

Structure and Magnetic Properties of Quenched $(\text{Mn}_x\text{Al}_{1-x})_3\text{O}_4$ Spinel and Hausmannites

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Abstract—Manganese aluminate spinels and Hausmannites, namely $(\text{Mn}_x\text{Al}_{1-x})_3\text{O}_4$, with compositions varying between $x = 0.33$ and $x = 1.00$ have been synthesized by sintering of MnO and Al_2O_3 mixtures. Lattice parameters of these spinels and Hausmannites increase linearly with increasing Mn content and depend on neither sintering temperature nor cooling rate. Magnetic hysteresis loops at 5 K show non-saturating features up to 5 T. Ferrimagnetic Curie temperatures of spinels and Hausmannites both increase monotonically with increasing Mn content.

I. INTRODUCTION

In ferromagnetic spinels cation disorder can influence such fundamental magnetic properties as saturation magnetization, exchange couplings and ferromagnetic ordering temperatures. Manganese aluminate spinels[1] are examined as a spinel system with only one magnetic species, Mn (which can exist in more than one valence state). This offers simplicity in a reduced number of exchange parameters required to describe magnetic interactions. On the other hand, the magnetic properties are richer due to non-collinear spin arrangements as observed in Hausmannite (Mn_3O_4)[2].

II. EXPERIMENTAL PROCEDURE

Manganese aluminate spinels and Hausmannites, namely $(\text{Mn}_x\text{Al}_{1-x})_3\text{O}_4$, $0.33 \leq x \leq 1.00$, have been made by a solid state synthesis route. Mixtures of MnO and Al_2O_3 were ground, pressed, and sintered in the spinel phase field or in the spinel and corundum, Al_2O_3 , phase field (Fig. 1). The reaction and sintering step was performed in air at 1473 K for 604.8 ks, 1623 K for 172.8 ks and 1823 K for 86.4 ks with the samples either water- or air-cooled to quench in the high temperature spinel phase. Several samples were chemically analyzed to confirm their metal to oxygen ratio after synthesis. Phases in the quenched and air-cooled samples were identified by X-ray powder diffraction and their magnetic properties were measured in fields between ± 5 T at 5 K for

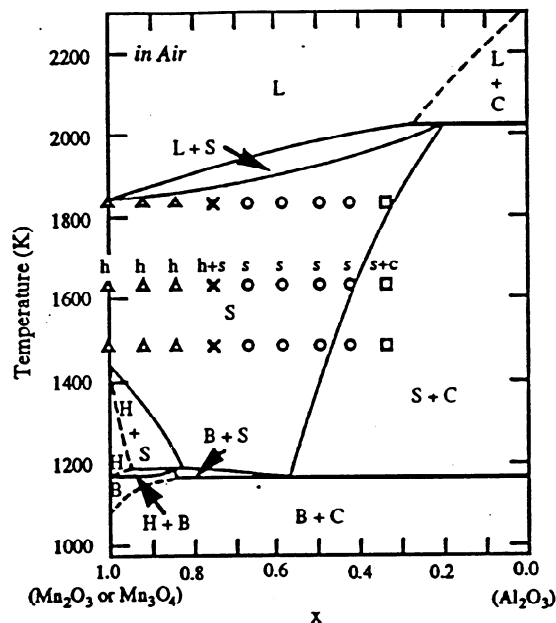


Fig. 1. The phase diagram of Mn_3O_4 - Al_2O_3 [1]. L = liquid, S = spinel, H = Hausmannite, B = Bixbyite, Mn_2O_3 , C = corundum Al_2O_3 . Symbols and lower case letters indicate observed phases by X-ray powder diffraction at room temperature. Symbols show compositions and sintering temperatures.

magnetic hysteresis curves and under 0.05 T in the temperature range between 5 and 300 K for the temperature dependence of magnetization, using a SQUID magnetometer.

III. RESULTS AND DISCUSSION

A. Structure

X-ray powder diffraction, using $\text{Cu K}\alpha$ radiation, has shown samples in the composition range $0.42 \leq x \leq 0.67$ to exhibit a single spinel phase. Samples with $x = 0.33$ and $x = 0.75$ contain the spinel phase and corundum, Al_2O_3 , and Hausmannite, tetragonal Mn_3O_4 , respectively. X-ray diffraction has also shown samples in the composition range $0.84 \leq x \leq 1.00$ to exhibit a single Hausmannite phase with Al substituted on Mn sites (Fig. 1). The presence of these observed phases depends on neither the synthesis temperature nor cooling rate, however the ratio of the amounts of phases seems to depend on the cooling rate. Hausmannite has a distorted spinel structure caused by the Jahn-Teller effect associated with a d^4 electronic configuration on Mn^{3+} [3] (Fig.2). Since the Hausmannite phase is not stable at 1473 K

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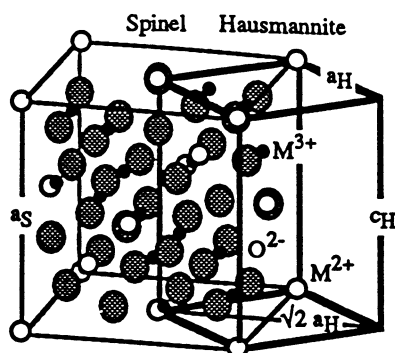


Fig. 2. The relationship between spinel and Hausmannite structures. Hausmannite does not have an ideal c/a ratio because of Jahn-Teller effect.

or higher, its occurrence is attributed to a phase transformation during cooling. This phase transformation can be explained well in terms of the T_0 concept. The T_0 curves for spinel and Hausmannite, where free energies of both spinel phase and Hausmannite phase are equal, falls between $x = 0.67$ and $x = 0.75$ at room temperature. Since Hausmannite is more stable than spinel below the T_0 curve, samples with $x \geq 0.75$ start to transform to Hausmannite during relatively rapid cooling. The lattice parameters of the spinel and Hausmannite phases increase linearly with Mn content (Fig. 3). These features of the spinel - Hausmannite transformation, both of the sintering temperature and the cooling rate independence of existing phases and of their lattice parameters, suggests this transformation to be a massive or a displacive phase transformation. These results are in qualitative agreement with the transformation of pure Hausmannite, Mn_3O_4 , reported by Pollert[4].

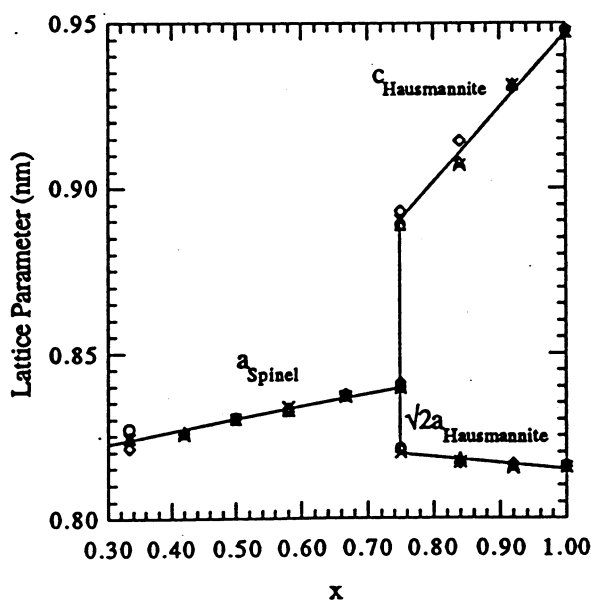


Fig. 3. The composition dependence of lattice parameters of spinels and Hausmannites at room temperature. This figure contains samples air-cooled from 1623 K, quenched from 1473 K, quenched from 1623 K and quenched from 1823 K.

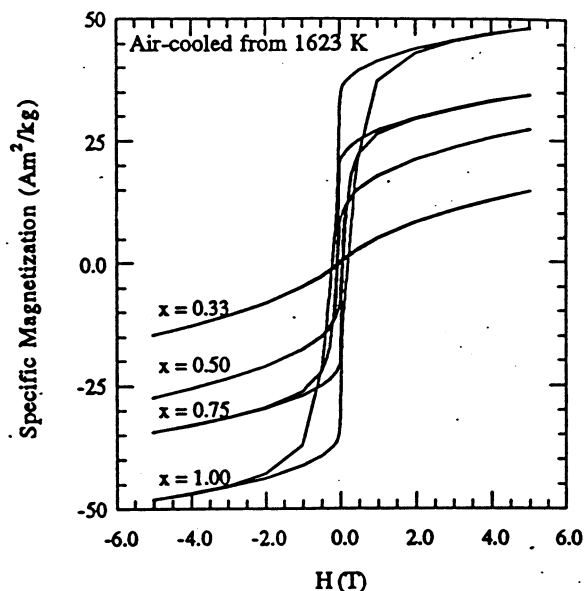


Fig. 4. Typical magnetic hysteresis curves and their composition dependence.

Chemical analysis reveals that the metal to oxygen ratio of samples air-cooled from 1623 K is in the range 3/3.7 - 3/4.0, so that these spinels and Hausmannites are oxygen deficient or non-stoichiometric. The sintering temperature and cooling rate dependence of the metal to oxygen ratio is unknown, so that the origin of the oxygen deficiency is also unknown. It is plausible that a non-equilibrium oxygen defect concentration could be quenched in from high temperatures.

B. Magnetic Properties

Fig. 4 shows typical magnetic hysteresis curves and their composition dependence. Specific magnetizations and coercivities of all samples are observed to increase with Mn content. Furthermore, all hysteresis curves do not saturate in fields up to 5 T. These non-saturating curves may suggest a Yafet-Kittel triangular spin arrangement[5]. The Curie temperature, T_C , is shown to increase with Mn content for the spinel phase (Fig. 5), consistent with predictions of mean field theory. The number of nearest neighbor Mn-Mn pairs is smaller in spinels with lower Mn content. The mean field should therefore be smaller than in spinels with higher Mn content and consequently T_C should be smaller. Also, the T_C 's of spinels with lower Mn content show stronger sintering and cooling rate dependence. There are two possible explanations for this observation. One is that lower sintering temperatures and slower cooling promote formation of more Al_2O_3 , enriching the Mn content of the spinel phase. The other possibility is that high temperature sintering and faster cooling introduce more cation [6] disorder which reduces the mean field. T_C of the Hausmannites varies only slightly.

The effective Mn moment (in μ_B) is calculated from the $H = 5$ T value of the non-saturating specific magnetization assuming ideal stoichiometry. It is seen to be relatively

invariant with composition, x (Fig. 6). An interesting result is that the effective moment per formula unit increases monotonically with increasing Mn content without a discontinuous change at the spinel - Hausmannite boundary (Fig. 7). The composition dependence of the lattice parameter and of the effective Mn moment suggest that ordered MnAl_2O_4 has antiferromagnetically coupled Mn^{2+} ions on A sites, while at higher concentrations Mn^{3+} ions substitute on Al^{3+} (B) sites, which couple ferrimagnetically with Mn^{2+} ions on A sites.

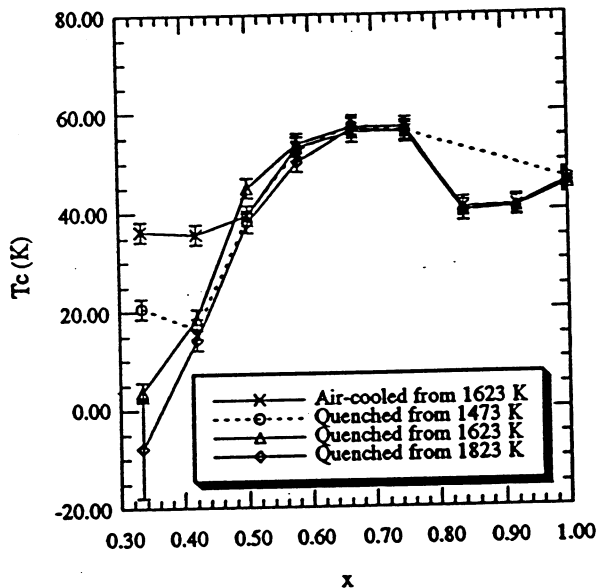


Fig. 5. Composition dependence of the Curie temperature.

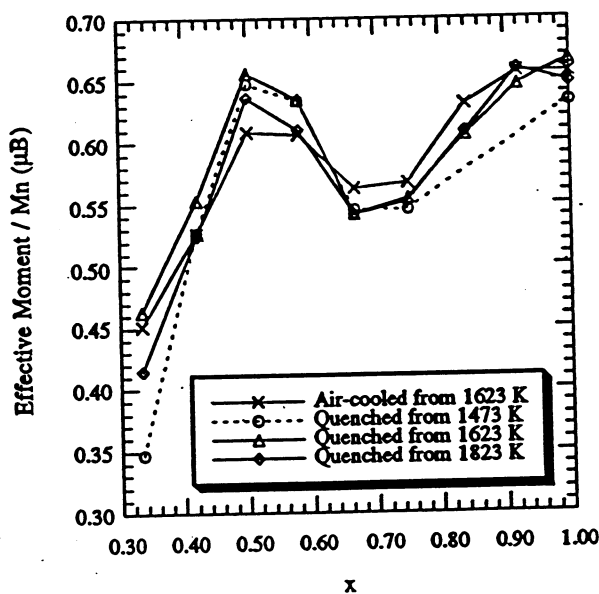


Fig. 6. Composition dependence of effective moment per Mn atom at $H = 5$ T.

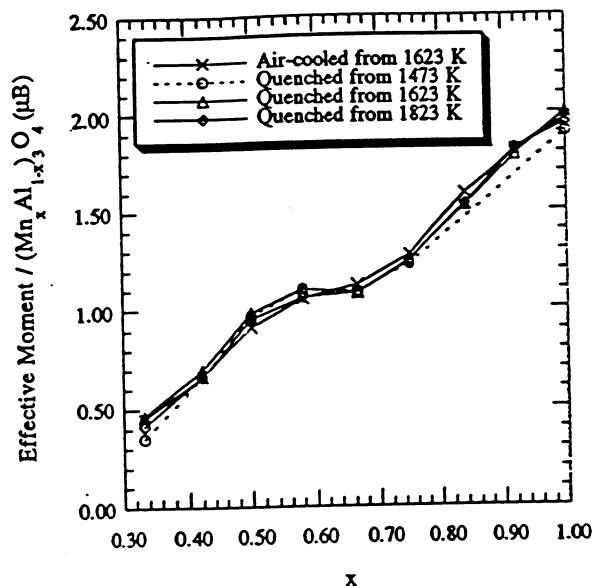


Fig. 7. Composition dependence of effective moment per formula, $(\text{Mn}_x\text{Al}_{1-x})_3\text{O}_4$, at $H = 5$ T.

IV. CONCLUSION

Manganese aluminate spinels and Hausmannites, namely $(\text{Mn}_x\text{Al}_{1-x})_3\text{O}_4$, with compositions varying between $x = 0.33$ and $x = 1.00$ have been investigated. Lattice parameters of these spinels and Hausmannites increase linearly with increasing Mn content and depend on neither sintering temperature nor cooling rate. The phase transformation between the spinel and Hausmannite phases can be explained using the T_0 concept and suggests a massive or displacive phase transformation. Magnetic hysteresis curves at 5 K show non-saturating features up to 5 T, and are consistent with a Yafet-Kittel triangular spin arrangement. Ferrimagnetic Curie temperatures of spinels and Hausmannites increase monotonically with increasing Mn content, respectively.

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