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Neutron diffraction analysis of Sr_2FeMoO_6 as influenced by temperature and elemental substitutions

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Abstract. *Sr_2FeMoO_6 is a half-metallic ferromagnetic material with a high Curie temperature, making it suitable for spintronic applications. Its crystal structure, consisting of alternating Fe and Mo ions, results in unique electronic and magnetic properties. This study investigates the structural behavior of Sr_2FeMoO_6 and its modified forms, $Sr_2FeMo_{1-x}Ta_xO_6$ ($x = 0.05$) and $Sr_2FeMo_{1-x}V_xO_6$ ($x = 0.15$), using neutron diffraction at various temperatures. The findings reveal how temperature fluctuations and cation substitutions influence the unit cell dimensions, providing insights into the material's structural and thermal properties for potential technological applications.*

Key words: *neutron diffraction, Rietveld refinement, substitutions, low temperature.*

Introduction

The double perovskite oxide Sr_2FeMoO_6 is known for its half-metallic ferromagnetic nature and elevated Curie temperature, making it a potential material for spintronic technologies. Its crystal structure consists of alternating Fe and Mo ions, which give rise to distinctive electronic and magnetic characteristics [1]. Furthermore, Sr_2FeMoO_6 has been explored for applications in solid oxide fuel cells due to its strong electronic conductivity and thermal resilience [2]. The study [3] revealed that increasing the total sintering time significantly improved Fe/Mo cation ordering in Sr_2FeMoO_6, reducing antisite defects and increasing the degree of ordering from 44.9 % to 80.2 %. Rietveld refinement showed a gradual decrease in unit cell volume and bond lengths (Fe-O and Mo-O) with extended sintering, indicating a more compact and ordered crystal structure. Additionally, the Fe-O1-Mo bond angle increased with sintering time, reflecting reduced octahedral tilting and enhanced linearity along the Fe-O-Mo chains. A structural phase transition from cubic ($Fm\bar{3}m$) to tetragonal ($I4/m$) symmetry occurs in Sr_2FeMoO_6 near 400 K, accompanied by octahedral rotations and the onset of ferrimagnetic ordering. Neutron diffraction and Mössbauer spectroscopy revealed a saturated Fe magnetic moment of ~ 4.3 μB and an intermediate Fe valence state, with approximately 6 % Mo-site vacancies contributing to local structural and magnetic inhomogeneity [4].

In this context, our research focuses on further understanding the structural behavior of Sr_2FeMoO_6-based systems under different doping strategies and temperature conditions using high-resolution neutron diffraction and Rietveld analysis.

Research methods

In this study, neutron diffraction experiments were carried out at various temperatures using the High Resolution Fourier Diffractometer (HRFD) located at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia. The purpose was to investigate the structural behavior of the parent compound Sr_2FeMoO_6 and its cation-substituted derivatives, namely $Sr_2FeMo_{1-x}Ta_xO_6$ ($x = 0.05$) and $Sr_2FeMo_{1-x}V_xO_6$ ($x = 0.15$). The samples were synthesized with carefully controlled compositions to ensure uniformity and consistency, which is essential for obtaining accurate and reliable diffraction measurements. The experimental results provide important insights into the effects of temperature variation and B-site substitution (with Ta and V) on the unit cell parameters. These findings contribute to a deeper understanding of the structural and thermal behavior of these double perovskite materials under different physical conditions. The Rietveld approach was used to obtain the lattice parameters.

Results and discussion

Neutron diffraction experiments were conducted on Sr_2FeMoO_6-based samples at varying dopant concentrations and temperatures. The diffraction spectra were refined using the Rietveld method implemented in the FullProf Suite software.

In the initial undoped state, the diffraction pattern illustrates a well-defined structure, from which changes in lattice parameters with temperature were identified (Fig. 1 a).

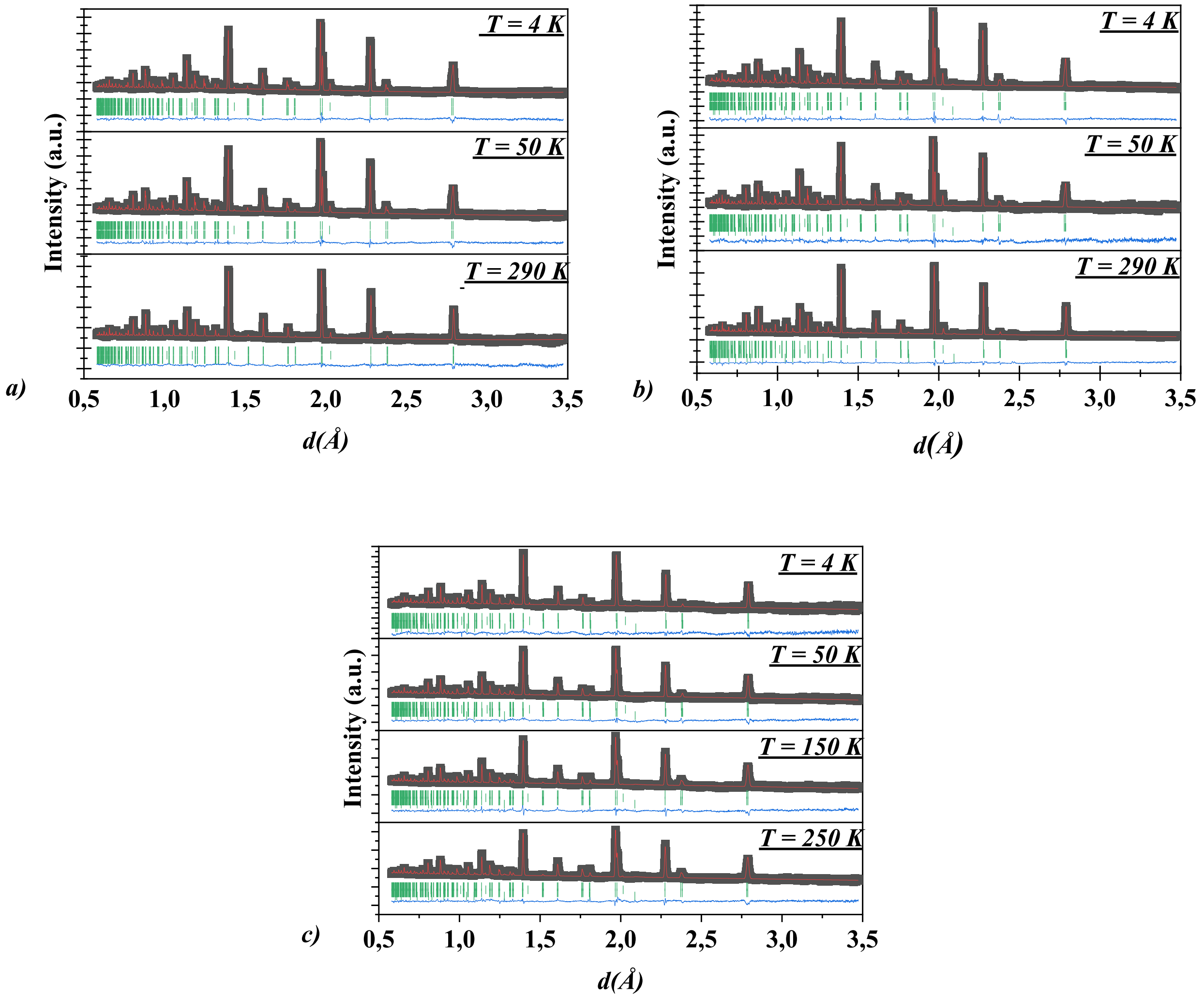

Fig. 1. Neutron diffraction patterns of (a) initial Sr_2FeMoO_6, (b) $Sr_2FeMo_{1-x}V_xO_6$ (x = 0.15), and (c) $Sr_2FeMo_{1-x}Ta_xO_6$ (x = 0.05) at different temperatures. Black dots represent experimental data, the red line is the Rietveld refinement fit, green vertical ticks indicate Bragg reflection positions, and the blue line shows the difference between observed and calculated intensities

Following vanadium doping (x = 0.15), diffraction patterns were recorded at three different temperatures. It is illustrated in Fig. 1 b. Additionally, further peaks are observed in the diffraction data that correspond to the presence of aluminum and copper. These reflections, which appear consistently, originate from the equipment used to secure the sample containers under the experimental conditions. In the Ta-doped compound $Sr_2FeMo_{1-x}Ta_xO_6$ (x = 0.05) (Fig. 1 c), the unit cell volume remains close to that of the undoped sample, with a slight increase observed at intermediate temperatures, reaching 245.95 Å^3 at 250 K. The a-axis shows minor expansion, while the c-axis remains relatively stable, indicating that the structural framework is largely preserved with Ta substitution. The structural evolution identified through Rietveld refinement is presented in

Table 1. In the undoped Sr_2FeMoO_6, the unit cell volume increases with temperature, rising from 244.63 Å³ at 4 K to 246.14 Å³ at 290 K.

In contrast, the V-doped sample $Sr_2FeMo_{1-x}V_xO_6$ (x = 0.15) exhibits a consistently smaller unit cell volume compared to both the undoped and Ta-substituted samples, with a minimum value of 243.99 Å³ at 4 K. The c-axis, in particular, shows a more significant reduction, suggesting that vanadium incorporation causes noticeable lattice contraction. This contraction is more pronounced than that observed with Ta doping, reflecting the stronger structural influence of vanadium.

Table 1

The changes in structural parameters after substitution

Space group_I 4/m m m	a	c	V
Sr_2FeMoO_6 T = 4K	5.5599(1)	7.9134(1)	244.627(6)
Sr_2FeMoO_6 T = 50 K	5.5607(1)	7.9138(2)	244.71(1)
Sr_2FeMoO_6 T = 290K	5.5785(1)	7.9096(2)	246.14(1)
$Sr_2FeMo_{1-x}T_{ax}O_6$ x = 0.05, T = 4K	5.5628 (2)	7.9059(2)	244.778(2)
$Sr_2FeMo_{1-x}Ta_xO_6$ x = 0.05, T = 50 K	5.5628(2)	7.9101(3)	244.78(1)
$Sr_2FeMo_{1-x}Ta_xO_6$ x = 0.05, T = 150 K	5.5676 (2)	7.9085 (3)	245.15(2)
$Sr_2FeMo_{1-x}TaxO_6$ x = 0.05, T = 250 K	5.576(1)	7.909(1)	245.95(5)
$Sr_2FeMo_{1-x}V_xO_6$ x = 0.15, T = 4 K	5.5560(1)	7.9040 (2)	243.994 (1)
$Sr_2FeMo_{1-x}V_xO_6$ x = 0.15, T = 50 K	5.5547(1)	7.9039(2)	243.98(1)
$Sr_2FeMo_{1-x}V_xO_6$ x = 0.15, T = 290 K	5.5730(1)	7.8986(2)	245.32(1)

These findings emphasize the role of B-site substitution in tuning the thermal and structural behavior of double perovskites. While Ta maintains structural integrity across temperature ranges, V leads to distinct lattice shrinkage, underlining the importance of dopant selection for potential applications where thermal and structural stability are critical.

Conclusion

In conclusion, the study demonstrates that temperature and elemental substitutions significantly influence the structural properties of Sr_2FeMoO_6. Thermal expansion caused a moderate increase in the unit cell volume of the pristine compound, with distinct behavior observed along the a- and c-axes. The introduction of Ta resulted in minimal changes, preserving structural stability, while V doping led to more substantial lattice contraction, particularly along the c-axis. These findings highlight the critical role of B-site doping in controlling the thermal and structural characteristics of double perovskites, offering insights for their potential applications in various technological fields such as spintronics and fuel cell technologies.

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