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Citation: *Journal of Applied Physics* **109**, 07E329 (2011); doi: 10.1063/1.3562917

View online: <http://dx.doi.org/10.1063/1.3562917>

View Table of Contents: <http://aip.scitation.org/toc/jap/109/7>

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Magnetization and neutron diffraction studies on $\text{Sr}_2\text{TiMnO}_6$

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(Presented 18 November 2010; received 25 September 2010; accepted 15 December 2010; published online 6 April 2011)

Magnetic properties of the double perovskite oxide, $\text{Sr}_2\text{TiMnO}_6$, have been studied by means of bulk magnetization and powder neutron diffraction experiments. Low field magnetization data reveal transitions at ~ 45 K (T_C) and at ~ 15 K (T_N). A magnetic moment value of only $\sim 0.23 \mu_B/\text{F.U.}$ is attained at 5 K in the 7 T field. Powder neutron diffraction studies suggest the possible antiferromagnetic order in this compound at 12 K with moments of $\sim 0.5 \mu_B$ at the Mn site.

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Recently, the double perovskite oxide, $\text{Sr}_2\text{TiMnO}_6$, has been identified as a colossal dielectric constant material.^{1,2} This material shows a large room temperature dielectric constant value that extends over a wide temperature and frequency range. Preliminary magnetic property study suggested a possible ferromagnetic transition at ~ 45 K.² However, the magnetic moment does not saturate in fields of 5 T below T_C for this sample. Since the nature of the magnetism is not well understood, this work aims to study the magnetic properties of $\text{Sr}_2\text{TiMnO}_6$ oxide and its magnetic structure.

A polycrystalline sample of $\text{Sr}_2\text{TiMnO}_6$ was prepared by solid state reaction starting with pure oxides and carbonates [SrCO_3 , MnO , MnO_2 and TiO_2 ; Sigma-Aldrich, USA] as described in Ref. 1. The sample was characterized by room temperature powder x-ray diffraction (XRD), and SEM-EDAX analyses. The magnetization was measured using commercial magnetometers [SQUID - MPMS XL and Physical Property Measurement System (PPMS), Quantum Design, USA]. The powder neutron diffraction (ND) investigation was carried out at 300 K and at 12 K (incident neutron wavelength of 1.478961 Å, MURR, USA). The powder x-ray and neutron diffraction patterns were indexed and the calculations were performed using the FULLPROF 98-program.³

The sample $\text{Sr}_2\text{TiMnO}_6$ is found to be single phase, crystallizing in a tetragonal structure (Space group $I4/m$) at room temperature [Fig. 1] as reported in Refs. 1 and 2. We have prepared two samples: sample S1, starting from MnO and sample S2, starting from MnO_2 . It was found that for the both samples the XRD patterns and microstructure are nearly the same. Sample 2 was prepared in order to check whether there is any possibility of oxygen deficiency induced magnetism in S1. The SEM micrographs confirm the well-sintered nature of the samples with grain sizes of ~ 1 – $10 \mu\text{m}$ [Fig. 2]. The EDAX analysis ascertains the nominal composition. [During the

course of the nuclear and magnetic structure analysis with neutron diffraction data it was found that the obtained data could be fitted to both tetragonal (space group, $I4/m$) and cubic (space group, $\text{Fm}\bar{3}m$) structures. Both the tetragonal ($I4/m$) and monoclinic ($\text{P}2_1/n$) structures result from a small distortion of the cubic ($\text{Fm}\bar{3}m$) structure. Phase transformations at elevated temperatures among these three structures have been reported in several double perovskite oxides, such as Sr_2MnWO_6 and A_2CoBO_6 (where $A = \text{Sr, Ca}$; $B = \text{Te, W}$)^{4–6}.

The temperature dependent magnetization, $M(T)$, of $\text{Sr}_2\text{TiMnO}_6$ indicates a slope change at ~ 45 K with a weak cusp centered at 15 K [Fig. 3]. In a field of 10 mT, the zero-field-cooled (ZFC) and field-cooled (FC) magnetization bifurcate well above T_C , suggesting the presence of possible competing interactions and short range correlations [inset in Fig. 3].

The magnetization versus the field, $M(H)$, isotherm at 5 K shows non-negligible hysteresis owing to the ferromagnetic (FM) correlations present in the sample as is evident from the $M(T)$ data. The magnetization does not saturate even in a 7 T field [Fig. 4]. The magnetic moment value at 5 K in 7 T field is only $\sim 0.23 \mu_B/\text{F.U.}$ Both samples, S1 and S2, displayed similar magnetic behavior. The previous report suggested that this system could be ferrimagnetic based on the ZFC-FC difference.²

In order to understand the nature of magnetism in this oxide, powder ND experiments were performed at 300 K and at 12 K [Figs. 5(a) and 5(b)]. Refinement of the 12 K data shows no deviation from the cubic double perovskite structure, i.e., no peak splitting or high angle peak broadening is observed. The oxygen site is found to contain a 3% excess (or comparable cation deficiency), which is a result similar to that observed in many simple perovskite manganites [Tables I and II]. The magnetic structure was refined in the space group $\text{P}-1$, allowing for complex magnetic structures to be modeled and the positions of the reflections in that space group are marked in Fig. 5(b). However, no intensity was observed at any position other than those corresponding to the original cubic structure. The magnetic structure appears to be a simple

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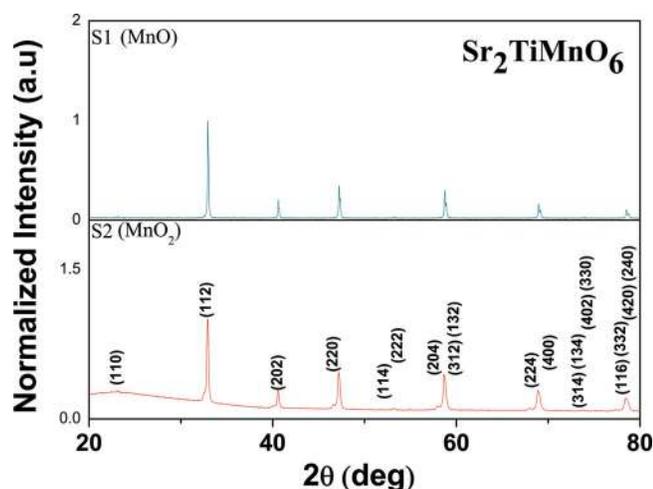


FIG. 1. (Color online) Powder x-ray diffraction patterns of $\text{Sr}_2\text{TiMnO}_6$ at room temperature.

antiferromagnetic (AFM), with the Mn atoms at $(0.5, 0, 0)$ and $(0, 0.5, 0)$ antiparallel to those at $(0.5, 0.5, 0.5)$ and $(0, 0, 0.5)$. In other words, the structure has ferromagnetic planes antiferromagnetically coupled along the direction of the moment. This should result in a tetragonal distortion, but the magnitude of the distortion is apparently too small to detect. The moment at 12 K is about $0.61 \pm 0.14 \mu_B$ per Mn ion, which is quite small. But, the ND measurements were made only 2 K below T_N and it is possible that the saturation moment is significantly larger. The χ^2 for the pattern, 2.02, is quite good for a pattern with the high peaks seen here, but the R_{mag} (84.5) is large due to the very small magnetic contribution and the overlap of nuclear and magnetic intensity.

X-ray photoelectron spectroscopy studies confirmed a 4+ state for Ti and Mn ions in $\text{Sr}_2\text{TiMnO}_6$.¹ The antiferromagnetic superexchange interactions between Mn^{4+} ions mediated by Ti^{4+} and oxygen anions could play a dominant role in this oxide. This could explain the observed $M(H)$ with small magnetic moment and no saturation. In the cubic structure, the mixing of Ti-Mn sites is possible. Such site

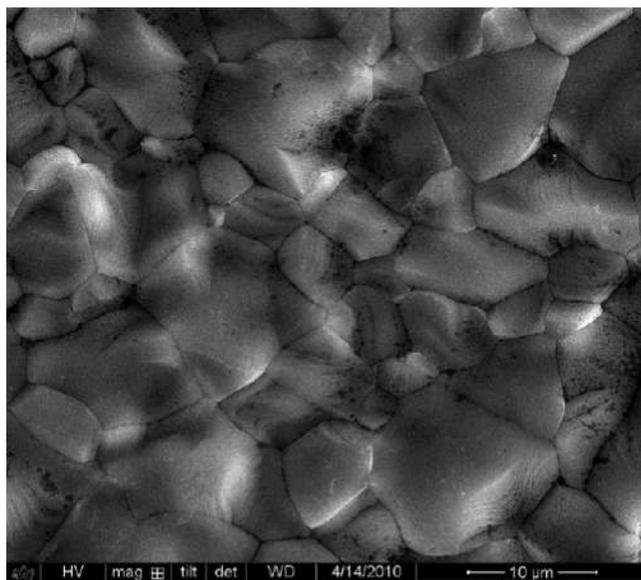


FIG. 2. Scanning electron micrograph (SEM) of $\text{Sr}_2\text{TiMnO}_6$.

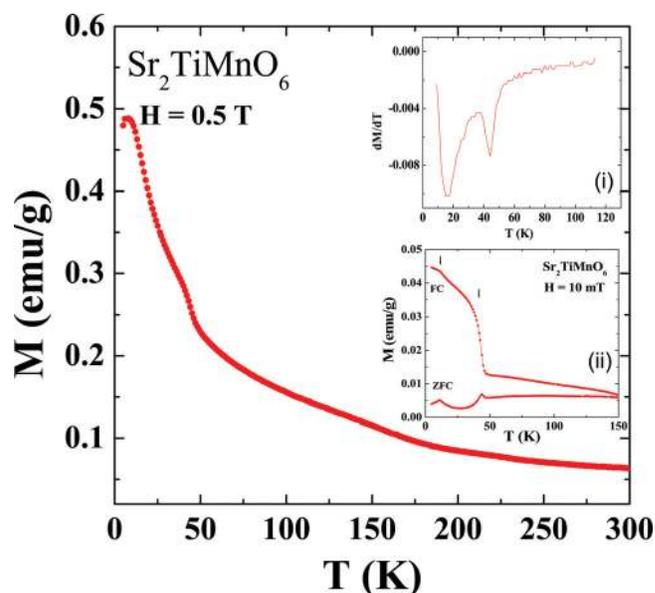


FIG. 3. (Color online) Magnetization vs temperature of $\text{Sr}_2\text{TiMnO}_6$ in 0.5 T field [Inset (i) shows a derivative plot of temperature dependence of magnetization in 0.5 T. Inset (ii) shows the zero-field-cooled (ZFC) and the field-cooled (FC) magnetization of $\text{Sr}_2\text{TiMnO}_6$ in 10 mT field].

mixing can lead to the difference between low field ZFC and FC magnetization. This difference in the ZFC and FC states could also arise from weak ferromagnetism originating from oxygen vacancies, if any, in the system, leading to a slight competition with the otherwise robust AFM interactions between Mn^{4+} ions. In addition, the neutron evidence of FM layers coupled by AFM interactions could also explain the weak FM interactions observed in this system.

In summary, the magnetic properties of the $\text{Sr}_2\text{TiMnO}_6$ oxide could be explained by dominant AFM interactions between Mn^{4+} ions mediated by nonmagnetic Ti^{4+} and oxygen ions superimposed by short-range FM interactions. The ND study indicates possible antiferromagnetic ordering of Mn moments with $\sim 0.5 \mu_B$ within statistical accuracy.

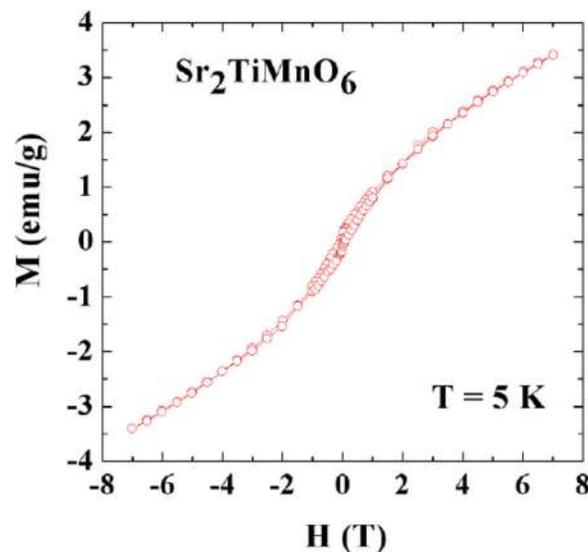


FIG. 4. (Color online) Magnetization vs field of $\text{Sr}_2\text{TiMnO}_6$ at 5 K in fields up to 7 T.

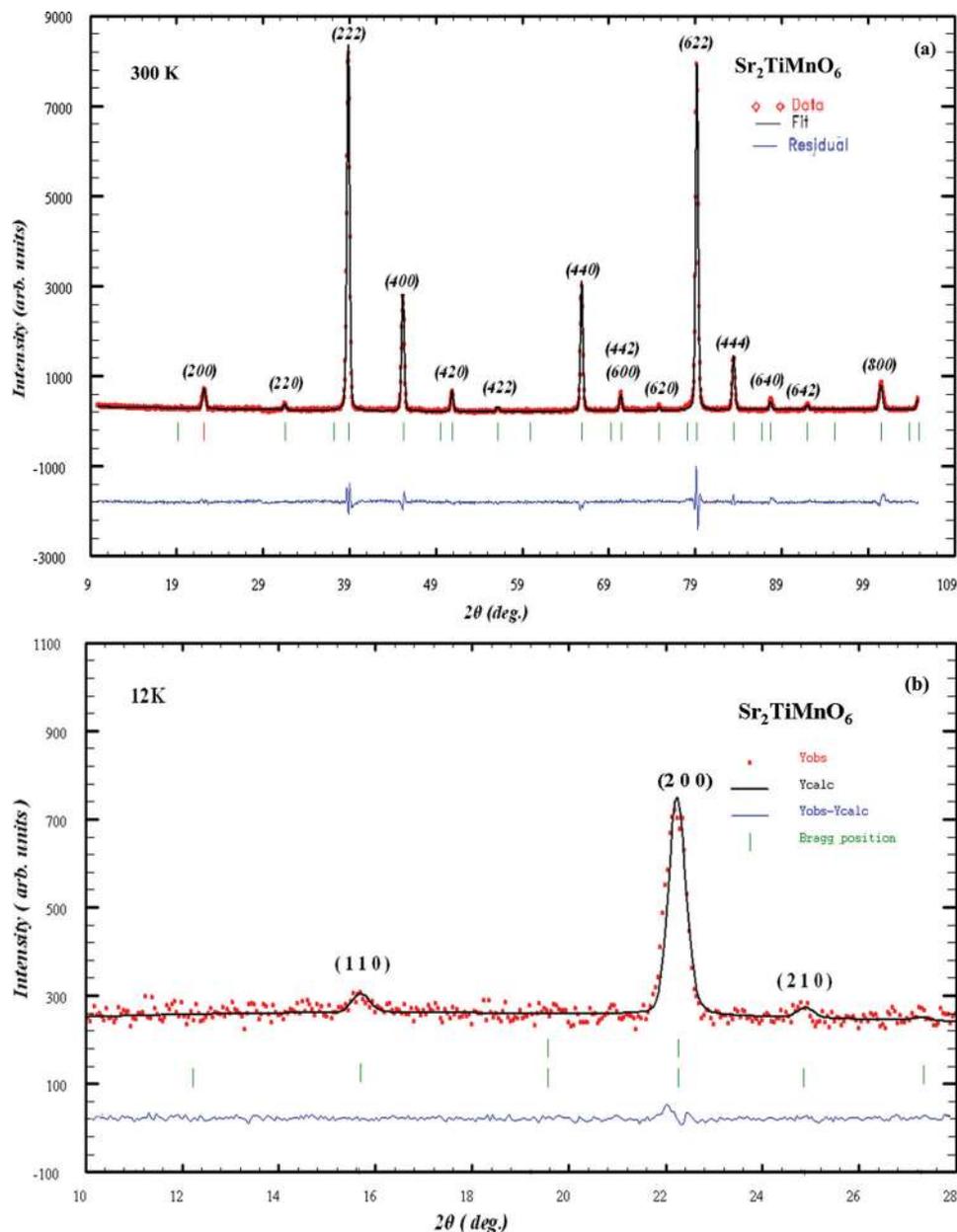


FIG. 5. (Color online) (a) Neutron diffraction data [red (diamond) symbols] and the Rietveld fit for the nuclear reflections (black line) at 300 K. The residual is shown in blue (bottom line). The top row of green tick marks shows the positions of the nuclear reflections. (b) Neutron diffraction data and Rietveld fit for the magnetic and nuclear reflections at 12 K.

TABLE I. The refined structural parameters of $\text{Sr}_2\text{TiMnO}_6$ at 300 K using the Rietveld method. Chemical cell: space group: Fm-3m (cubic). Cell parameters: $a = 7.69308 \text{ \AA}$, $R_p = 5.73$, $R_{wp} = 7.34$, $R_{Bragg} = 4.39$, $\chi^2 = 2.32$.

Atom	Positions	x	y	z	B (\AA) ²	Occupancy
Sr	8c	0.25	0.25	0.25	0.194(50)	0.041 7(50)
Ti	4a	0.00	0.00	0.00	0.240(99)	0.020 8(0)
Mn	4b	0.50	0.50	0.50	0.320(59)	0.020 8(0)
O	24e	0.250 1(17)	0.00	0.00	0.387(32)	0.128 4(8)

R.N. thanks IITMadras for project support under a New Faculty Research Grant. The authors thank NFMTTC and Metallurgy, IITMadras for extending their SEM-EDAX facilities.

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TABLE II. The refined structural parameters of $\text{Sr}_2\text{TiMnO}_6$ at 12 K using the Rietveld method after adding the magnetic phase in the refinement. Chemical cell: space group: Fm-3m (cubic), $a = 7.679721 \text{ \AA}$, $R_p = 5.68$, $R_{wp} = 7.32$, nuclear R-factor = 3.94, magnetic R-factor = 84.5, $\chi^2 = 2.02$.

Atom	Positions	x	y	z	B (\AA) ²	Occupancy
Sr	8c	0.25	0.25	0.25	0.154(41)	0.041 7(50)
Ti	4a	0.00	0.00	0.00	0.223(91)	0.020 8(0)
Mn	4b	0.50	0.50	0.50	0.300(53)	0.020 8(0)
O	24e	0.2502(18)	0.00	0.00	0.312(39)	0.128 4(8)

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