Crystal Structures, Magnetic and Transport Properties of Calcium Based Perovskites

E. Burzo

Faculty of Physics, Babes-Bolyai University, 400084, Cluj-Napoca

Double perovskites

$Ca_2Fe_{1-x}Ni_xMoO_6$ $x \leq 0.2$

$Ca_{1.5}La_{0.5}FeMo_{1-x}W_xO_6$ $x \leq 0.3$

Preparation: Solid state reaction

- mixed powders calcinated in argon atmosphere at 900 ^oC
- pelletized
- sintered at 1300 ^oC, 8 h in argon with 3 % hydrogen

1. Crystal structure

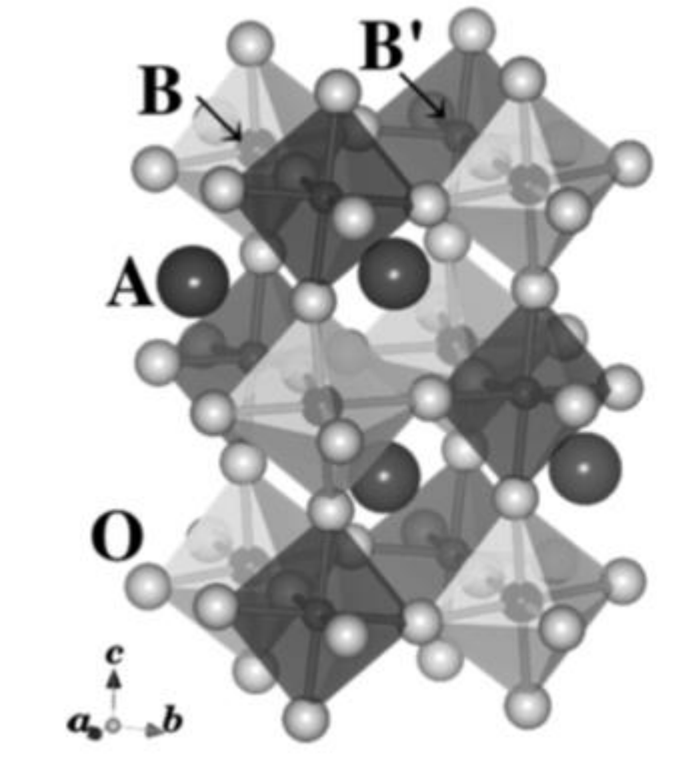
$Ca_{1.5}La_{0.5}FeMo_{1-x}W_xO_6$ $x \leq 0.3$

monoclinic $P2_1/n$ type structure

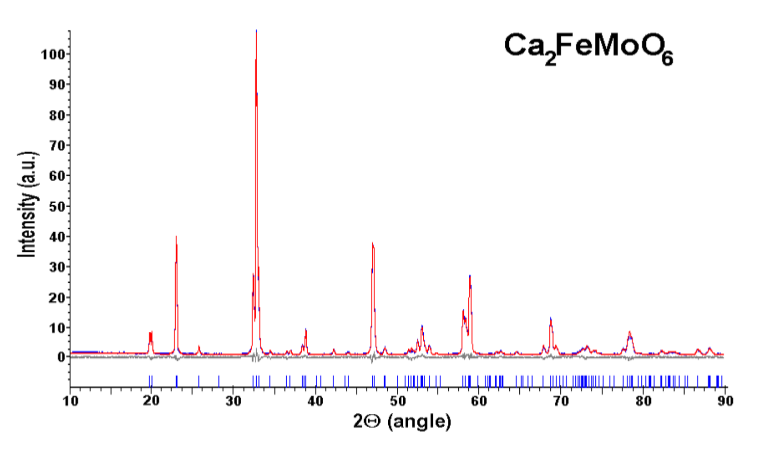
$Ca_2Fe_{1-x}Ni_xMoO_6$

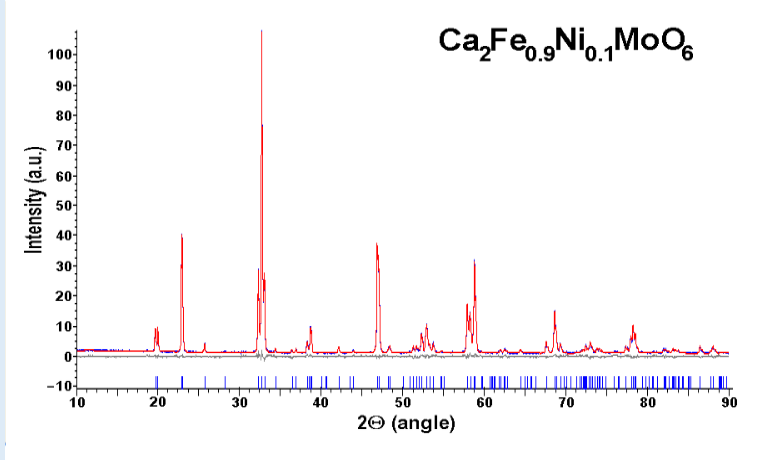
$x \leq 0.2$ solid solutions

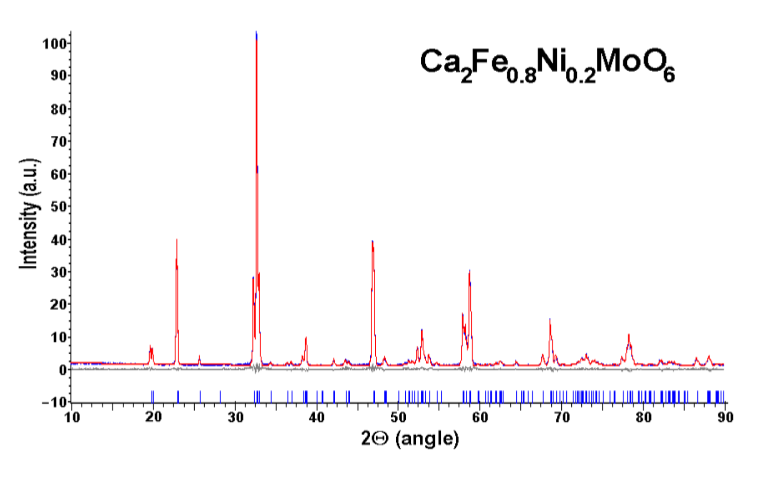
$P\ 2_1/n$ space group



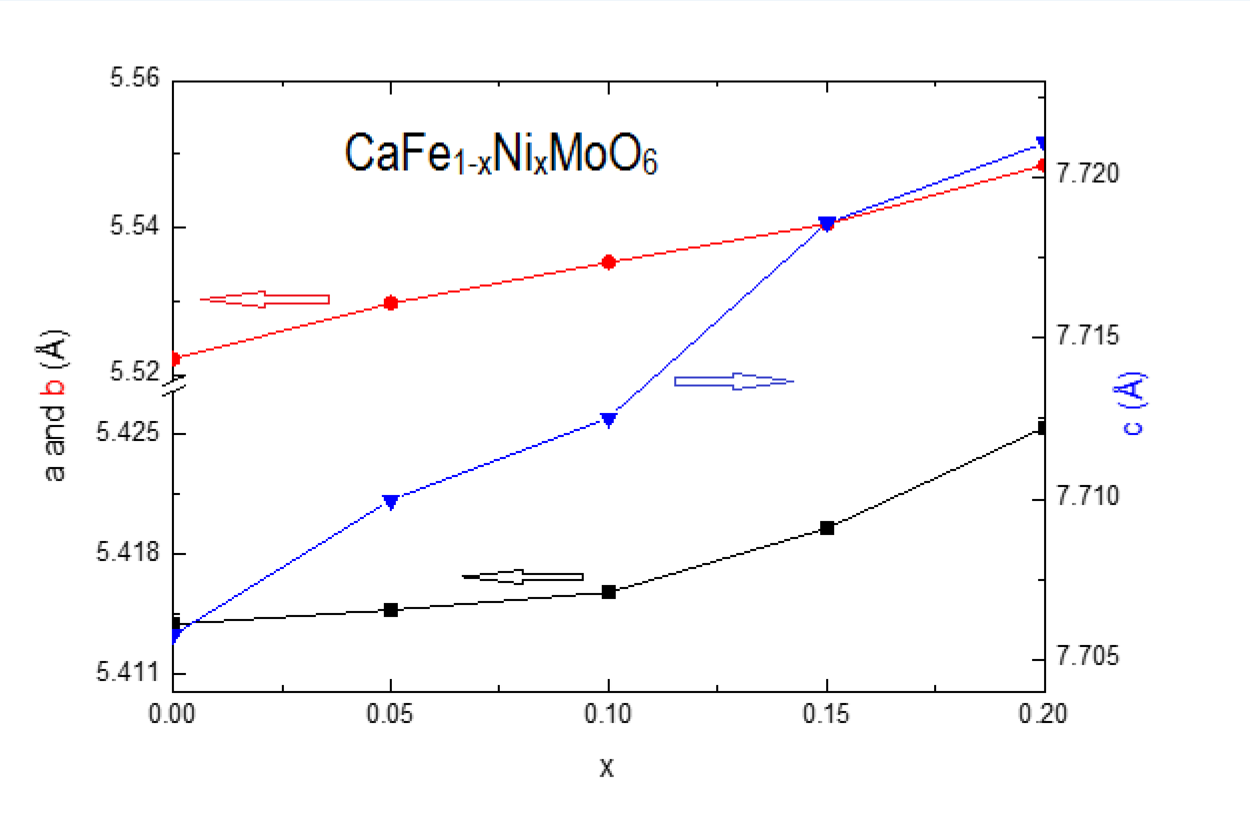
Crystal structure

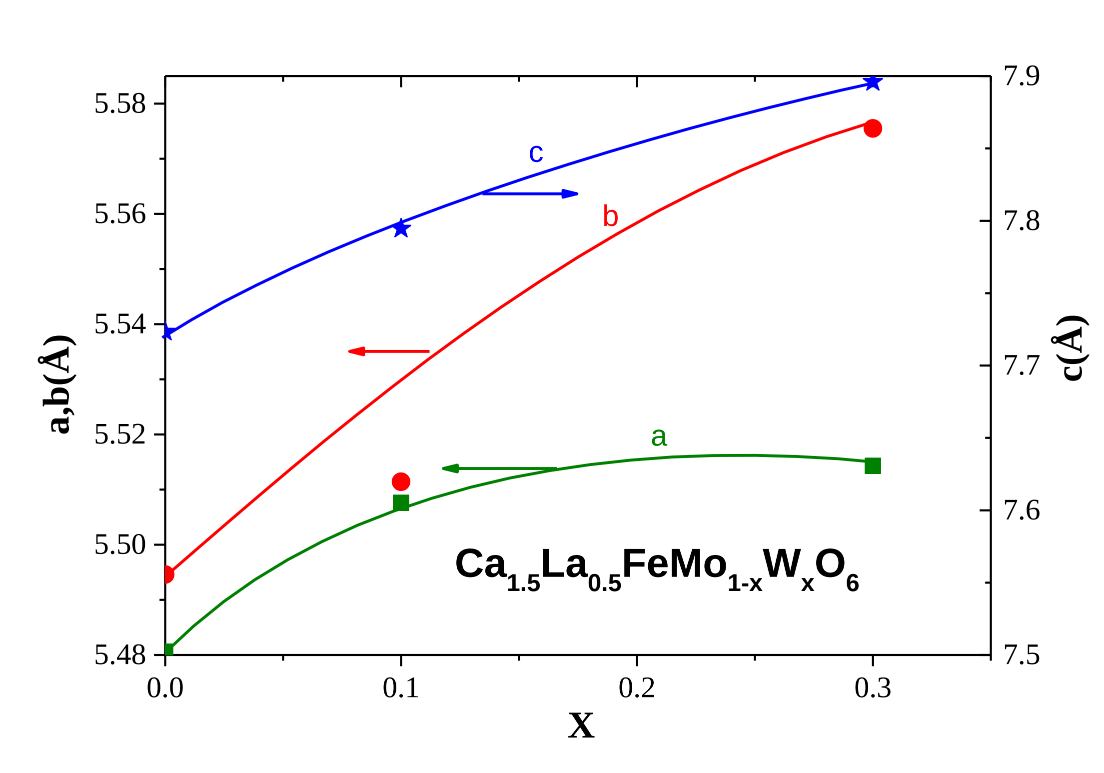






Lattice parameters increase with x

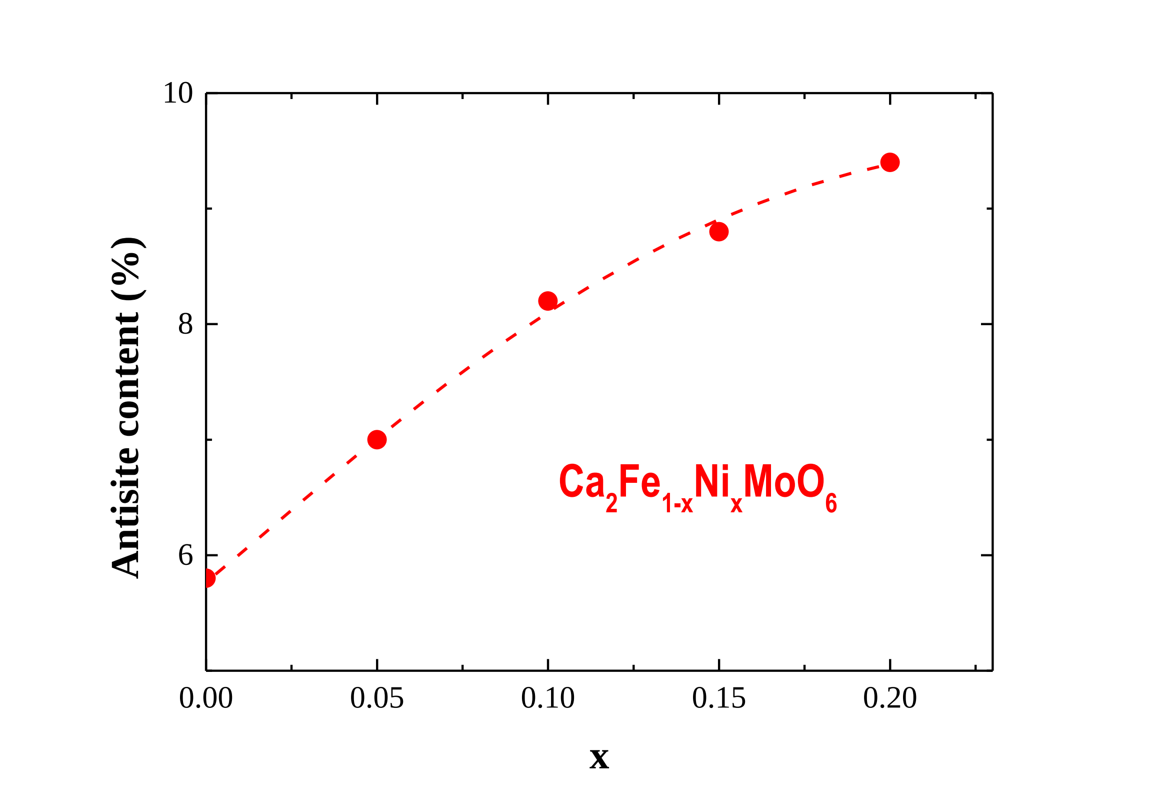




$Ca_2Fe_{1-x}Ni_xMoO_6$

monoclinic $P2_1/n$ space group

($x \leq 0.2$)

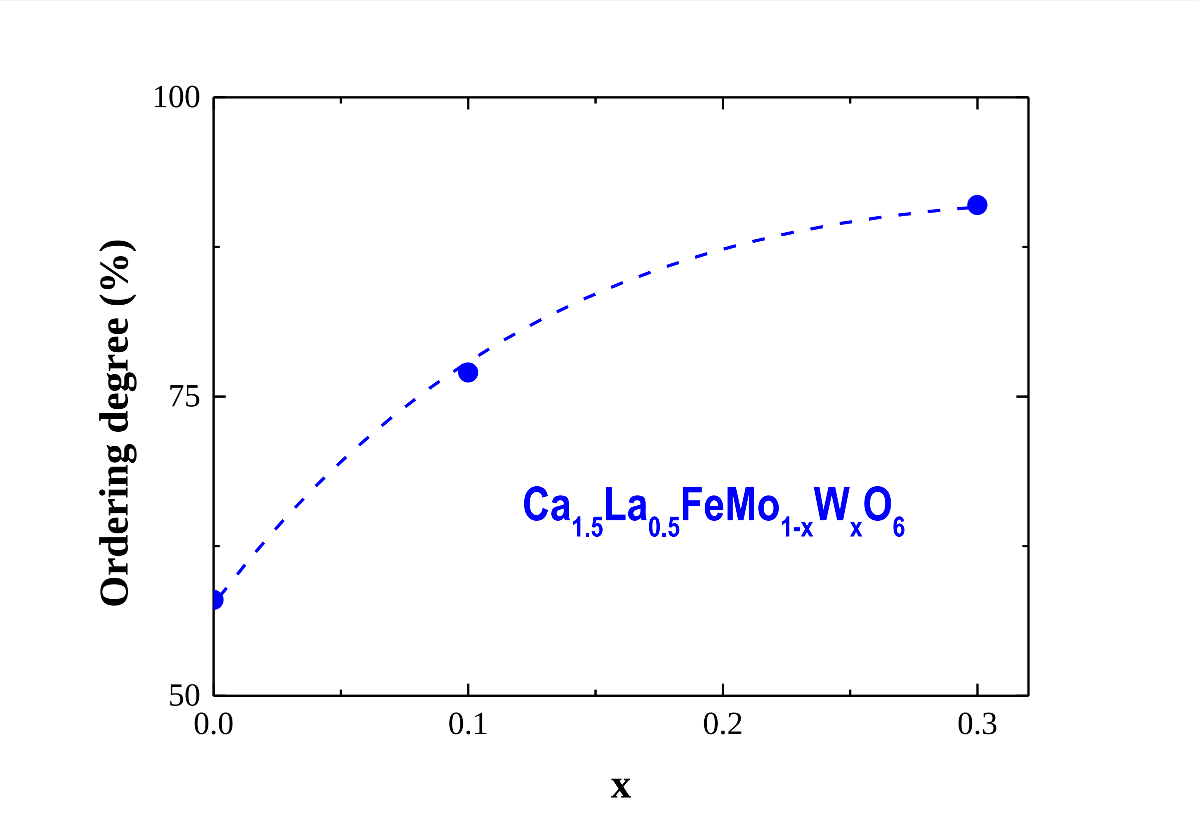


Antisite content increases with Ni^{2+} substitutions

$Ca_{1.5}La_{0.5}FeMo_{1-x}W_xO_6$

monoclinic $P2_1/n$ space group

($x \leq 0.3$)

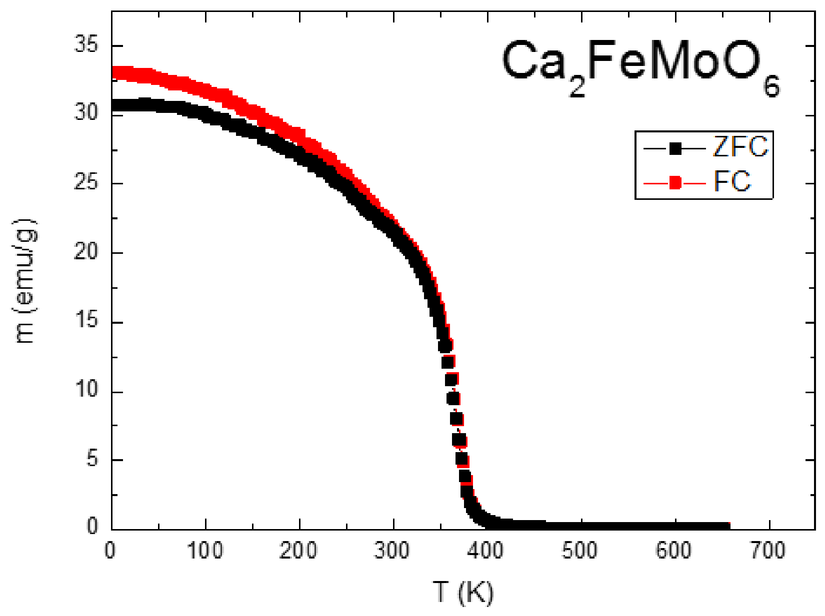


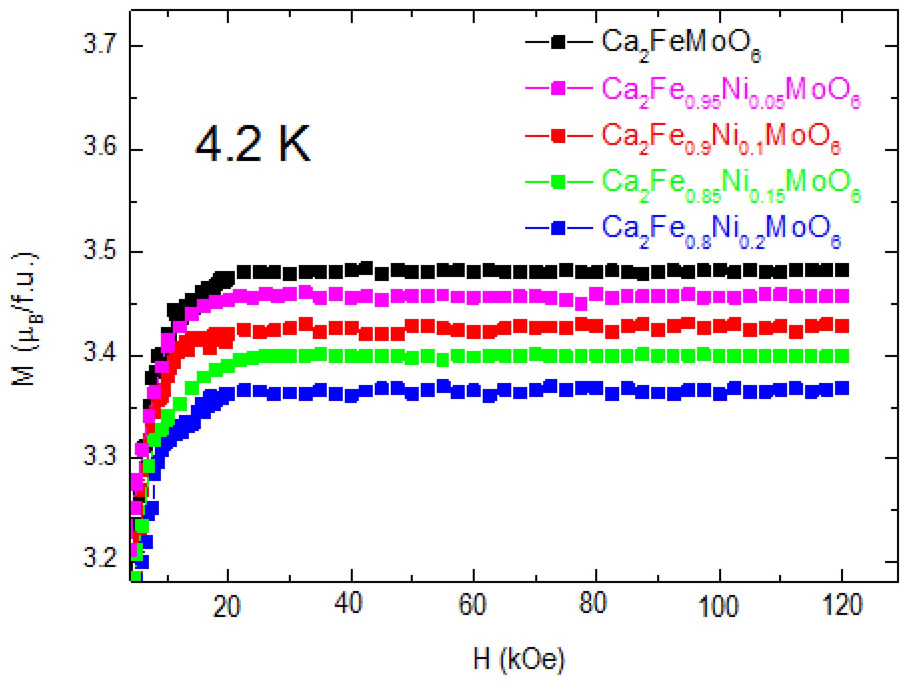
Crystallographic ordering increases with W content

2. Magnetic properties

$Ca_2Fe_{1-x}Ni_xMoO_6$

- cluster glass behaviour superposed on essentially ferrimagnetic ordering
- moderate irreversibility T ≤ 240 K





H > 20 kOe

Magnetic moments of clusters aligned

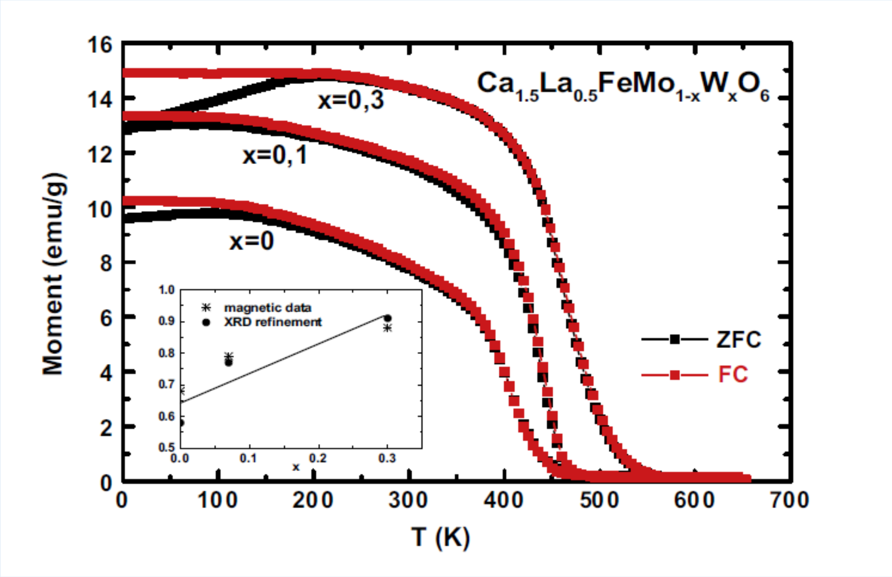
Magnetic moments at B and B’ sites antiparalelly oriented

x ≤ 0.2 $\Delta M_s = -0.12\ \mu_B$

$\Delta M_s = -0.6\ \mu_B$/Ni atom

$Ca_{1.5}La_{0.5}FeMo_{1-x}W_xO_6$

cluster glass on mainly ferrimagnetic behaviour



Magnetic saturation

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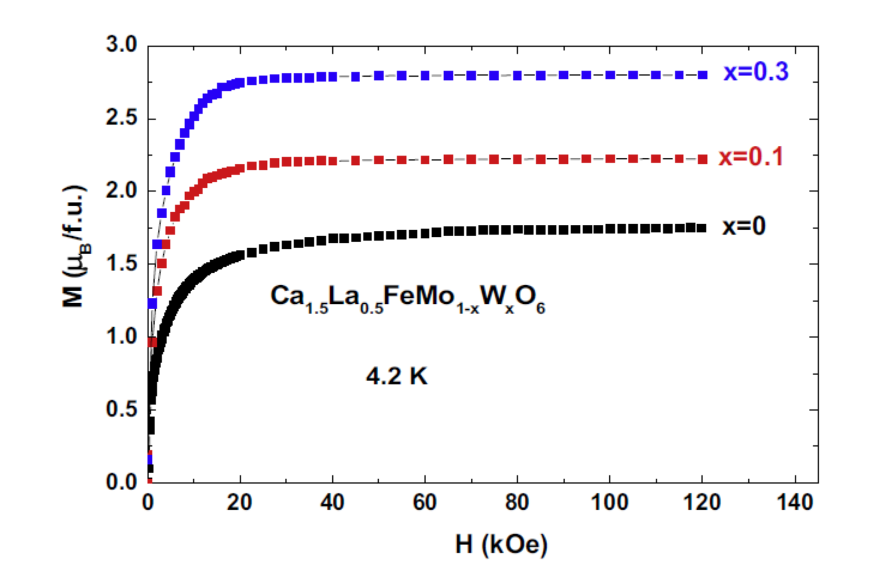
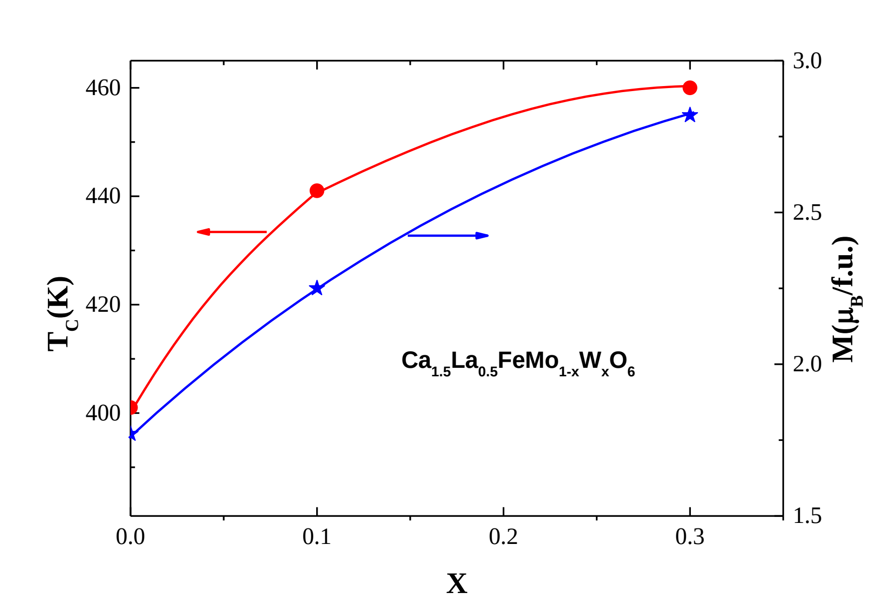
at lower fields as W content increases





$\Delta M_s \cong +3.5\ \mu_B$/W atom

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increase degree of ordering

Ca_2FeMoO_6

T > T_C

$$\chi^{-1} = -85 + \frac{T}{3.58} - \frac{3530}{T-390}$$

Néel-type dependence

- ionic model

$C = xC_{Fe^{2+}} + (1-x)\,C_{Fe^{3+}} + (1-x)\,C_{Mo^{5+}}$

66 % Fe^{2+}; 34 % Fe^{3+}; 34 % Mo^{5+}

$$\chi^{-1} = \chi_0^{-1} + TC^{-1} - \sigma(T-\theta)^{-1}$$

C-Curie constant, χ_0, σ, θ = f($J_{BB'}$, $J_{B'B'}$, J_{BB})

Exchange interactions

Mean field approximation; two sublattices: B,B'

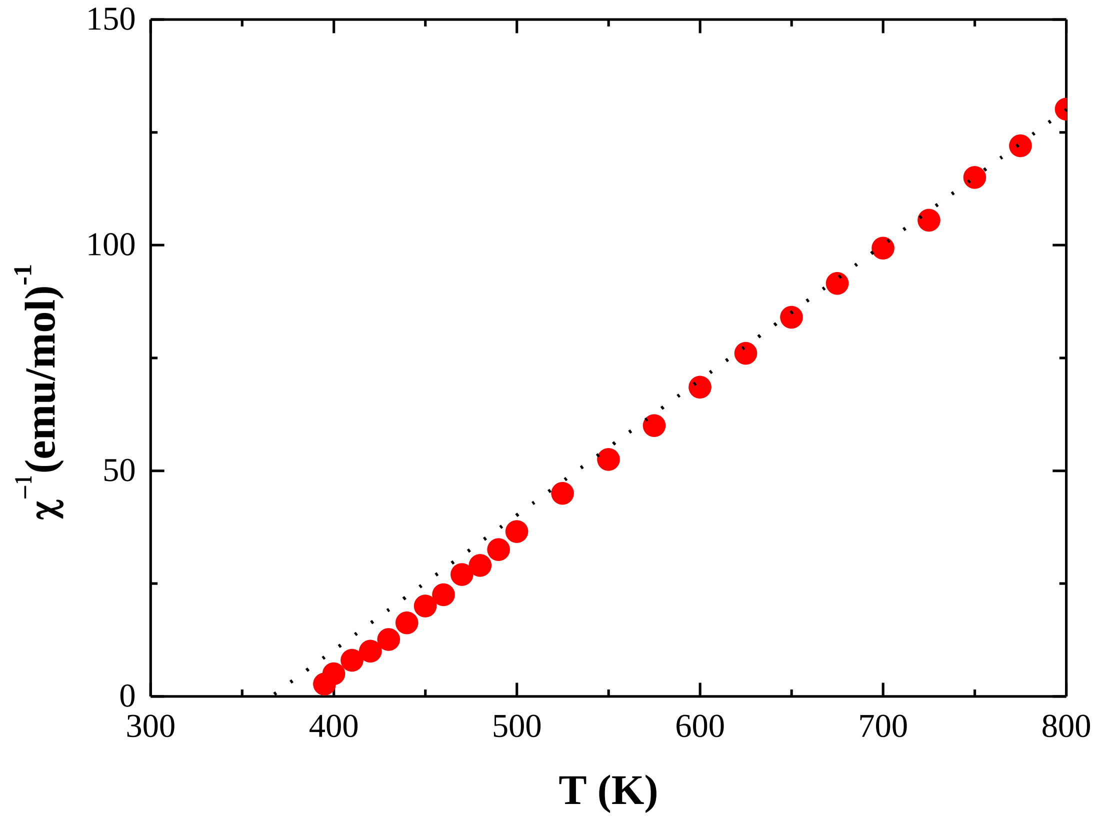
$J_{BB'}$= -58 $|J_{BB'}| < |J_{BB}| < |J_{B'B'}|$

small coupling between sublattices

$C = C_B + C_{B'} \rightarrow C_B >> C_{B'}$

$\Downarrow$

χ^{-1} = f(T) close to Curie –Weiss behaviour



$Ca_2Fe_{1-x}Ni_xMoO_6$

Distribution of ions in B and B' sites

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- number of antisites Mo^{5+} in B site
- number of ions in different valence states
- nickel has +2 valence state

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to fit the saturation magnetization at T = 4 K

- Fe^{2+} ions only B sites
- Ni^{2+} replaces Fe^{2+} up to x = 0.1 in B sites, then located also in B' ones
- Fe^{3+} ions mainly in B site; small fraction in B'

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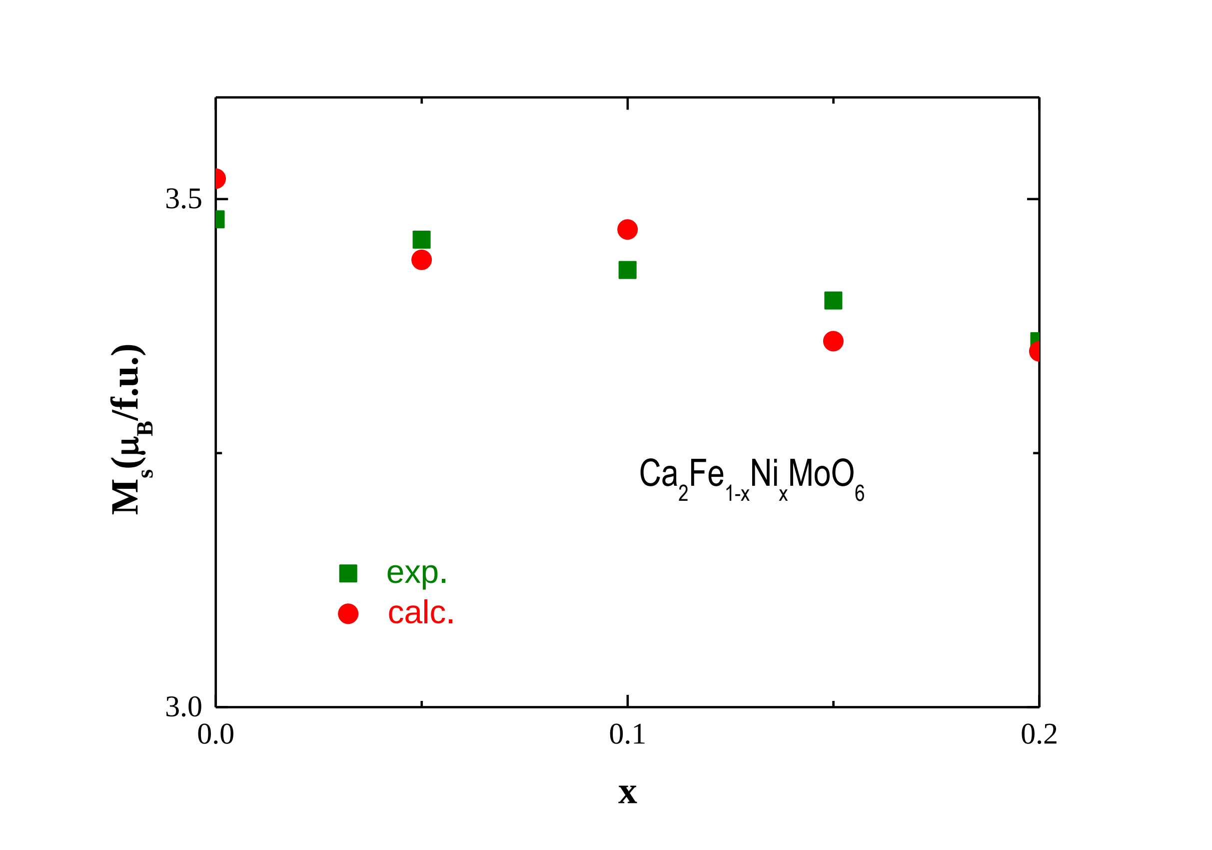
good agreement with measured values



$Ca_{1.5}La_{0.5}FeMo_{1-x}W_xO_6$

$$\chi^{-1} = \chi_0^{-1} + TC^{-1} - \sigma(T-\theta)^{-1}$$

$J_{BB'}$, J_{BB} negative values

J_{BB}= -270 (x = 0), -190 (x=0.3)

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diminution of cluster glass contribution

$J_{BB'}$= -130 (x = 0), -170 (x=0.3)

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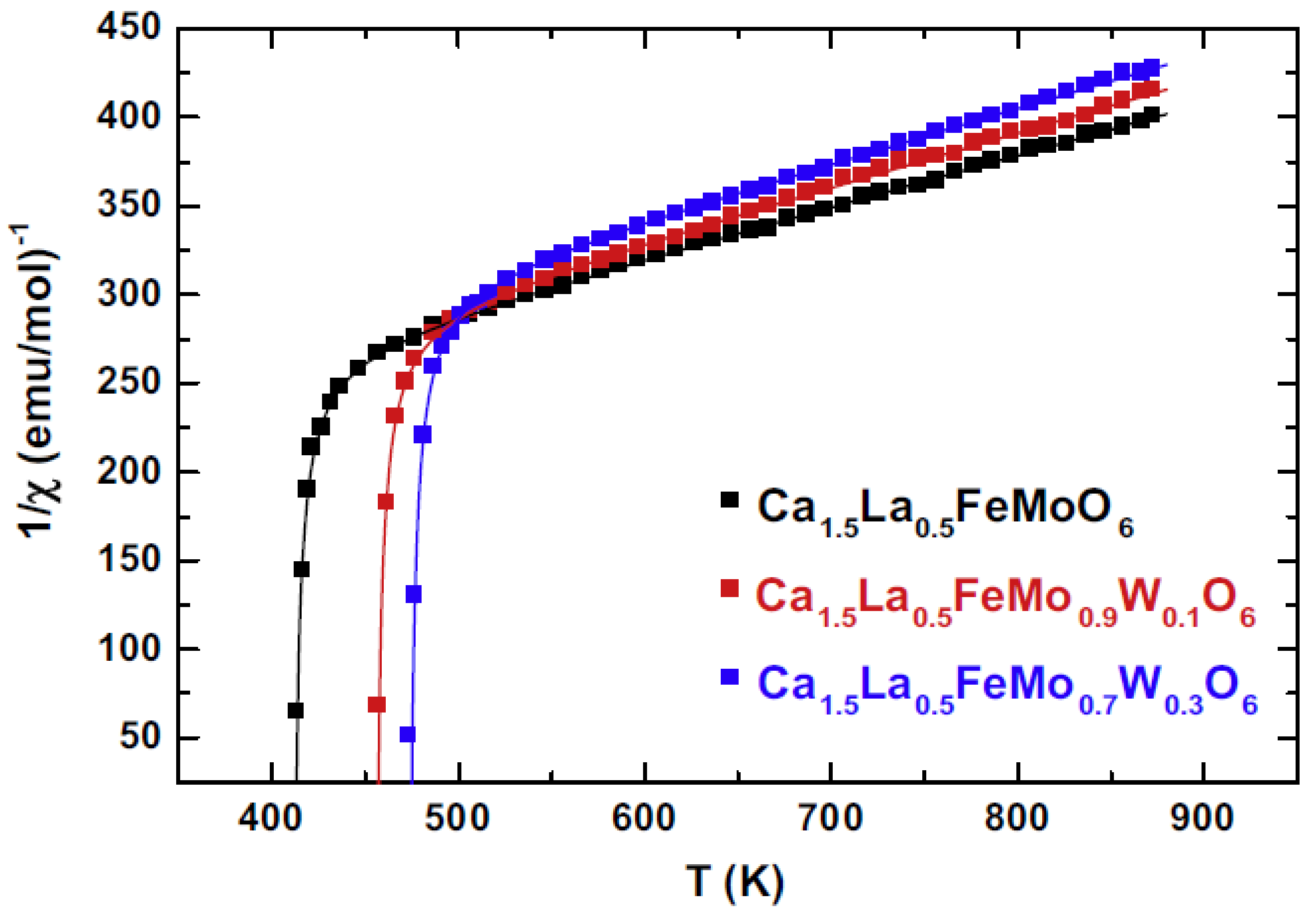
increase T_C values



$Ca_{1.5}La_{0.5}FeMoO_6$: 70 % Fe^{2+}, 68 % Mo^{5+}

increasing W content to x = 0.3

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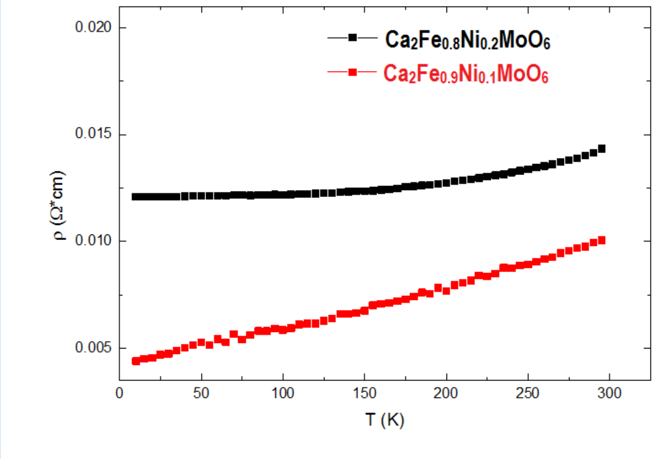
increase number o Fe^{2+} by 10 %

decrease number of Mo^{5+} by 19 %

3 Transport properties

3.1 Resistivities

$Ca_2Fe_{1-x}Ni_xMoO_6$



metallic

Resistivities increases with x

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$Fe^{3+}+Mo^{5+} \rightarrow Ni^{2+}+Mo^{6+}$

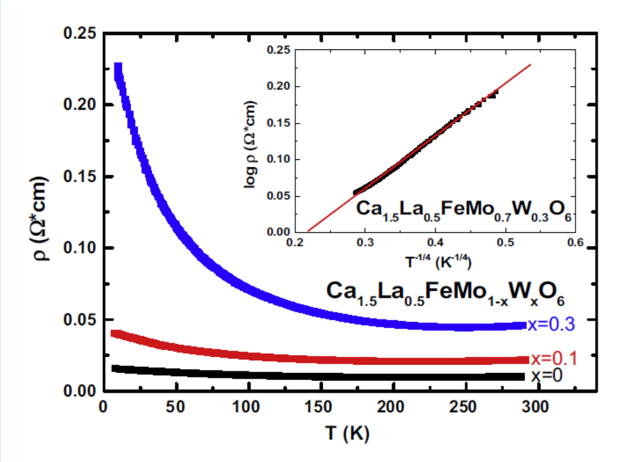
$\rho \propto T^2$ 40 K ≤ T ≤ 300 K

$\frac{\partial \rho}{\partial T^2}=0.82\cdot10^{-6}$ (x=0); $0.69\cdot10^{-6}$ (x=0.1)

$=0.024\cdot10^{-6}$ (x=0.2) Ω cm K^{-2}

electron-electron → scattering
electron-magnon →

$Ca_{1.5}La_{0.5}FeMo_{1-x}W_xO_6$



Resistivities increase with x:
higher W^{6+} content

for x = 0.3; 18 K < T < 160 K
Variable range hopping
(VRH)
$\rho \propto T^{1/4}$

Semiconducting-metallic transition at
T_{sm}=204 K (x = 0); 221 K (0.1)
= 249 K (x = 0.3)

3.2 Magnetoresitivities

$Ca_2Fe_{1-x}Ni_xMoO_6$

Contributions:

- intergrain tunneling magnetoresistance (ITMR) across a single barrier

$MR_I = -Pm(H)^2[1-Pm(H)^{-2}]^{-1}$

P polarization degree

m(H) approach to saturation

near grain boundary (spin glass)

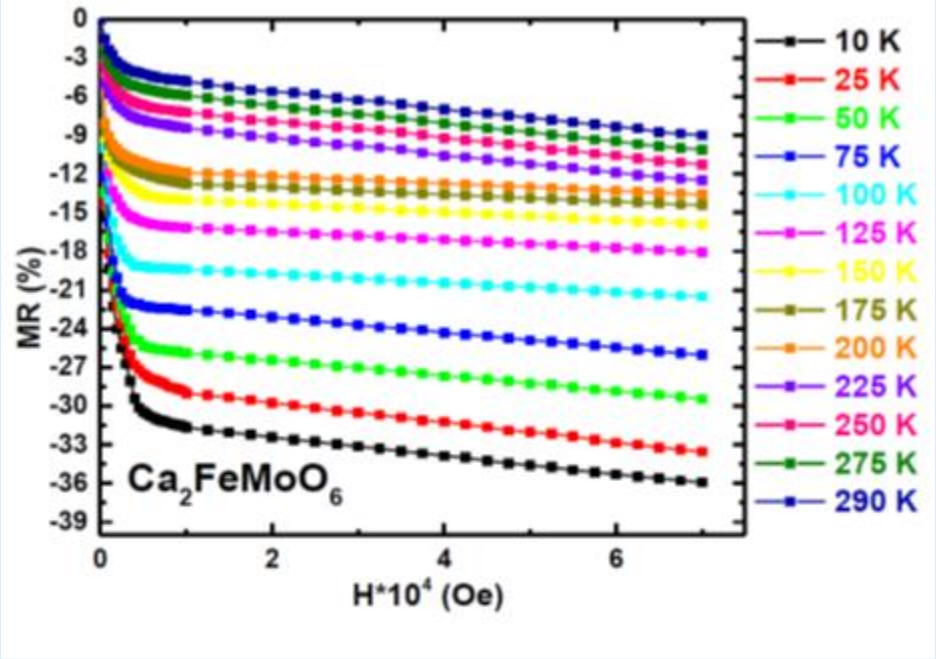
$m(H) = (1-aH^{1/2})$

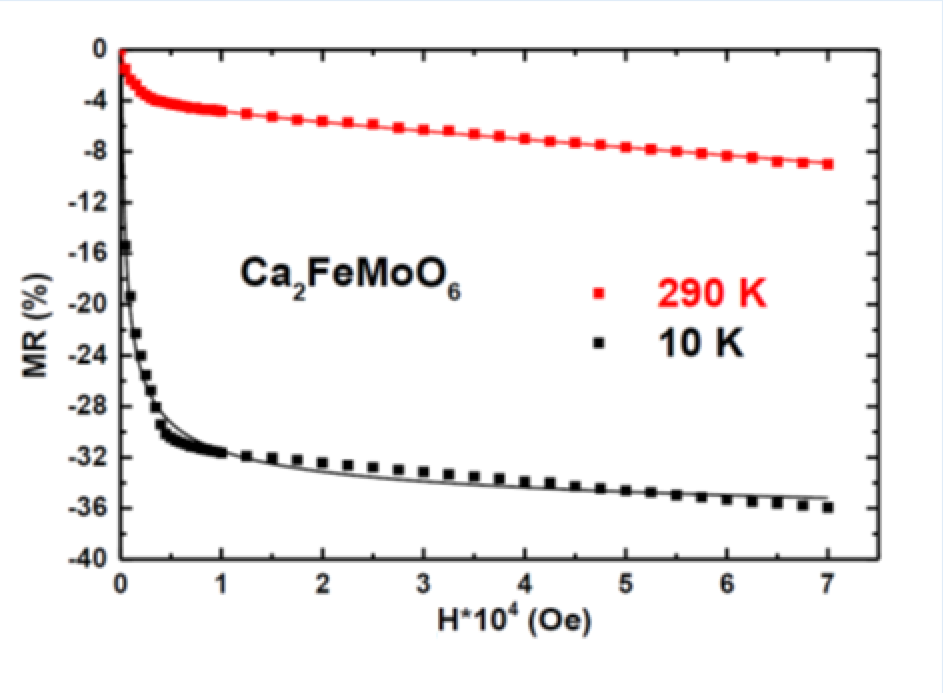
- intragrain magnetoresistance

spin disorder inside grains

$MR_H=-bH$

$MR = MR_I+MR_H$

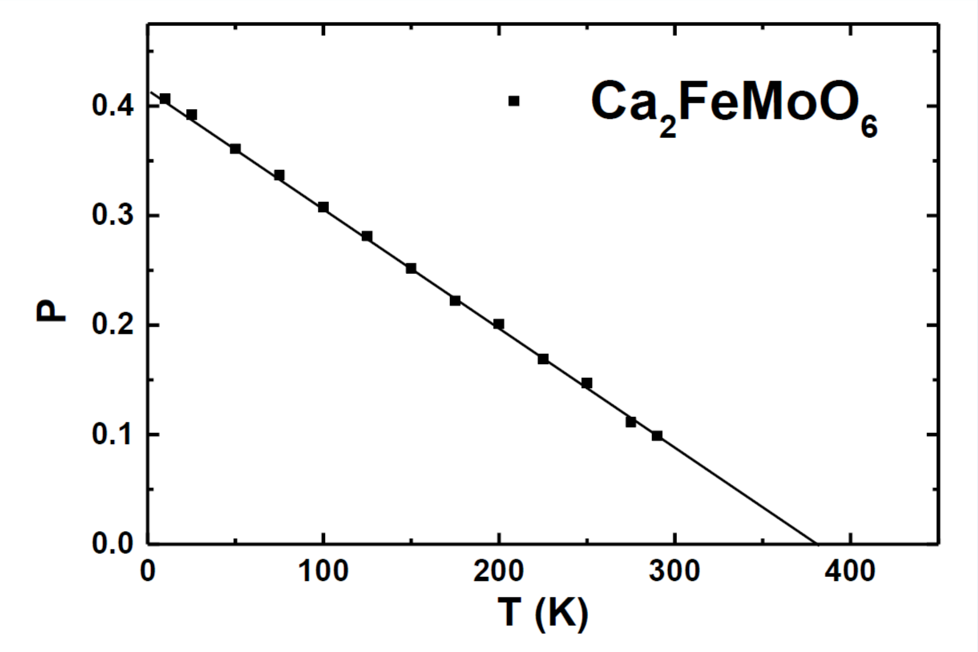


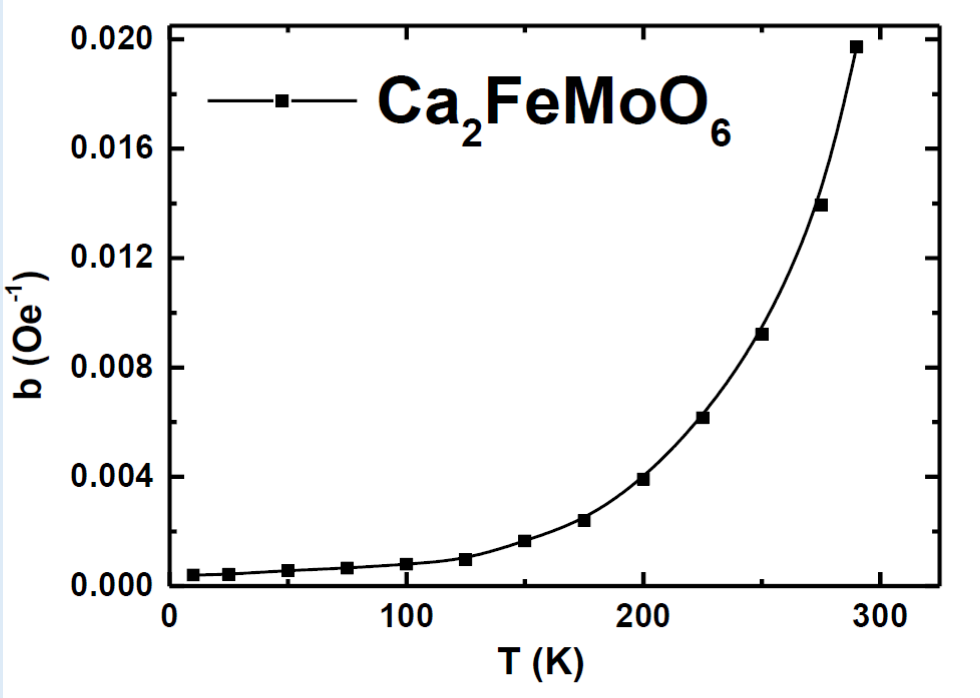


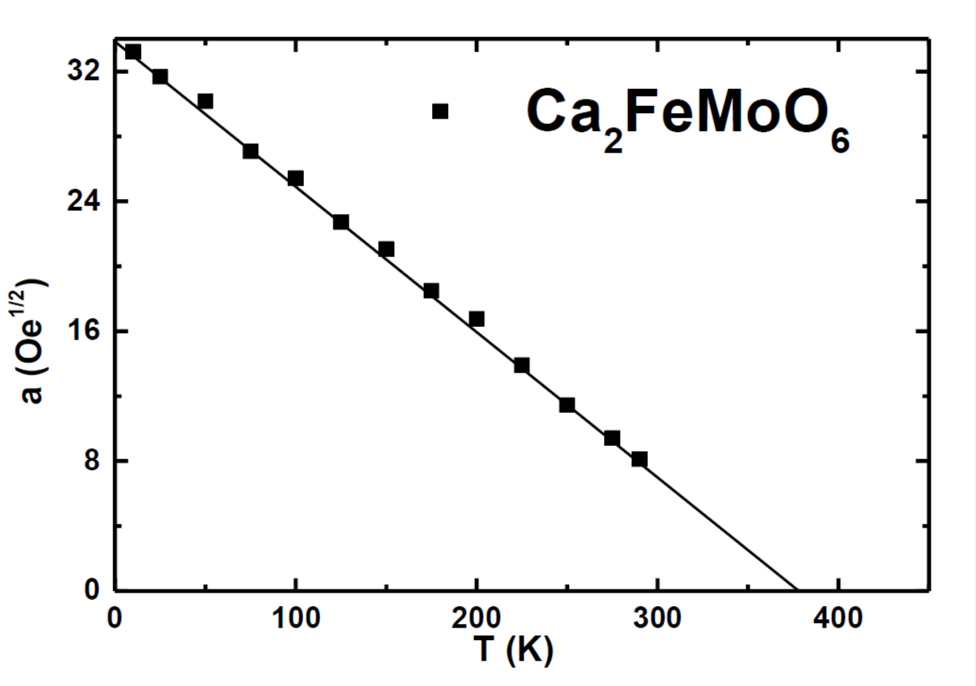
Model describes good experimental data

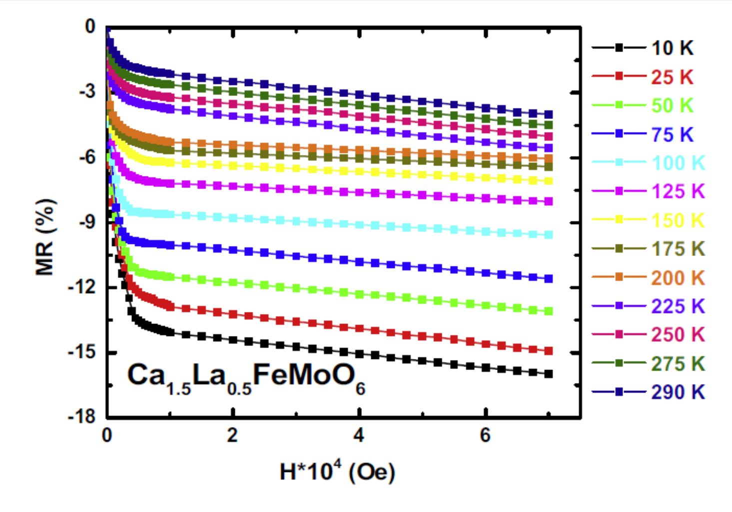
P = 41 % at 10 K

P = 10 % at 300 K

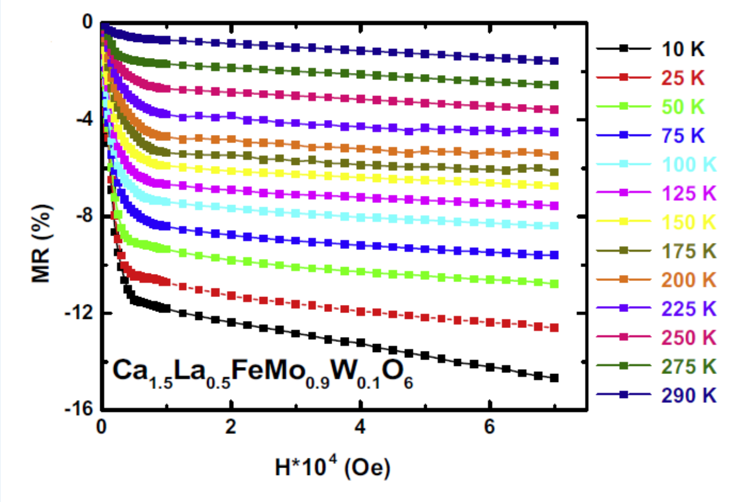




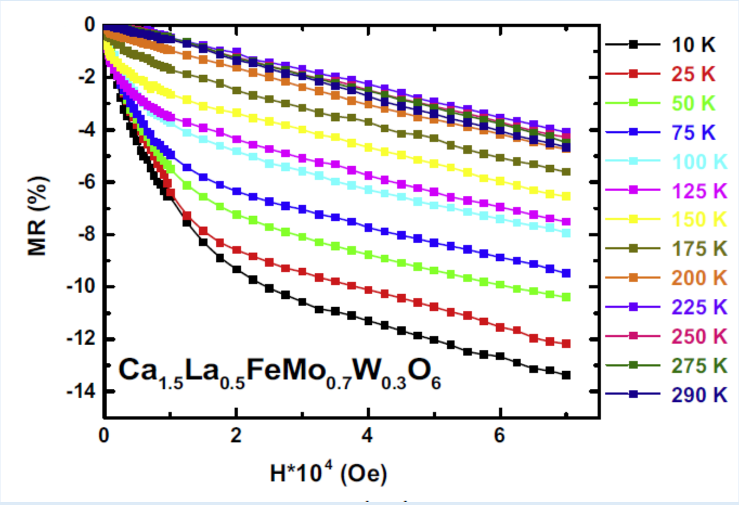




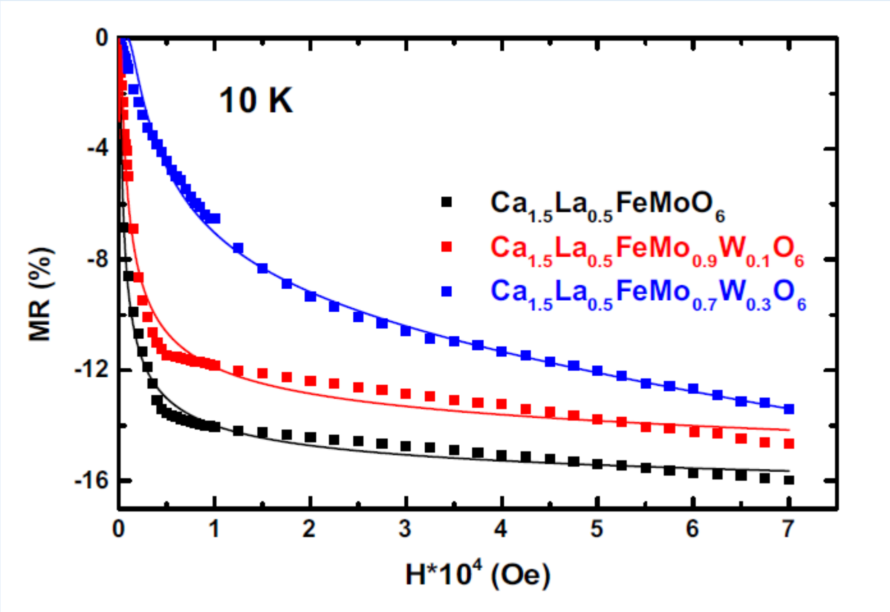
MR (%)
H*10^4 (Oe)
Ca1.5La0.5FeMoO6
10 K
25 K
50 K
75 K
100 K
125 K
150 K
175 K
200 K
225 K
250 K
275 K
290 K



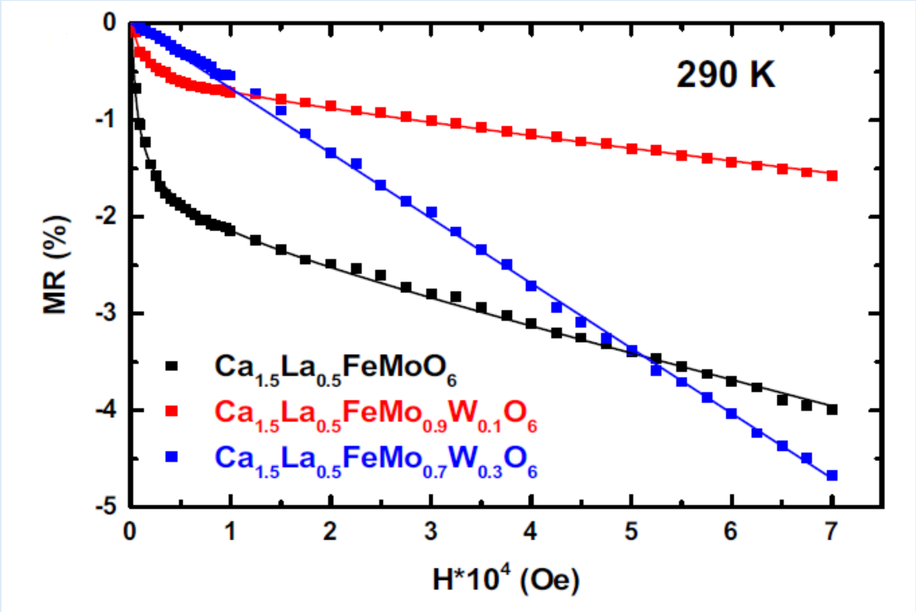
MR (%)
H*10^4 (Oe)
Ca1.5La0.5FeMo0.9W0.1O6
10 K
25 K
50 K
75 K
100 K
125 K
150 K
175 K
200 K
225 K
250 K
275 K
290 K



MR (%)
H*10^4 (Oe)
Ca1.5La0.5FeMo0.7W0.3O6
10 K
25 K
50 K
75 K
100 K
125 K
150 K
175 K
200 K
225 K
250 K
275 K
290 K



10 K
MR (%)
H*10^4 (Oe)
Ca1.5La0.5FeMoO6
Ca1.5La0.5FeMo0.9W0.1O6
Ca1.5La0.5FeMo0.7W0.3O6



290 K
MR (%)
H*10^4 (Oe)
Ca1.5La0.5FeMoO6
Ca1.5La0.5FeMo0.9W0.1O6
Ca1.5La0.5FeMo0.7W0.3O6

$Ca_{1.5}La_{0.5}M_{1-x}W_xO_6$

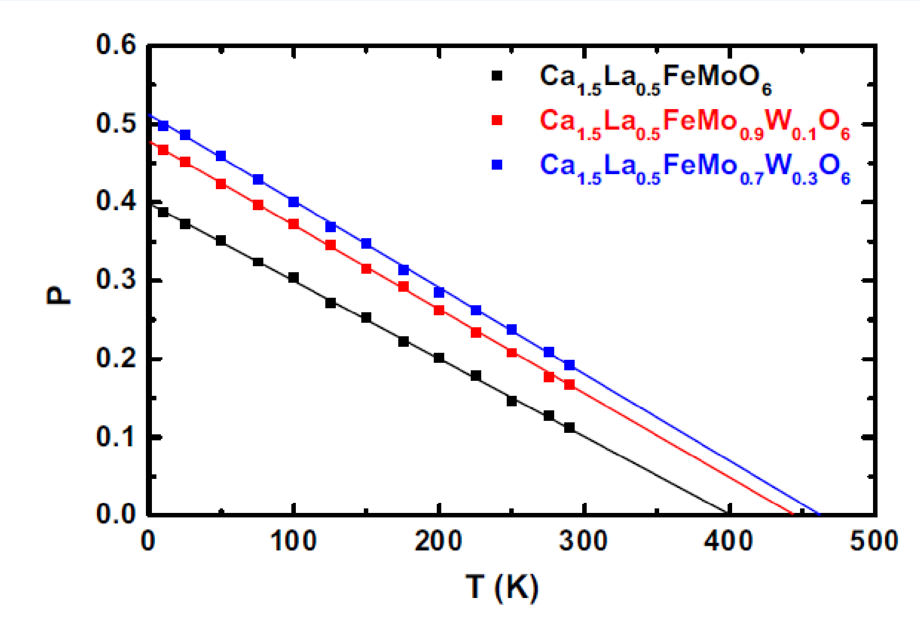
Polarization

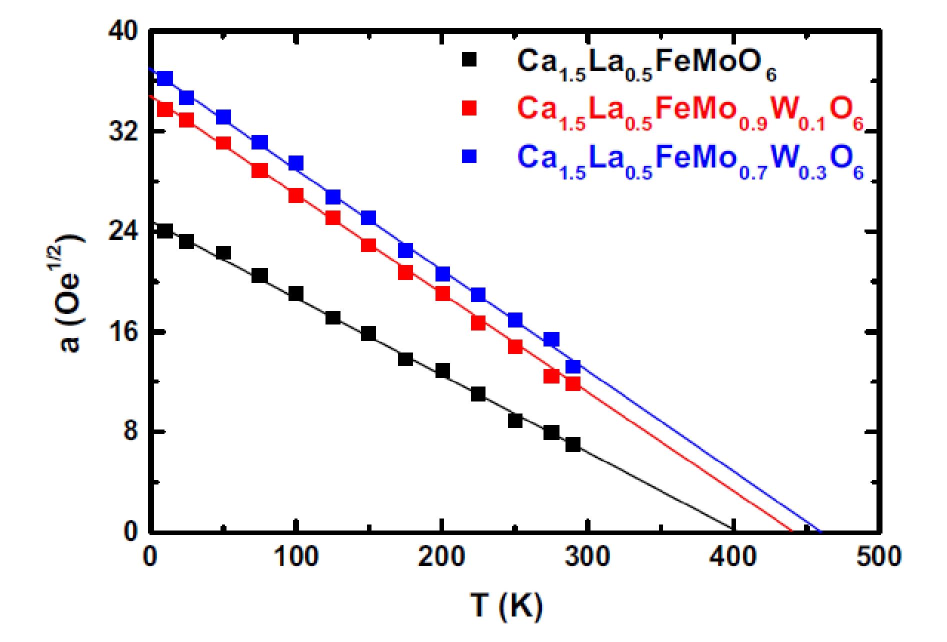
P = 0.50 (x = 0.3)

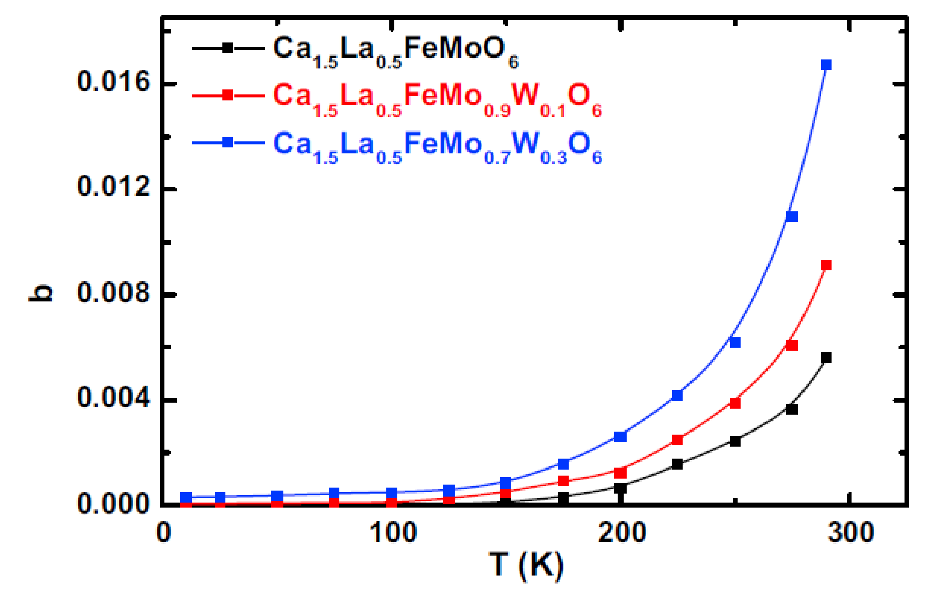
0.47 (x = 0.1) → T = 10 K

0.40 (x = 0)

P = 0.20 (x = 0.3) T = 300 K







CONCLUSIONS

- Crystal structure

monoclinic P_21/n — $Ca_2Fe_{1-x}Ni_xMoO_6$ — $x \leq 0.2$

$Ca_{1.5}La_{1.5}FeMo_{1-x}W_xO_6$ — $x \leq 0.3$

- Magnetic properties: ferrimagnetic with small cluster glass contribution

M_s decrease — $Ca_2Fe_{1-x}Ni_xMoO_6$

with x

M_s increase — $Ca_{1.5}La_{0.5}FeMo_{1-x}W_xO_6$; at T = 4 K greatly influenced by degree of ordering

$T > T_C$ — χ^{-1} — Néel-type dependences

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ferrimagnetic system

- Resistivities
  - metallic type $Ca_2Fe_{1-x}Ni_xMoO_6$; ρ increases with x: Fe^{3+}-$Mo^{5+} \rightarrow Ni^{2+}+Mo^{6+}$
  - semiconductor-metallic transition $Ca_{1.5}La_{0.5}FeMo_{1-x}W_xO_6$ ($T \cong 200$ K)
- Magnetoresistivities
  - intergrain tunneling
  - intragrain disorder

Polarization higher in $Ca_{1.5}La_{0.5}FeMo_{1-x}W_xO_6$

$\Downarrow$

10 K increases with ordering degree 40 % (x = 0) $\rightarrow$ 51 % (x= 0.3)

$Ca_2FeMo_{1-x}Ni_xO_6$ x = 0; P = 41 %

decreases with increasing antisite positions

ACKNOWLEDGMENTS
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Thank you very much for your attention