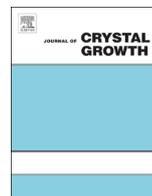




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journal homepage: www.elsevier.com/locate/jcrysgrOptical floating zone crystal growth and magnetic properties of MgCr_2O_4 S.M. Koohpayeh^{a,*}, J.-J. Wen^a, M. Mourigal^a, S.E. Dutton^b, R.J. Cava^b, C.L. Broholm^a, T.M. McQueen^{a,c}^a Institute for Quantum Matter and Department of Physics and Astronomy, Johns Hopkins University, Baltimore, MD 21218, USA^b Department of Chemistry, Princeton University, Princeton, NJ 08544, USA^c Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, USA

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ABSTRACT

Large, high-quality single crystals of the magnesium chromate spinel, MgCr_2O_4 , have been grown by the optical floating zone technique. The impact of experimental parameters including the feed rod density, growth atmosphere, temperature gradient, and the growth rate on eventual crystal quality have been studied. The best single crystals were obtained by growing in purified argon, at high growth rates of 8–24 mm/h and using a slow cooling procedure. The crystals were characterized using Laue and powder X-ray diffraction, energy dispersive X-ray analysis, and magnetization measurements. Lattice parameter measurements taken from the crystals prepared at various growth conditions combined with the magnetic data show that off-stoichiometric crystals have larger lattice constants and a higher magnetic susceptibility at T_N . Our results demonstrate the importance of correlating growth conditions with structural and physical properties to produce high quality single crystals that have physical properties commensurate with stoichiometric powder samples.

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1. Introduction

Magnesium chromium oxide, MgCr_2O_4 , is among a large group of spinel ceramic materials, sometimes called double oxides, that crystallize in the cubic crystallographic system (FCC, face centered cubic, space group $Fd\bar{3}m$). They have the general formula AB_2O_4 : 'A' is a divalent element, such as Mg, Fe, Zn, Mn, Ni, Co, V or Cu, and is tetrahedrally coordinated by oxygen; 'B' is a trivalent element such as Al, Fe, In, Ga or Cr, and is octahedrally coordinated by oxygen (Fig. 1a). Spinel, including MgCr_2O_4 and MgAl_2O_4 , have found many applications as refractory materials, catalysts, and catalyst supports due to an excellent combination of physical and chemical properties (e.g., melting point above 2000 °C, high mechanical strength and resistance to harsh chemical environments) [1].

More recently, spinels containing transition metals or rare earth elements have been extensively investigated as prime candidates to exhibit geometric magnetic frustration, as the 'B' site atoms form a three dimensional network of corner-sharing tetrahedra, with 'B' site atoms at the vertices, akin to one sublattice of the pyrochlore structure [2]. Chromium-rich spinels,

such as ZnCr_2O_4 and MgCr_2O_4 , have attracted particular attention due to antiferromagnetic ordering transitions at low temperature that are coupled to lattice distortions [3–8].

Single crystal growth of MgCr_2O_4 using the flux method has been reported [8–10]; however, only relatively small (mm size) crystals have been obtained, and there has been no systematic study of their quality. Growth of MgCr_2O_4 whiskers (several mm in length and μm in diameter) through a vapor–solid mechanism has also been reported [11]. Larger size $\text{Mg}_{1-x}\text{Cr}_2\text{O}_{4-x}$ ($0.02 \leq x \leq 0.11$) crystals, up to 30 mm long and 4 mm in diameter, were recently grown using an optical floating zone (FZ) furnace at a zoning rate of 20 mm/h under 6 bar argon [12]. In this case, excess MgO was added before performing the growth process, but no further details were described.

Porosity formation, thermal dissociation and volatilization at high temperatures (above 1500 °C) are known challenges during high temperature synthesis of MgCr_2O_4 as reported in several studies [13–17]. The spinel MgCr_2O_4 begins to lose Cr at 1500 °C in a vacuum of 1.3×10^{-7} bar by vaporization of Cr_2O_3 in the form of Cr, CrO and O_2 , while considerable simultaneous vaporization of MgO and Cr_2O_3 occurs at temperatures above 1600 °C (the rate of vaporization at 1660 °C was reported to be 1.54×10^{-5} g/cm² s) [14,15]. Further investigations of the kinetics of vaporization, in which constant vaporization rates were measured, also confirmed a nearly congruent vaporization of the phases in this system, with

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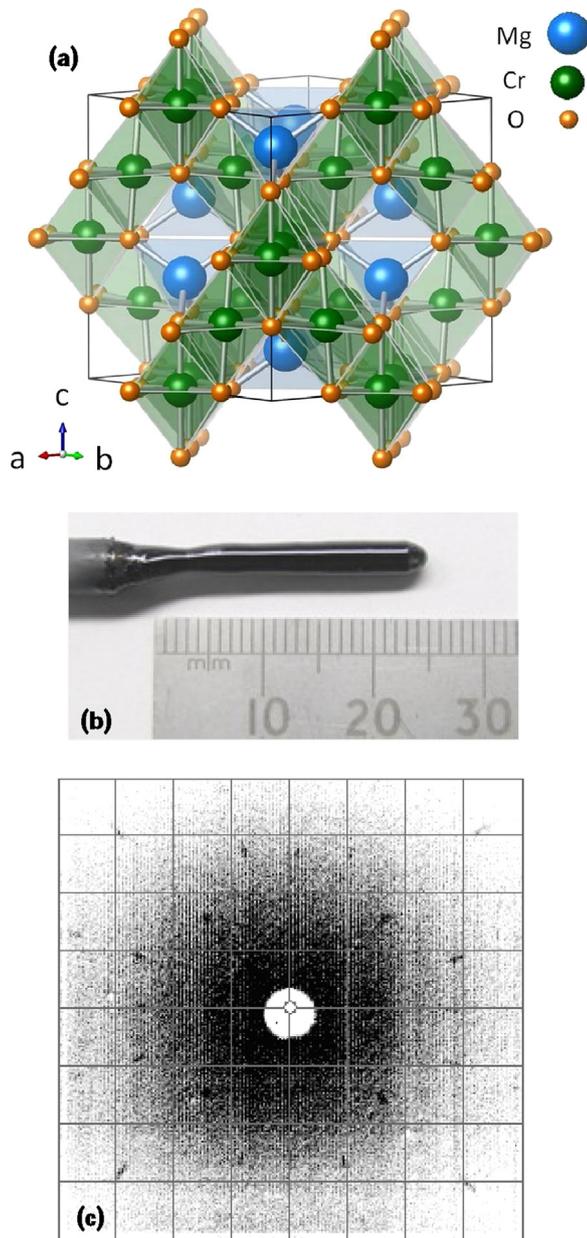


Fig. 1. (a) Unit cell representation of spinel MgCr_2O_4 illustrating the octahedrally coordinated Cr^{3+} and tetrahedrally coordinated Mg^{2+} ions. (b) A typical dark green MgCr_2O_4 single crystal grown by the optical floating zone technique under 3 bar static high purity argon at the growth rate of 8 mm/h. (c) X-ray Laue picture taken from the as-grown crystal. The substantial background is due to chromium fluorescence. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the vaporization coefficient of MgCr_2O_4 increasing with temperature and reaching a value of unity near the melting point [16]. Synthesis of MgCr_2O_4 in other atmospheres, such as an oxidizing atmosphere of air at elevated temperatures ($\geq 1500^\circ\text{C}$), also led to abundant formation of Cr vacancies ($\text{MgCr}_{2-x}\text{O}_4$, $0 < x < 0.49$), affecting the chemical bonding and electronic structure of the material [18–20].

Despite these studies of crystal growth kinetics, it is not clear how the magnetic properties of single crystals are affected by factors such as impurity concentration, phase distribution, or crystallinity. As it is now known that small changes in stoichiometry have a dramatic effect on the physical properties of powder MgCr_2O_4 [6], optimizing crystal growth conditions to control the type and number of defects is critical. The aim of the present study

was to prepare large and high quality single crystals of MgCr_2O_4 by the floating zone technique, and to investigate the effects of varying growth conditions upon the quality of grown crystals and their structural and magnetic properties.

2. Experimental procedures

2.1. Synthesis and crystal growth

Stoichiometric amounts of Cr_2O_3 (Alfa Aesar, 99.97% purity) and MgO (Alfa Aesar, 99.99% purity) were thoroughly ground together and then heated in air at 1300°C for 20 h with an intermediate grinding after 10 h. The powder was then sealed into a rubber tube, evacuated using a vacuum pump, and compacted into a rod (typically 6 mm in diameter and 80 mm long) using a hydraulic press under an isostatic pressure of 7×10^7 Pa. After removal from the rubber tube, the rods were sintered at 1550°C for 12 h under 1 bar static argon atmosphere. Powder X-ray diffraction taken from the green sintered feed rods confirmed the spinel structure of pure MgCr_2O_4 with a measured lattice parameter of $a = 8.33564$ (2) Å. (All quoted error bars for lattice parameters includes only the statistical contribution to the error.)

Single crystals of approximately 4 mm in diameter and 40 mm in length were grown from the feed rods in a four-mirror optical floating zone furnace (Crystal Systems Inc. FZ-T-12000-X-VPO-PC) with 4×3 kW xenon lamps. During all of the growths, the molten zone was moved upwards with the seed crystal being at the bottom and the feed rod above it. This was accomplished by holding the mirrors in a fixed position and translating both the seed and feed rods downwards. Growths were carried out under 3 bar static high-purity argon atmosphere (gaseous impurities were below 1 ppb due to the use of an inert gas purifier) at rates of travel between 4 and 24 mm/h, rotation rates of 6 rpm for the growing crystal (lower shaft) and 3 rpm for the feed rod (upper shaft) in the opposite direction. In all runs, only one zone pass was performed.

2.2. Crystal characterization

Powder X-ray diffraction patterns were obtained using a Bruker D8 Focus X-ray diffractometer operating with $\text{CuK}\alpha$ radiation and a Lynxeye silicon strip detector. Phase identification and unit cell determinations were carried out using the Bruker TOPAS software (Bruker AXS). Back-reflection X-ray Laue diffraction (with the X-ray beam of about 1 mm in diameter) was utilized to check the crystalline qualities of the crystals. The compositional homogeneities (taken from the polished surface of samples cut directly from the cross sections of the as-grown crystals) were analyzed by energy dispersive X-ray (EDX) technique using a JEOL 6700F scanning electron microscope (SEM) operating in backscatter mode. Magnetic susceptibility measurements were carried out using a Quantum Design Physical Properties Measurement System (PPMS). Temperature-dependant magnetization measurements were collected under an applied field of $\mu_0 H = 0.1$ T between 2 and 300 K after cooling in zero field (ZFC). No apparent change in physical properties was observed for samples left on the benchtop for an extended period, i.e., the crystals are stable for at least months in ambient conditions.

3. Results and discussion

3.1. Floating zone crystal growth

Growth attempts using feed rods sintered at 1400°C in air were not successful due to low densification, excess porosity and higher

exposed surface area, which led to a large amount of vaporization and molten zone instability on heating to the melting temperature of MgCr_2O_4 under an argon atmosphere in the image furnace. It is well-known that dense feed rods are needed to achieve a stable molten zone and perform a successful zoning process [21]. Studies on the sintering behavior of MgCr_2O_4 showed that it cannot be densified to more than 70% of the theoretical density at temperatures up to 1700 °C if the oxygen activity exceeds 10^{-6} bar, while decreasing oxygen activity to $< 10^{-10}$ bar helped to achieve more than 90% of the theoretical density [17]. Significant improvements in feed rod density were obtained by increasing the sintering temperature of feed rods to 1550 °C for 12 h under a static argon atmosphere using a vacuum furnace.

Crystal growth experiments in oxygen-containing atmospheres (regardless of the growth rate and gas pressure applied) were found to lead to a significant evaporation from the feed rod. Successful crystal growth attempts were performed under 2–3 bar static high purity argon at fast zoning rates of 8–24 mm/h to minimize evaporation. No further reduction of vaporization occurred by increasing the argon pressure to 7 bar. Despite using high purity argon as the growth atmosphere, the slower growth rate of 4 mm/h still led to extensive vaporization from the sample that ultimately prevented light from reaching the sample after a few millimeters of crystal growth, due to deposition of the vaporized material on the quartz containment tube.

While vaporization during the crystal growth process is inevitable, the feed rods appeared to melt congruently over the growth period, as expected from the $\text{MgO-Cr}_2\text{O}_3$ phase diagram [13]. A typical as-grown MgCr_2O_4 crystal obtained using the image furnace is shown in Fig. 1b. The as-grown crystals are very dark green in color, when crushed into small pieces however, they turn to the lighter green color of the starting feed rod (as expected for a Cr^{3+} -containing oxide).

X-ray Laue patterns taken at regular intervals along the lengths and cross sections of the crystals indicated that they all exhibited an equally high crystalline quality with no detectable variation of the orientation between pictures and no evidence of spot splitting or distortion. Fig. 1c shows a typical X-ray Laue picture taken from the as-grown crystal.

Phase identification using powder X-ray diffraction taken from crushed sections of the crystals grown at different rates of 4–24 mm/h indicated pure MgCr_2O_4 phase with no detectable evidence of second phases or inclusions (Fig. 2a). Powder X-ray diffraction was also performed on the evaporated materials collected from the growth chamber. The majority phase was found to be the MgCr_2O_4 spinel, with trace amounts of Cr_2O_3 , indicating a nearly congruent vaporization under argon atmosphere. The existence of a very small quantity of MgO (which would balance the stoichiometry and indicate a perfectly congruent melt) cannot be ruled out due to the lower scattering power of Mg relative to Cr. Congruent vaporization from the $\text{MgO-Cr}_2\text{O}_3$ system has been reported in vacuum (1.3×10^{-8} bar) [16], while changing the atmosphere to oxygen results in excess Cr vaporization [18,19].

Back scattered SEM micrographs taken from polished cross sections of the crystals grown at 4–24 mm/h also showed similar microstructural morphology and compositional homogeneity with no indication of any visible second phase inclusions in the crystals (a representative image is shown in Fig. 2b).

3.2. Magnetic measurements

The temperature dependence of the zero-field cooled magnetization was measured under a $\mu_0 H = 0.1$ T applied field on disk shaped samples cut directly from the cross section of the crystals. The calculated susceptibility (χ) for crystals grown using stoichiometric feed rods shows that the shape of the feature at T_N changes

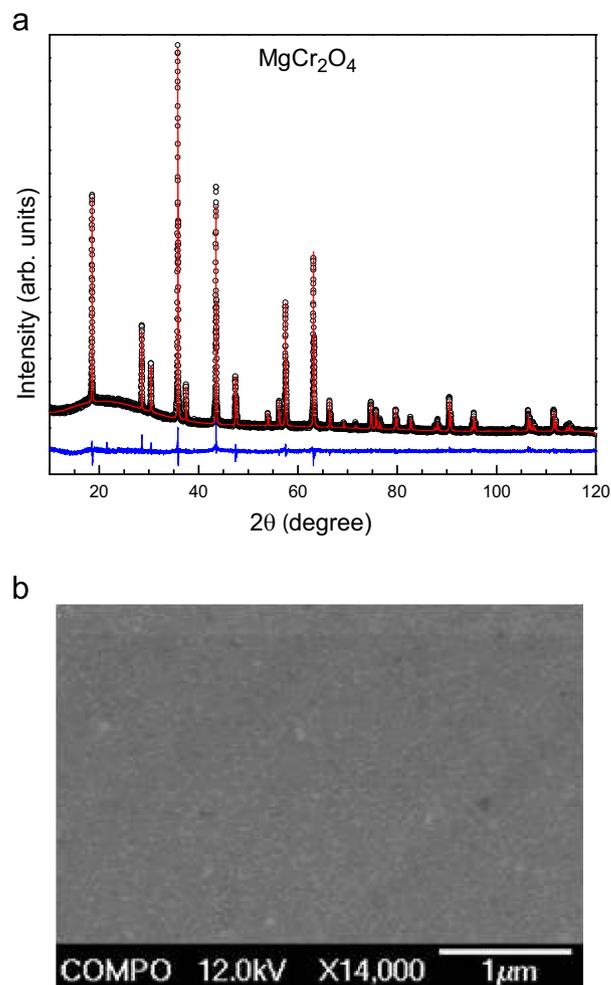


Fig. 2. (a) Powder X-ray diffraction data taken from the crushed MgCr_2O_4 single crystal indicating a pure phase of the as-grown crystals. The data in black circles, calculated profile in red line, and their difference in blue line are shown. (b) Back scattered SEM micrograph taken from the polished cross section of the as-grown crystal with no indication of any visible second phase inclusions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

for the crystal grown at 4 mm/h, with a divergence of the magnetic susceptibility prior to a drop at T_N (Fig. 3), while crystals grown at 8, 16 and 24 mm/h showed magnetization curves similar to stoichiometric MgCr_2O_4 [6]. Powder X-ray diffraction together with lattice parameter measurements (which are consistent with a change in stoichiometry) indicated that all crystals are phase-pure MgCr_2O_4 ; however, a larger lattice parameter of $a = 8.33676(2)$ Å was measured for the slowly grown crystal at 4 mm/h, compared to the lattice parameter of $a = 8.33565(2)$ Å measured for the crystal grown at 8 mm/h (which is close to the lattice parameter of the sintered feed rod).

The increase in the susceptibility near T_N of the 4 mm/h specimen is similar to increases seen in nonstoichiometric chromite spinels, an indicative to the presence of Cr^{4+} [6]. The existence of Cr^{4+} in the grown crystals can come from either a deficiency of Cr (i.e., $\text{MgCr}_{2-x}\text{O}_4$) [6] or Mg (i.e., $\text{Mg}_{1-x}\text{Cr}_2\text{O}_{4-y}$, $y < x$) [12]. Initially, a Cr deficiency seemed the more likely possibility since a small amount of oxygen inclusions can drive Cr vaporization [18,22], and trace amounts of Cr_2O_3 was detected in the XRD pattern of the evaporated MgCr_2O_4 . Therefore, 4–6 wt% extra Cr_2O_3 was added to the starting feed rods, and single crystals were then produced under similar growth conditions. Magnetic measurements performed on these crystals (Fig. 4) showed an

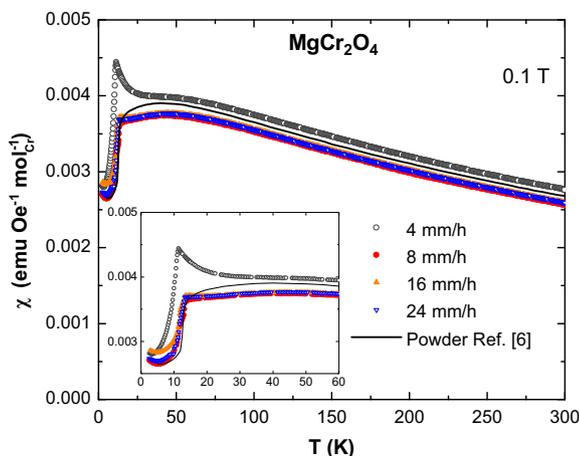


Fig. 3. Temperature dependence of the magnetic susceptibility of MgCr_2O_4 crystals illustrating the effect of changing the growth rate on the susceptibility values at T_N compared to stoichiometric MgCr_2O_4 powder [6]. Higher zoning rates of 8–24 mm/h led to the growth of crystals with properties similar to the stoichiometric powder [6], while the crystal grown at 4 mm/h has an upturn prior to T_N .

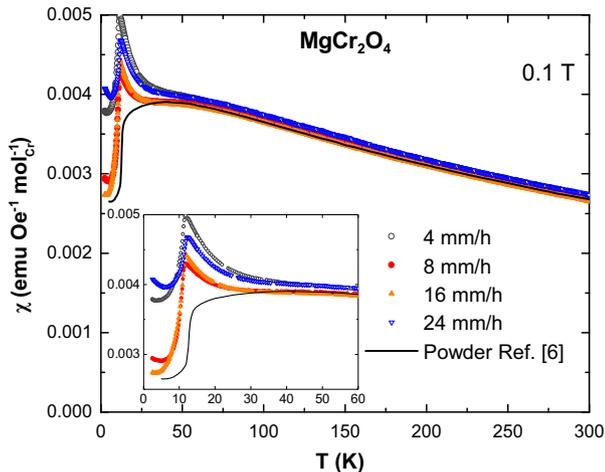


Fig. 4. Magnetic susceptibility vs. temperature for MgCr_2O_4 crystals grown using feed rods with 6 wt% extra Cr_2O_3 illustrating the effect of changing the growth rate on the susceptibility values at T_N compared to stoichiometry MgCr_2O_4 powder [6]. Adding more Cr to the starting feed rods led to the growth of non-stoichiometric crystals for all the growth rates applied.

even larger increase in magnetic susceptibility just prior to T_N . The measured lattice parameters (e.g., $a=8.33827(2)$ Å and $a=8.33723(2)$ Å for the crystals grown at 4 and 8 mm/h, respectively) were even larger and further away from the lattice parameter of stoichiometric powders. This indicates Cr deficiency is not likely responsible for the upturn in the susceptibility just prior to T_N . Instead, our results point to deviations from nominal Mg stoichiometry as being the origin of trace Cr^{4+} in MgCr_2O_4 crystals. (A summary of magnetic properties of all the grown crystals is provided in Table 1, along with values for a stoichiometric powder and flux-grown crystals from the literature.)

Non-stoichiometry of Mg can occur either due to removal of some Mg from the growing crystal through vaporization (in particular, from the molten zone), or a change of Mg arrangement (e.g., movement to an interstitial position or substituting for Cr on the 'B' site) in the crystal structure. The magnetic susceptibilities of a series of samples taken from different positions within a single boule grown at 8 mm/h are shown in Fig. 5. These samples were selected from the lower region (where the growth started and the growing crystal had the longest time to anneal), middle, and upper

Table 1

Magnetic parameters for MgCr_2O_4 crystals grown at the rates of 4–24 mm/h. (C and θ were determined by fitting over the temperature range 150–300 K).

Samples	T_N (K)	C ($\text{emu Oe}^{-1} \text{molCr}^{-1} \text{K}^{-1}$)	θ (K)
Crystals grown using stoichiometric feed rods			
4 mm/h	11.4	2.05	–442
8 mm/h	13.4	1.83	–414
16 mm/h	13.2	1.86	–415
24 mm/h	13.2	1.88	–423
Crystals grown using feed rods with 6% extra Cr_2O_3			
4 mm/h	11.8	1.91	–409
8 mm/h	11.8	1.95	–428
16 mm/h	11.6	1.91	–416
24 mm/h	12.3	1.99	–428
MgCr_2O_4 powder Ref. [6]	12.8	1.97	–433
Flux grown crystals [3]	~13.0	–	–380(10)

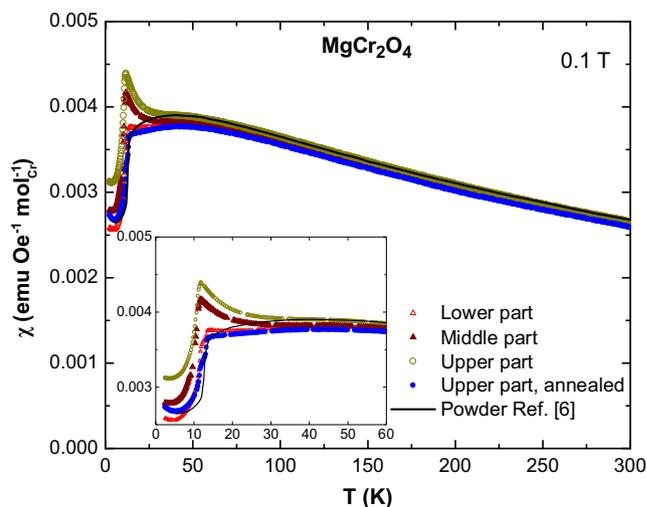


Fig. 5. Magnetic susceptibility as a function of temperature for different parts of MgCr_2O_4 crystal grown at 8 mm/h. The annealing process either due to the temperature gradient that takes place longer for the lower part of the growing crystal, or through a slow cooling of the upper part led to the growth of stoichiometric crystals with smaller susceptibilities prior to T_N .

region close to the molten zone (where the growth was rapidly finished without much annealing). As shown in Fig. 5, the sample from the lower part of the crystal had the smallest susceptibility at T_N and the smallest lattice parameter ($a=8.33614(2)$ Å) close to the nominal value, while the upper part had the largest susceptibility and lattice parameter ($a=8.33672(2)$ Å). As a result, stoichiometric large crystals were grown by holding the upper part of the growing crystal at high temperatures through a lengthy finishing (or slow cooling) procedure for about 5 h. Growth of such long stoichiometric crystals indicates that Mg deficiency (through a gradual vaporization of some Mg from the molten zone) is unlikely since the most upper part of the crystal, which is expected to be highly Mg deficient, was found to be stoichiometric after the annealing procedure.

Since no indications of phase segregation or inclusions were observed in the XRD patterns and SEM backscattered images taken from different parts of the as grown crystal, it is difficult to explain the origin of this annealing effect. However, it suggests that during the float-zoning crystal growth some stoichiometric atomic scale disorder occurs that ultimately is rectified by the annealing process. Such complex disordering phenomena involving the two cation sites with temperature in the spinel structure have been previously reported [23–26].

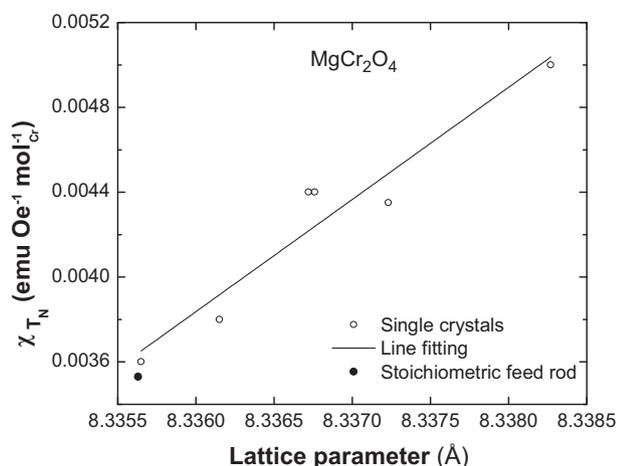


Fig. 6. Lattice parameter vs. magnetic susceptibility at T_N for MgCr_2O_4 crystals prepared under different growth conditions. Crystals with smaller lattice parameters showed susceptibilities similar to stoichiometric MgCr_2O_4 .

Lattice parameter measurements of the crystals prepared under different growth conditions showed that the crystals with larger susceptibility values at T_N (due to the presence of Cr^{4+}) had larger lattice parameters, while the higher quality crystals with lower magnetic susceptibilities showed smaller lattice constants close to that of stoichiometric MgCr_2O_4 (Fig. 6). The increase in lattice parameter as Cr^{4+} concentration increases likely arises due two competing effects: while the ionic radius of Cr^{4+} is smaller than Cr^{3+} , the second kind of defect that then must be present to maintain charge neutrality (e.g., Mg or Cr vacancies) may then have a larger effective size, resulting in a net increase in the lattice parameter. This happens quite commonly in oxides, e.g., the large expansion of c lattice parameter in Na_xCoO_2 as x is reduced even though Co^{3+} is oxidized to Co^{4+} , or the increase in the lattice parameter of magnetite (Fe_3O_4 spinel) as cation vacancies are introduced despite the oxidation of Fe^{2+} to Fe^{3+} [23]. This observed change in the lattice parameter of MgCr_2O_4 spinel crystals can be related to the stoichiometry, which depends on the temperature and synthesis conditions [24–27].

4. Conclusions

Using well densified feed rods, successful floating zone growth of MgCr_2O_4 crystals was performed under high purity argon, during which a nearly congruent vaporization of the phases was observed. The growth rate was found to have a significant impact on both the structural and magnetic properties of the grown crystals. The slower growth rate of 4 mm/h led to significant vaporization from the sample that ultimately prevented the light from reaching the growing crystal, while faster growth rates of 8–24 mm/h limited evaporation and yielded a successful growth of more stoichiometric crystals. Annealing of the crystals using the temperature gradient (which exists along the growing crystal during the float-zoning technique) helped to produce crystals with improved physical properties. Lattice parameter measurements of the crystals prepared under different growth conditions showed that the crystals with larger lattice constants have larger susceptibilities just prior to T_N . The results clearly demonstrate that a strong correlation exists between the structural and magnetic properties of MgCr_2O_4 single crystals, and that careful

optimization of floating zone growth parameters is required to produce high quality single crystals.

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