



Complete, reversible H^+/Li^+ ion exchange reaction between rhombohedral $LiMO_3$ and perovskite-type HMO_3 ($M = Nb, Ta$)

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Abstract

We demonstrate for the first time the complete, reversible H^+/Li^+ ion exchange reaction between HMO_3 and $LiMO_3$ ($M = Nb, Ta$) using molten $LiNO_3$ at $320^\circ C$ for 5 days. HMO_3 were prepared from $LiMO_3$ by ion exchange reactions using dilute HNO_3 . The results reveal that both $LiMO_3$ prepared by normal solid state reaction between Li_2CO_3 and M_2O_5 , and by ion exchanged from HMO_3 using molten $LiNO_3$ are isostructural. $LiMO_3$ prepared using HMO_3 yields nearly uniformly sized crystallites in contrast to those prepared by conventional solid state synthesis. The present method is simple and inexpensive compared to other methods of preparation of high purity $LiMO_3$ powders.

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1. Introduction

Both lithium niobate and tantalate are typical ferroelectric and nonlinear optical materials, which have drawn much attention due to potential applications in surface acoustic wave devices and integrated optics [1,2]. It has also been reported that rhombohedral $LiMO_3$ ($M = Nb, Ta$) [3,4] shows an exchange [5–7] of Li^+ for H^+ and

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yields new proton conducting [8] solids with the perovskite-type HMO_3 [5,7]. This proton exchange property of LiMO_3 has been studied by a number of researchers [5–9]. For example, detailed structural investigations revealed that the $\text{Li}_{1-x}\text{H}_x\text{NbO}_3$ system exhibits a complex structural chemistry with several phase transformations depending on the x value [6]. A variety of distinct phases with different structures have been isolated rudimentary phase diagram has been constructed for the LiNbO_3 – HNbO_3 system [10]. Furthermore, a new monoclinic phase with the chemical composition $\text{Li}_{0.23}\text{H}_{0.77}\text{NbO}_3$ ($a = 8.906(3) \text{ \AA}$, $b = 5.191(3) \text{ \AA}$, $c = 13.944(8) \text{ \AA}$, $\beta = 90.77(5)^\circ$) was found for x approximately equal to 0.77 [6].

The complete reversible exchange of H^+ to Li^+ in HMO_3 has not been reported in the literature. Recently, Ohsaka et al. [10] reported that the reverse lithium ion exchange of cubic perovskite HNbO_3 occurred through a homogeneous solid solution of cubic $\text{Li}_x\text{H}_{1-x}\text{NbO}_3$ for x from 0 to 0.2 using 0.1 M LiNO_3 and 0.1 M LiOH . A rhombohedral phase of $\text{Li}_x\text{H}_{1-x}\text{NbO}_3$ appeared for $x > 0.2$ along with the cubic

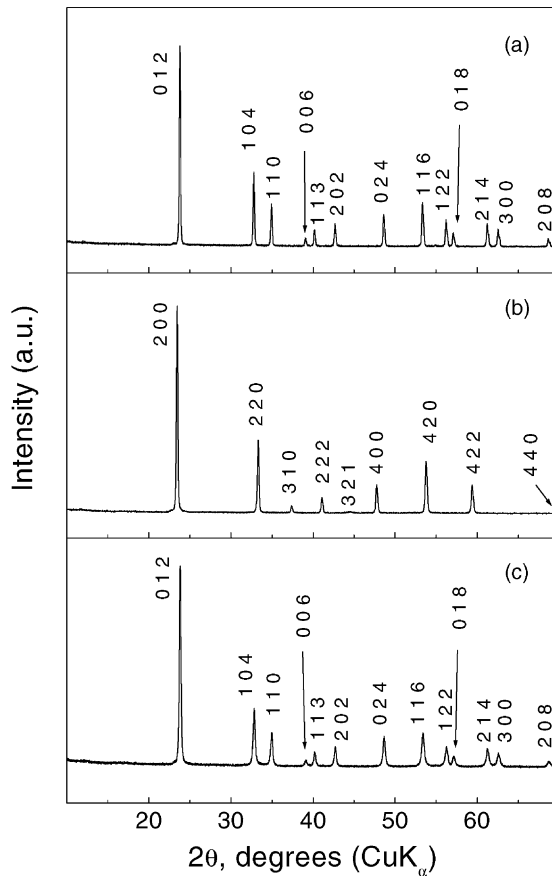


Fig. 1. Powder XRD patterns of (a) solid state synthesized LiNbO_3 , (b) HNbO_3 obtained from LiNbO_3 by ion exchange reaction, and (c) LiNbO_3 prepared from HNbO_3 using molten LiNO_3 at 320°C for 5 days.

phase. The maximum value of x was found to be 0.45 and 0.61 at 30 and 60°C, respectively. The irreversible ion H^+/Li^+ exchange was related to the low mobility of protons and lithium ions in $Li_xH_{1-x}NbO_3$ with increasing lithium content [10]. In this paper, we show that it is possible, however, to exchange rapidly Li^+ and H^+ between HMO_3 and $LiMO_3$ by making use of molten $LiNO_3$.

2. Experimental aspects

$LiMO_3$ ($M = Nb, Ta$) were prepared by a solid state reaction using stoichiometric amounts of Li_2CO_3 and M_2O_5 at 900°C for 24 h [5]. The powder HMO_3 sample was prepared from $LiMO_3$ by stirring the compound in 8 M hot HNO_3 at 90–100°C for 5 days with intermediate replacement of acids after 3 days. Following the ion exchange reactions, the products were washed with water and dried in air at 120°C.

The reversible Li^+/H^+ ion exchange reaction was investigated by using aqueous 2 M $LiOH$ at 60–100°C and molten $LiNO_3$ (six-fold excess) at 320°C for 5 days. The

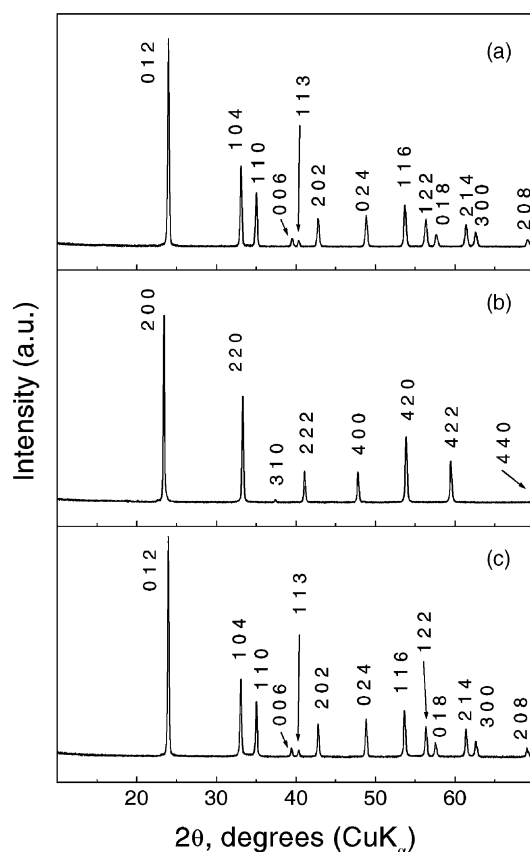


Fig. 2. Powder XRD patterns of (a) solid state synthesized $LiTaO_3$, (b) $HTaO_3$ obtained from $LiTaO_3$ by ion exchange reaction, and (c) $LiTaO_3$ prepared from $HTaO_3$ using molten $LiNO_3$ at 320°C for 5 days.

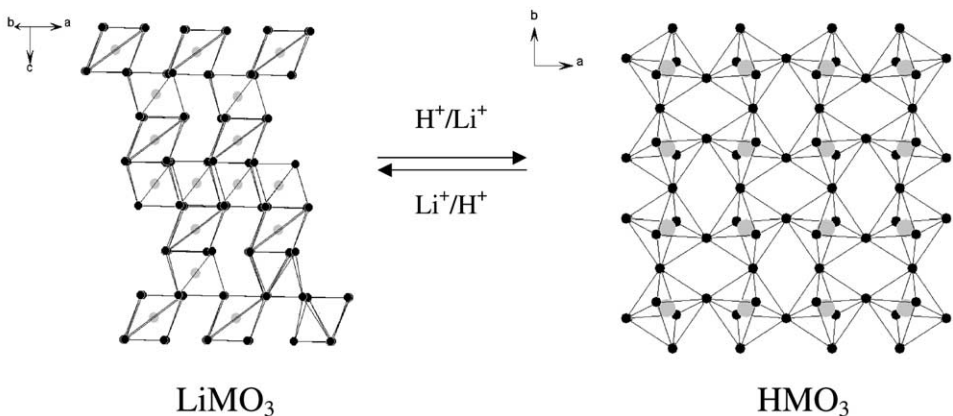


Fig. 3. Schematic representation of the reversible H^+/Li^+ ion exchange reaction between HMO_3 and LiMO_3 ($M = \text{Nb}, \text{Ta}$).

reaction products were washed with distilled water and dried in an oven at 120°C in air. Powder X-ray diffraction (XRD) (SEIFERT 3000 powder X-ray diffractometer ($\text{CuK}\alpha$)), thermogravimetric analysis (TGA) (Netzsch thermal analyzer (Model STA 409)), FTIR (Nicolet FTIR spectrometer using KBr) and scanning electron microscope (SEM) (PHILIPS SEM XL 30 electron microscope) techniques were employed for characterization of all the synthesized oxides.

3. Result and discussions

The formation of rhombohedral LiMO_3 (Figs. 1a and 2a) and perovskite-type HMO_3 (Figs. 1b and 2b) ($M = \text{Nb}, \text{Ta}$) was confirmed by powder XRD and TGA analysis, which is in agreement with literature data [11]. The attempt to exchange H^+

Table 1

Lattice constant of LiMO_3 (hexagonal) prepared from HMO_3 ($M = \text{Nb}, \text{Ta}$) by ion exchange reaction, solid state synthesized LiMO_3 and precursor HMO_3

Compound	Lattice constant (\AA)		Reference
	<i>a</i>	<i>c</i>	
LiNbO_3 from HNbO_3	5.141(2)	13.83(5)	Present study
LiNbO_3 solid state synthesized	5.142(9)	13.84(3)	Present study
LiNbO_3	5.1494	13.862	JCPDS no. 20-0631
LiTaO_3 from HTaO_3	5.141(1)	13.81(1)	Present study
LiTaO_3 solid state synthesized	5.141(1)	13.71(7)	Present study
LiTaO_3	5.1530	13.755	JCPDS no. 20-0836
HNbO_3	7.633(1)		Present study
HTaO_3	7.614(1)		Present study
HNbO_3	7.645(2)		JCPDS no. 36-0794
HTaO_3	7.6225(9)		JCPDS no. 38-0964

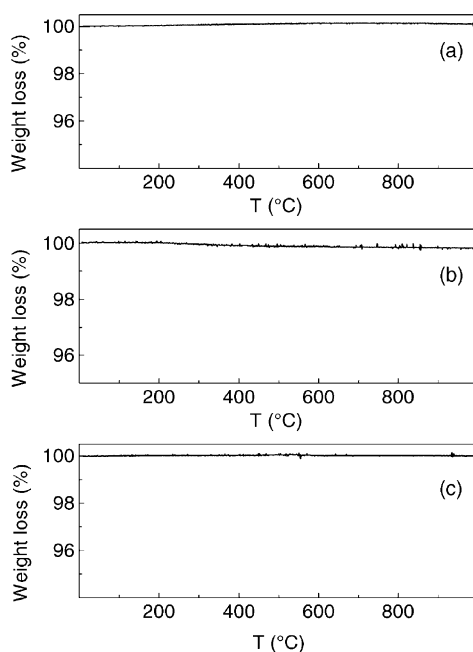


Fig. 4. TGA curves of (a) LiNbO_3 obtained from HNbO_3 by ion exchange reaction using molten LiNO_3 at 320°C for 5 days, (b) solid state synthesized LiNbO_3 , and (c) LiTaO_3 prepared from HTaO_3 by ion exchange reaction using molten LiNO_3 at 320°C for 5 days.

for Li^+ in HNbO_3 by using 2 M LiOH at $60\text{--}100^\circ\text{C}$ resulted in the formation of $\text{Li}_{0.61}\text{H}_{0.39}\text{NbO}_3$ showing that the Li^+/H^+ ion-exchange is incomplete under these conditions. This result is similar to that of Ohsaka et al. [10] who used 0.1 M LiNO_3 and 0.1 M LiOH at 60°C .

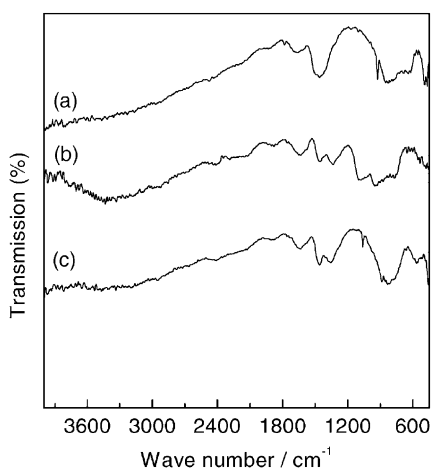


Fig. 5. FTIR spectra of (a) solid state synthesized LiNbO_3 , (b) HNbO_3 obtained from LiNbO_3 by ion exchange reaction, and (c) LiNbO_3 prepared from HNbO_3 using molten LiNO_3 at 320°C for 5 days.

However, when using molten LiNO_3 at 320°C for 5 days, we observed the formation of rhombohedral LiNbO_3 (Fig. 1c) instead of the perovskite-type structure modification. A similar ion-exchange reaction was found for HTaO_3 (Fig. 2). The mechanism of ion exchange appeared to be just in the reverse direction of the H^+ exchange against Li^+ in LiMO_3 since the cubic perovskite-type structure ($a = 7.6 \text{ \AA}$) of HMO_3 was obtained from rhombohedral LiMO_3 using diluted acids [5,7].

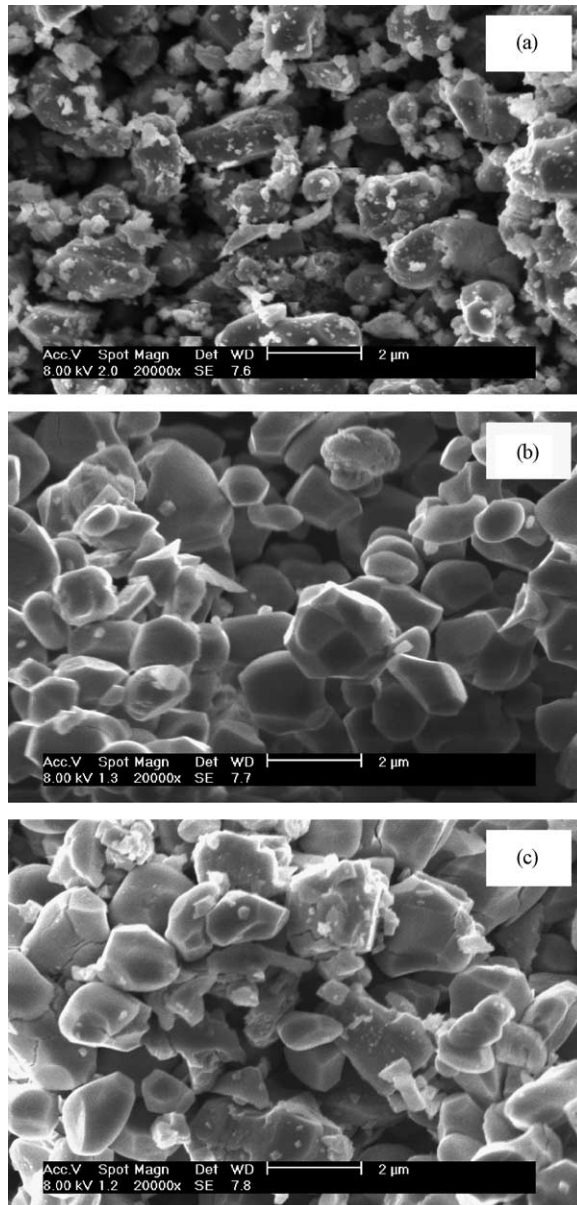


Fig. 6. SEM photographs of (a) solid state synthesized LiNbO_3 , (b) HNbO_3 obtained from LiNbO_3 by ion exchange reaction, and (c) LiNbO_3 prepared from HNbO_3 using molten LiNO_3 at 320°C for 5 days.

Fig. 3 shows the schematic representation of the reversible H^+/Li^+ ion exchange reaction between HMO_3 and $LiMO_3$ ($M = Nb, Ta$). Both $LiMO_3$ and HMO_3 belong to ABO_3 perovskite-like structures, consisting of MO_6 octahedral units. In the $LiMO_3$ structure, the oxygen atoms are hexagonal-close-packed, in which $2/3$ of the

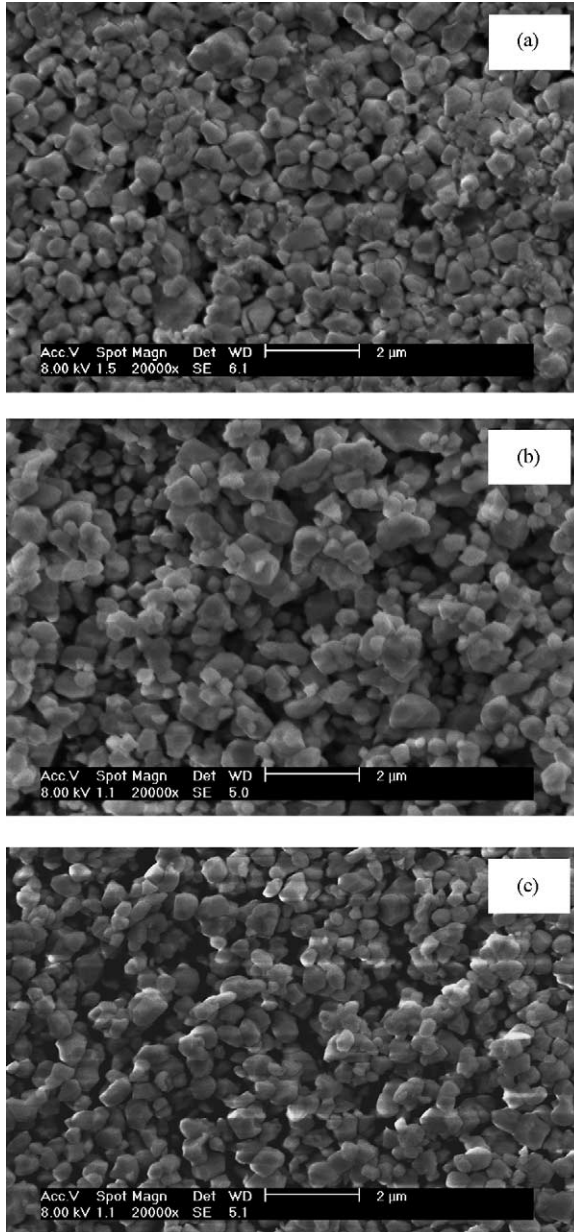


Fig. 7. SEM photographs of (a) solid state synthesized $LiTaO_3$, (b) $HTaO_3$ obtained from $LiTaO_3$ by ion exchange reaction, and (c) $LiTaO_3$ prepared from $HTaO_3$ using molten $LiNO_3$ at $320^\circ C$ for 5 days.

octahedral sites are occupied in an ordered manner with the sequences Li, M, vacancy, Li, M, vacancy, etc. for adjacent face-sharing octahedral sites along the *c*-axis of the rhombohedral unit cell. The M–O–M bond angles are close to 157° [5]. In an ideal perovskite structure the B–O–B angles are 180° and there is one large interstice per BO₃ unit, which is occupied by A ions with 12-fold coordination. The HMO₃ structure is built of NbO₆ corner sharing octahedra as in the ReO₃ structure (A-site deficient perovskite-like ABO₃ structure). The H atoms are found to statistically distribute on two types of positions at room temperature. The doubling of the edge of the primitive cell arises due to the tilts of the octahedra from the cube axis by 15.8° [7]. Table 1 lists the hexagonal lattice constants of LiMO₃ prepared from HMO₃ using the LiNO₃ melt together with LiMO₃ prepared by solid state reaction and precursor HMO₃ as well as literature data [11]. TGA data (Fig. 4) and FTIR spectra (Fig. 5) reveal that LiMO₃ obtained from HMO₃ is anhydrous, similar to the compound obtained by solid state reaction.

SEM images of LiMO₃ prepared from HMO₃ are shown together with those of HMO₃ and LiMO₃ prepared by solid state reactions in Figs. 6 and 7. We see LiMO₃ derived from HMO₃ (Figs. 6c and 7c) are crystallites of rather uniform size, which differs from that of the solid state reaction products (Figs. 6a and 7a). LiMO₃ prepared by solid state reaction shows crystals of irregular size and small agglomerated particles at the surface of the crystals. For the purpose of comparison the intermediate HMO₃ SEM images are shown in Figs. 6b and 7b. We see that HMO₃ phases are uniform in size, which leads to the formation of rather uniform sized LiMO₃. This is remarkable since the larger grain growth during the conventional solid state reaction lowers the surface area of the material, which is disadvantageous for many catalytic applications. LiMO₃ prepared from HMO₃ is quite uniform in size and shows clean surfaces without any second phase. Accordingly, LiMO₃ obtained from HMO₃ by ion exchange is considered to be phase-pure.

4. Conclusion

In summary, we have shown the reversible H⁺/Li⁺ ion exchange reaction between HMO₃ and LiMO₃ (M = Nb, Ta) using molten LiNO₃ at 320°C for 5 days. The present method yields nearly uniformly sized crystallites of LiMO₃ in contrast to those prepared by conventional solid state synthesis. The present method is very convenient and easily produces high purity ferroelectric LiMO₃. It is also relatively simple and inexpensive compared to other methods of preparation of high purity LiMO₃ including the sol–gel and Pechini methods.

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