Journal of Crystal Growth 344 (2012) 65–68

Contents lists available at SciVerse ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Crystal growth and magnetic properties of spinel $(Co,Mn)_3O_4$

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ARTICLE INFO

Article history:
Received 16 October 2011
Received in revised form
26 January 2012
Accepted 27 January 2012
Communicated by K. Jacobs
Available online 6 February 2012

Keywords:
A1. Crystal structure
A1. X-ray diffraction
A2. Growth from high temperature solutions
A2. Single crystal growth
B1. Oxides
B2. Magnetic materials

ABSTRACT

Single crystals of cubic and tetragonal spinel $Co_{3-x}Mn_xO_4$ ($x=1.0$ and 1.5) were successfully grown using a solvent evaporation method with PbF_2 flux. Single crystals in octahedral shape with a size of about 4 mm on edge were obtained from 100 cm^3 Pt crucibles. Ferrimagnetic transitions were detected at 170 K and 160 K from the measurements of temperature dependent magnetization and specific heat of Co_2MnO_4 and $Co_{1.5}Mn_{1.5}O_4$, respectively. Low temperature field-dependent magnetization curves give a strong indication of the non-collinear spin structure, offering an insulating $Co_{3-x}Mn_xO_4$ system as a possible candidate for examining the multiferroicity.

1. Introduction

A number of studies have been performed on the magnetic oxide spinel compounds and their solid solutions because of interesting crystallographic, magnetic, dielectric, and electrical properties [1]. More recent researches even extend their horizons to the multiferroic phenomena, focusing on the coupling between magnetization and electric polarization within a single compound of both oxides [2–4] and sulfides [5]. Furthermore a variety of magnetic spin structures observed in spinel compounds are boosting a new research activity of searching for a new type of multiple order parameter system with a strong coupling between them.

Spinel structure provides us a unique structural characteristic. Two different local symmetric sites for magnetic ions, tetrahedral (8a) and octahedral (16b) sites make the configuration more complicated both magnetically and crystallographically. Even the spinel mineral itself, $MgAl_2O_4$ has a controversy over the exact space group and a possibility of antiferroelectricity resulting from the interplay of distortions of octahedral and tetrahedral groups has been proposed [6]. In the case of the famed loadstone Fe_3O_4 magnetite, even though it is the ancestor of all the magnetic materials in our planet, Verwey transition has still been a big open question and even the observation of electric polarization has been reported at low temperatures [7].

Solid solutions of spinel Co_3O_4(Cubic Fd-3m)–Mn_3O_4(Tetragonal $I4_1/amd$) have been studied with an emphasis on their cubic–tetragonal phase transition depending on the content of manganese due to the cooperative Jahn-Teller distortion of Mn^{3+} ions of octahedral sites in the percolative manner and the accompanying change from the inverse to the normal spinel configuration. Unusual magnetic property was mentioned [8] in the polycrystalline samples since the early report on the ferrimagnetic nature of the compounds [9]. Previous researches on the construction of phase diagram [10] and the structural and magnetic studies of a complete range of solid solutions $Co_{3-x}Mn_xO_4$ polycrystalline specimens [11] have been the guide for the growth of single crystals. Here in this paper, we report the experimental results on the growth of single crystals $(Co,Mn)_3O_4$ and their novel magnetic properties such as non-collinear and forced magnetization behavior.

2. Sample synthesis and experimental methods

Single crystals of spinel $Co_{3-x}Mn_xO_4$ were grown by a slow cooling solvent evaporation method. Stoichiometric amounts of Co_3O_4 (99.99%) and MnO_2 (99.99%) raw powders were mixed with two different flux materials, PbF_2 (99.9%) and Bi_2O_3–B_2O_3 ($>99.9\%$) for the purpose of growing the prototypical cubic ($x=1.0$) and tetragonal ($x=2.0$) phases of $Co_{3-x}Mn_xO_4$ single

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doi:10.1016/j.jcrysgro.2012.01.053

Table 1
Summary of growth conditions of $Co_{3-x}Mn_xO_4$ single crystals. In all growth processes furnace was turned off at 860 °C and allowed to cool to room temperature. Nominal contents x are from the composition ratio of the starting raw powders. Real contents x indicate the results of experiments by both electron probe microanalysis and structural data of the grown single crystals.

Crystal		Growth conditions				
Nominal x	Real x	Flux	Weight ratio	Soaking temperature and time	Cooling rate	Mean size (mm^3)
Co_2MnO_4 ($x=1.0$)	Co_2MnO_4 ($x=1.0$)	Bi_2O_3–B_2O_3	$Bi_2O_3-B_2O_3+Co_2MnO_4=20:1$	1200 °C, 70 h	10 K/h	Not available
		PbF_2	$PbF_2+Co_2MnO_4=30:1$	1200 °C, 70 h	10 K/h	Not available
			$PbF_2+Co_2MnO_4=30:1$	1200 °C, 70 h	10 K/h	Not available
			$PbF_2+Co_2MnO_4=25:1$	1170 °C, 50 h	3 K/h	$4\times4\times4$
$CoMn_2O_4$ ($x=2.0$)	$Co_{1.5}Mn_{1.5}O_4$ ($x=1.5$)	PbF_2	$PbF_2+CoMn_2O_4=25:1$	1170 °C, 40 h	2 K/h	Not available
			$PbF_2+CoMn_2O_4=25:1$	1170 °C, 40 h	3 K/h	Not available
			$PbF_2+CoMn_2O_4=25:1$	1170 °C, 30 h	10 K/h	$3\times3\times3$

crystals in 100 cm^3 Pt crucibles. In order to allow the evaporation of solvents during various growth conditions, Pt crucibles were not tightly sealed with high temperature cement but sealed with crimped Pt lids. Optimized weight ratios between solutes and solvents, crystal growth conditions, and the resultant crystal sizes are summarized in Table 1. The grown single crystals were easily separated from the molten flux materials by rinsing the Pt crucibles in a diluted H_2SO_4 solution for several minutes. We estimated the actual content of composition by comparing with the published experimental polycrystalline data [11] of lattice parameters and magnetic ordering temperatures versus manganese content. Data on composition from electron probe microanalysis in our single crystals also showed a consistent result on the sample stoichiometry estimated from the structural data.

Crystal structure and quality were examined by X-ray diffraction with both laboratory source powder diffraction set up and PLS 11 A BL synchrotron facility. The commercially available physical property measurement system (PPMS) by Quantum Design was used for magnetic property measurements with VSM option under various temperatures and applying magnetic fields. For the orientation dependent magnetization measurement, crystals were cut into the (110) planes. Relaxation calorimeter installed in PPMS was also used for specific heat measurement.

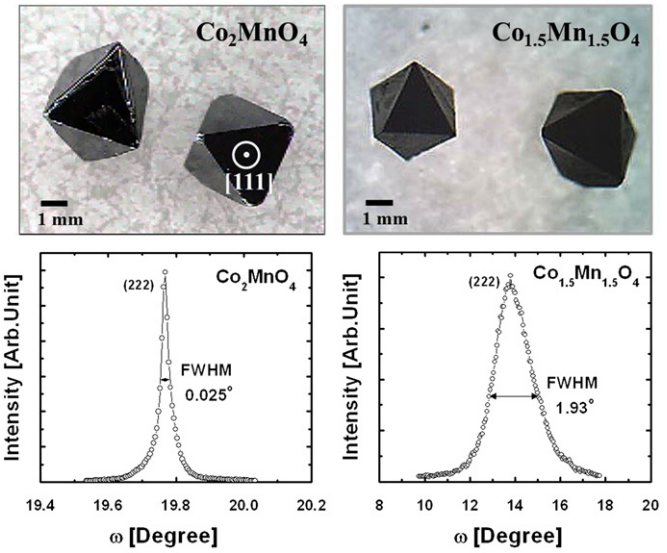

Fig. 1. PbF_2 flux grown single crystals of $Co_{3-x}Mn_xO_4$ ($x=1.0$ and 1.5) and synchrotron X-ray rocking curves of (222) Bragg peak with X-ray wavelength of $\lambda=0.15498$ nm.

3. Results and discussion

In Table 1, the conditions of crystal growth of $Co_{3-x}Mn_xO_4$ are summarized. As indicated, the cooling rate during the growth process turned out to play an important role to grow single crystals successfully in the solvent evaporation method. With Bi_2O_3–B_2O_3 flux, crystal growth process was not successful to produce crystals with a size larger than about 100 μm. However $Co_{3-x}Mn_xO_4$ single crystals with nominal manganese content of $x=1.0$ and 2.0 were successfully grown in PbF_2 flux with high crystalline quality and well defined octahedral crystal habit with a size larger than 1 mm. All the successfully grown crystals were black and their typical size distribution was about 1–4 mm on edges of octahedron. Pictures of the grown crystals are depicted in Fig. 1. The triangular plane corresponds to the {111} plane index of spinel structure. The full width at half maximum (FWHM) of (222) Bragg peak X-ray rocking curve of the cubic Co_2MnO_4 was 0.025°, indicating good sample quality. However in the case of tetragonal $Co_{1.5}Mn_{1.5}O_4$ (nominal content in starting raw powders was $x=2.0$) a very broad peak of 1.93° FWHM was observed because of twining structure in the tetragonal phase and the surface quality both in the flatness and luster was also much worse than that of the cubic phase.

From our previous study of polycrystalline $Co_{3-x}Mn_xO_4$ samples that were obtained by a conventional solid state reaction, we found that always a 2-phase region consisting of the cubic and tetragonal spinel phases occurs in the region $x>1.3$ near the structural phase boundary. The exact position of this boundary between the cubic single phase region and the cubic+tetragonal 2-phase region depended on the previous history of the sample synthesis conditions, especially on the cooling rate after the final process of sintering. This is also consistent with the previous report on the phase diagram study of Mn_3O_4–Co_3O_4 [10]. It should be noted that for pure hausmannite Mn_3O_4 ($x=3$) the cubic→tetragonal transformation occurs at 1180 °C and extends for compositions $3>x>1.3$ over a finite T range, starting from low $T<1180$ °C. The $x=2.0$ material has to cross upon cooling the 2-phase region of the phase diagram, and consequently the preparation of homogeneous sample is difficult. In the polycrystalline case, one can utilize quenching to overcome this issue, however in the case of single crystal growth this problem becomes more severe. At least it becomes obvious from Table 1 that tetragonal crystals could be grown only with relatively rapid cooling rate (10 K/h), whereas the cubic phase requires slow cooling (3 K/h).

X-ray powder diffraction results of the crunched single crystal samples of both Co_2MnO_4 and $Co_{1.5}Mn_{1.5}O_4$ are shown in Fig. 2(a) and (b). Through the Rietveld refinement procedure, we determined the lattice parameters of the cubic ($a=0.826$ nm) and tetragonal ($a=0.821$ nm, $c=0.866$ nm) structure with Fd-3m (SG-227) and $I4_1/amd$ (SG-141) space group, respectively. Upper