Hexagonal Ferrites in the System Sr-La-Zn-Fe-O Crystal Chemistry and Phase Relations

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Hexagonal ferrites are important permanent magnetic materials. Sr-Hexaferrite (M-type = $SrFe^{3+}_{12}O_{19}$) compounds are generally used for ceramic magnets with high values of saturation magnetization and coercivity force. Nevertheless there are possibilities to enhance their magnetic properties. To reach this aim its fundamental for the understand the phase relations and crystal chemistry of such compounds.

This study deals with co-doping of Sr-Hexaferrite (SrFe₁₂O₁₉) by La³⁺ and Zn²⁺. A suggested substitution formula could be $Sr_1-xLa_xZn_xFe_{12}-xO_{19}$. Different studies of the similar systems like Sr-La-Co-Fe-O do not support this assumption. Besides of Fe^{3+} the divalent iron (Fe^{2+}) is stabilized by Co^{2+} . Therefore, the 1:1 replacement of La^{3+} $+ Zn^{2+}$ instead of $Sr^{2+} + Fe^{3+}$ is not necessarily present and the mechanism of replacement in M-type hexaferrites should be more closely investigated. The knowledge of the correct substitution is essentially for interpretation of magnetic properties.

For the evaluation of phase relations suitable compositions have been prepared. Conventional solid state methods ere applied. Oxide and carbonate powder mixtures were decalcinated, pressed to pellets and equilibrated at chosen temperatures (1200, 1300 and 1380 \pm 5°C) in vertical furnaces in air. Finally the samples were quenched in water. The examination of the phase assemblages by BSE images and characterization by electronprobe microanalysis (EPMA) employing WDX-mode leads to the following conclusions.

The results shows clearly that at the chosen temperatures a quaternary system SrO-La₂O₃-ZnO-Fe₂O₃ can not be assumed. The measured amounts of ZnO are not sufficient to compensate the substitution of Sr^{2+} by La^{3+} . Subsequently it has to be assumed that at all temperatures studied Fe^{2+} is incorporated in the M-type structure. Because of the presence of FeO one has to deal actually with the quinary system SrO-La₂O₃-ZnO-Fe₂O₃. The Fe²⁺ content rises with the temperature. Results of the investigation are shown in the following substitution formulas:

 $\begin{array}{l} Sr_1 - xLa_x Fe^{3+}{}_{12} - xFe^{2+}{}_x - yZn_yO_{19} \text{ with } 0 \leq x \leq 0,8 \text{ and } 0 \leq y \leq 0,6 \text{ at } 1200^\circ C \text{ ,} \\ Sr_1 - xLa_x Fe^{3+}{}_{12} - xFe^{2+}{}_x - yZn_yO_{19} \text{ with } 0 \leq x \leq 1,0 \text{ and } 0 \leq y \leq 0,4 \text{ at } 1300^\circ C \text{ and} \\ Sr_1 - xLa_x Fe^{3+}{}_{12} - xFe^{2+}{}_x - yZn_yO_{19} \text{ with } 0 \leq x \leq 0,9 \text{ and } 0 \leq y \leq 0,4 \text{ at } 1380^\circ C. \end{array}$

Phase relations and crystal chemical aspects in this quinary system due to the modified substitution mechanism will be presented and discussed.

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