Growth and characterization of MnO doped near stoichiometric $LiNbO_3$ crystals

Z. J. SUN, H. T. LI, X. H. ZHEN, L. C. ZHAO
School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China

$LiNbO_3$ (LN) crystal is an excellent photorefractive material which has been used in many fields [1]. The conventional LN crystal is generally of congruent composition (CLN) with a [Li]/[Nb] ratio of 0.946 [2]. CLN crystals have, however, disadvantages such as low response speed and low resistance to photodamage, which limit their usage for holograph storage [3]. The stoichiometric LN (SLN) crystal shows significant improvement in some photorefractive properties and the response speed of SLN crystals is two orders higher than that of CLN crystals [4, 5]. However, for holograph storage, the diffraction efficiency of the SLN crystal has to be increased by doping with ions such as Fe, Cu, and Mn. In the present study, SLN crystals were grown by the top-seeded solution growth (TSSG) method with K_2O flux added to Li_2O-Nb_2O_5 melt [6]. Because MnO-doped SLN crystals have not been studied systematically, and because CLN crystals doped with high concentrations of Mn ions show better storage properties than when doped with Fe and Cu ions [7], Mn ions were chosen as the dopant for the SLN crystals. The domain structures, IR spectra, and Curie temperature of the crystals were investigated.

The MnO-doped SLN crystals were grown from congruent composition melts (48.6 mol% Li_2O) containing 6 wt% K_2O. MnO was added to melt at concentrations of 0, 0.05 wt%, 0.16 wt%, and 0.32 wt%. CLN crystals were grown for comparison. The raw material compositions of different samples were given in Table I. CLN seeds were used to grow the MnO-doped SLN crystals, and the crystals were grown along the *c* axis. Since the concentration of doped MnO was low, it had little effect on the growth conditions. The MnO-doped SLN crystals were grown under the optimal conditions: the temperature gradient above the melt of 25 °C/mm, the pulling speed of 0.2 mm/h, and the rotation rate of seeds of 15 rpm. The growth conditions of CLN crystals were as follows: temperature gradient above melt of 5 °C/mm, pulling speed of 2 mm/hr and rotation rate of seeds of 20 rpm.

In order to study the ferroelectric domain structure, the as-grown crystals were cut into 2-mm thick slices perpendicular to the growth direction. The slices were ground using SiC powders and polished using a 0.2-μm diamond solution. The surfaces of the slices were etched in an acid solution ($HF:HNO_3 = 1:2$ by volume) for 20 min, and then they were observed using an MC80DX ZEISS optical microscope. For measuring IR spectra, 3-mm thick samples were cut from the as-grown SLN-0, SLN-0.05, SLN-0.16, SLN-0.32, and CLN-0 crystals and polished to optical quality. A Nicolet-710 FT-IR spectrometer was used in the 3000–4000 cm^{-1} wavenumber range at room temperature. The Curie temperatures of the crystal powders were measured using a differential thermal analysis (DTA) ZRY-2P system.

TABLE I Raw material compositions of samples

Samples	Concentration of MnO (wt%)	Concentration of K_2O (wt%)	[Li]/[Nb]
SLN-0	0	6	0.946
SLN-0.05	0.05	6	0.946
SLN-0.16	0.16	6	0.946
SLN-0.32	0.32	6	0.946
CLN-0	0	0	0.946

Under the optimal growth condition of TSSG method, SLN-0, SLN-0.05, SLN-0.16, and SLN-0.32 single crystals were harvested with good optical qualities. As an example, a photograph of an SLN-0 crystal is shown in Fig. 1.

Figs 2a and b are micrographs showing the ferroelectric domain structures of SLN-0, as revealed on the etched surfaces in the direction of $-c$ axis and $+c$ axis. It was found that the surfaces of samples SLN-0.05, SLN-0.16, and SLN-0.32 showed the same triangular corrosion pits in the direction of $-c$ axis and no obvious changes in the direction of $+c$ axis as for SLN-0. The surfaces of CLN-0 showed no obvious changes in both $-c$ axis (Fig. 2c) and $+c$ axis directions (Fig. 2d). The results indicate that the SLN-0, SLN-0.05, SLN-0.16,

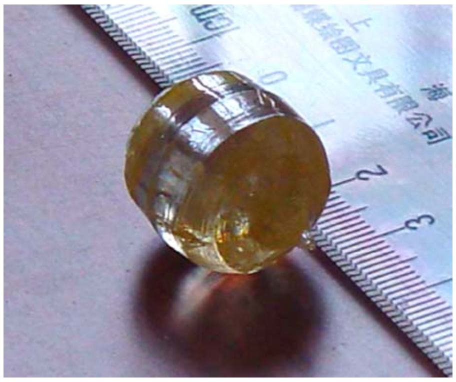

Figure 1 Photograph of SLN-0 crystal.

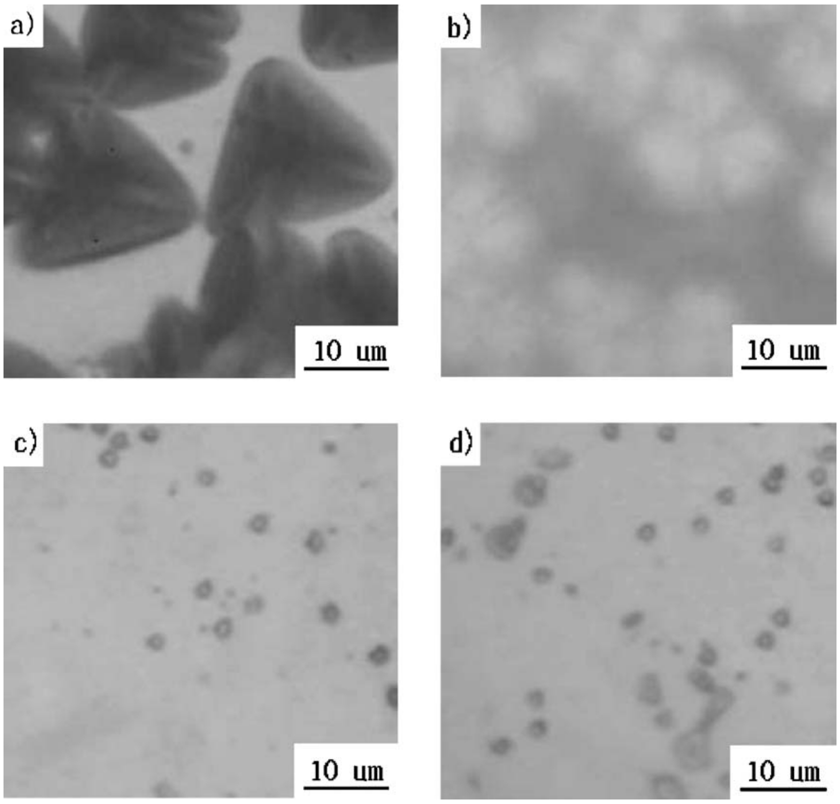

Figure 2 Domain structure of stoichiometric LN and congruent LN crystals: (a) the direction of $-c$ axis of SLN-0 crystal, (b) the direction of $+c$ axis of SLN-0 crystal, (c) the direction of $-c$ axis of CLN-0 crystal, and (d) the direction of $+c$ axis of CLN-0 crystal.

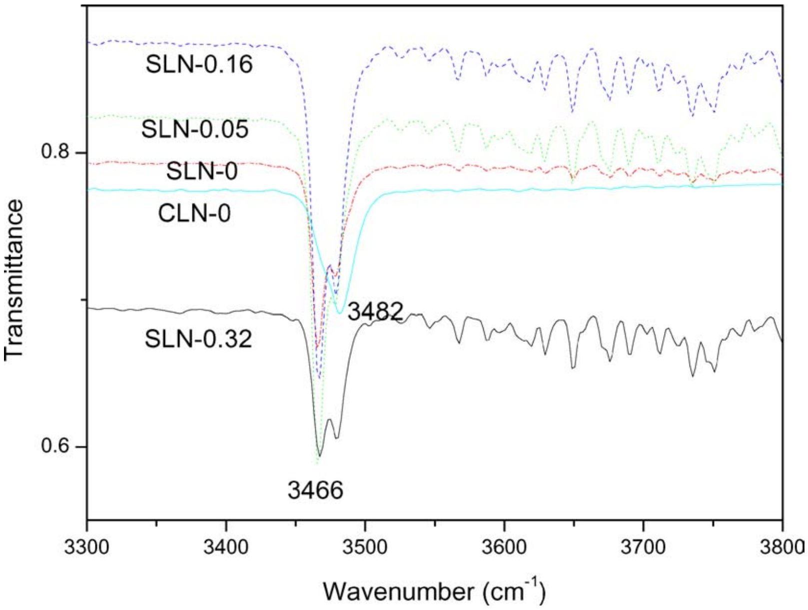

Figure 3 The IR absorption band related to the OH$^-$ vibration.

and SLN-0.32 crystals grown by TSSG methods have a single-domain structure, which is one of the characteristics of stoichiometric LiNbO$_3$ crystals. However, the CLN crystals exhibited a multidomain structure and will require a poling treatment before being suitable for holograph storage.

As shown in Fig. 3, the OH$^-$ vibration band of the CLN-0 crystal was broader than those of SLN-0, SLN-0.05, SLN-0.16, and SLN-0.32 crystals in the IR transmittance spectra. The main band for CLN-0 is located at 3482 cm^{-1}, whereas the main bands of SLN-0, SLN-0.05, SLN-0.16, and SLN-0.32 are located at 3466 and 3481 cm^{-1}. The former at 3466 cm^{-1} is a marker of stoichiometric LN crystal [8]. The IR spectra show that the SLN-0, SLN-0.05, SLN-0.16, and SLN-0.32 crystals were near stoichiometric.

Fig. 4 shows that the Curie temperature is dependent on the MnO concentration in the melt. The Curie temperatures of SLN-0, SLN-0.05, SLN-0.16, and SLN-0.32 were 1191.5, 1195.3, 1201.5, and 1219 °C respectively. As shown in Fig. 4, the Curie temperature increased with increasing MnO concentration. In CLN

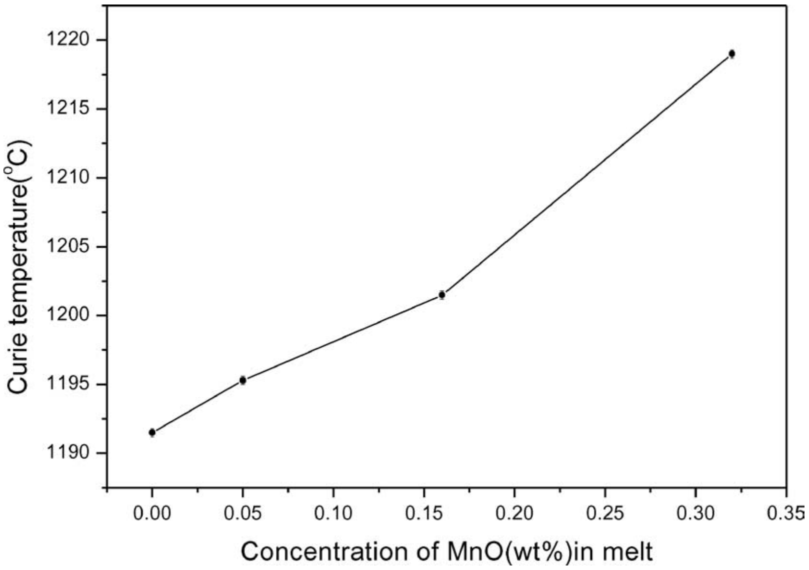

Figure 4 The dependence of the Curie temperature on the MnO concentration in melt.

crystals, the Curie temperature is a function of the antisite defect (Nb_{Li}) concentration, and it decreases proportionally to the Nb_{Li} concentration [9]. However, the concentration of Nb_{Li} defects in the SLN-0 crystals was two orders less than that in CLN crystals [10]. The doped Mn ions replace not only all the Nb ions on the Li ion site (Nb_{Li}) but also part of the Li ions on the Li ion site (Li_{Li}) [11]. So it is the increase in Mn_{Li} defects that induces the Curie temperature increase with increasing MnO concentration.

In conclusion, good quality SLN-0, SLN-0.05, SLN-0.16, and SLN-0.32 single crystals were grown by the TSSG method. The domain structure and IR spectra showed that these single crystals were near stoichiometric. The Curie temperature of MnO-doped SLN crystals was dependent on the MnO concentration in the melt.

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