# Room temperature ferromagnetism of nonmagnetic element Ca-doped LiNbO₃ films*

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The nonmagnetic element Ca-doped LiNbO₃ films were prepared on Si (111) substrates by radio frequency (RF) magnetron sputtering technique. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) indicate that the Ca atoms enter the LiNbO₃ lattice in the form of $Ca^{2+}$ ions. Superconducting quantum interference device (SQUID) results show that the Ca-doped LiNbO₃ films have room-temperature ferromagnetism and a maximum saturation magnetization of 4800 A/m at the 3% of Ca atom doping concentration. The room temperature ferromagnetism of the Ca-doped LiNbO₃ films can be attributed to the occurrence of vacancies due to Ca doping and is the intrinsic property.

In recent years, the multiferroic materials with simultaneous ferromagnetism and ferroelectricity have attracted much attention because of their interesting physical properties and a wide range of potential applications in some devices, such as magnetic data storage, non-volatile memories, and sensors[1-3]. However, the single-phase multiferroic materials are relatively rare[4], due to two reasons: the ferromagnetism and ferroelectricity turn out to be mutually exclusive[5-7] and ferromagnetism tends to be metallic while ferroelectricity coexists with insulating state[8]. Therefore, in order to resolve these problems, many investigations are being extensively carried out.

Some researches suggested that the ABO₃-type ferroelectric oxide can be easily doped by the 3d transition metal to produce ferromagnetism. For this reason, as a representative of the ABO₃-type ferroelectric oxide, LiNbO₃ is worth investigating for its unexceptionable ferroelectric and crystal structural properties, such as a strong room temperature spontaneous polarization of 70 $\mu C/cm^2$ and a high ferroelectric transition temperature of 1483 K[9,10]. Recently, some investigations showed that the ferromagnetism of LiNbO₃ can be obtained by the introduction of transition metal (TM) ions into LiNbO₃. Song et al[11,12] reported that the implantation of cobalt ions into the LiNbO₃ wafers induces the ferromagnetic behavior of LiNbO₃ at room temperature. Chen et al[13] also reported that the LiNbO₃ wafers implanted with manganese ions exhibit ferromagnetism. Lately, Sheng et

al[14] reported that vanadium can induce the room temperature ferromagnetic behavior of LiNbO₃ by doping it into LiNbO₃. These researches are beneficial to the exploration of new ABO₃-type multiferroic materials.

However, the TM-doped LiNbO₃ easily produces the TM clusters and magnetic secondary phases, which obscures the intrinsic magnetic property of the TM-doped LiNbO₃. But the nonmagnetic element doped LiNbO₃ can effectively avoid the above disadvantages if the nonmagnetic element doped LiNbO₃ has magnetic property, because unlike TM elements, the nonmagnetic element itself and related compounds are not magnetic. Therefore, the nonmagnetic element doped LiNbO₃ is an ideal system to investigate the magnetic mechanism of the doped LiNbO₃. As far as we know, there is no report on the room temperature ferromagnetism of nonmagnetic element doped LiNbO₃.

In this work, we choose Ca as doping element of LiNbO₃ films to investigate the magnetic properties of LiNbO₃ and the results exhibit that the Ca-doped LiNbO₃ films present room temperature ferromagnetism. Because the Ca clusters and its secondary phases are not magnetic, the magnetic property of the Ca-doped LiNbO₃ films should be an intrinsic property. The origin of the ferromagnetic behavior is also discussed in this paper.

The Ca-doped LiNbO₃ films were deposited on Si (111) substrates with a SiO₂ buffer layer by radio frequency (RF) magnetron sputtering technique. The base pressure

of the sputtering system was about $9 \times 10^{-5}$ Pa and the films were deposited at the sputtering pressure of 1.6 Pa for 2 h. A mixture of $O_2/Ar$ with a flow ratio of 5:10 was introduced into the deposition chamber as the sputtering gas. The deposition temperature and RF power were controlled at 575 ℃ and 85 W, respectively. The $LiNbO_3$ target on top of some Ca chips (square in 3 mm × 3 mm, 99.99% purity) symmetrically attached as the co-sputtering target was used to fabricate the Ca-doped $LiNbO_3$ films. By adjusting the number of Ca chips, the $LiNbO_3$ films with different Ca-doped concentrations were obtained. In order to improve the crystalline quality of the films, the deposited-films were annealed by a tube furnace at 1000 ℃ for 1 h in air.

X-ray diffraction (XRD) analysis with Cu Kα radiation ($\lambda$=0.15406 nm) was used to determine the crystal structure and phases in the films. The thickness of the films was estimated using a scanning electron microscopy (SEM). The composition and the element valence of the films were characterized by X-ray photoelectron spectroscopy (XPS) spectra. The 1%, 2% and 3% Ca atom doping concentrations in $LiNbO_3$ films were determined by the elemental sensitivity factor method based on the XPS measurement. The ferromagnetism of the films was recorded using a superconducting quantum interference device (SQUID) magnetometer at 300 K.

Fig.1(a) shows the XRD patterns of the undoped, 1%, 2% and 3% Ca-doped $LiNbO_3$ films annealed at 1000 ℃. From Fig.1(a), it can be seen that the diffraction peaks of the films are indexed as a typical R3c structure of $LiNbO_3$[15] and no diffraction peaks connect with the metallic calcium or its secondary phases, suggesting that the $LiNbO_3$ film is formed and there are not the calcium clusters or secondary phases in the Ca-doped $LiNbO_3$ films. Fig.1(b) shows the enlarged view of (104) diffraction peaks of the Ca-doped $LiNbO_3$ films. The clear shift of the (104) peak to lower $2\theta$ angles is observed with the increase of Ca doping concentration, because the Ca doping results in the change of lattice parameter of $LiNbO_3$, indicating that the Ca atoms are incorporated into the lattice of $LiNbO_3$.


(b)
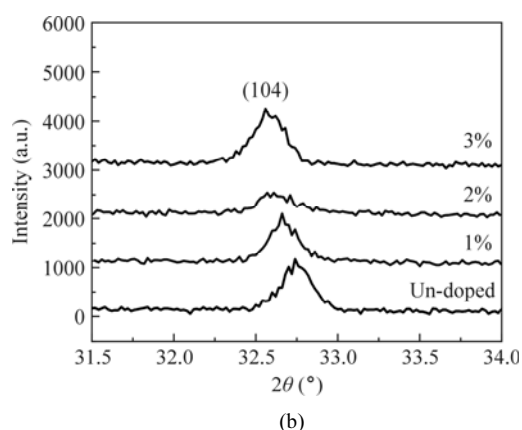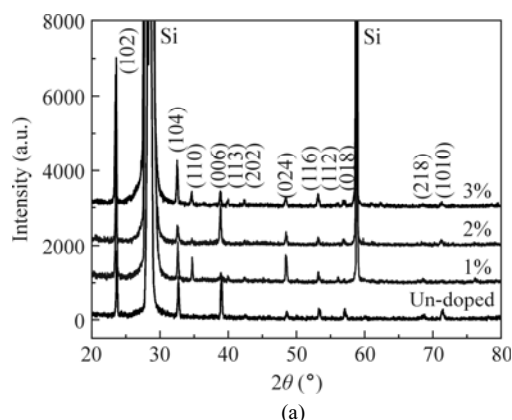
**Fig.1 (a) X-ray diffraction patterns of the un-doped, 1%, 2% and 3% Ca-doped $LiNbO_3$ films; (b) Enlarged view of (104) diffraction peaks of the Ca-doped $LiNbO_3$ films**

Fig.2 shows the Ca 2p, Li 1s (with the nearby Nb 4s level), Nb 3d and O 1s XPS spectra of the 2% Ca-doped $LiNbO_3$ films. The charge-shifted spectra were corrected using the adventitious C 1s photoelectron signal at 284.6 eV. The Ca 2p XPS spectrum is depicted as shown in Fig.2(a). The peaks located at 346.78 eV and 350.78 eV can be ascribed to Ca $2p_{3/2}$ and Ca $2p_{1/2}$ binding energy, respectively. The Ca $2p_{3/2}$ binding energy of the Ca-doped $LiNbO_3$ film located at 346.78 eV is clearly different from that of metallic calcium (345.9 eV) and is very close to that of CaO (346.65 eV)[16]. This suggests that Ca atoms in the form of $Ca^{2+}$ ions are incorporated into the $LiNbO_3$ lattice. Fig.2(b) shows the Li 1s XPS spectrum. Li 1s binding energy is located at 55.08 eV, indicating that the Li remains in a typical $Li^+$ valence. Fig.2(c) shows the Nb 3d XPS spectrum. The Nb $3d_{5/2}$ and Nb $3d_{3/2}$ peaks are located at 206.38 eV and 209.08 eV, respectively, indicating that Nb is $Nb^{5+}$ valence[17]. Fig.2(d) shows the O1s XPS spectrum. The peaks located at 529.56 eV and 531.75 eV respectively, can be ascribed to the $LiNbO_3$ lattice oxygen and the oxygen deficient regions[18, 19].

Fig.3 shows the room temperature M-H curves of the Ca-doped $LiNbO_3$ films with different Ca concentrations. From Fig.3, it can be seen that the Ca-doped $LiNbO_3$ films exhibit the room temperature ferromagnetism and the clear hysteretic behavior at lower fields (the inset of Fig.3), and the saturation magnetization ($M_s$) increases from 1870 A/m to 4800 A/m with Ca atom doping concentration from 1% to 3%. This proves that the Ca doping is effective for the room temperature ferromagnetism of $LiNbO_3$ films. From above XRD and XPS results, we know that the Ca atoms enter the $LiNbO_3$ lattice in the form of $Ca^{2+}$ ions. Because the valence of Ca ions is different from that of Nb and Li ions, the O vacancies and Li vacancies are induced to compensate the charge non-equilibrium[20]. The Li vacancies could induce the spin-


(a)

polarization of O 2p electrons[21] and O vacancies would result in the exchange interactions between located electron



(a)



(b)



(c)



(d)
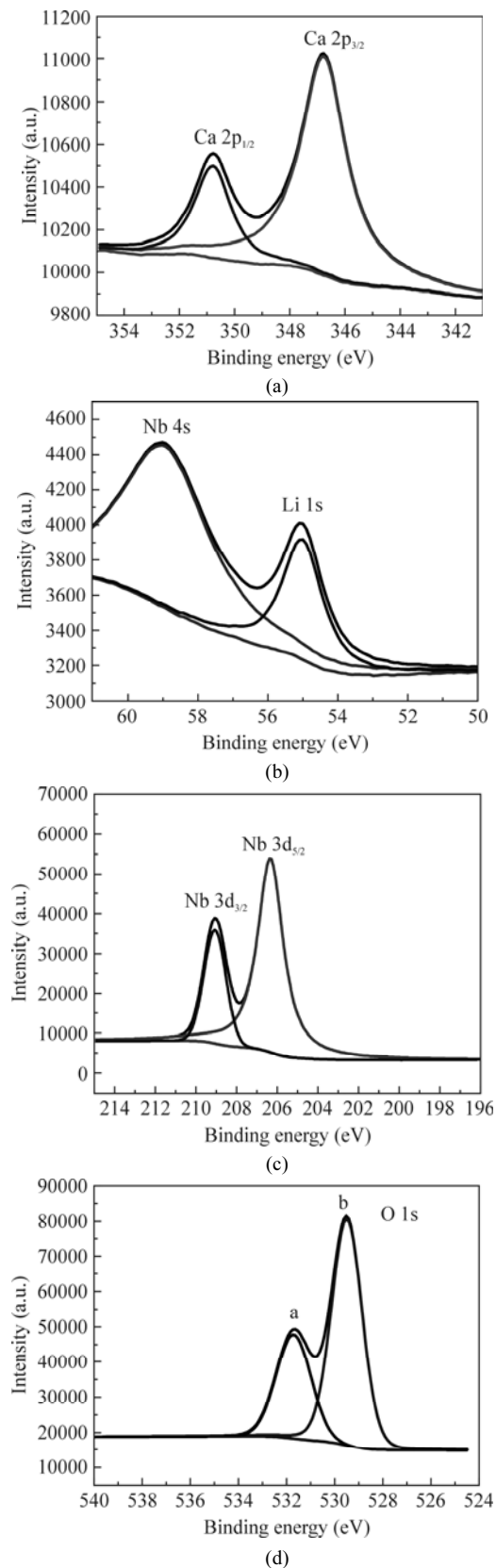
**Fig.2 (a) Ca 2p, (b) Li 1s, (c) Nb 3d and (d) O 1s XPS spectra of the 2% Ca-doped LiNbO₃ film**
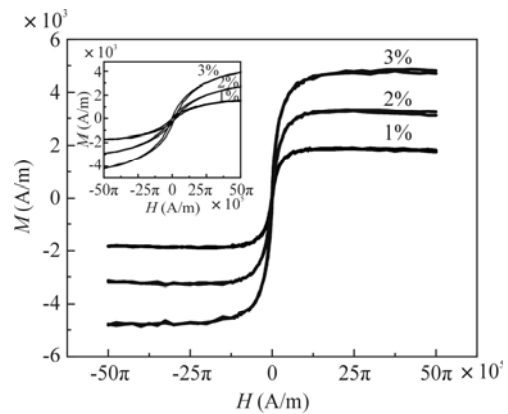


**Fig.3 Magnetization curves of the 1%, 2% and 3% Ca-doped LiNbO₃ films at room temperature (Inset shows an enlarged view of M-H curves.)**

spin moments[22], so the vacancies should be responsible for the ferromagnetism of the Ca-doped LiNbO₃ films. Recent first principle calculation indicated that the magnetic properties of the A (A = Ca, Sr, Ba) substitution for Li in LiNbO₃ result from the s orbital of Nb atoms around the doping element[23]. Anyways, the room-temperature ferromagnetism induced by the nonmagnetic element Ca doping in LiNbO₃ film is the instinct property and deserves careful investigation.

In summary, the undoped, 1%, 2% and 3% Ca-doped LiNbO₃ films were deposited on Si (111) substrates by radio frequency magnetron sputtering technique. The Ca-doped LiNbO₃ films show room-temperature ferromagnetism. The saturation magnetization increases from 1870 A/m to 4800 A/m with Ca atom doping concentration from 1% to 3%. The Ca atoms in the form of $Ca^{2+}$ ions enter the LiNbO₃ lattice and the $Ca^{2+}$ incorporation can induce the formation of the Li vacancies or O vacancies for the charge compensation. The vacancies are responsible for the intrinsic ferromagnetism of the Ca-doped LiNbO₃ films.

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