JOURNAL OF SOLID STATE CHEMISTRY 12, 270 (1975)

The Structural Behavior of Oxidized Lanthanum Manganite and Related Materials

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Received July 11, 1974

The structure of $LaMnO_{3.12}$ has been investigated (*1*) by powder neutron diffraction and the defect arrangement is best described by $(La_{0.94\pm0.02}\square_{0.06\pm0.02})$ $(Mn^{3+}_{0.745}Mn^{4+}_{0.235}\square_{0.02})O_3$ with partial elimination of La_2O_3 and vacancies on both *A* and *B* sites. Oxidative nonstoichiometry was also observed (*1*) for $LaVO_{3+x}(x \leqslant 0.05)$ and $(Ba_{0.8}La_{0.2})Ti^{4+}O_{3.1}$, but not for Ba-doped $SrTiO_3$, $LaCrO_3$, $LaFeO_3$ or $EuTiO_3$ (at 1200°C). The only previous example of *B*-site vacancies in perovskites ABX_3 maintaining cubic close-packed AX_3 stacking was demonstrated by power X-ray diffraction (*2*) for La-doped $PbTiO_3$ (other perovskite-like materials with *B*-site vacancies are known (*3*, *4*)). A large decrease in radius of the dopant higher oxidation state ion relative to the normal ion seems to be a feature of systems showing oxidative nonstoichiometry, and it is predicted that $KCrF_{3+x}$ may also behave in this fashion. Phases $AB_{1-x}O_3$ (e.g., $La(Mn^{3+}_{1-x}Mn^{4+}_x)_{3/(3+x)}O_3$ $(Ba_{1-x}La_x)Ti_{(1-(x/4)}O_3$) do not seem to have been much studied and might be of interest both structurally and with regard to the effect of nonstoichiometry on magnetic and dielectric properties.

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