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Journal of Solid State Chemistry 180 (2007) 2641–2642

JOURNAL OF SOLID STATE CHEMISTRY

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Corrigendum

Corrigendum to “$EuBaFe_2O_{5+w}$: Valence mixing and charge ordering are two separate cooperative phenomena” [J. Solid State Chem. 180 (2007) 148–157]

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Received 11 July 2007; accepted 15 July 2007
Available online 27 July 2007

Abstract

An error in the expression for the Fe^{2+}, Fe^{3+} valence-mixing probability in $R$$BaFe_2O_{5+w}$ is acknowledged and correct formula is derived. The new formula slightly improves the least-squares fit to the experimental concentrations of the Mössbauer component $Fe^{2.5+}$ as a function of the oxygen-nonstoichiometry parameter w for $R = Eu$.
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Keywords: Oxygen nonstoichiometry versus valence-mixing probability

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Formula (3) in Ref. [1] for the probability of the Fe^{2+}, Fe^{3+} valence mixing in $R$$BaFe_2O_{5+w}$ under oxygen nonstoichiometry describes incorrectly the model shown in Fig. 11 of Ref. [1]. The formula starts with the correct term 2(0.5−w), which is the double of the concentration of the minority divalent iron. Not all divalent iron is involved in valence mixing: In addition to the trivial oxidation already expressed in 2(0.5−w), every added oxygen (the probability of its occurring at the given site is w) will face two Fe^{3+} atoms, thus ruining one valence-mixing pair across each of the two adjacent square-pyramidal double layers (up and down along c) by trapping the large Fe^{2+} on the other side of the double-pyramidal apex. The probability of the oxygen’s ruining a valence-mixing pair is therefore 2w, and the probability of not ruining is (1–2w). Because this must not happen on either side along c of an actual valence-mixing pair, the latter probability is squared. The correct formula for the concentration of the valence-mixed Mössbauer component $x_{Fe}^{2.5+}$ as a function of the oxygen nonstoichiometry w is given in Eq. (1),

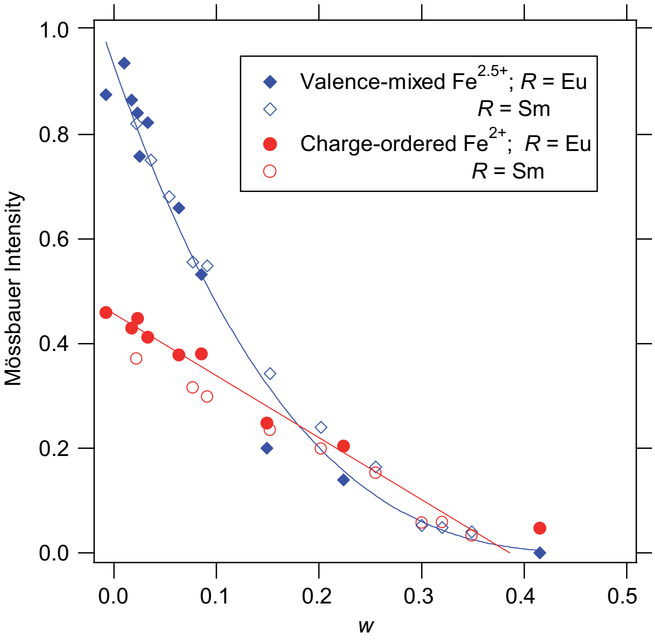

Fig. 1. Mössbauer-based fraction of iron atoms in valence-mixed state at 310 K (full diamonds; curve fitted by Eq. (1)) and fraction of divalent charge-ordered iron atoms at 77 K (bullets; line drawn as a guide for eye). Analogous data for $R = Sm$ from Ref. [2] are in open symbols.

DOI of original article: 10.1016/j.jssc.2006.09.031

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doi:10.1016/j.jssc.2007.07.014

which replaces Eq. (3) in Ref. [1]:

$$x_{\mathrm{Fe}}^{2.5+} = 2(0.5 - w)(1 - 2w)^2 \, P_R. \tag{1}$$

Least-squares fitting for $R = \mathrm{Eu}$ gives $P_R = 0.93(3)$. The new fit is shown in Fig. 1, which replaces Fig. 10 of Ref. [1]. The difference in these two figures is small and none of conclusions in Ref. [1] is affected.

The existence of two or more equally good formulas that describe the probability of valence mixing under oxygen nonstoichiometry in $R\mathrm{BaFe_2O_{5+w}}$, cfr Ref. [2], is not surprising, as they all reflect the general fact that the added oxygen not only alters the valence ratio of $\mathrm{Fe^{2+}}$ and $\mathrm{Fe^{3+}}$, but also ruins the valence-mixing pairs by various scenarios of sterically induced valence trapping.

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