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**STRUCTURAL, MAGNETIC AND ELECTRONIC PROPERTIES
OF VANADIUM-SUBSTITUTED IRON WARWICKITE**

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Up to now, there are only three homometallic warwickites Fe_2BO_4 , Mn_2BO_4 and V_2BO_4 which exhibit quite different magnetic and electronic properties [1–3]. The Fe_2BO_4 shows the monoclinic–orthorhombic phase transition at $T_{CO} = 340$ K associated with charge-ordering of Fe^{2+} and Fe^{3+} ions. The Mössbauer spectroscopy and synchrotron x-ray scattering have revealed both commensurately and incommensurately modulated charge ordered phases at low temperatures ($T < T_{CO}$) and the valence fluctuating states above T_{CO} .

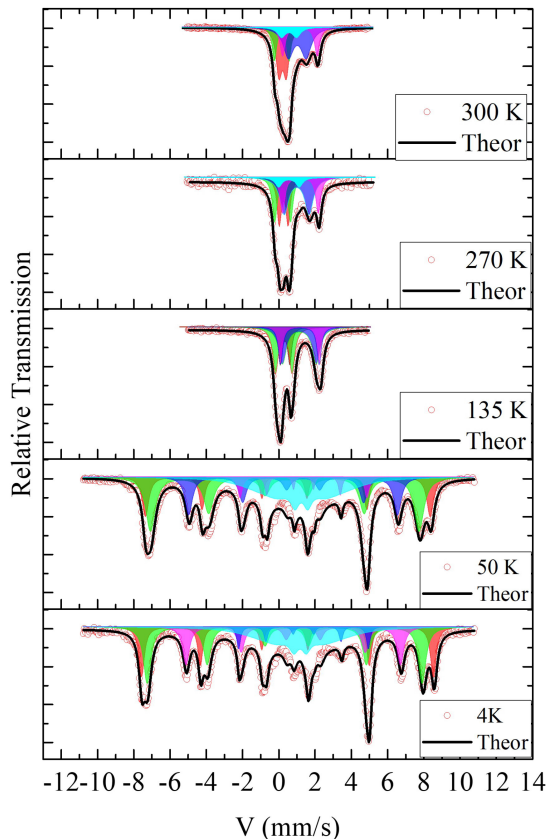


Figure 1. Mössbauer spectra for $\text{Fe}_{2-x}\text{V}_x\text{BO}_4$ ($x = 0.25$) at the temperature range of 4 – 300 K

The single crystals of the vanadium-substituted iron warwickite $\text{Fe}_{2-x}\text{V}_x\text{BO}_4$ ($x = 0.25$) have been synthesized using flux method [4]. The crystallographic structures have been solved in detail by means

of single-crystal x-ray diffraction at 390 and 100 K. The XRD patterns have been refined in a orthorhombic symmetry ($Pnma(62)$) with lattice parameters: $a = 9.2410(11) \text{ \AA}$, $b = 3.1672(3) \text{ \AA}$, $c = 9.3833(12) \text{ \AA}$, $V = 274.63(5) \text{ \AA}^3$ at 100 K and $a = 9.255(4) \text{ \AA}$, $b = 3.1786(14) \text{ \AA}$, $c = 9.401(4) \text{ \AA}$, $V = 276.6(2) \text{ \AA}^3$ at 390 K. Refinements of the occupancies of Fe and V have indicated $(0.87 \cdot \text{Fe} + 13 \cdot \text{V})$ and $(0.88 \cdot \text{Fe} + 0.12 \cdot \text{V})$ at M1 and M2 distinct sites, respectively. The coordination octahedra $(\text{M1})\text{O}_6$ and $(\text{M2})\text{O}_6$ are compressed along the main axis. The mean octahedral bond-lengths $\langle \text{M1-O} \rangle = 2.0929 \text{ \AA}$, $\langle \text{M2-O} \rangle = 2.0866 \text{ \AA}$ at 390 K and 2.0862 \AA and 2.0820 \AA at 100 K are almost intermediate between the expected $\text{Fe}^{2+} - \text{O}$ and $\text{Fe}^{3+} - \text{O}$ bond lengths. This finding suggests that Fe^{2+} and Fe^{3+} ions are distributed over both sites. The main component V_{zz} of the tensor $G_{\alpha\beta}$ of the electrical field gradient has indicated the local distortions of both octahedra almost same at 100 K and the difference increases at the heating.

The Mössbauer spectroscopy has revealed the coexistence of localized (Fe^{2+} , Fe^{3+}) and delocalized ($\text{Fe}^{2.5+}$) iron states (Fig. 1). Namely, five Fe sites (two Fe^{2+} , two Fe^{3+} and one $\text{Fe}^{2.5+}$) exist at room temperature. As temperature decreases the area of $\text{Fe}^{2.5+}$ doublet decreases and below 230 K the delocalized states were not observed. The charge delocalization was found to appear between 230 – 240 K. Below this temperature four iron sites ($\text{Fe}^{3+}:\text{Fe}^{3+}:\text{Fe}^{2+}:\text{Fe}^{2+}$) exist in a 2:1:2:1 ratio. According to the electroneutrality principle, the vanadium enters both in divalent and trivalent states. At low temperatures, the Mössbauer spectra show Zeeman splitting indicating the magnetic ordering of iron ions. Observed temperature of magnetic transition $T_N = 122 \text{ K}$ is lower than that $T_N = 155 \text{ K}$ found for end member Fe_2BO_4 [1]. The values of hyperfine fields obtained at 4 K are 50.1 T, 47.2 T for Fe^{3+} and 36.8 T, 13.2 T for Fe^{2+} , respectively.

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