$a= 5.479(2)$	$\alpha= 90$		$a= 9.551(4)$	$\alpha=90$		
	$b= 5.479(2)$	$\beta= 90$		$b= 5.490(2)$	$\beta=92.07(2)$		
	$c= 33.89(3)$	$\gamma= 120$		$c=13.223(4)$	$\gamma=90$		
Lattice Volume (Å ³)	880.0(1)		Lattice Volume (Å ³)	698.2(6)			



Supp. Figure 3: PXRD and Rietveld refinement of $\text{Sr}_{0.25}\text{Ca}_{0.75}\text{CrO}_{3-\delta}$. The top green vertical lines represent the 6H phase and the bottom ones represent the 15R phase.

Table 3: Space groups, agreement factors, lattice parameters, lattice volumes of $\text{Sr}_{0.25}\text{Ca}_{0.75}\text{CrO}_{3-\delta}$ phases.

Sr _{0.25} Ca _{0.75} CrO _{3-δ}				
Superstructure phase	15R		Superstructure phase	6H
Space Group	$R\bar{3}m$		Space Group	$P2/m$
Phase Composition	0.17(1)		Phase Composition	0.83(1)
χ^2	2.787			
R_{wp}	0.0591			
Lattice Parameters	Constants (Å)	Angles (°)	Lattice Parameters	Constants (Å)
	$a=5.406(2)$	$\alpha=90$		$a=9.465(3)$
	$b=5.406(2)$	$\beta=90$		$b=5.419(1)$
	$c=33.50(2)$	$\gamma=120$		$c=13.394(4)$
Lattice Volume (Å ³)	847.7(7)		Lattice Volume (Å ³)	688.3(7)