

Electronic State and Local Surrounding of ^{119}Sn in Calcium-Substituted Holmium Orthochromites

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Received October 27, 2016

Abstract—The influence of Ca^{2+} doped into the holmium sublattice on the magnetically active surrounding of Sn^{4+} ions located in the chromium sublattice of $\text{Ho}_{1-x}\text{Ca}_x\text{Cr}_{0.997}\text{Sn}_{0.003}\text{O}_3$ ($x = 0, 0.003$, and 0.1) compounds was studied by ^{119}Sn Mössbauer spectroscopy. At concentrations $[\text{Ca}] = [\text{Sn}] = 0.3 \text{ mol } \%$, an increase was observed in the spectral contribution of Sn^{4+} sites, having the full number of nearest-neighbor Cr^{3+} cations ($n = 6$), where they perceived a magnetic field $H(\text{Sn})_{4.2\text{K}} = 82 \text{ kOe}$, compared to the contribution of the relevant sites in the undoped chromite ($x = 0$). This observation was interpreted as resulting from a reduced probability of appearance of Cr^{3+} vacancies in the nearest surrounding of heterovalent Sn^{4+} ions. For $x = 0.1$, on the contrary, the ^{119}Sn spectrum revealed a reduced contribution from the Sn^{4+} sites with $n = 6$. This evolution is shown not to be due neither to the appearance of Cr^{4+} nor Cr^{6+} ions in the nearest neighborhood of Sn^{4+} in the chromium sublattice to balance the charge deficiency of the Ca^{2+} ions doped into the holmium sublattice. This allowed us to suggest that the observed effect was due to the onset of Sn^{4+} segregations in the structure of $\text{Ho}_{0.9}\text{Ca}_{0.1}\text{Cr}_{0.997}\text{Sn}_{0.003}\text{O}_3$, which contained a far greater amount of Ca^{2+} ions whose charge deficiency was balanced mostly by Cr^{4+} formation. Studies of samples that were prepared under a hydrogen atmosphere revealed the reduction of Sn^{4+} to the oxidation state $+2$, with the concomitant stabilization of the formed Sn^{2+} ions on crystallite surfaces on sites having low coordination numbers.

DOI: 10.1134/S0036023617100126

The elucidation of charge compensation mechanisms upon heterovalent substitutions, used to optimize the functional properties of materials, is one of the important problems of solid state chemistry. Various physical and chemical characterization methods were used to study the effect of heterogeneous substitution on the electrical, magnetic, and other properties of rare-earth orthochromites. One of such methods was the ^{119}Sn Mössbauer spectroscopy, which succeeded in studying many oxide systems, including rare-earth orthochromites [1–4]. Rare-earth orthochromites are antiferromagnetic compounds having a G-type magnetic structure [5]. The Sn^{4+} ions entering Cr^{3+} substitution sites experience spin polarization induced by the neighboring Cr^{3+} spin moments in the $\text{Cr}^{3+}\text{--O}^{2-}\text{--Sn}^{4+}$ chains at temperatures below the Néel point [6]. The changing cationic surrounding of a ^{119}Sn probe atom will affect its magnetic hyperfine interactions, whose analysis will accordingly provide information on the properties of the studied material.

For the development of such studies, of interest are perovskite-like phases of orthochromites where rare-

earth cations are partially substituted by heterovalent alkaline-earth cations M^{2+} . The literature [7, 8] shows no common opinion on the way the M^{2+} charge deficiency is balanced under oxidizing conditions; the charge compensation can be provided by formation of both $\text{Cr}^{4+}(3d^2)$ ions and $\text{Cr}^{6+}(3d^0)$ ions. The appearance of any one of them near ^{119}Sn should be accompanied by a specific change of the Mössbauer spectrum, whose interpretation would make it possible to clarify the mechanism of charge compensation.

On the other hand, because of instability of the higher oxidation states of chromium under reducing conditions, the predominant mechanism of M^{2+} charge compensation may be expected to involve the loss of oxygen producing vacancies V_{O} , which can also affect the spectrum of ^{119}Sn probe atoms.

Here, we present new data on hyperfine interactions of tin ions both in the bulk and on the surface of holmium orthochromite crystals of composition $\text{Ho}_{1-x}\text{Ca}_x\text{Cr}_{0.997}\text{Sn}_{0.003}\text{O}_3$ ($x = 0, 0.003$, and 0.1).