

## Synthesis of Spinal $\text{Mg}_{1.5}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_3$ by a Solid State Reaction Method and Study of Its Exchange for $\text{Li}^+$

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**Abstract.** Spinel-type metal oxides, magnesium-manganese- titanium oxide ( $\text{Mg}_{1.5}\text{Mn}_{0.25}\text{Ti}_{0.5}\text{O}_3$ ) was prepared by a solid state reaction crystallization method. The acid treatments of  $\text{MgMn}_{0.25}\text{Ti}_{0.75}\text{O}_3$  caused  $\text{Mg}^{2+}$  extractions of more than 74%, while the dissolutions of  $\text{Mn}^{4+}$  and  $\text{Ti}^{4+}$  were less than 9.0%. The experimental results have proved that the acid-treated sample has a capacity of exchange 12.6mmol • g<sup>-1</sup> for  $\text{Li}^+$  in the solution.

### Introduction

At present, the studies on lithium-mentioned mainly focus on inorganic ion exchangers. The inorganic ion-exchange preparation has the advantage of thermo-stability and radiation resistance, synthesis simple and good selectivity etc. Apart from that, it appears the fine speciality in dealing with nuclear waste, gathering and separating of metal ions and chromatogram analysis [1-2]. In this paper, solid state reaction crystallization method was used to synthesize the  $\text{MgMn}_{0.25}\text{Ti}_{0.75}\text{O}_3$  of spinel-type oxide, whose composition and structure are different from those in literature[3-4], The experimental result have proved that the inorganic material has better selectivity and higher capacity of exchange for  $\text{Li}^+$  in the solution removed  $\text{Li}^+$  previously. Moreover, the cost is cheap and its application prospect is significant.

### Experimental Section

**Reagent and Instruments.**  $\text{MgO}$ ,  $\text{MnO}_2$  and  $\text{TiO}_2$  were all analytical reagents; pure ethanol; D/max-A type X-ray diffraction instrument; Dx-170 type ion chromatogram instrument; XQM planetary ball mill; AA-670 atom absorption spectrum instrument; tubular-furnace.

**Synthesis and Identifiable of  $\text{MgMn}_{0.25}\text{Ti}_{0.75}\text{O}_3$ .** The pure ethanol was dropped into a XQM planetary ball mill mixed powder of  $\text{MgO}$ ,  $\text{MnO}_2$  and  $\text{TiO}_2$  with a Mg/Mn/Ti mole ration of 1:0.25:0.75 at the condition of constant rate churning. After 8 hours, the mixture was mixed completely. After mixing fully, the mixture was pressed to tablet by tablet press machine. Then the tablet was heat-treated for 4.5h at 900°C to obtain the Mg-Mn-Ti metal compound, the sample was designed as MgMnTi-900, whose theoretical formula was  $\text{MgMn}_{0.25}\text{Ti}_{0.75}\text{O}_3$ . Then it was analysed of x-ray diffraction and compared to literature [3-4].

Composition analysis: A 0.2g portion of sample was dissolved with acid. The Mg, Mn and Ti contents were determined by atomic absorption spectrometry.

**The Cation Extraction of Mg-Mn-Ti metal compound and Acid Modification.** Four 0.200g portions of sample (MgMnTi-900 compound) were immersed in a  $\text{HNO}_3$  solution (50ml) of 0.01M, 0.1M, 1M and 10M respectively with shaking in constant temperature water at 25°C. After 3 days, take the supernatant solution to determine the cation concentration, test its acid proof ability and the extraction ration of  $\text{Mn}^{4+}$ ,  $\text{Ti}^{4+}$ .

A 5g portion of sample (MgMnTi-900) was immersed in a 1M  $\text{HNO}_3$  solution (500mL) with intermittent shaking in constant temperature water at 25°C. After 7 days, remove the supernatant solution and add new  $\text{HNO}_3$  solution. Repeating that for twice, then the initial sample was

transformed to H-type sample, washed with water and air-dried. The sample obtained by thermal crystallized at 900°C and acid modified was designated as MgMnTi-900 (H).

**Saturation Capacity of Exchange.** Weigh five 0.5g portions of MgMnTi-900 (H), then each portion was immersed in a 0.1M solution (10mL), containing Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> respectively, diluted to 100mL, shaken in constant temperature water at 25°C. After saturation exchanging (namely, after 10 days by literature[3-4]) the solutions were filtered by subminiature aperture sieve, and the cation concentration was determined. At the same time, do vacant experiment. Last, the inorganic exchanger saturation capacity of exchange for alkali-metal-ions is obtained by decrease quantity.

**Distribution Coefficient (Kd).** After weighing four 0.100g portions of MgMnTi-900 (H), each portion of sample was immersed in a 0.05M mixed solution (0.200mL) containing Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> (Cl<sup>-</sup>/OH<sup>-</sup> ratios are different in each solution, C(Cl<sup>-</sup>)+C(OH<sup>-</sup>)=0.1M, C= Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup>). The alkali-metals ions total concentration all was 1.0×10<sup>-3</sup>M by adding 9mL distilled water. After the samples were shaken for 7 days in constant temperature water at 25°C and were filtered, cation concentrations in each samples were obtained.

## Results and Discussion

**Compound and Appraisalment of MgMn<sub>0.25</sub>Ti<sub>0.75</sub>O<sub>3</sub>.** The X-ray diffraction pattern of compound metal oxide (MgMn<sub>0.25</sub>Ti<sub>0.75</sub>O<sub>3</sub>), crystallized was shown in figure 1. The structure of compound metal oxide MgMn<sub>0.25</sub>Ti<sub>0.75</sub>O<sub>3</sub> crystallized at 900°C was much perfect.

We know from chemical analysis, the composition of MgMnTi-900 is Mg<sub>0.98</sub>Mn<sub>0.24</sub>Ti<sub>0.74</sub>O<sub>2.98</sub>, whose chemical component is basically corresponded with the composition of inverse spinel-type metal oxides.

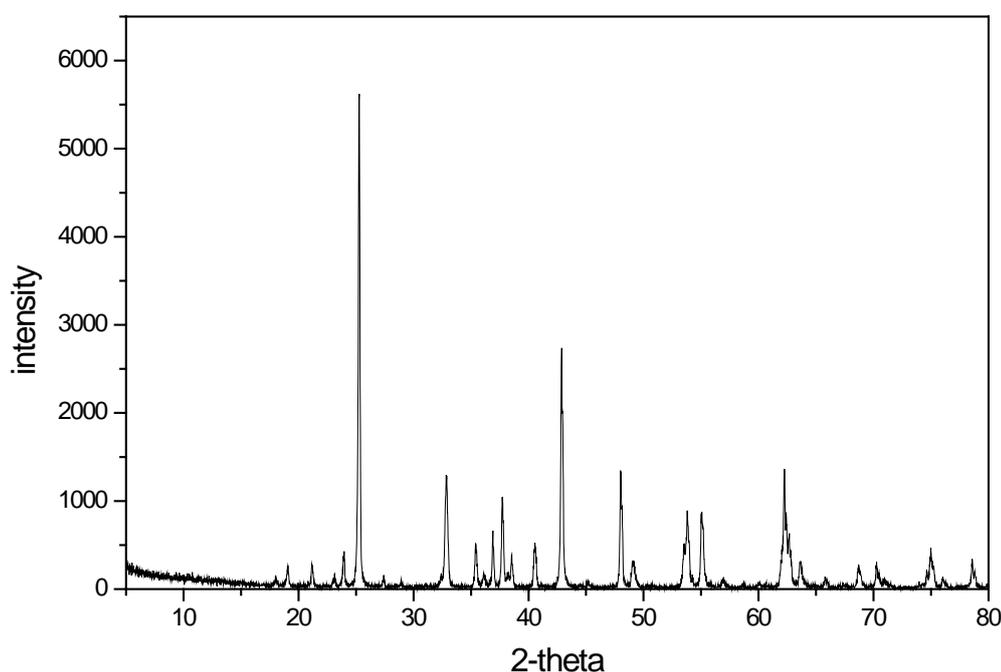


Fig.1 The powder's X-ray figures of Mg<sub>0.98</sub>Mn<sub>0.24</sub>Ti<sub>0.74</sub>O<sub>2.98</sub> crystal

**Cation Extraction of Metal Compound Mg-Mn-Ti and Acid Modification.** The extraction ration of Mg<sup>2+</sup>, Mn<sup>4+</sup> and Ti<sup>4+</sup> from MgMnTi-900 in different concentration HNO<sub>3</sub> solution is shown in Figure2. we know from Figure2, the extractabilities of Mg<sup>2+</sup> are 35%~80%, Mn<sup>4+</sup> are 6.6%~13.8, and Ti<sup>4+</sup> are 2.7%~8.7%. Those indicate that the extractabilities of Mg<sup>2+</sup> are higher than those of Mn<sup>4+</sup> and Ti<sup>4+</sup> when exchanger was immersed in 1 M acid solution, correspondding with the exchanger condition was better.(1 N, Mg<sup>2+</sup>74%, Mn<sup>4+</sup>9.0%, Ti<sup>4+</sup>6.4%)

X-ray diffraction of MgMnTi-900 (H), which is the acid modification product, is shown in Figure 1. As shown, the structure of MgMnTi-900(H) is nearly constant, which is spinel oxide type too. It indicates that the exchanger is steady. The analysis indicates the composition of MgMnTi-900 (H) was  $H_{1.45}Mg_{0.25}Mn_{0.22}Ti_{0.69}O_{2.68}$ , whose component of 74%  $Mg^{2+}$  transformed to  $H^+$  compared with the composition  $Mg_{0.98}Mn_{0.24}Ti_{0.74}O_{2.98}$  before acid-treated. Then the specific  $Mg^{2+}$  of exchanger were extracted basically and remained the H-type identified with initial type.

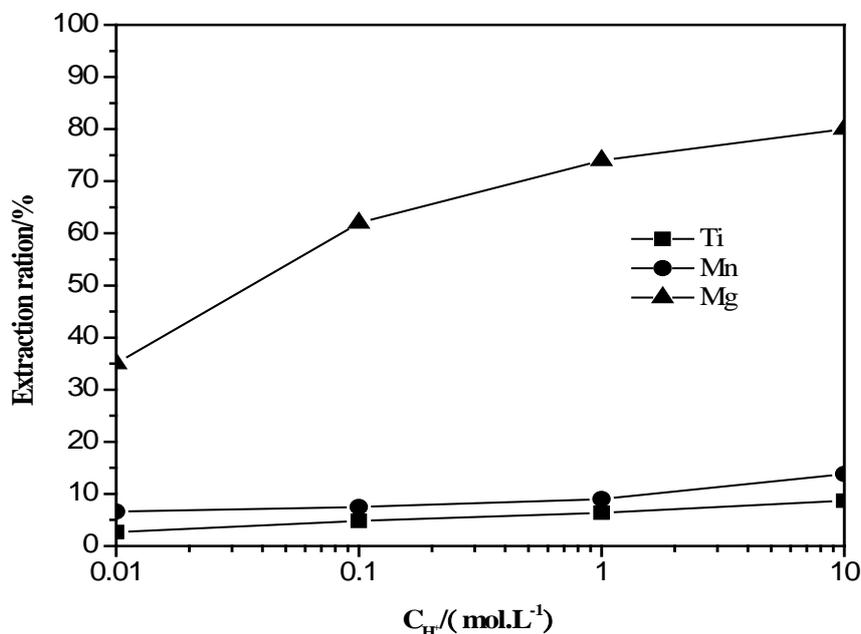


Fig.2 Extraction ration of cations from MgMnTi-900 in nitric acid solution

**Saturation Capacity of Exchange.** The relation between radius and saturated ion exchange capacity of MgMnTi-900 (H) for alkali was shown in figure 3. Known from figure 3, the capacity of exchange for  $Li^+$  was much higher than those for other alkali ions. The capacity for  $Li^+$  is  $12.6 \text{ mmol} \cdot \text{g}^{-1}$ . It proved that the ion exchange synthesized has higher capacity of exchange, and better remembering of exchange for  $Li^+$ . The effect factors of saturation capacity of exchange of MgMnTi-900 (H) are: 1) The  $Li^+$  in exchange solution must be removed previously, because  $Li^+$  exchanged with exchanger vacancy site when existing too much  $Li^+$ ; 2) The experimental results shown that the exchange capacity of ion exchanger for  $Li^+$  is much higher than those for other alkali ions in thin solution, which indicate that the ion-exchange reaction is carried out between and bare ions; 3) At the time of exchange, a  $Li^+$  was replaced by one  $H^+$ .  $Li^+$  not only entered the vacancy site but also exchanged with the  $H^+$  of surface. Therefore, MgMnTi-900 (H) has a higher exchange capacity for  $Li^+$ .

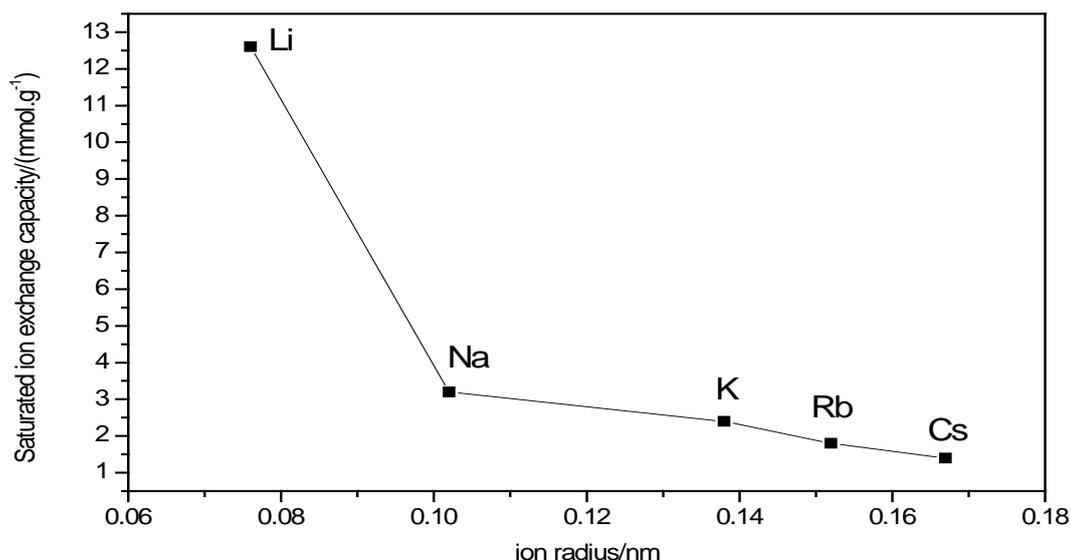


Fig.3 Relation between ion radius and saturated ion exchange capacity of MgMnTi-900 for alkali ions

**Distribution coefficient(K<sub>d</sub>).** K<sub>d</sub> values can be the token of exchange selectivity of MgMnTi-900 (H) for correlate ions. Shown in figure 4, K<sub>d</sub> values of MgMnTi-900 (H) for alkali ions are larger and larger with an increase pH over the pH region studied. The selectivity sequence of MgMnTi-900 for alkali metal ions as follows:

$$Li^+ > Cs^+ > Rb^+ > K^+ > Na^+ \quad (1)$$

It indicates that MgMnTi-900 (H) has a better ion selectivity for Li<sup>+</sup>. Ion-exchange reaction is reversible reaction. The reaction of H<sup>+</sup> in ion-exchanger with alkali metal ions in solution as follows(example for Li<sup>+</sup>):

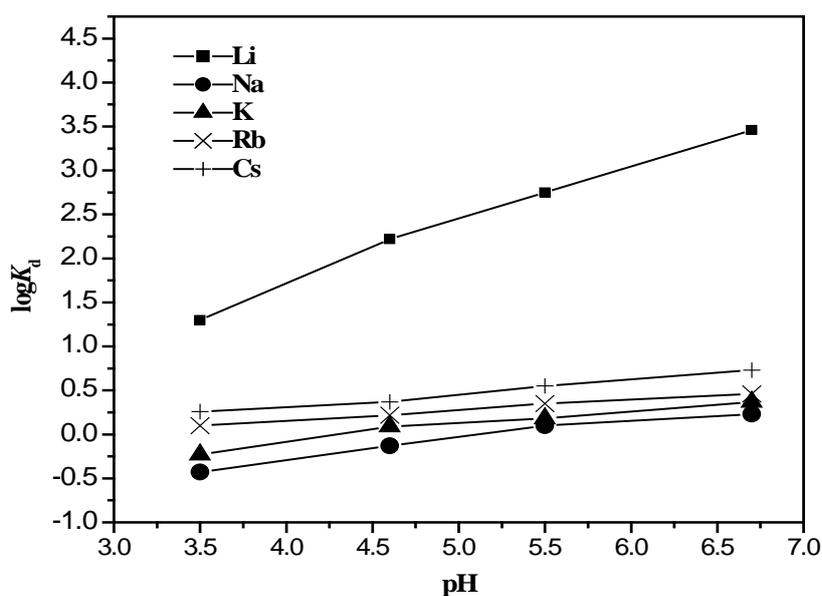


Fig.4 Distribution coefficient of MgMnTi-900(H) for alkali ions

## Conclusions

The inverse spinel-type metal oxide ( $\text{MgMn}_{0.25}\text{Ti}_{0.75}\text{O}_3$ ) show a capacity extraction/insertion of  $\text{Li}^+$  in the aqueous phase, mainly by an ion-exchange mechanism. The  $\text{Li}^+$ -extracted samples show a high selectivity and a large capacity for  $\text{Li}^+$  among alkali metal ions.

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## References

- [1] Q Liu, Y J Wang, Q Lu, et al . Synthesis and characterization of spinel type high-power cathode material  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  ( M= Ni, Co, Cr) [J]. Journal of Physics and Chemistry of Solids, 2007, 68: 780-784.
- [2]Dan Li, Tian Long Deng, Bai Sun. Inorganic ion exchange extraction of lithium from brine research [J]. Guangdong Trace Elements Science, 2007, 14 (1): 6-10.
- [3]Sui Lian Luo, Wei Shan Li, Shi Zhou Qiu, et al.  $\text{LiMn}_2\text{O}_4$  doped elements on the structure and properties [J]. Battery, 2001, 31 (1): 44-47.
- [4]Rong Guo Zhang, Lin Yang Shun, Heng Lei, etc. lithium manganese oxide lithium ion-sieve Salt Lake Research and application prospects [J]. Chemical and Biological Engineering, 2004 (4): 4-6.