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Structural and magnetic properties of $FeCr_2S_4$ spinel prepared by field-activated sintering and conventional solid-state synthesis

V. Zestrea · V. Y. Kodash · V. Felea · P. Petrenco ·
D. V. Quach · Joanna R. Groza · Vladimir Tsurkan

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Abstract We report on the fast preparation of the ternary magnetic semiconductor spinel $FeCr_2S_4$ using the Field-Activated Sintering Technique (FAST). The structural (X-ray) and magnetic (Squid) characterization demonstrates a similarity of the properties of the FAST crystals and those prepared by conventional solid-state synthesis. Residual structural disorder in FAST samples has a pronounced influence on the ferrimagnetic–paramagnetic transition and the orbital ordering at low temperatures.

Introduction

Ternary magnetic oxides and chalcogenides crystallizing in the spinel structure have attracted recently considerable attention both from theoretical and experimental point of view. Within the last decade a number of new physical phenomena were discovered in these compounds, like colossal magneto-resistance [1], heavy-fermion behavior [2], complex spin order and spin dimerization [3–5], spin-orbital liquids [6], and orbital glasses [7, 8], multiferroic behavior related to coexistence of ferromagnetism and ferroelectricity and colossal magneto-capacitive coupling [9–11]. These novel phenomena present an increased interest for spintronic and advanced multifunctional device applications.

The phase purity and non-stoichiometry appear to be ones of the most important problems in materials science of complex materials. Spurious phases and deviations from the stoichiometry considerably complicate the preparation procedure of the pure compounds and have a pronounced effect on their properties. For the ternary chalcogenides, and particularly sulfides, the temperature of conventional solid-state synthesis in closed systems is additionally limited by high vapor pressure of sulfur and usually does not exceed 700–750 °C. At these temperatures the interaction of the initial reactants (either pure elements or binary sulfides) is rather slow. As a result, in order to reach complete reaction and to obtain of the ternary phase, several synthesis cycles with long homogenization heat treatment (on the order of several weeks and even months) are usually necessary. Therefore, the alternative methods for preparation of such compounds are strongly desirable. One of such promising methods is the Field-Activated Sintering Technique (FAST), also known as Spark Plasma Sintering (SPS). FAST/SPS is a novel effective method for fast preparation of a variety of different types of materials [12, 13]. This method utilizes a pulsed DC voltage applied to powders under a modest pressure (<100 MPa). Due to direct heating, the heating rate may reach very high values (up to 1,000 K/min) and the total synthesis time is of the order of minutes. The FAST processing has been proven as highly effective for reactive sintering, i.e., simultaneous synthesis and sintering. FAST was successfully applied for the synthesis of a number of binary compounds and ternary oxides such as MgB_2 from constituent elements [14], BPSCCO superconductors [15] and perovskites from a mixture of oxide powders [16]. In addition, a considerable activation of the reaction between Al_2O_3 and TiO_2 to form Al_2TiO_5 (tialite) was shown during sintering under applied electrical field in comparison with conventional sintering [17].

V. Zestrea · V. Y. Kodash · P. Petrenco ·
D. V. Quach · J. R. Groza
Department of Chemical Engineering and Materials Science,
University of California, Davis, CA 95616, USA

V. Zestrea · V. Felea · V. Tsurkan (✉)
Institute of Applied Physics, Academy of Science of Moldova,
Chisinau 2028, Republic of Moldova
e-mail: vtsurkan@yahoo.co.uk

Here, we present the results on the preparation of the ternary magnetic sulfide spinel $FeCr_2S_4$ using FAST. We analyze the structural and magnetic properties of the grown samples and compare them with those of the $FeCr_2S_4$ samples synthesized by conventional solid-state reaction method.

Experimental

To prepare the sulfide spinel by FAST, powders of commercial binary compounds FeS (99.9% metal basis), and Cr_2S_3 (99% metal basis) were mixed in “U.S. StoneWare” mill using iron balls. FeS and Cr_2S_3 powders were mixed for 44 h. Such a preliminary grinding was necessary to reduce the grain size of the starting powders and to enhance their reactivity. The $FeCr_2S_4$ sample was sintered at 1,000 °C using a FAST unit (Sumitomo, Model 1050, Coal Mining Company, Tokyo, Japan) with pulsed DC voltage. The pulsing cycle is 12 on and 2 off, with a duration of each pulse of 3.3 ms. Powders were loaded into a graphite die-and-punch unit with a diameter of 19 mm. A vacuum of 3 Pa and a uniaxial pressure of 45 MPa were used in all experimental runs. The temperature was measured by a thermocouple inserted into the hole in the wall of the die. The sample was heated in two steps firstly to 970 °C in 5 min then to avoid overheating to 1,000 °C in 1 min and maintained at 1000 °C for 10 min. Total time of sample sintering was 16 min.

The conventional solid-state synthesis of $FeCr_2S_4$ was performed from the high purity Fe (99.99%) and Cr (99.99%) powders and elemental S (99.999%) in a closed quarts ampoules at 750 °C. Four successive sintering cycles with the total time of about 1 month were necessary to reach full reaction and to eliminate the spurious binary sulfides.

The X-ray diffraction analysis was performed using a Scintag XDS 2000 diffractometer with Cu Kα radiation. The X-ray data were analyzed by standard Rietveld refinement using the FULLPROF program [18]. The microstructure of the synthesized compounds was studied utilizing an FEI XL30 SEM scanning electron microscope. The chemical composition of the samples was checked by EDX analysis. Magnetic properties were measured using a commercial SQUID magnetometer MPMS-5 (Quantum Design) in the temperature range $2\ \text{K} \le T \le 400\ \text{K}$.

Results and discussion

X-ray diffraction of the $FeCr_2S_4$ samples prepared by FAST revealed nearly single-phase ternary compound. As a secondary phase, Cr_2O_3 impurity was found at about 6 mol%. This oxide, however, did not form during the sintering step, but was also found in the starting binary chromium sulfide (Cr_2S_3). The results of the EDX analysis of the chemical composition of the “as-sintered” FAST sample are given in Table 1. The data are averaged over 10 measurements on the random areas of 3 μm × 3 μm and on a larger area of 500 μm × 500 μm. The composition of the main phase $FeCr_2S_4$ was close to the stoichiometric one within the accuracy of the measurements. An additional treatment of the “as-sintered” FAST sample in a sulfur atmosphere at temperature of 750 °C for 1 week was found to reduce the amount of the oxide impurity.

Representative X-ray diffraction profiles for the samples prepared by different methods together with the Rietveld refinement and the difference pattern are shown in Fig. 1. Within the Rietveld refinement, 12 parameters have been fitted: scale factor, zero point shift, resolution parameters, lattice constant, sulfur positional parameter *x*, and isotropic temperature factors for Fe, Cr, and S ions. The refined structural parameters are given in Table 2. The refinement shows that the values of the lattice parameter and of the sulfur positional parameter (the later being related to deviation from the ideal cubic position) are very close for the samples prepared by conventional and FAST techniques. We must note, however, the nearly two times larger values of the width of the diffraction lines and enhanced values of the isotropic temperature factors (Table 1) for all ions in “as-sintered” sample prepared by FAST compared to those for the conventional synthesis (CS). This might be related to strong deviation from the equilibrium conditions during the FAST sintering which results in residual structural disorder. Average crystallite size estimated from the Rietveld-refined linewidths of the diffraction patterns is of the order of 40 nm for the FAST sample and is nearly two times smaller than that of the CS sample. Post-sintering annealing of the FAST sample in sulfur atmosphere, which probably promotes relaxation, increases the crystallite size and reduces the values of the temperature factors approaching them to those of the conventional synthesis. However, the atomic structure of the FAST sample is yet not fully relaxed, even after this post-sintering annealing. It is important to mention also the much higher values of the

Table 1 Results of the EDX analysis of the composition of the $FeCr_2S_4$ samples prepared by the FAST method

Element (at.%)	Measurement area (μm^2)		Stoichiometry (theoretical)
	3 × 3	500 × 500	
Fe	12.5	11.4	14.3
Cr	30.0	30.5	28.6
S	52.8	50.3	57.1
O	4.7	7.8	–

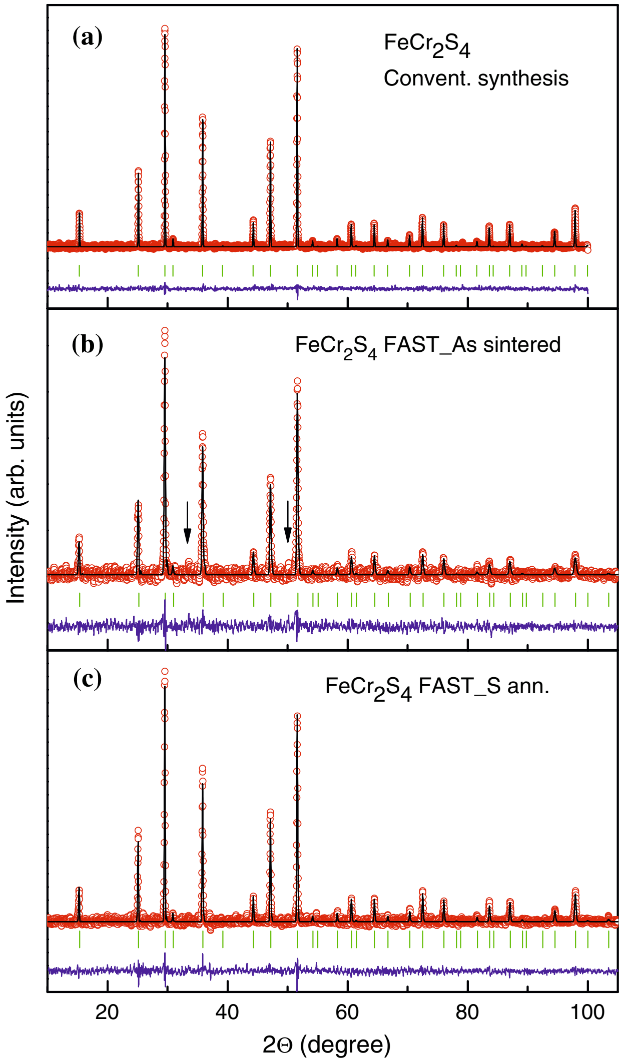


Fig. 1 X-ray diffraction profiles of $FeCr_2S_4$ samples prepared by different methods: (**a**) conventional solid-state synthesis, (**b**) and (**c**) by Field-Activated Sintering Technique, "as-sintered" and annealed in sulfur, respectively. The measured intensities (red open circles) are compared with the calculated profile using Rietveld refinement (black solid line). Bragg positions of the normal cubic spinel structure are indicated by vertical (green) bars and the difference pattern is shown by the bottom thin (blue) solid line. Arrows show the spurious phase in FAST as-sintered sample

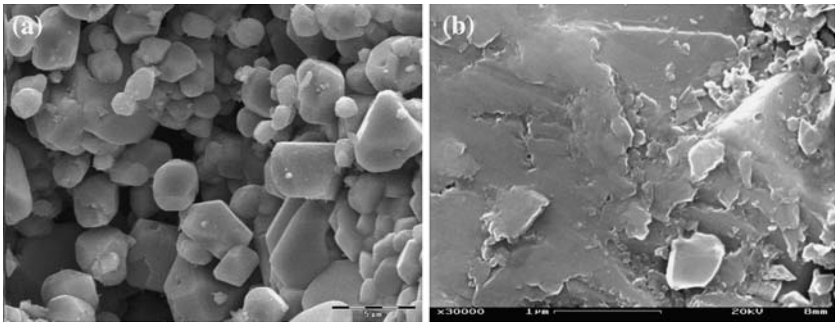
background and of the residuals χ^2 and *R*-factors for the FAST samples compared to CS sample which are also can probably be attributed to deviation from the equilibrium during the FAST synthesis. Additional annealing in sulfur reduced the amount of the spurious oxide phase and gives the narrower diffraction lines in the equilibrated sample.

The SEM images for two different types of samples are presented in Fig. 2. $FeCr_2S_4$ prepared by conventional synthesis is porous and consists of an agglomerate of grains of well-shaped octahedra and plates with a dimension between 2 and 5 μm. About 200 grains were counted

Table 2 Lattice constants *a*, sulfur positional parameter *x* in fractional coordinates (f.c.), and temperature factors of Fe, Cr, and S ions of $FeCr_2S_4$ samples obtained by Rietveld analysis

Sample $FeCr_2S_4$	Lattice parameter (Å)	Sulfur positional parameter (f.c.)	Temperature factors (Å^2)			R_{Bragg}	R_f	Crystallites size (nm)
			Fe	Cr	S			
Convent. synthesis	10.007 (1)	0.260 (1)	1.20 (9)	0.70 (10)	1.20 (10)	4.86	3.90	75–80
SPS_"as-sintered"	10.008 (1)	0.258 (1)	2.80 (19)	2.27 (21)	2.31(18)	16.8	11.7	40–45
SPS_annealed in sulfur	10.004 (1)	0.258 (1)	1.75 (15)	1.14 (10)	1.72 (16)	13.0	8.88	60–65

Fig. 2 (**a**) Microstructure of $FeCr_2S_4$ sample prepared by conventional synthesis. (**b**) Microstructure of $FeCr_2S_4$ sample prepared by FAST



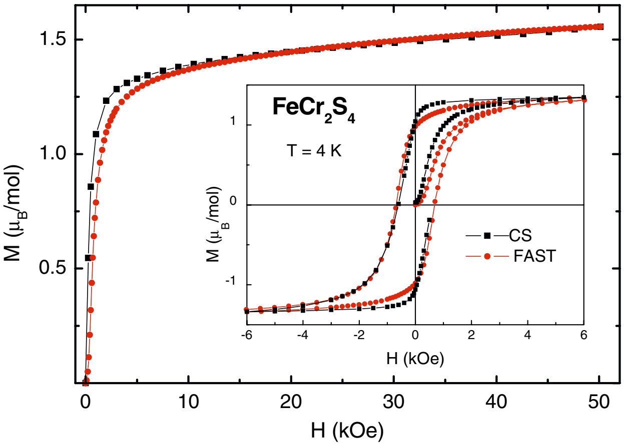


Fig. 3 Magnetization curves for the samples prepared by Field-Activated Sintering Technique (FAST) and conventional synthesis (CS) measured at a temperature of 4 K. *Inset*: Hysteresis loops at 4 K

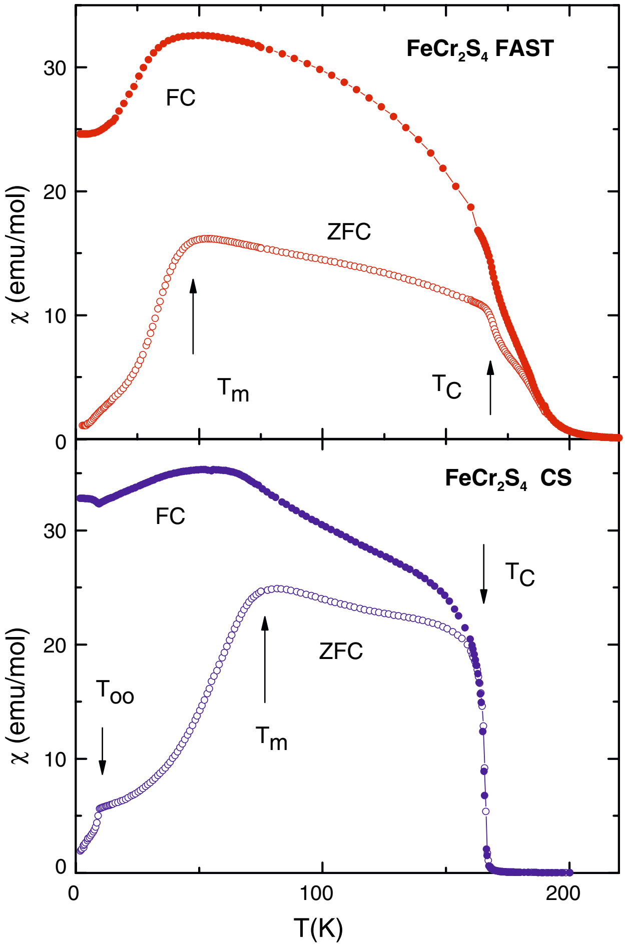


Fig. 4 Magnetic susceptibilities of the samples prepared by Field-Activated Sintering Technique (FAST) and conventional synthesis (CS) measured in a field of 50 Oe in zero-field cooled (ZFC) and field cooled (FC) regime. The arrows indicate the magnetic anomalies at the Curie temperature T_C, the temperature T_m, and the orbital ordering at T_{OO}

and the average grain size was 2.5 μm with a standard deviation of 1 μm. There are also some larger grains at some random locations. In contrast, FAST sample shows almost no porosity, which is consistent with a density close to the single crystalline samples (3.84 g/cm^3). The visible grains of the FAST sample have a size varying in a larger range than conventional sample including sub-micrometer particles.

The magnetization curves for two types of prepared samples as measured at a temperature of 4 K are shown in Fig. 3. Both samples show a similar behavior of magnetization M in high magnetic fields with a value of saturation magnetization typical for polycrystalline $FeCr_2S_4$. The inset of this figure presents the hysteresis loops measured for these samples which again indicate their very close values of the remnant magnetization and coercitive force. Slight difference in M in low fields for the FAST and CS samples can be connected with the difference in demagnetizing coefficient due to different sample shape and possible influence of the surface anisotropy due to difference in the grain size and their distribution.

Magnetic susceptibilities of the FAST and CS samples in low field (50 Oe) are shown in Fig. 4. They demonstrate all prominent magnetic irreversibility features found earlier in $FeCr_2S_4$ single crystals [19, 20] and attributed to spin and orbital degrees of freedom. The ferrimagnetic transition at around $T_C = 165$ K in the FAST sample is less sharp compared to the CS sample. This may be ascribed to structural disorder present in the FAST sample, which emphasizes its significant influence on the critical behavior.

The second magnetic anomaly at T_m in the FAST sample is shifted to lower temperatures compared to that of the CS sample and correlates well with that observed in the $FeCr_2S_4$ single crystals [21]. In addition, the third magnetic anomaly at $T_{OO} = 10$ K related to orbital ordering [22] is not present in the FAST sample similarly to that in non-stoichiometric $FeCr_2S_4$ single crystals [8]. This indicates that the state of the orbital glass recently proposed for this compound [7, 8] must be also attributed to a mechanism related to structural disorder.

Conclusion

Using Field-Activated Sintering we successfully prepared the nearly single-phase magnetic spinel $FeCr_2S_4$ in a 300 shorter time compared to that of conventional solid-state synthesis. The structural analysis and magnetic characterization of the prepared samples show similar properties between samples prepared by FAST and conventional techniques. Residual structural disorder present in the FAST samples has a pronounced influence on the ferrimagnetic–paramagnetic transition at T_C and suppresses the orbital ordering at low temperatures.

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