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LETTERS TO THE EDITOR

State of Manganese in Solid Solutions of Complex Bismuth Niobates with a Layered Perovskite Structure

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Recently interest has renewed in layered complex bismuth niobates similar to Aurvillis phases, in connection with studies on the effect of defects and constituents metals on the physical properties of these compounds. A number of perovskite-like complex oxides containing manganese have been found to exhibit a high magnetoresistivity [1]. In this context studying the states of manganese atoms and interatomic interactions in perovskite-like structures of various composition appears to be urgent. This work deals with the possibility of formation of solid solutions preserving the layered perovskite structure typical of the $Bi_2BaNb_2O_9$ compound. According to neutron-diffraction data, this structure belongs to the $A2_1am$ space group [2]. Solid solutions $Bi_2BaMn_x \cdot Nb_{2-x}O_9$ ($0.01 < x < 0.25$) were obtained by calcination of stoichiometric amounts of the corresponding metal oxides (in the case of manganese it was Mn_2O_3) at 1220 K in air for 30 h with precalcination of the oxide mixture at 850 K. These solid solutions were obtained in a wide concentration range, which is associated with the isomorphous substitution of manganese atoms for the close-in-size niobium. The X-ray diffraction study of the resulting solid solutions showed that they all crystallize in the $Bi_2BaNb_2O_9$ structure. The unit cell parameters of the solid solutions under study remain almost unchanged as the manganese content increases, and for the most manganese-rich solid solution $Bi_2BaMn_{0.2}Nb_{0.8}O_9$ they are as follows: a 5.571(5), b 0.576(1), and c 25.61(6) Å, which is sufficiently close to the unit cell parameters for $Bi_2BaNb_2O_9$: a 5.567(1), b 5.567(1), and c 25.674(1) Å [2].

The magnetic susceptibilities of the synthesized solid solutions and the diamagnetic matrix $Bi_2Ba \cdot Nb_2O_9$ were measured in the range 77–320 K by the Faraday method. The accuracy of relative measurements was ~2%. The paramagnetic magnetic susceptibilities ε_{Mn}^{para} and the effective magnetic moments μ_{eff} of manganese atoms, corrected for the diamagnetic matrix, were calculated.

The dependence of the paramagnetic magnetic susceptibility calculated per mole of manganese atoms on the manganese content in the solid solutions ($\varepsilon_{Mn}^{para} - x$) is characterized by a maximum near x ~0.06. Note that similar isotherms were earlier obtained for $LaMn_xM_{1-x}O_3$ solid solutions [3]. Extrapolation of ε_{Mn}^{para} to infinite dilution of the solid solution ($x = 0$) allows estimation of the effective magnetic moments of a conventionally single manganese atom. In our case μ_{eff} 5.54 (77 K) and 5.44 BM (293 K) were obtained. It should be borne in mind that manganese in all the valence states possible in the solid solutions under study has orbital nondegenerate or twice degenerate ground states $^6A_{1g}$ [Mn(II)], ^5E_g [Mn(III)], and $^4A_{2g}$ [Mn(IV)]. The effective magnetic moment for these states is independent of temperature, which facilitates subsequent estimations. Extrapolated μ_{eff} are higher than the spin only values for Mn(III) and Mn(IV) (4.9 and 3.87 BM, respectively), but lower than for Mn(II) (5.92 BM). Further information about manganese atomic states was obtained from the ESR spectra. The ESR spectrum of the most dilute solid solution with $x = 0.01$ almost precisely reproduces those obtained earlier for $LaMn_xAl_{1-x}O_3$ solid solutions [3]. It contains a well-resolved sextet from Mn(II) and a stronger broad signal, presumably from Mn(IV). All these data show that in the systems under study, like in cubic $LaMn_xAl_{1-x}O_3$ perovskites, the Jahn–Teller Mn(III) atoms disproportionate into Mn(II) and Mn(IV). The only slight rhombic distortion in the structure of the solid solutions suggests that this disproportionation is not complete, and a small fraction of Mn(III) atoms is still present in the solution. From the viewpoint of structure electroneutrality, substitution of Mn(IV) for Nb(V) is strongly preferred. We estimated the fraction of tetravalent manganese from data for an infinitely dilute solid solution, where the magnetic susceptibility can be represented as a sum of the susceptibilities of single manganese atoms in various valence states. The estimate for the fraction of Mn(IV) in the system under study was ~80%. The minor decrease in the effective magnetic moment with increasing temperature for the infinitely dilute solid solution is attributable to distortion of Mn(IV)-containing octahedra, which results in zero field splitting [4]. The presence of manganese atoms in various valence states seems to be responsible for ferromagnetic exchange interactions within small clusters of dilute solutions and, consequently, for the nonmonotonic variation in the magnetic susceptibility with dilution.

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REFERENCES

1. Jin, S., Teifel, T.H., McCormack, M., Fastnacht, R.A., and Ramesh, R., *Science*, 1994, vol. 264, pp. 413–415.
2. Kennedy, I.J. and Kennedy, B.J., *Solid State Chem.*, 1996, vol. 26, pp. 135–141.
3. Brach, B.Ya., Dudkin, B.N., and Chezhina, N.V., *Zh. Neorg. Khim.*, 1979, vol. 24, no. 8, pp. 2064–2067.
4. Rakitin, Yu.V. and Kalinnikov, V.T., *Sovremennaya magnetokhimiya* (Modern Magnetochemistry), St. Petersburg: Nauka, 1994.