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Growth rate dependence of the $NdFeO_3$ single crystal grown by float-zone technique

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ABSTRACT

Rare-earth orthoferrite single crystal $NdFeO_3$ has been successfully grown by the floating-zone technique using a four-mirror-image furnace with flowing air. The polycrystalline feed and seed rods were prepared at a pressure of 150 MPa and sintered at 1200 °C. Structural characteristics of $NdFeO_3$ single crystal were studied using a metallurgical microscope and by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction pattern of the crystal with perfect shape indicated the excellent quality of the crystal grown at 9 mm/h without any shoulder, clarifying the absence of sub-grain. Particular attention was given to the influence of growth rate on structural properties of the crystals. The X-ray rocking curve of the crystal has a small full-width at half-maximum (FWHM), confirming the high crystal quality of the sample. The results indicate that the optimal growth condition was 9 mm/h growth rate and 5 L/min air flow, compared with the use of other growth rates (3 and 6 mm/h). The growth rate plays an important role in $NdFeO_3$ single crystal growth by the floating-zone technique.

1. Introduction

Magneto-optical materials are known as special functional materials with magneto-optical effects, which have resulted in many optical devices having been designed, such as the optical isolator, optical switch, gas sensor, storage, etc. [1,2]. YIG and other rare-earth substituted crystals are used in the near-infrared region. In order to meet the demands of miniaturized and integrated devices, designers are in desperate need of new materials with fast response and high sensitivity. Because of its high magneto-optical figure in the near-infrared range, $RFeO_3$ (where R is rare-earth ion) with orthorhombic perovskite-type structure has gained considerable interest due to its peculiar magneto-optical and magnetic properties. In the range of 1300–1550 nm, the specific Faraday rotation of $YFeO_3$ is between 400° and 250° cm^{-1}, while that of YIG is 180° cm^{-1} [3]. Because of magnetic interactions between the iron ions and the rare-earth ions, it has many remarkable properties such as high domain-wall velocity, spin orientation, weak ferromagnetic behavior with rectangular hysteresis loop and smaller magnetic field needed for application in magnetic field sensors and magneto-optical data storage devices [4–7].

Most of the devices require ideal single crystals, which have been grown using several techniques by many groups [8,9], but it is difficult to get high-quality single crystals. As $RFeO_3$ single crystal congruently melts at 1700 °C, just like the growth of RIG ($R_3Fe_5O_{12}$), most of the $RFeO_3$ samples are grown through the flux method [10–12]. But the crystals still suffer from many kinds of disadvantages such as very small size, voids, dislocation, cracks and so on. During the growth of high quality $RFeO_3$ single crystal, various problems were encountered in other technologies like hydrothermal method, Czochralski pulling, liquid-phase homoepitaxial method and the seeded Bridgman method [13–17]. The optical floating-zone technique, with the advantages of being container-free, non-polluting and possessing high growth rate, is the most effective method for the growth of $RFeO_3$ single crystal [18,19]. For the orthoferrite single crystal grown by the floating-zone method, the quality of crystal usually depends on factors such as stability of the molten zone, quality of feed and seed rods, rotating rate, temperature distribution, atmosphere environment, chemical composition, and especially the growth rate.

This paper aims to study the effect of growth rate on the quality of $NdFeO_3$ single crystals grown by the floating-zone method. Previous research on erbium orthoferrite [9] suggests that the quality of single crystal is better at slower growth rate. However, we found that the quality of $NdFeO_3$ single crystal becomes poor with the decrease in growth rate.

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2. Experimental procedures

$NdFeO_3$ polycrystalline feed and seed rods were synthesized by the conventional solid-state reaction technique. We started with a stoichiometric mixture of Nd_2O_3 (99.9%) and Fe_2O_3 (99.99%) powders that was calcined at a temperature of 1000 °C for 12 h in air. The milled presintered material was isostatically pressed into a cylindrical sample 120 mm length and 8 mm diameter at 150 MPa and sintered at 1200 °C for 24 h. Then we reground, pressed and sintered the obtained rods again under the same conditions in order to obtain high-quality polycrystallite that was confirmed by X-ray diffraction.

A single crystal of $NdFeO_3$ was successfully grown in a four-mirror optical floating-zone furnace (FZ-T-10000-H-VI-P-SH, Crystal Systems Corp.) using four 1.5 kW halogen lamps as the infrared radiation source with flowing air. The temperature of the molten zone focused by mirrors was precisely controlled by adjusting the power of the lamps. During the growth process, the molten zone moved upwards at rates of 3, 6 and 9 mm/h, with the seed rod (lower shaft) and the feed rod (upper shaft) counter rotating at 30 rpm in air flow of 5 L/h.

Along the growth direction, the composition homogeneities, orientations of the as-grown crystal prepared and crystalline qualities were analyzed by X-ray diffraction (Beamline BL14B1, Shanghai Synchrotron Radiation Facility), using a metallographic microscope, by energy-dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM) of the disk-shaped samples cut directly from the cross-sections of the single crystal perpendicular to the growth direction using a diamond wheel.

3. Results and discussion

The X-ray powder diffraction pattern of the feed rod for single crystal growth at room temperature is shown in Fig. 1. The desired crystallographic phase of the sample was confirmed by the Joint Committee on Powder Diffraction Standards (JCPDS, file no. 25-1149). All the peaks shown match very well with those of $NdFeO_3$. All the diffraction peaks were assigned to the perovskite-type structure with a space group Pbnm. High-quality polycrystalline feed rods always play very important role in the growth of single crystal by the floating-zone method.

$NdFeO_3$ boules obtained at different growth rates of 3, 6 and 9 mm/h are shown in Fig. 2. Being distinct from the two other rates, it

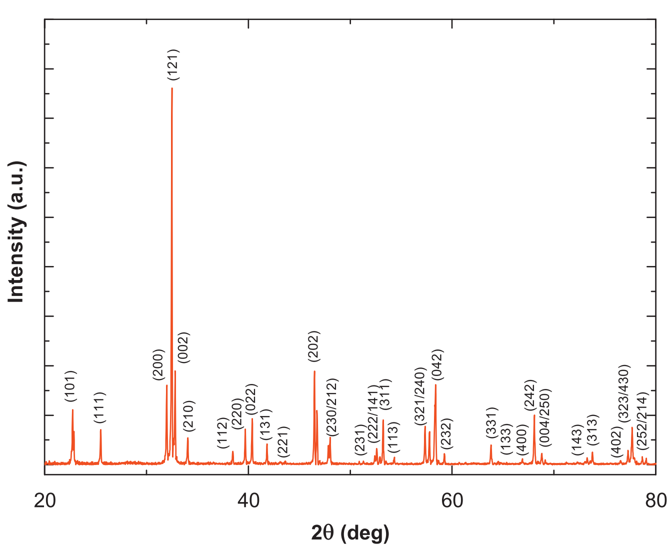

Fig. 1. Powder XRD pattern of polycrystalline $NdFeO_3$ rod for single crystal growth.

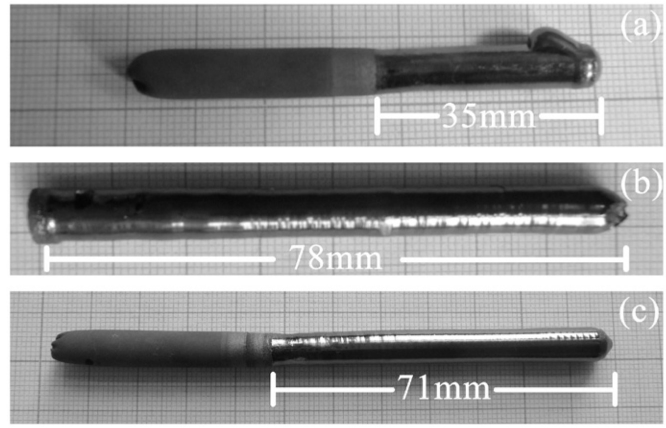

Fig. 2. Feature of entire $NdFeO_3$ crystals grown at (a) 3 mm/h, (b) 6 mm/h and (c) 9 mm/h.

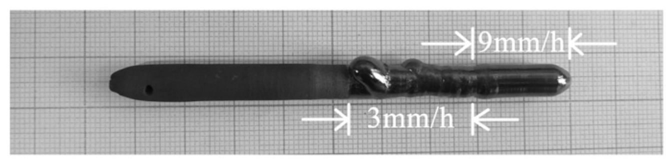

Fig. 3. Feature of one $NdFeO_3$ crystal grown at 9 mm/h after growth at 3 mm/h.

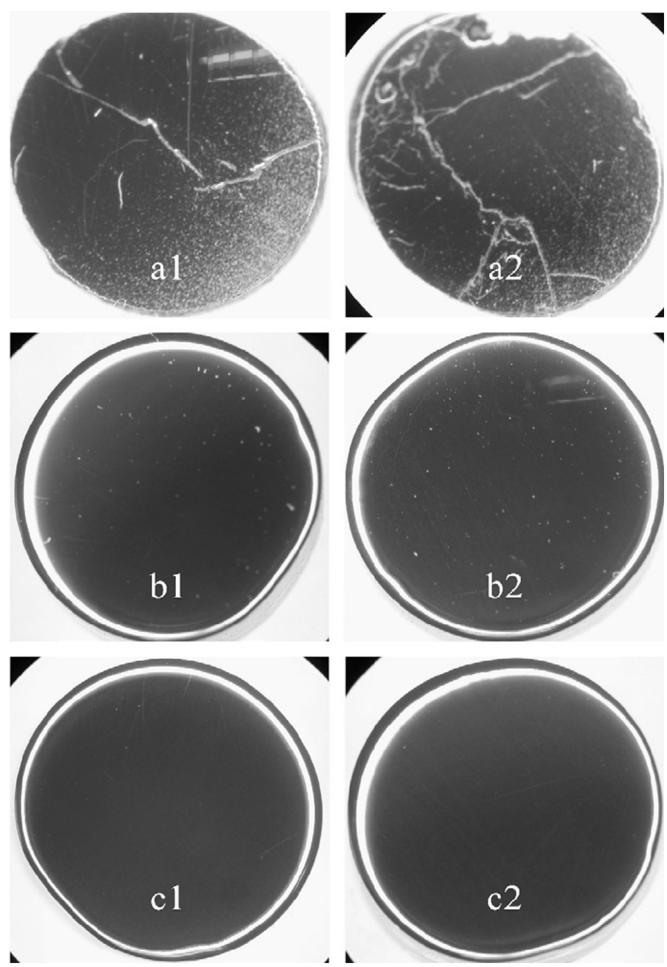

Fig. 4. Metallurgical microscope for surfaces of cross-section along the growth direction. Images a(1)–c(1) were taken at 15 mm distance from the beginning of growth. Images a(2)–c(2) were taken at 30 mm distance from the beginning of growth.

was hard to stabilize the molten zone at rate of 3 mm/h, which spontaneously fell out as the crystal grew to 34 mm while the length of the feed rod was 120 mm. However, others were manually broken off when the feed rods were used up. In order to make further understanding of the relation between growth rate and stabilization, one crystal was grown at two different melting rates of 3 and 9 mm/h. As shown in Fig. 3, it was very easy to maintain the stabilization of growth as we changed the rate from 3 to 9 mm/h. As is known, melting growth is a process of heat quantity accumulation that directly depends on the times of heating. With decrease in zoning speed, the hotter melt formed by focused light caused a more drastic mass transport in the molten zone. The growth would fall out when

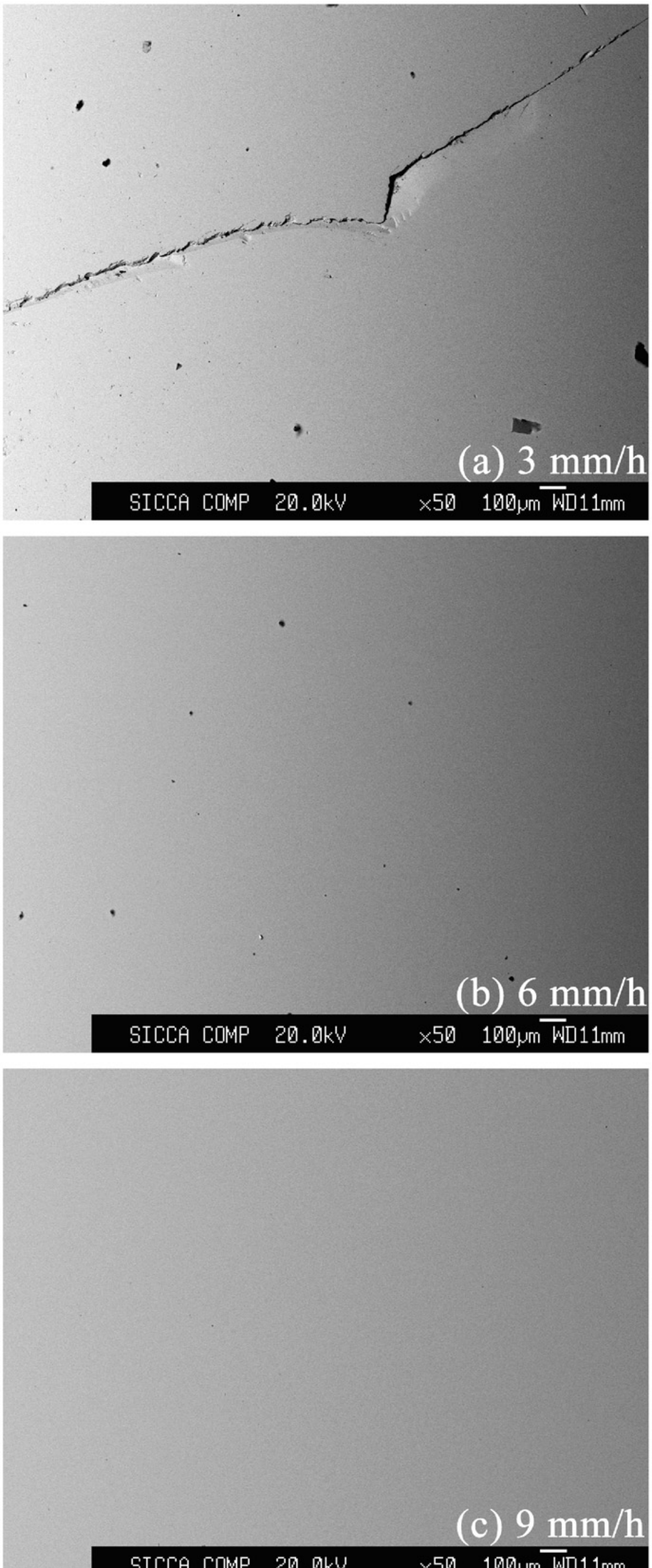

Fig. 5. SEM back-scattered micrographs of cross-sections cut from $NdFeO_3$ crystals grown at (a) 3 mm/h, (b) 6 mm/h and (c) 9 mm/h.

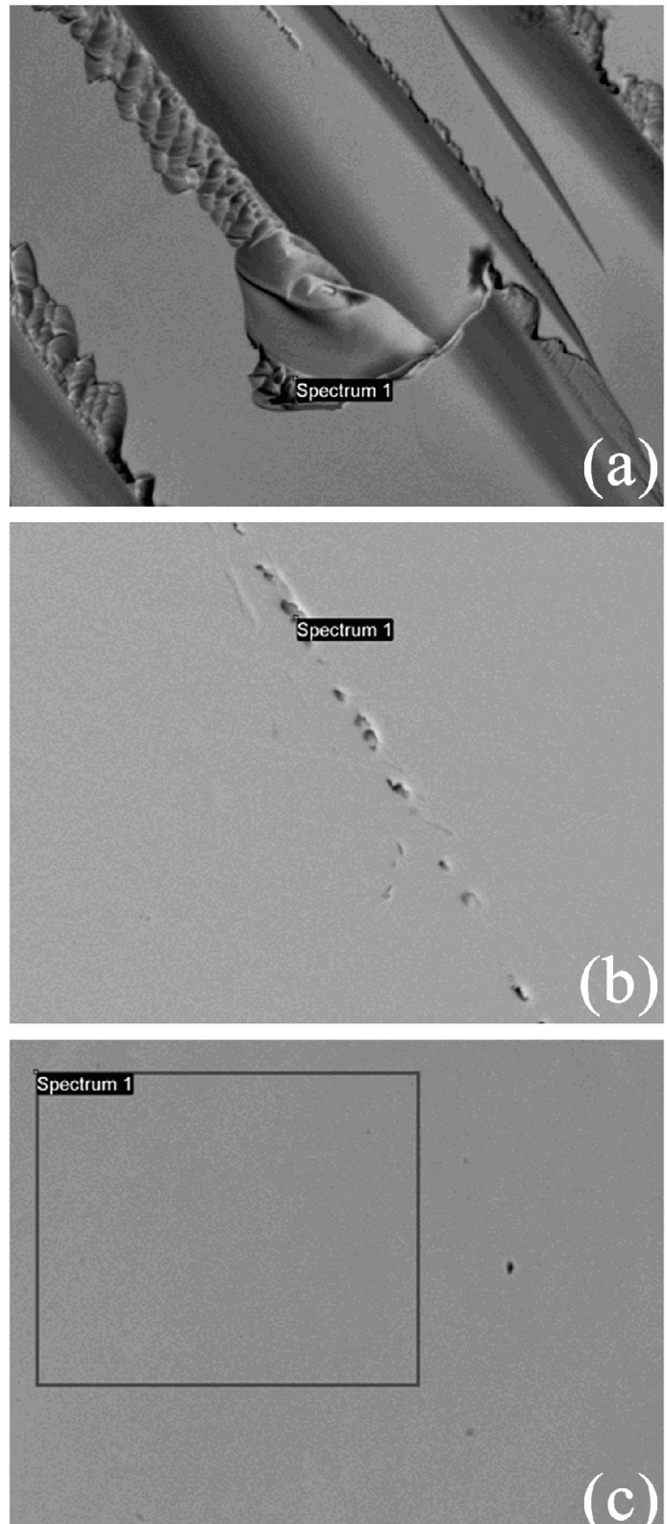

Fig. 6. EDX analysis of cracks and defects on surfaces of single crystals grown at (a) 3 mm/h, (b) 6 mm/h and (c) 9 mm/h.

the feature got to a certain extent. One apparent difference between crystals grown at different rates was that the surfaces were smooth and shiny at growth rates of 6 and 9 mm/h, whereas they were non uniform and rough at 3 mm/h.

To study the crystal habit, the crystals were cut into small pieces along the direction perpendicular to the growth direction, and polished pieces were observed using a metallographic microscope. Fig. 4 shows the presence of the core region and cracks on the surface of cross-sections 15 and 30 mm apart from the starting point of growth. A large number of cracks and defects were found in crystals grown at the lowest rate while the sample of 9 mm/h shows a perfect pattern. It is worthwhile to note that the degree of cracking does not show obvious change in the growth direction from the beginning to the end of growth at different rates. We further examined the surface morphology of the polished cross-sections of $NdFeO_3$ single crystals with a scanning electron microscope (SEM) shown in Fig. 5. Back scattered SEM shows sensibly different images taken of the crystals grown at 3, 6 and 9 mm/h. At a relatively high rate of 9 mm/h, the main feature of micrographs is very perfect. Differing from the $ErFeO_3$, for $NdFeO_3$ single crystal, the lower the growth speed, the poorer the crystal quality. In order to study how and why the cracks and defects appeared, EDX was conducted on several special spots on the surface of disk-shaped crystals at different rates (see Fig. 6). Through calculations based on the data of EDX analysis, we found that the mole ratio of iron to neodymium dropped with decrease in growth rate (see Fig. 7), although the nominal ratio is 1 in ideal $NdFeO_3$. The lowest Fe/Nd mole ratio (about 0.72) at the spot of cracks in the single crystal grown at 3 mm/h proves that the deficiency of Fe plays a very important role, resulting in defects giving rise to cracks. This implies that one should properly increase the content of Fe in synthesizing polycrystalline rods, especially for the growth at slower rates. Besides evaporation of the Fe element, which causes poor crystal quality, expansion of domains of slightly different lattice constants also plays an indispensable role in this characteristic feature of the $NdFeO_3$ single crystal. For the crystallite grown at a lower rate, the quantity of evaporation and the expansion of lattice will be increased with duration of melting. As a result, the cracks are reduced with the growth rate shifting from 3 to 9 mm/h.

Further works were carried out in order to ascertain the influence of zoning rate on the quality of the $NdFeO_3$ crystallite. Because of spontaneous nucleation, it is difficult to obtain $NdFeO_3$ single crystals grown along the expected crystalline direction if one does not use a seed crystal with definite direction. After orientation, XRD was used to scan the surface of the same crystallographic plane of the crystals with different growth rates, as shown in Fig. 8. Full-width at half-maximum (FWHM) is still an effective method to confirm the integrality of crystal structure. The crystal integrality is higher due to the smaller FWHM. To check and compare the crystalline quality of the crystals grown at different rates, a high-resolution X-ray rocking curve (inset of Fig. 8) was measured. Fig. 9 shows that the quality of crystallite gets better with decrement in FWMH, as the growth speed

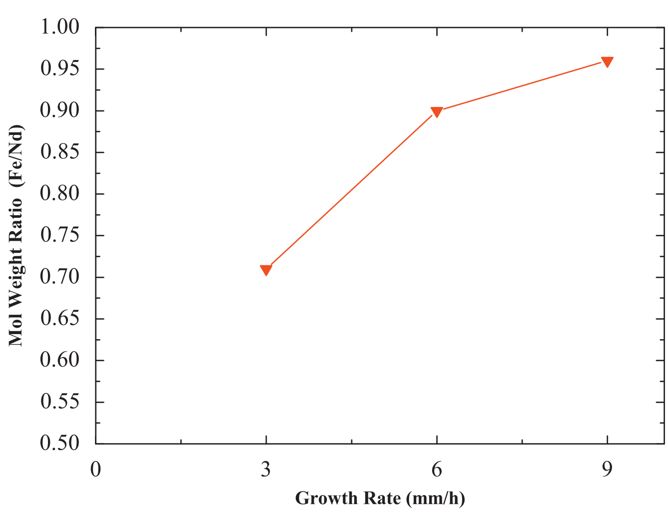

Fig. 7. Mole ratios of iron to neodymium at 3, 6 and 9 mm/h estimated from EDX data.

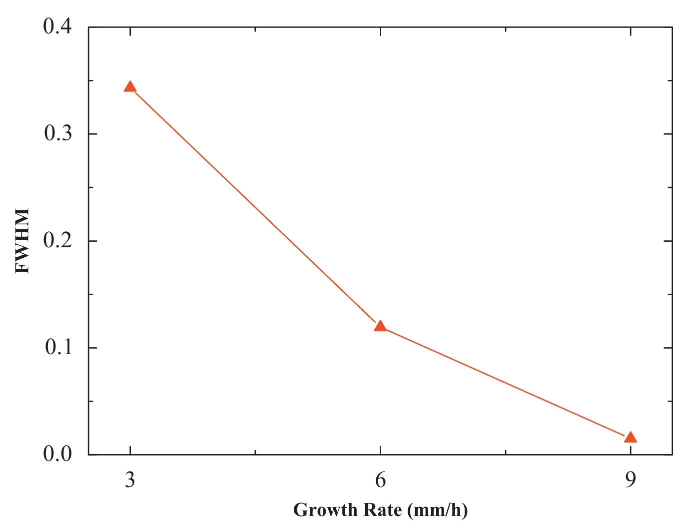

Fig. 9. FMWH for disk-sharped samples cut directly from the cross-sections of $NdFeO_3$ crystals grown at 3, 6 and 9 mm/h.

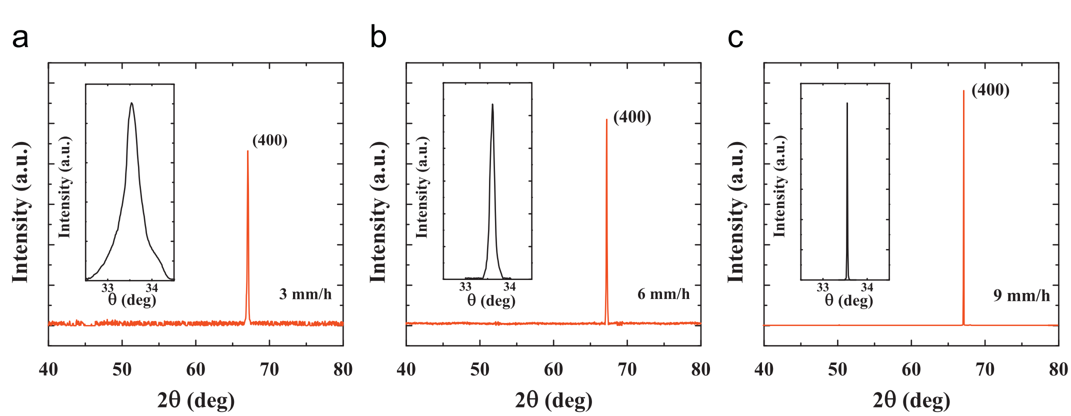

Fig. 8. XRD pattern of the same plane cut from $NdFeO_3$ crystals grown at (a) 3 mm/h, (b) 6 mm/h and (c) 9 mm/h. Inset shows the high-resolution X-ray rocking curve of the same plane at different zoning speeds.

increases from 3 to 9 mm/h. The influence of defects on rocking curve mainly shows the effect of broadening FWHM. Corresponding exactly with the defects, the rocking curve of the sample at rate 3 mm/h shows the maximum width of peaks in the rocking curve.

4. Conclusion

The optical floating-zone technique was successfully used to prepare an $NdFeO_3$ single crystal. The growth rate has a noticeable influence on the crystalline quality. With reduced zoning speed, stabilization of molten zone for the $NdFeO_3$ crystal is very hard to maintain and thus evident cracks and defects resulted, in accordance with the metallurgical microscope and SEM images, which were obtained from the cross-sections cut at the same distance as the beginning of growth for the samples at different grown rates. EDX analysis indicates that the cracks and defects were a result of deficiency in Fe element. A lower zoning speed results in more duration of evaporation of the Fe element. The worst crystalline quality was observed in $NdFeO_3$ crystal grown at the rate of 3 mm/h, which was further confirmed by FWHM of the high-resolution X-ray rocking curve. Although there are many factors such as atmosphere, rotation rate, thermal stress and so on, we suggest that growth rate plays an important role in single crystal growth for the rare-earth orthoferrites system.

Acknowledgments

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