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A Study of Phase Transitions in $\text{Sr}_2\text{FeVO}_{6-\delta}$ by X-Ray Diffraction

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Abstract. The thermal expansion of $\text{Sr}_2\text{FeVO}_{5.6}$ (SFVO) has been measured in the temperature interval 20-300K by the powder X-ray diffraction technique to elucidate the relationship between the crystal symmetry and its magnetic behaviour. The thermal expansion coefficients α_a , α_b and α_c revealed a sudden decrease at 80 K and 240 K, although the crystal symmetry of the compound remained unchanged. Moreover, for $100 \text{ K} < T < 240 \text{ K}$ as well as $T > 270 \text{ K}$, a high anisotropy of the thermal expansion was observed. This effect is expected to be related to changes in the magnetic ordering of the compound studied [1].

1. INTRODUCTION

Compounds with a perovskite crystal structure ABO_3 have been investigated especially in view of the ferroelectric properties that they commonly exhibit. For several years "mixed valency" perovskite, described by the formula $\text{A}_2(\text{BB}')\text{O}_6$ have been known to exhibit ferroelectric properties with magnetic ordering [2-7]. However, extensive data on the relationship between the crystal symmetry and magnetic properties in these compounds are not available. In this work we have complemented the available information on the magnetic properties of SFVO by the results of X-ray diffraction studies.

2. EXPERIMENTAL

The method of preparation of SFVO single crystals has been described elsewhere [8]. Chemical analysis and XPS measurements revealed that our crystals of SFVO were homogeneous and of proper stoichiometry.

The crystallographic system of SFVO was resolved on the basis of X-ray diffraction data on powdered monocrystals, at two temperatures 10 K and 300 K. Moreover, the temperature changes of its lattice parameters were observed. Measurements were carried out on a DRON-2 type diffractometer (K_αFe radiation, 20 mA, 35 kV) equipped with an automatic system enabling scanning of each profile. At a given point the pulses were counted for 10 or 20 seconds, depending on the line intensity and then the pulse counter was moved with a step of 0.01° . The temperature measurements were performed in the range 20K - 300K with the temperature stabilization to within $\pm 1\text{K}$. Temperature changes of the lattice parameters were determined on the basis of the positions of maxima of the profiles: (200), (020), (002). Each profile contained close lines but the applied method of fast recording of the lines permitted accurate determination of the profile maximum.

3. RESULTS AND DISCUSSION

The unit cell parameters were determined from 10 reflection observed for SFVO at 10K and 300K. All the reflections at both temperatures considered are indicative of the monoclinic system with the parameters: $a = 0.7398(2) \text{ nm}$, $b = 0.5032(1) \text{ nm}$, $c = 0.5421(1) \text{ nm}$, $\beta = 95^\circ 50.1'$ at 10K and $a = 0.7415(2) \text{ nm}$, $b = 0.5037(1) \text{ nm}$, $c = 0.5426(1) \text{ nm}$, $\beta = 95^\circ 54.5'$ at 300K, respectively. The values of the lattice parameters determined at 300K are in good agreement with those obtained for single crystals of SFVO [8] at the same temperature. Fig. 1 shows the temperature dependence of the lattice parameters for SFVO. This dependence indicates a multiple transition at 80K, and at about 240K a sudden decrease in the volume of this compound, however, the crystal symmetry remains unchanged.

Figure 1: Temperature dependence of the lattice parameters for $\text{Sr}_2\text{FeVO}_{5.6}$.

Table I lists the anisotropic thermal expansion values of α_a and α_v of SFVO for various of temperature.

Table I. Thermal expansion coefficients α_i $10^6[\text{K}^{-1}]$ and α_v $10^6[\text{K}^{-1}]$ of $\text{Sr}_2\text{FeVO}_{5.6}$

Temperature ranges [K]	α_a	α_b	α_c	$\langle \alpha_i \rangle$	$\langle \alpha_v \rangle$
T<50	7.0	7.0	7.0	7.0	21.0
100<T<240	16.6	4.6	8.5	9.9	29.7
240<T<290	-22.2	11.2	12.0	0.33	1.0

A comparison of the principal coefficients α_a , α_b , α_c at T>50K shows an increasing anisotropy of expansion. Such as increase in the anisotropy of expansion is possible even for T>240K, when the expansion occurs in two directions (b and c) and contraction in the third direction (a). In the first approximation the coefficients of volume expansions are three times greater than those of linear expansion $\alpha_v \approx 3\alpha_i$. The coefficient of volume expansion for SFVO below 240 K is of the same order as that for SrTiO_3 ($\alpha=28.3 \cdot 10^{-6} \text{ K}^{-1}$; 110K<T<300K)[9] and SrZrO_3 ($\alpha=26.3 \cdot 10^{-6} \text{ K}^{-1}$; 298K<T<590K) [10] in a similar range of temperatures, which for ABO_3 perovskites indicates that the influence of the B cation on the thermal expansion is not negligible. Above the temperature of the magnetic transition ($T_M=256 \text{ K}$), the volume expansion of SFVO is very small and has the invar behaviour [11]. An alloy of 34% Ni-Fe (invar) is characterized by a very small coefficient of expansion $\alpha \approx 1 \cdot 10^{-6} \text{ K}^{-1}$ [11] at 300K while Fe and Ni have $\alpha=11\text{-}12 \cdot 10^{-6} \text{ K}^{-1}$ [11]. The anomalous properties of invar are related to the influence of spontaneous magnetostriction compensating the normal Debye thermal expansion. In view of the results obtained we suggested that the perovskite type compound SFVO should be regarded as an invar of a new class.

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