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Mosaics of $KMnCl_3$, undoped and Mg-doped $LiNbO_3$ single crystals measured by neutron scattering

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중성자 산란을 이용한 $KMnCl_3$, $LiNbO_3$ 및 Mg-$LiNbO_3$ 단결정의 mosaic 연구

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Abstract Bulk properties of single crystals $KMnCl_3$, undoped and Mg-doped $LiNbO_3$ were examined by using the neutron scattering technique. This study shows that the good-looking samples by polarized light have to be examined by the neutron scattering to ensure the bulk properties of single crystal. Large mosaic spread in $KMnCl_3$ indicated the crystal is not in a single domain. Many parts are relatively randomly directed against crystal axis with close angle each other. For the small mosaic spread of $LiNbO_3$ in the scattering pattern, it is found that some large domains have close orientations. Mg doped $LiNbO_3$ is turned out to be a well grown one.

요 약 단결정 $KMnCl_3$, $LiNbO_3$ 및 Mg-$LiNbO_3$의 bulk 성질을 중성자 산란을 이용하여 측정하였다. 본 연구는 편광 빛을 사용하여 보이는 좋은 단결정이라도 이들의 bulk 성질을 정확히 파악하기 위하여는 중성자 산란으로 재측정하여야 함을 보여 준다. 중성자 산란에서 나타나는 $KMnCl_3$의 큰 mosaic 분포는 이 결정이 단일 구역을 갖는 단결정이 아니고 축에 대해 작은 각으로 분포되어 있는 구역 군들이 상대적으로 여러 방향으로 존재함을 보여준다. $LiNbO_3$에서 나타나는 작은 mosaic 분포는 큰 구역들이 서로 가까이 정렬되어 있고 Mg가 첨가된 $LiNbO_3$는 잘 키워진 단결정으로 나타났다.

1. Introduction

ABX_3 compounds where A and B are cations and X an anion have been a peculiar interest in studying transitions. These materials show various chemical structural transitions including order-disorder and commensurate-incommensurate in the wide range of temperatures [1-4]. Magnetic properties of the system have been also intensively studied. Especially, at low temperatures, many of those compounds have low dimensional magnetic long range order, which enables one to investigate a theoretical magnetic model experimentally [5,6].

$LiNbO_3$ is widely used for optical elements and surface acoustic wave devices. Optical wave guides can be produced by adding impurities because implantation can modify the refraction index in defined regions. One of the great importances of impurity is an improvement of resistance to optical damage. High Mg doping leads to optical device where the light wave fronts are not distorted and can be a promising laser material with high optical damage threshold [7-10].

Achieving single crystal has been a crucial point in doing many basic science and application. Because of the different crystal forming conditions for every crystal, many efforts have been devoted to determine the optimum conditions of stabilization in cooling from melting. Temperature step and delay time are especially important to get clean samples. Crystal growing techique has to be selected based on the circumstance required. It can be air or inert gas. Vacuum is required when the system is hygroscopic or active with gases. Crystals grown with good-care normally represent good-looking. But it doesn't necessarily mean nice crystal. There are a few ways of investigating crystal quality. X-ray and electron microscope can be used to measure the bulk properties when sample is transparent or has large penetration depth for these beams. But in many of the cases those are useful for surface measurements. Optical method is one of the easist ways but it is limited for the certain cases because the interference of long

disorientations of domains. Neutron scattering is the unique technique to measure the surface as well as bulk. Instead of reacting with atomic electrons as for the X-ray, electrons and other electromagnetic waves, neutron react with nuclei when it passes through the material because it doesn't have electric charges. It has large penetration depth for the most of the atoms in this reason. Most of the cases, neutron has short wavelength which is comparable to that of X-ray and thus has high resolving power. Many atoms are even very transparent for the neutron [11]. By using these advantages, three crystals of $KMnCl_3$, undoped and Mg-doped (0.1 mol%) $LiNbO_3$ were investigated. The aim of this study is to measure the mosaic spread to investigate the bulk properties of the single crystals.

2. Experiments

Single crystals were grown by Czochralski technique at the different batches. The measurements were carried out on the two axis spectrometer at the McMaster Nuclear Reactor. The spectrometer used a fixed incident neutron energy 3.36 THz with corresponding wavelength beam of 2.4258 Å which were scattered from a pyrolytic graphite monochromator. The instrument collected the scattered neutron beam at the single detector. Recently installed control and plotting program from Riso National Laboratory provided a lot of advantages in performing the crystal quality measurements and aligning the single crystals. The $KMnCl_3$ was placed at the aluminium sample cell in the helium atmosphere because the sample was very hygroscopic. The other two samples were measured in the open air. During the measurements, $KMnCl_3$ crystal was oriented with $(h00)$ and $(00l)$ in the scattering plane. Undoped and Mg-doped $LiNbO_3$ crystals were in the $(00l)$.

3. Results

For coherent elastic scattering, differential scattering cross section of scattered neutron can be explicitely written as [11]

$$\frac{d\sigma}{d\Omega} = \frac{N(2\pi)^3}{v} \sum_{\vec{\tau}} \delta(\vec{q}-\vec{\tau}) \mid F(\vec{q}) \mid^2$$

where unit cell structure factor is

$$F(\vec{q}) = \sum_d b_d \exp(i\vec{q} \cdot \vec{d}) \exp(-W_d).$$

On the above equations, N is the number of atoms in the unit volume, v is the unit cell volume, $\vec{q}$ is the scattering wave vector, $\vec{\tau}$ is a wave vector in the reciprocal space, b_d is the scattering length of a atom, $\vec{d}$ is a lattice position and $exp(-W_d)$ is the Debye-Waller factor. For the Bragg position, $\vec{q}=\vec{\tau}$ and Debye-Waller factor can be neglected on a narrow wave vector scan. Thus scattering intensity is proportional to the structure factor and written as

$$I(\vec{q}) = \mid F(\vec{q}) \mid^2 \text{ with } q = \frac{4\pi \sin\theta}{\lambda},$$

where λ and 2θ are wave length and scattering angle, respectively. In this way the crystal structure can be directly investigated by measuring scattered intensities.

The compound of $KMnCl_3$ has two kinds of structures at room temperature. One is perovskite-like structure which is an orthorhombic distortion of tetragonal. The other is also orthorhombic of the type for $KFeCl_3$ with lattice constant a = 8.77 Å, B = 3.88 Å, c = 14.42 Å [12], Fig. 1 shows rocking curve at (200). As can be seen, there are many scattering peaks. The resolution of the incident beam through the collimator is about 0.4 degrees in full width at the half maximum (HWHM). This diffraction pattern can be well investigated with following scenario. Most of the cases, if the diffraction pattern is well defined elastic Bragg peak, it should have the Gaussian profile. But the diffraction pattern in this sample shows many uncorrelated peaks. If we force to fit the peak with Gaussian, FWHM of largest

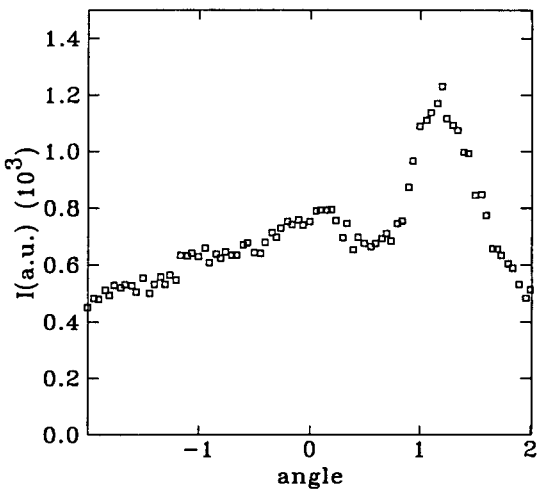

Fig. 1. Rocking curve for $KMnCl_3$ on the (200) reflection. The square is measured data and the angle is the sample rotation (ψ). The pattern represents there are many domains.

one is about 0.7 degrees. There are also large background scattered from many domain boundaries. This indicated that many crystal axis are oriented at the different angles. If large domains are well seperated with different orientations, the scattered Bragg peak can be resolved within the incident beam resolution limit. When bulk is not single crystal but has domains with same orientation, small peak brodening from the result of scattering at the domain boundaries can be detected. Diffraction pattern doesn't show such an narrow peak width. After all, this sample can be thought as having multi-domains with relatively random orientations. From the sight of scientific research and applications, this kind of sample is hard to be used to determine the chemical structure. This one can not be used to study dynamics either, because it is hard to place all the atoms at the right position in the reciprocal space.

$LiNbO_3$ has hexagonal structure with lattice constant a = 5.148 Å and c = 13.863 Å at room temperature [13]. Scattering pattern at (002) looked good. In order to improve scattering angle resolution, since at higher scattering angle diffracted angle distribution becomes narrower for a incident energy, a scan was made at (004) reflection plane. Fig. 2 shows this diffraction pattern. The peak is asymmetric and wider than resolution limit. The peak can be fitted with two Gaussians with small seperation of center. This can be understood that two or a few domains are closely oriented along the

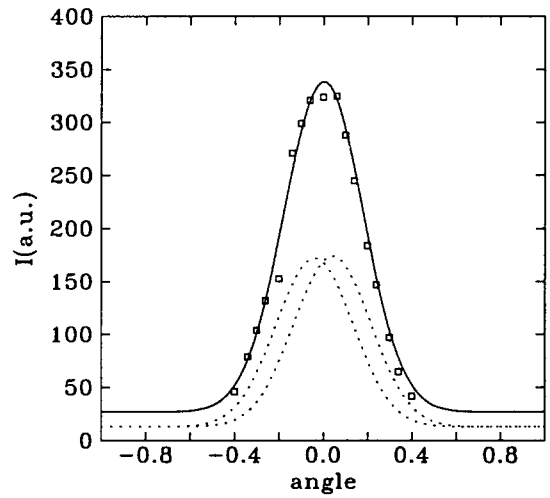

Fig. 2. Rocking curve for $LiNbO_3$ on the (004) reflection. The square is measured data, dotted are 2 Gaussians from fit and the solid line is the summation of those Gaussians. The angle is the sample rotation (ψ).

same axis. This small mosaic spread sample can be used for applications and some scientific researches as studying electric and dielectric properties. But one has to keep in mind the small disorientation when the sample is used as for studying ordering process and existence of spin density waves. A long incident wave length has very large resolving power in the reciprocal space and the small disorientation can lead satellite which can be thought as incommensurate ordering. The incident low energy beam also has high energy resolution and the diffractions from electron density wave may lead wrong positions of ordering wave vector. Fig. 3 is the picture of $LiNbO_3$ crystal. The poling axis does not have to be same as that of the crystal axis as shown. The crystal axis can be aligned as exactly as we need within a beam resolution limit. To located the better axis positions, a incident beam can be narrowed.

Fig. 4 represents the diffraction from Mg doped $LiNbO_3$ at (004) reflection. The pattern is symmetric and fit results the peak width within the resolution limit. This is really well grown sample.

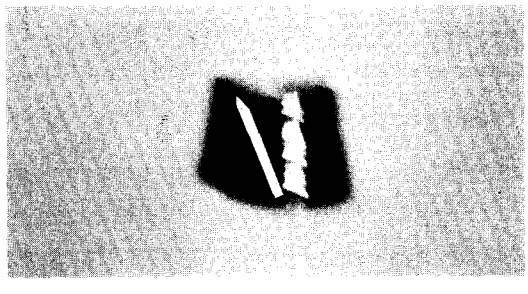

Fig. 3. Cylindrical shape $LiNbO_3$ crystal with diameter 10 mm. The vertical arrow represents poling axis and leaning arrow shows crystal c axis aligned by using neutron scattering.

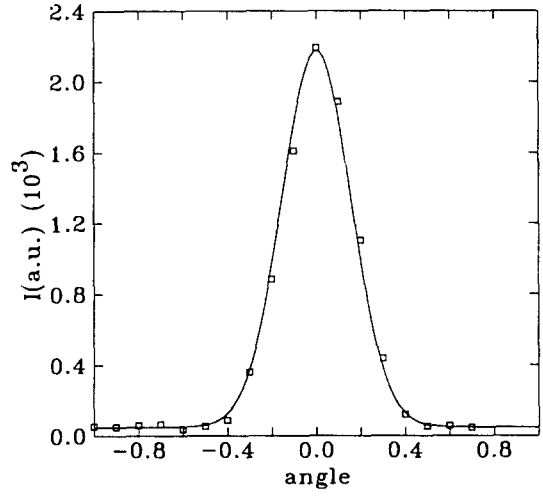

Fig. 4. Rocking curve for Mg-dopped $LiNbO_3$ on the (004) reflection. The square is measured data. The solid line is the result of a fit with Gaussian. The angle is the sample rotation (ϕ).

In summary, three single crystals have been investigated to search mosaic spread which gives crucial informations of crystal qualities. Among these, impurity doped one is best grown.

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