Stability Region of Eu$_{2-x}$Mn$_x$O$_3$+δ Solid Solutions in Air

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Abstract—The homogeneity range of EuMnO$_3$ has been determined using x-ray diffraction analysis of single- and mixed-phase Eu$_{2-x}$Mn$_x$O$_3$+δ samples (0.90 ≤ x ≤ 1.20, Δx = 0.02) prepared from oxide mixtures by solid-state reactions in air between 900 and 1400°C. The results have been used to construct a partial phase diagram of the Eu–Mn–O system in air. The dependences of unit-cell parameters on x and synthesis temperature are presented for the samples synthesized at 1100 and 1400°C and for EuMnO$_3$, respectively. The solubility of europium oxide in EuMnO$_3$ is tentatively attributed to structural defects, and that of manganese oxides is interpreted in terms of structural defects, oxygen nonstoichiometry of europium manganese, the disproportionation reaction 2Mn$^{3+}$ = Mn$^{2+}$ + Mn$^{4+}$, and partial substitution of the resulting Mn$^{2+}$ for Eu$^{3+}$ on the cuboctahedral site of the perovskite-like structure. To check these assumptions, systematic studies of the oxygen nonstoichiometry and structure of Eu$_{2-x}$Mn$_x$O$_3$+δ solid solutions synthesized at different temperatures are needed.

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INTRODUCTION

Rare-earth manganites are now receiving a great deal of attention for several reasons: from attempts to understand the physicochemical and crystal-chemical aspects of the cooperative Jahn–Teller effect [1] to the colossal magnetoresistive response of rare-earth man-

EXPERIMENTAL

We studied phase-pure solid solutions and mixed-phase samples with the general formula Eu$_{2-x}$Mn$_x$O$_3$+δ. The logic behind the choice of sample compositions and synthesis temperatures is clear from Fig. 1.

RESULTS AND DISCUSSION

Our results are displayed in Fig. 1 as a more detailed portion of the phase diagram of the Eu–Mn–O system in air compared to earlier studies [3]. The Eu$_{2-x}$Mn$_x$O$_3$+δ solid-solution region (orthorhombic perovskite-like structure, sp. gr. Pbnm [2, 3, 5]) is labeled O. The horizontals separating phase fields were taken from [3]. In particular, at 1095 ± 5°C in air europium manganese (O-phase) is in equilibrium with EuMn$_2$O$_5$ and β-Mn$_3$O$_4$ [3]. The points in Fig. 1 repre-
sent the present experimental data. The boundaries of the europium manganite field in Fig. 1 are drawn midway between single-phase ($O$) and two-phase ($O + \gamma$-Mn$_3$O$_4$) compositions, as determined by XRD. Attempts to more accurately locate the phase boundaries using the composition dependences of unit-cell parameters for europium manganite in single- and two-phase samples were unsuccessful. As an example, Fig. 2 presents such data for the samples synthesized at 1100 and 1400°C. The inflections that should occur at the boundaries between single- and two-phase regions in the phase diagram cannot be identified in Fig. 2. Note that, in Figs. 2 and 3, the uncertainty in the unit-cell volume is no greater than the size of the points.

At least two features of the data in Fig. 2 warrant attention. First, in the range 1100–1400°C the synthesis (firing) temperature has an insignificant effect on the shape of the composition dependences of unit-cell parameters for Eu$_{2-x}$Mn$_x$O$_{3+\delta}$. Second, the metal composition of Eu$_{2-x}$Mn$_x$O$_{3+\delta}$ ($x$) and synthesis temperature in the range 1100–1400°C have no effect on the $a$ cell parameter to within the present experimental uncertainty, except for the boundary composition Eu$_{0.86}$Mn$_{1.14}$O$_3$. At $x > 1.14$, the solid solution coexists with Mn$_2$O$_3$ ($\gamma$-Mn$_2$O$_3$ at 1100°C and $\beta$-Mn$_2$O$_3$ at 1400°C (Fig. 1)). As shown by repeated syntheses of samples with $x = 1.14$, the anomaly in question is well reproducible. A similar anomaly was observed in the $c$ parameter, which is a weak function of $x$, just as $a$. The present experimental data are insufficient to understand the origin of these anomalies. The composition dependence of $b$ also defies interpretation. To clarify this issue, x-ray structure analysis of Eu$_{2-x}$Mn$_x$O$_{3+\delta}$ is necessary. What matters in the context of this study is that we identified no inflections in the composition dependences of unit-cell parameters for Eu$_{2-x}$Mn$_x$O$_{3+\delta}$, which impeded accurate determination of its composition stability range.

Among the possible reasons for the nonmonotonic behavior of the unit-cell parameters in Fig. 2 are (1) the variation in the oxygen content of Eu$_{2-x}$Mn$_x$O$_{3+\delta}$ with $x$ and (2) the processes that take place during sufficiently slow cooling in the $O + \gamma$-Mn$_3$O$_4$ phase region when the amount of EuMn$_2$O$_4$ resulting from the oxidation of the $O$-phase is too small to be detected by XRD, but the oxidation of europium manganite causes its unit-cell parameters to vary nonmonotonically with composition. Thus, the behavior in question may be due not only to oxygen nonstoichiometry but also to internal quasi-heterogeneity of the material, i.e., the formation of structured regions, without interfaces, in phase-pure Eu$_{2-x}$Mn$_x$O$_{3+\delta}$, which may be enriched in both europium oxide and manganese oxide. Oxygen nonstoichiometry of europium manganite, EuMnO$_{3+\delta}$, was documented by Kasper and Troyanchuk [6]. Indirect evidence that it influences the unit-cell parameters of Eu$_{2-x}$Mn$_x$O$_{3+\delta}$ solid solutions is provided by the data in Fig. 3, which plots the unit-cell parameters of Eu$_{2-x}$Mn$_x$O$_{3+\delta}$ against synthesis temperature. We find a pronounced tendency for the $a$, $b$, and $c$ of europium manganite to increase with firing temperature.

Turning back to Fig. 1, we note that the solubility of europium oxide in europium manganite is independent of the synthesis temperature to within the present experimental uncertainty and slightly exceeds the uncertainty in the Eu$_2$O$_3$ solubility in EuMnO$_3$. Given that europium manganite has a perovskite-like structure, it is easily seen that Eu$^{3+}$ is very unlikely to occupy...