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# Order–disorder at Fe sites in $\text{SrFe}_{2/3}\text{B}''_{1/3}\text{O}_3$ ( $\text{B}'' = \text{Mo}, \text{W}, \text{Te}, \text{U}$ ) tetragonal double perovskites

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## Abstract

We have prepared  $\text{SrFe}_{2/3}\text{B}''_{1/3}\text{O}_3$  ( $\text{B}'' = \text{Mo}, \text{U}, \text{Te}, \text{and W}$ ) double perovskites in polycrystalline form by ceramic methods. Phases with  $\text{B}'' = \text{U}, \text{Te}$  and  $\text{W}$  have been studied by X-ray powder diffraction and the results have been compared with neutron diffraction data available for  $\text{B}'' = \text{Mo}$ . At room temperature, the stoichiometric samples crystallize in the tetragonal crystal system (space group  $I4/m$ ,  $Z = 4$ ). Cell parameters when  $\text{B}'' = \text{U}, \text{Te}$  and  $\text{W}$  are  $a = 5.6936(1) \text{ \AA}$ ,  $c = 8.0637(1) \text{ \AA}$ ;  $a = 5.5776(1) \text{ \AA}$ ,  $c = 7.9144(3) \text{ \AA}$  and  $a = 5.5707(3) \text{ \AA}$ ,  $c = 7.9081(5) \text{ \AA}$ , respectively.

The Mössbauer spectra at room temperature for all compounds show hyperfine parameters belonging to two  $\text{Fe}^{3+}$  sites located at lattice positions with different degrees of distortion. This is in agreement with diffraction data that indicate that the series of compounds display different degrees of Fe-site disorder, which increases in the following sequence:  $\text{Mo} < \text{U} < \text{Te} < \text{W}$ .

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## 1. Introduction

The discovery of tunneling magnetoresistance (TMR) at room temperature and at low-magnetic fields in the ordered ferrimagnetic metallic double-perovskite  $\text{Sr}_2\text{FeMoO}_6$  [1] and structural related compounds [2–4] has shown the great potentiality of this oxide for magnetic recording compared to manganites for which the appearance of intergrain TMR is much smaller and requires to work below room temperature [2].

Further studies on other members of the  $A_2\text{B}'\text{B}''\text{O}_6$  ( $\text{AB}'_{1/2}\text{B}''_{1/2}\text{O}_3$ ) family seem to indicate that the occurrence of TMR properties is a feature common to some of them [5–8]. Viola et al. have recently reported the induction of colossal magnetoresistance (CMR) in  $\text{Sr}_2\text{CoMoO}_6$  [9] upon chemical reduction, via topotactical removal of oxygen atoms. The most remarkable

result was the induction of magnetoresistance as high as 30% at 12 K for  $H = 9 \text{ T}$ .

The magnetic and magnetotransport properties of these double perovskites are strongly dependent on their  $B$  cations order–disorder. For example, when  $B$  cations are disordered (randomly distributed among the two crystallographic sites), spin-glass-like behavior is observed at low temperatures [10–12], because of the spin frustration due to the structural/chemical disorder in the solid. On the other hand,  $B$ -site ordered ones exhibit ferrimagnetism [3,7], ferromagnetism [4,7] or antiferromagnetism [8,13]. When  $\text{B}''$  is a non-magnetic ion and  $\text{B}'$  and  $\text{B}''$  are in different crystallographic sites (ordered  $B$  sites) an array of  $\text{O}-\text{B}''-\text{O}$  exists between every two magnetic  $B$  ions, and the superexchange interactions, even if weak, are still present. Consequently, an anti-ferromagnetic order is expected with a relatively low ordering temperature. This type of interaction is usually called super–superexchange. Magnetotransport properties are particularly dependent on  $B$  site order–disorder.

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For example, in the case of  $\text{Sr}_2\text{FeMoO}_6$  an almost fully ordered arrangement of Fe and Mo is observed. In a simple picture,  $\text{FeO}_6$  and  $\text{MoO}_6$  octahedra alternate along the three directions of the crystal structure of  $\text{Sr}_2\text{FeMoO}_6$ . Its ferrimagnetic structure can be described as an ordered arrangement of parallel  $\text{Fe}^{3+}$  ( $S = \frac{5}{2}$ ) magnetic moments, antiferromagnetically coupled to  $\text{Mo}^{5+}$  ( $S = \frac{1}{2}$ ) spins [14]. On the other hand, Alonso and co-workers [15] have shown recently that the presence of low-field magnetoresistance (LFM) is associated with antisite disorder at the Fe and Mo sites. This is explained in terms of a spin-dependent crossing of intergranular barriers originated from the presence of antiferromagnetic  $\text{SrFeO}_3$  patches that naturally develop when antisite disorder occurs in the double perovskite. These reasons explain why the study of order–disorder phenomena in double perovskites is of crucial importance to design new magnetoresistant perovskites.

The  $AB'_{2/3}B''_{1/3}O_3$  family has attracted our attention because the majority of their members are isostructural to the analogues of  $A_2B'B''O_6$  ( $AB'_{1/2}B''_{1/2}O_3$ ) series.

The elements Mo, W, Te and U are the only ones in the periodic table with a 6+ oxidation state stable in perovskites under the synthesis conditions (besides  $\text{Re}^{6+}$ ) (see Ref. [16]).  $B''$  cations with a 6+ oxidation state are necessary to stabilize Fe in the 3+ oxidation state in  $\text{SrFe}_{2/3}B''_{1/3}O_3$  perovskites (when no O vacancies are present).

Order–disorder in these structures may be determined by X-ray and/or neutron diffraction and Mössbauer spectroscopy [17]. However, the information about the Mössbauer spectra of these compounds is scarce as far as we know [18,19], in spite of several recent Mössbauer papers that look into the stoichiometry of the  $\text{Sr}_2\text{FeMoO}_6$  phase [20–22].

In this work, we describe the synthesis and the order–disorder phenomena at the  $B$  sites of the series of compounds  $\text{SrFe}_{2/3}B''_{1/3}O_3$  ( $B'' = \text{Mo, U, Te, W}$ ) using Mössbauer spectroscopy and Rietveld analysis of X-ray diffraction patterns of powder samples (except for Mo).

## 2. Experimental section

We have synthesized  $\text{SrFe}_{2/3}B''_{1/3}O_3$  (with  $B''$ : U, Te, and W), via a solid-state reaction of stoichiometric mixtures of high-purity oxides and carbonates. The initial materials were ground in an agate mortar and fired in a Pt crucible in air.  $\text{SrFe}_{2/3}\text{Mo}_{1/3}O_3$  was synthesized via citrate precursor mixtures in stoichiometric amounts of analytical grade  $\text{SrCO}_3$ ,  $\text{Fe}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  dissolved in citric acid. The samples  $\text{SrFe}_{2/3}M_{1/3}O_3$  with  $M$ : Mo, U, W were heated up to 1150°C with intermediate heating and grindings whereas  $\text{SrFe}_{2/3}\text{Te}_{1/3}O_3$  was heated only up to

950°C because  $\text{TeO}_2$  volatilize at higher temperatures. Although the oxygen stoichiometry has not been experimentally verified, because Mössbauer results show that all iron is in the 3+ oxidation state, it is reasonable to assume that there are no oxygen vacancies since, under the synthesis conditions, all  $B''$  ions must stabilize in the 6+ oxidation state, to be consistent with the formula  $\text{SrFe}_{2/3}B''_{1/3}O_3$ .

For the structural refinement powder X-ray diffraction patterns were recorded in a Philips 1710 diffractometer with  $\text{CuK}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation with an exit beam graphite monochromator and Si as an external standard. The  $2\theta$  ranged from 10° to 70° with increments of 0.05° and a counting time of 4 s.

The Fullprof program [23] was used to refine the crystal structures by the Rietveld method. Refinements were carried out always assuming an  $I4/m$  space group and a pseudo-Voigt shape function.

The Mössbauer spectra were taken in a conventional constant acceleration spectrometer of 512 channels with a 50 mCi nominal activity  $^{57}\text{CoRh}$  source in transmission geometry. The absorbers were powder samples of about 36, 22, 30, and 17  $\text{mg/cm}^2$  for the compounds of Mo, U, Te and W, respectively, calculated after the method described by Rancourt et al. [24] that yields the optimum absorber thickness. The parameters were obtained by fitting the data with a least-squares program to sites of static hyperfine field distributions. Isomer shifts were calibrated against an  $\alpha$ -Fe foil at room temperature.

## 3. Results and discussion

In the space group  $I4/m$  there are two possible sites for  $B$  type cations, namely,  $2a$  and  $2b$ . For double perovskites with stoichiometry  $A_2B'B''O_6$  there is the possibility of total order of  $B$  type cations between these two sites, which would correspond to a crystallographic formula  $A_2(B'_{2a}(B''_{2b})O_6$ . For perovskites with stoichiometry  $A_3B'_2B''O_9$ , total order is impossible. Thus, if one wants to assure a certain degree of disorder in this kind of perovskites, the  $A_3B'_2B''O_9$  stoichiometry would be ideal. In order to make a better representation of the distribution of the  $B$  cations in the two crystallographic sites, we can write the crystallographic formula  $A_2(B'_{2a}(B'_{1/3}B''_{2/3})_{2b}O_6$ . This actually corresponds to a situation where site  $2a$  is fully occupied by  $B'$  cations, which is the maximum degree of order attainable for this stoichiometry. A more general situation would be  $A_2(B'_{1-\delta}B''_{\delta})_{2a}(B'_{1/3+\delta}B''_{2/3-\delta})_{2b}O_6$ , where  $0 \leq \delta \leq \frac{1}{3}$ . Thus, if  $\delta = 0$  we have maximum order (but not full order), and if  $\delta = \frac{1}{3}$  we have maximum disorder. The composition for maximum disorder, i.e.  $A_2(B'_{2/3}B''_{1/3})_{2a}(B'_{2/3}B''_{1/3})_{2b}O_6$ , corresponds to  $B$  cations randomly distributed. Based on the preceding discussion we can

define the degree of order (DO) as  $DO = 1 - 3\delta$ . For maximum order  $DO = 1$  and for random distribution  $DO = 0$ . DO values are obtained from the refinements of occupancies of  $B$  cations in  $2a$  and  $2b$  sites.

Rietveld refinements from laboratory X-ray diffraction data are shown in Fig. 1. Cell parameters, cell volume and DO values obtained from the refined occupancies for the different compounds are shown in Table 1. Our results for  $B'' = W$  are in agreement with the structural data recently reported by Ivanov et al.

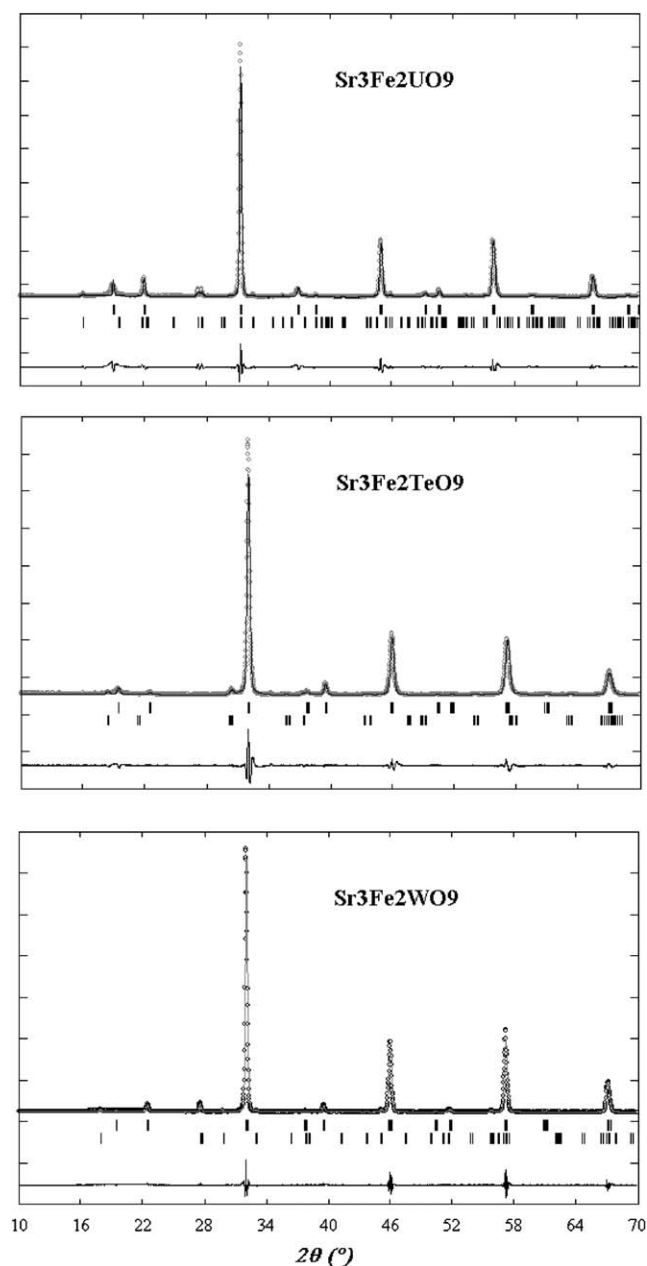


Fig. 1. Observed (circles), calculated (full line), and difference (bottom) XRD Rietveld profiles for  $Sr(Fe_{2/3}B''_{1/3}O_3)$  with  $B'' = U, Te, W$ . The second series of tick marks correspond to the Bragg reflections of the impurity phases.

Table 1

Cell parameters, cell volume and degree of order (DO) for  $SrFe_{2/3}B''_{1/3}O_3$  compounds. Space group  $I4/m$ .  $Z = 4$

Compound	Cell parameters (Å)	Volume (Å) <sup>3</sup>	Degree of order
$Sr_3Fe_2MoO_9^a$	$a = 5.5599(1)$ $c = 7.8493(4)$	242.65(1)	0.60
$Sr_3Fe_2UO_9$	$a = 5.6936(1)$ $c = 8.0637(1)$	261.40(1)	0.53
$Sr_3Fe_2TeO_9$	$a = 5.5776(1)$ $c = 7.9144(3)$	246.21(1)	0.50
$Sr_3Fe_2WO_9$	$a = 5.5707(3)$ $c = 7.9081(5)$	245.41(3)	0.06

<sup>a</sup> Neutron diffraction data from Ref. [25].

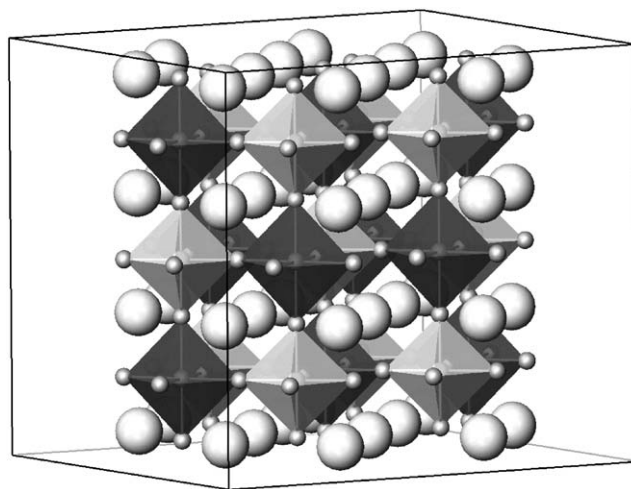


Fig. 2. View of the structure of tetragonal  $Sr(Fe_{2/3}B''_{1/3}O_3)$  with  $B'' = Mo, U, Te, W$ .  $c$ -axis is vertical;  $a$ -axis from left to right. Large spheres represent Sr; small spheres represent O. The corner-sharing  $(B''_{1-\delta}B''_{\delta})O_6$  octahedra at  $2a$  sites (dark) and the  $(B''_{1/3+\delta}B''_{2/3-\delta})O_6$  octahedra at  $2b$  sites (light shaded) are rotated in anti-phase about the  $c$ -axis, in order to optimize Sr–O bond lengths.

[25]. For  $B'' = Mo$  we have used the neutron diffraction data obtained for the same sample [26]. A view of the structure of tetragonal  $Sr(Fe_{2/3}B''_{1/3}O_3)$  with  $B'' = Mo, U, Te, W$  is shown in Fig. 2.

As previously discussed, the assessment of the order-disorder at the structural sites of these oxides is very important to anticipate their magnetic and magneto-transport properties. In our case, the most disordered sample is  $SrFe_{2/3}W_{1/3}O_3$ . The other ones have higher DO.

The Mössbauer spectra at room temperature for all compounds (Fig. 3) show hyperfine parameters (Table 2) belonging to two  $Fe^{3+}$  sites located at lattice positions with different degrees of distortion. Within the statistical uncertainty of the spectra, no  $Fe^{2+}$  ions

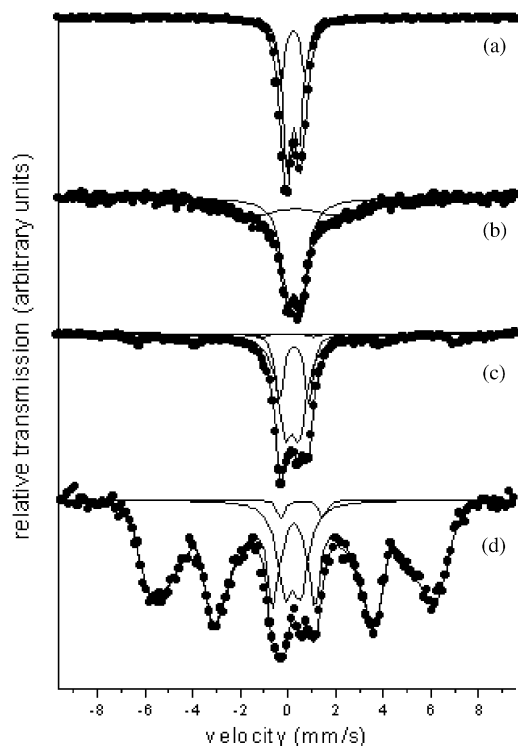


Fig. 3. Room temperature Mössbauer spectra of  $\text{Sr}_3\text{Fe}_2\text{B}''\text{O}_9$  where  $\text{B}''$  is (a) Mo, (b) U, (c) Te, and (d) W. The thicker solid lines are the simulated spectra, least-squares fitted as described in the text. The thinner solid lines are the magnetic and quadrupole components that make up the spectra.

exist in the samples; the isomer shifts values for  $\text{Fe}^{2+}$  found in the literature lie in the range 0.7–1.2 mm/s, while  $\text{Fe}^{3+}$  ions are characterized by isomer shifts between 0.3 and 0.6 mm/s.

The spectrum of the Mo compound does not display magnetically split signals within the statistical errors. The other three compounds exhibit magnetically split signals whose different spectral areas and dispersion are probably related to the increase in crystallographic disorder:  $\text{U} < \text{Te} < \text{W}$ . To arrive at this result, we have made several assumptions.

Based on the values of the Mössbauer linewidths, and considering that the main contribution to the electric field gradient at the Fe sites in closed-shell  $\text{Fe}^{3+}$  ions arises from the lattice term (see below) we assign the smaller linewidths to signals coming from Fe ions located at sites (2b) surrounded by the more homogeneous octahedra at sites 2a. For the Mo compound this is almost the only reasonable assumption coherent with the DO data, and because it shows the lowest  $\text{Fe}^{3+}$  occupancy at site 2a (0.468), it is likely that the spectral area of its magnetic signal is hidden in the  $\approx 9\%$  statistical uncertainty of the background. This tentative assumption shows the trend—which would need to be checked by further experiments—that the Fe atoms located at the 2a sites are the only ones experiencing

Table 2  
Mössbauer hyperfine parameters obtained by the procedure described in the text

$\text{Sr}_3\text{Fe}_2\text{MoO}_9$			
$\Delta_1$ (mm/s)	$\delta_{1\text{Fe}}$ (mm/s)	$\Gamma_1$ (mm/s)	$I_1$ (%)
0.98	0.33	0.36	28
$\pm 0.03$	$\pm 0.01$	$\pm 0.03$	$\pm 6$
$\Delta_2$ (mm/s)	$\delta_{2\text{Fe}}$ (mm/s)	$\Gamma_2$ (mm/s)	$I_2$ (%)
0.49	0.33	0.44	72
$\pm 0.02$	$\pm 0.01$	$\pm 0.02$	$\pm 7$
$\text{Sr}_3\text{Fe}_2\text{UO}_9$			
$\langle H \rangle$ (kOe)	$\delta_{\text{Fe}}$ (mm/s)		$I$ (%)
180	0.40		24
$\pm 20$	$\pm 0.03$		$\pm 9$
$\Delta$ (mm/s)	$\delta_{\text{Fe}}$ (mm/s)	$\Gamma$ (mm/s)	$I$ (%)
0.58	0.39	0.61	76
$\pm 0.01$	$\pm 0.01$	$\pm 0.01$	$\pm 7$
$\text{Sr}_3\text{Fe}_2\text{TeO}_9$			
$\langle H \rangle$ (kOe)	$\delta_{\text{Fe}}$ (mm/s)		$I$ (%)
404	0.37		21
$\pm 7$	$\pm 0.03$		$\pm 4$
$\Delta_1$ (mm/s)	$\delta_{1\text{Fe}}$ (mm/s)	$\Gamma_1$ (mm/s)	$I_1$ (%)
0.40	0.41	0.43	29
$\pm 0.06$	$\pm 0.04$	$\pm 0.03$	$\pm 5$
$\Delta_2$ (mm/s)	$\delta_{2\text{Fe}}$ (mm/s)	$\Gamma_2$ (mm/s)	$I_2$ (%)
1.18	0.42	0.50	50
$\pm 0.09$	$\pm 0.03$	$\pm 0.02$	$\pm 6$
$\text{Sr}_3\text{Fe}_2\text{WO}_9$			
$\langle H \rangle$ (kOe)	$\delta_{\text{Fe}}$ (mm/s)		$I$ (%)
318	0.37		80
$\pm 7$	$\pm 0.01$		$\pm 5$
$\Delta_1$ (mm/s)	$\delta_{1\text{Fe}}$ (mm/s)	$\Gamma_1$ (mm/s)	$I_1$ (%)
0.72	0.33	0.60	8
$\pm 0.04$	$\pm 0.02$	$\pm 0.04$	$\pm 1$
$\Delta_2$ (mm/s)	$\delta_{2\text{Fe}}$ (mm/s)	$\Gamma_2$ (mm/s)	$I_2$ (%)
1.69	0.38	0.71	12
$\pm 0.04$	$\pm 0.02$	$\pm 0.04$	$\pm 1$

hyperfine magnetic fields resolvable at room temperature.

The other three cations, U, Te, and W, display magnetic signals whose spectral areas increase in approximately the same way as the DO. It must be recalled that the Mössbauer area is not only proportional to the Fe atom occupancy but also to the recoil-free fraction at each site, which may vary from compound to compound. Moreover, because the 2a sites of different compounds may have diverse magnetic ordering temperatures, the areas of the magnetically split signals obtained at room temperature are only indicative. In this sense the comparison of X-ray and Mössbauer results should be considered only as semi-quantitative.

The Mössbauer spectrum is the superposition and not the average of the different hyperfine fields sensed by the probes. In particular, the quadrupole splitting is proportional to the electric field gradient, and thus a measure of the degree of the charge distortion around

each atom. For the half-filled  $3d$  shell  $\text{Fe}^{3+}$  ions, its main contribution arises from the arrangements of near and next-near neighbors departing from symmetries, like cubic or octahedral, which do not produce electric field gradients at the iron site. In a perfectly ordered structure, only one quadrupole doublet with a narrow linewidth will be observed for each Fe lattice site. If there is chemical or structural disorder around the iron probe, the different quadrupole splittings will be reflected in broader linewidths. The degree of disorder sensed by the Fe ions at  $2b$  sites (which we assume to yield only quadrupole split doublets at room temperature) is thus approximately reflected by the increasing linewidths of the quadrupole signals. It should be noted that the only broad quadrupole signal required to fit the uranium compound spectrum (on top of the magnetic one) is probably comprising the contribution of two doublets originated in  $\text{Fe}^{3+}$  sites with very similar electric field gradients. The disorder inferred from this assignment in the sequence: Mo, U, Te, W, is thus coherent with the assignment for the magnetic site and also with the X-ray results.

Order–disorder phenomena in perovskites with two or more kinds of  $A$  and/or  $B$  cations are mainly governed by the differences in charge or size of the corresponding cations [27]. In the present series of compounds the charge cannot be responsible for the different DO values since in all cases we have  $\text{Fe}^{3+}$  and  $B''^{6+}$  ions. The differences in size between the different  $B''$  cations based on the ionic radii [28] are too small to explain the different values of DO. Actually, the ionic radii for  $B''^{6+}$  ions in octahedral coordination lie in a narrow range:  $0.70 \text{ \AA}$  ( $\text{Te}^{6+}$ ),  $0.73 \text{ \AA}$  ( $\text{Mo}^{6+}$ ),  $0.74 \text{ \AA}$  ( $\text{W}^{6+}$ ) and  $0.87 \text{ \AA}$  ( $\text{U}^{6+}$ ). Moreover, the ionic radius ( $0.785 \text{ \AA}$ ) for  $\text{Fe}^{3+}$  (HS) in octahedral coordination is in the middle of this range. Consequently, we cannot find a simple explanation for the observed trend in DO values for the different  $B''$  cations based on crystallochemical considerations. Detailed studies including a larger number of different  $B'$  and  $B''$  cations would be necessary to fully understand the order–disorder phenomena in double perovskites.

Although in this work magnetotransport properties have not been measured, because of the reasons mentioned in the introduction, the knowledge of the DO is crucial as an additional information for the understanding of magnetotransport properties. For example, highly ordered double perovskites with  $B'$  cations having high  $S$  values, and  $B''$  cations belonging to the second or third transition metals series with a small number of  $d$  electrons, will favor half-metallic and ferrimagnetic behavior, and, consequently, could give rise to magnetotransport properties. On the other hand, highly disordered perovskites will tend to display spin-glass or ferromagnetic behavior.

#### 4. Conclusions

We have synthesized the series of isostructural compounds  $\text{SrFe}_{2/3}B''_{1/3}\text{O}_3$  ( $B'' = \text{Mo, U, Te, W}$ ) and have refined their structures by the Rietveld method. The diffraction results allowed us to estimate a degree of cation disorder at the two crystallographic inequivalent Fe sites that increases in the sequence  $\text{Mo} < \text{U} < \text{Te} < \text{W}$ . The hyperfine parameters determined from Mössbauer spectra at room temperature show the same increasing disorder, denoting, in addition, some disorder at the  $B''$  sites, which are occupied by  $\text{Fe}^{3+}$  cations.

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