ALaFeVO$_6$ (A = Ca, Sr): New Double-Perovskite Oxides

K. Ramesha and J. Gopalakrishnan

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore, 560012, India
E-mail: gopal@sscu.iisc.ernet.in

and

V. Smolyaninova and R. L. Greene

Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742

   We describe the synthesis and structural characterization of two new double perovskites, ALaFeVO$_6$ (A = Ca, Sr), where Fe^{3+}/V^{4+} are partially ordered at the octahedral sites. The small charge difference between Fe^{3+}/V^{4+} precludes the formation of a long-range ordered double-perovskite structure even on prolonged annealing at 1000°C. Electrical conductivity and magnetic susceptibility measurements show that both phases are weakly ferrimagnetic semiconductors where disordered Fe^{3+} – O – V^{4+} pairs persist even up to ∼ 350 K. © 2001

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   Key Words: double perovskite; ALaFeVO$_6$ (A = Ca, Sr).

1. INTRODUCTION

   Among the several original contributions made by Professor Paul Hagenmuller to solid state chemistry during his long and distinguished career (see, for example, (1)), his work on perovskite oxides is especially singular. For example, he and his co-workers have prepared several novel perovskites (ABO_3) and double perovskites ($A_2BB'O_6$) (2–4) such as LaCuO$_3$ and La$_2$LiMO_6 (M = Fe, Ru, Os), where unusual oxidation states for the transition metals are stabilized. Ordered double perovskites exhibiting ferrimagnetic and metallic properties (5, 6) such as Sr$_2$FeMoO$_6$ and Ba$_2$FeReO$_6$ have attracted recent attention (7, 8) in view of their half-metallicity and consequent magnetoresistance properties. In our efforts to synthesize new double perovskites of this kind, we believed that phases containing Fe$^{3+/2+}$ and V$^{4+/5+}$ would be similar to Sr$_2$FeMoO$_6$ and Ba$_2$FeReO$_6$, considering the redox potentials of the oxidation states involved (9). We have been able to prepare two new double perovskites, ALaFeVO$_6$ (A = Ca, Sr) where this possibility is realized. Here we describe the synthesis, structure, and properties of these phases.

EXPERIMENTAL

   ALaFeVO$_6$ (A = Ca, Sr) oxides were prepared by a two-step route. First, a precursor oxide of the composition ALaFeO$_4$ was prepared by reacting stoichiometric quantities of ACO$_3$, La$_2$O$_3$, and Fe$_2$O$_3$ in air at 1000°C for 24 h, to which required quantities of V$_2$O$_3$ and V$_2$O$_5$ were added to get the desired composition, ALaFeVO$_6$. The pellets of this oxide mixture were heated in evacuated sealed silica tubes at 1000°C for 8 days with intermediate grindings to obtain single-phase materials.

   X-ray powder diffraction (XRD) patterns were recorded using a Siemens D5005 diffractometer with Cu$K\alpha$ radiation. The indexed powder patterns are given in Table 1. The structures were refined from the powder XRD data using the Rietveld program FULLPROF (10). Data collection and the refinement conditions are given in Table 2. Refinements were carried out using the cubic double-perovskite $A_2BB'O_6$ structure, space group $Fm3m$ (6). We have refined unit cell parameters, position parameters, and isotropic thermal parameters along with the usual profile parameters defining pseudo-Voigt profile functions. La^{3+} and A^{2+} ions were assumed to be disordered over the A site of the cubic perovskite structure. Occupancy of Fe and V atoms over the B and B' sites of the $A_2BB'O_6$ double perovskite were refined with the constraint that the Fe:V cation ratio is 1:1 in these samples. The structural parameters and interatomic distances derived from the refinements are given in Tables 3 and 4 respectively. Observed, calculated, and difference profiles are shown in Fig. 1.

TABLE 1
X-Ray Powder Diffraction Data for *A*LaFeVO$_6$ (*A* = Ca, Sr)

	CaLaFeVO$_6^a$			SrLaFeVO$_6^b$		
hkl	d_{obs} (Å)	d_{calc} (Å)	I_{obs}	d_{obs} (Å)	d_{calc} (Å)	I_{obs}
111	4.468	4.466	1.0	4.507	4.504	1.7
200	3.858	3.859	4.7	3.880	3.883	14.8
220	2.728	2.728	100	2.749	2.750	100
311	2.333	2.332	1.3	2.350	2.352	1.3
222	2.229	2.228	13.8	2.248	2.248	13.9
400	1.929	1.929	27.8	1.947	1.947	27.5
331	1.775	1.775	0.9	1..791	1.790	1.3
420	1.729	1.729	1.7	1.744	1.744	4.3
422	1.575	1.575	29.2	1.588	1.589	25.3
511	1.488	1.489	0.5	1.500	1.501	0.4
440	1.364	1.364	10.3	1.377	1.377	12.2
531	1.307	1.308	0.7	1.318	1.318	0.5
442	1.289	1.289	1.0	1.300	1.300	1.7
620	1.220	1.220	7.8	1.231	1.231	2.1
622	1.167	1.167	1.7	1.176	1.176	1.7
444	1.114	1.114	2.6	1.124	1.124	1.9
642	1.034	1.034	7.7	1.043	1.043	8.7
800	0.967	0.967	1.2	0.975	0.975	1.7
820	0.938	0.938	1.0	0.946	0.946	0.8
822	0.912	0.912	6.0	0.919	0.919	4.3

$^a a$ = 7.736(1) Å.
$^b a$ = 7.802(1) Å.

Electrical resistivities were measured on sintered pellets by a four-probe technique in the range 15–300 K. Magnetization measurements were made with a SQUID (MPMS Quantum Design) magnetometer. The oxidation state of vanadium in the samples was determined by

TABLE 2
Data Collection and Refinement Conditions for *A*LaFeVO$_6$ (*A* = Ca, Sr)

Condition	CaLaFeVO$_6$	SrLaFeVO$_6$
Diffractometer	Siemens-D5005	Siemens-D5005
Geometry	Bragg–Brentano	Bragg–Brentano
Radiation	Cu*K*α	Cu*K*α
Counting time (h)	12	12
2θ range (°)	10–110	10–110
Z	4	4
Profile function	Pseudo-Voigt	pseudo-Voigt
Number of refined parameters	14	14
R_{wp} without structural information	4.5	3.72
R_{exp}	3.91	2.99
R_P, R_{wp}, χ^2 with structural constraint	4.01, 5.32, 1.85	3.91, 5.61, 3.52
R_{Bragg}, R_F	6.69, 13.7	7.84, 10.2

TABLE 3
Atomic Positions, Isotropic Temperature Factors, and Occupancy for CaLaFeVO$_6$ and SrLaFeVO$_6$ (Space Group *Fm3m*)

Atom	Site	*x*	*y*	*z*	B(Å^2)	Occupancy
La/Ca	8c	0.25	0.25	0.25	0.10(1)	2.00
Fe1	4a	0	0	0	0.20(3)	0.69(2)
Fe2	4b	0.5	0.5	0.5	0.15(2)	0.31(2)
V1	4a	0	0	0	0.20(3)	0.31(2)
V2	4b	0.5	0.5	0.5	0.15(2)	0.69(2)
O	24e	0.2517(4)	0	0	0.50(2)	6.00
La/Sr	8c	0.25	0.25	0.25	0.12(1)	2.00
Fe1	4a	0	0	0	0.15(2)	0.65(2)
Fe2	4b	0.5	0.5	0.5	0.15(2)	0.35(2)
V1	4a	0	0	0	0.15(2)	0.35(2)
V2	4b	0.5	0.5	0.5	0.15(2)	0.65(2)
O	24e	0.2524(4)	0	0	0.40(2)	6.00

a redox potentiometric titration using Ce(IV) as an oxidizing agent.

RESULTS AND DISCUSSION

Powder XRD data (Table 1) show formation of single-phase perovskite oxides for both *A*LaFeVO$_6$ (*A* = Ca, Sr). Occurrence of weak reflections that could be indexed only on a cell with *a* = 7.736(1) Å for *A* = Ca and *a* = 7.802(1) Å for *A* = Sr phases reveals formation of a double-perovskite structure. Rietveld refinements of the powder XRD data (Fig. 1 and Tables 2 and 3) however show that ordering of Fe/V atoms at the *B* site of the double-perovskite structure is not complete. From the site occupancies (Table 3), we calculate that the ordering is around 38 and 30% respectively for the *A* = Ca and *A* = Sr phases.

We could consider *A*LaFeVO$_6$ as 1:1 solid solutions between *A*VO$_3$ and LaFeO$_3$ or *A*FeO$_3$ and LaVO$_3$. The unit cell volumes of CaLaFeVO$_6$ (463.10 Å^3) and SrLaFeVO$_6$ (474.95 Å^3) do not distinguish between the two possibilities, because the calculated cell volumes for both formulations are nearly the same (456.92 Å^3 for CaVO$_3$/LaFeO$_3$, 469.29 Å^3 for SrVO$_3$/LaFeO$_3$, 455.65 Å^3

TABLE 4
Interatomic Distances for *A*LaFeVO$_6$ (*A* = Ca, Sr)

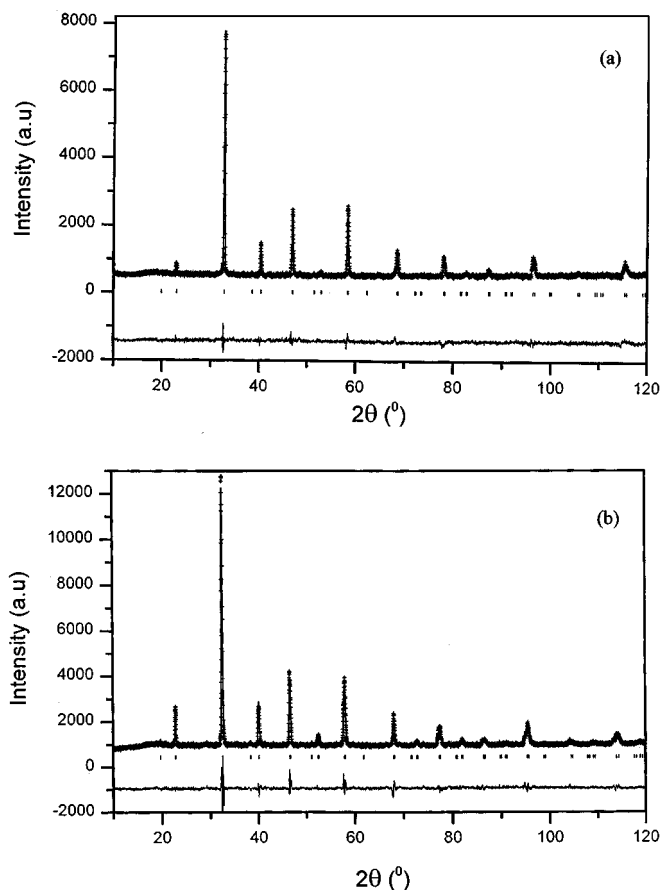|	CaLaFeVO$_6$	SrLaFeVO$_6$
Space group	*Fm3m*	*Fm3m*
Lattice parameter, *a* (Å)	7.736(1)	7.802(1)
Fe1/V1–O (Å)	1.947(2)	1.964(1)
Fe2/V2–O (Å)	1.921(1)	1.937(1)
A/La–O (Å)	2.735(1)	2.758(1)

FIG. 1. Rietveld refinement of powder XRD data for (a) $CaLaFeVO_6$ and (b) $SrLaFeVO_6$. Calculated (full line), experimental ($+$), and difference (bottom) profiles as well as Bragg reflection positions are shown.

FIG. 2. Log resistivity ($\log \rho$) versus inverse temperature ($1/T$) plots for $A LaFeVO_6$. (a) $A = $ Sr and (b) $A = $ Ca. Inset shows the log resistivity ($\log \rho$) versus $1/T^{1/4}$ plots for the same compounds.

exhibiting a conventional thermally activated hopping and the $A = $ Sr compound showing a variable range hopping of charge carriers. We are however unable to account for this difference in terms of the structure, except to point out that the Fe^{3+}/V^{4+} is more ordered in the $A = $ Ca case than in the $A = $ Sr case.

for $CaFeO_3/LaVO_3$, and 469.90 Å^3 for $SrFeO_3/LaVO_3$). Redox titrations using Ce(IV)/Fe(II) solutions show that the oxidation state of vanadium is 4.01 ± 0.03, indicating that the most likely formulation of the compounds is $A LaFe^{3+}V^{4+}O_6$. Since the formal charge difference between Fe^{3+} and V^{4+} in $A LaFe^{3+}V^{4+}O_6$ is only one unit, a fully ordered double-perovskite structure is not obtained even on prolonged annealing. Double perovskites with near-complete ordering of B site cations are obtained when the charge difference between the B site cations is ≥ 2, as for example in Ba_2FeReO_6 and Sr_2FeMoO_6 (6, 11). However, B-site ordering in $LaCaMnCoO_6$ was observed by electron diffraction, although powder X-ray diffraction did not reveal it (12).

The temperature dependence of dc resistivities (Fig. 2) show that both $A LaFeVO_6$ phases are semiconducting. The $\log \rho$ vs $1/T$ plot is linear for $A = $ Ca, but not linear for $A = $ Sr. Log ρ vs $1/T^{1/4}$ plot however is linear for $A = $ Sr. This difference indicates that the nature of charge transport is not the same in both materials, the $A = $ Ca compound
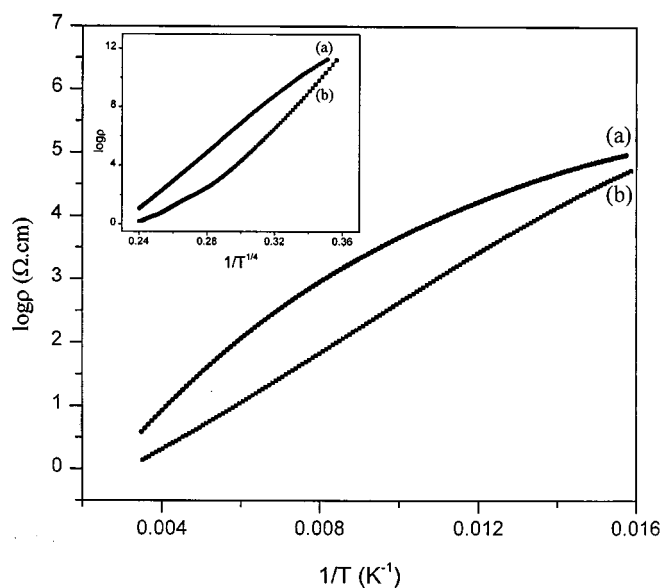

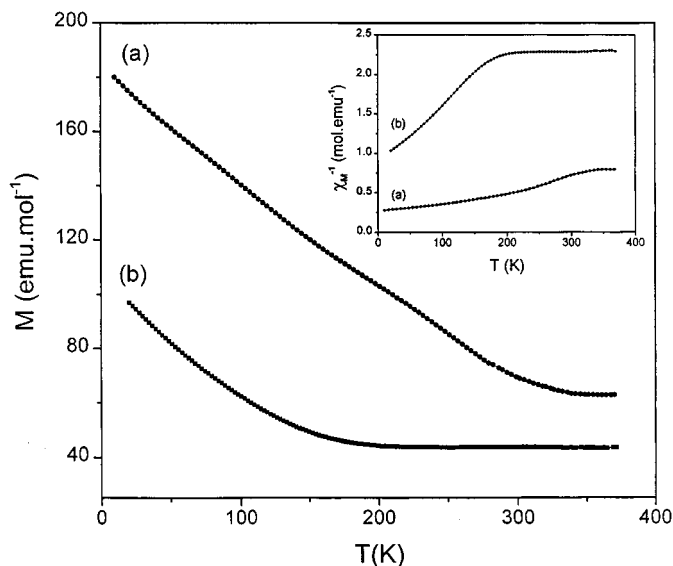FIG. 3. Magnetization (M) versus temperature (T) plots for $A LaFeVO_6$. (a) $A = $ Sr and (b) $A = $ Ca. Inset shows inverse molar magnetic susceptibility (χ_M^{-1}) versus temperature (T) plots for the same compounds.

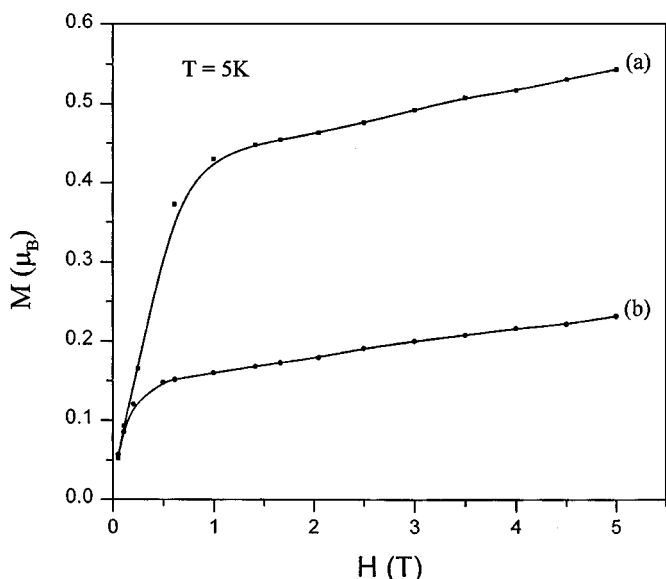**FIG. 4.** Magnetization (*M*) versus magnetic field (*H*) plots at 5 K for *A*LaFeVO$_6$. (a) *A* = Ca and (b) *A* = Sr.

The temperature dependence of magnetization measured with *H* = 50 Oe for both CaLaFeVO$_6$ and SrLaFeVO$_6$ is shown in Fig. 3. Both samples display a weak ferrimagnetic behavior. For *A* = Ca, magnetization remains almost constant down to 150 K, thereafter increasing steadily as the temperature is lowered. For *A* = Sr, magnetization increases steadily below 300 K. χ_M^{-1}–*T* plots (inset of Fig. 3) however show that the magnetic behavior is not Curie–Weiss at high temperatures (> 300 K). Considering that the oxidation states of iron and vanadium are Fe^{3+}:3d^5 (high spin) and V^{4+}:3d^1, we calculate a spin-only moment of 6.17 μ_B for *A*LaFe^{3+}V^{4+}O$_6$. The experimental values are however much higher (87 μ_B for *T* < 200 K and 33 μ_B for *T* > 200 K for *A* = Sr), suggesting that ferrimagnetically coupled Fe^{3+}–O–V^{4+} pairs exist even at temperatures > 300 K. The *M*–*H* data (Fig. 4) show small magnetic moments (0.43 μ_B for *A* = Ca and 0.23 μ_B for *A* = Sr phases) that are considerably smaller than the expected value (4 μ_B) for a long-range ordered Fe^{3+}–O–V^{4+} double-perovskite structure. This result is consistent with the structure refinement of powder XRD data (Table 3), which shows a partial ordering of Fe^{3+}/V^{4+} ions in the double perovskite, *A*LaFeVO$_6$.

CONCLUSIONS

We have prepared two new double perovskites, *A*LaFeVO$_6$ (*A* = Ca, Sr), where the Fe^{3+}/V^{4+} are partially ordered. The small charge difference between Fe^{3+} and V^{4+} most likely precludes a long-range ordering of transition metal ions at the *B* site, unlike in the cases Ba$_2$FeReO$_6$ and Sr$_2$FeMoO$_6$. Magnetic measurements suggest the presence of disordered ferrimagnetic Fe^{3+}–O–V^{4+} units that persist even up to 350 K.

REFERENCES

1. P. Hagenmuller, *Proc. Indian. Acad. Sci.* (*Chem. Sci.*) **92,** 1–26 (1983).
2. G. Demazeau, C. Parent, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **7,** 913 (1972).
3. J. B. Goodenough, N. F. Mott, M. Pouchard, G. Demazeau, and P. Hagenmuller, *Mater. Res. Bull.* **8,** 647 (1973).
4. G. Demazeau, B. Buffat, F. Menil, L. Fournes, M. Pouchard, J. M. Dance, P. Fabritchnyi, and P. Hagenmuller, *Mater. Res. Bull.* **16,** 1465 (1981).
5. T. Nakagawa, *J. Phys. Soc. Jpn.* **24,** 806 (1968).
6. A. W. Sleight and J. F. Weiher, *J. Phys. Chem. Solids* **33,** 679 (1972).
7. K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, *Nature* **395,** 677 (1998).
8. J. Gopalakrishnan, A. Chattopadhyay, S. B. Ogale, T. Venkatesan, R. L. Greene, A. J. Millis, K. Ramesha, B. Hannoyer, and G. Marest, *Phys. Rev. B* **62,** 9538 (2000).
9. D. F. Shriver, P. W. Atkins, and C. H. Langford, "Inorganic Chemistry," pp. 651–652. Oxford Univ. Press, Oxford, 1990.
10. J. Rodriguez-Carvajal, FULLPROF, version 3.1d-LLB-JRC, October 1998, ILL, France.
11. M. T. Anderson, K. B. Greenwood, G. A. Taylor, and K. R. Poeppelmeier, *Prog. Solid State Chem.* **22,** 197 (1993).
12. M. Vallet-Regi, E. Garcia, and J. M. González-Calbet, *J. Chem. Soc. Dalton Trans.* 775 (1988).