Preparation of $Li_xNd_{10-x}Si_6O_{27-x}$ sinters and its Application to Potentiometric CO_2 gas sensor

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Introduction

New classes of lithium ion conductors formulated by $LiLnSiO_4$ (Ln =Lanthanoid) and related materials were reported [1-3]. In 1993, as part of a screening program for dense and ionic conductive solid state electrolytes, the electrical properties of some rare earth silicates, M_2O-Ln_2O_3-$2SiO_2$ (M=Li, Na, K, Rb, Cs; Ln=La, Nd, Sm, Gd, Dy, Ho, Er, Yb) had been proceeded [1]. In the Li_2O-Ln_2O_3-$2SiO_2$ system, the sintering was well progressed for Ln=Nd and Sm. For the sintered $LiNdSiO_4$ the most of the XRD signals could be assigned to an apatite structure with hexagonal $P6_3/m$ and some peaks due to Li_2SiO_3 were also detected.

The increase need of a reliable and continuous monitoring of CO_2 levels in the ambient has promoted the development of potentiometric gas sensor, based on an alkali ion conducting solid electrolyte, because of their preferable selectivity to CO_2.

In this work, the sensing characteristics of CO_2 gas sensor composed with $Li_xNd_{10-x}Si_6O_{27-x}$ sinters as alkali ionic conductor were examined and the stability of the electrolyte and the reactivity of Li_2CO_3 with the electrolyte were also examined.

Experimental

$Li_6Nd_6Si_6O_{24}$ and $Li_xLn_{10-x}Si_6O_{24}O_{3-x}$ ($1 \le x \le 3$) powders were prepared from the mixture of Li_2CO_3, Nd_2O_3 and SiO_2 in the prescribed ratio by the heating at 1000 ^oC in atmosphere with box furnace. The sample after cooled was ball-milled, compacted and then heated again at some temperatures in atmosphere. The materials were examined by XRD (Kα-Cu), SEM-EDX, SEM, TG-DTA and XPS. For the separate type CO_2 gas sensor, porous Pt electrodes were formed by screen-prints with Pt paste on both side on the sintered discs and then heated at 600 ^oC. As an auxiliary electrode, the mixture of Li_2CO_3 and α-terpineol was printed on the surface of the disc. After settled in the measuring test chamber, the temperature raised in steps from the room temperature to 460^oC. Test gases were repeatedly injected in 20 min interval into the test chamber. The gas flow rate during the tests was maintained a constant, i.e., 50 ml/min. The resulting EMF of the sensor was continuously monitored using a digital electrometer.

Results and Discussion

Fig. 1 shows the XRD patterns of $Li_6Nd_6Si_6O_{24}$ and $Li_xLn_{10-x}Si_6O_{24}O_{3-x}$ in disc. The observed peak positions were mostly independent on the sintering temperature from 1000 ^oC to 1400 ^oC. Li_2SiO_3 phase was detected as a minor phase especially for $Li_6Nd_6Si_6O_{24}$ and $LiNd_9Si_6O_{24}$ but not for the other two samples. The major product suggests that the stable phase is $Li_xLn_{10-x}Si_6O_{24}O_{3-x}$ with an Apatite type crystal structure for Li-Nd-Si oxides.

The sinter with x=1 was porous and the morphology of the surface was similar to that of the bulk. For x=2, the surface was composed with well-sintered fine particles. In addition, the bulk was composed with well-sintered phase with some closed pore. For x=3, the surface was composed with well-grown particles like single crystals and the bulk was a mixture of well-sintered phase and finer single crystals. Similar morphology was observed for $Li_6Nd_6Si_6O_{24}$ sinter. The conductance was in the order of x=1 > 3 > 2. Especially for x=2, it was increased with the sintering period and its activation energy remained a constant (~0.95 eV), suggesting that the sinters of x=2 is the most stable electrolyte. From the TG analysis with the powder mixture of quartz and $LiCO_3$, the $LiCO_3$ decompostion to form Li_2SiO_3 and Li_4SiO_4 occurred at 550 ^oC and 700 ^oC in syn-air and in 100 $\%CO_2$, respectively. However, for the powder mixture of $Li_2Nd_8Si_6O_{25}$ and $LiCO_3$, it was found that the weight loss due to the decomposition of $LiCO_3$ started to be observed at 925 ^oC in 100$\%CO_2$. Furthermore no change was observed for XRD pattern for $Li_2Nd_8Si_6O_{25}$ up to 1000^oC, indicating that the $Li_2Nd_8Si_6O_{24}O$ is unreactive with Li_2CO_3.

It is expected that the interlayer between Li_2CO_3 and $Li_2Nd_8Si_6O_{25}$ is very stable in ambient containing CO_2 as mentioned above. Thus, the sensing characteristic of the sensor with Pt,Li_2CO_3/$Li_2Nd_8Si_6O_{25}$/Pt structure was examined at 460 ^oC in the separate type mode. The result was shown in Fig.2. After arrived at 460 ^oC, the sensitivity increased with time with an increase in the EMF. In a stable region, the sensitivity was estimated to 60.2 mV which was slightly lower than that (72 mV) for n=2 (electron number) in $E=E_o - A(RT/nF)\ln(Pco_2)$. A more detailed discussion will be appeared after the examination of the cross sensitivity for other gases and the field test in a longer period.

References

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[3] Y.Sadaoka, S.Nakayama, Y.Sakai, and M.Wake, Sensors and Actuators, B24-25 (1995) 282-286.

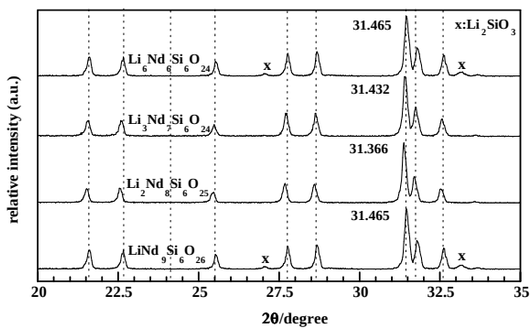

Fig.1 XRD patterns of the sinters at 1300 ^oC in air

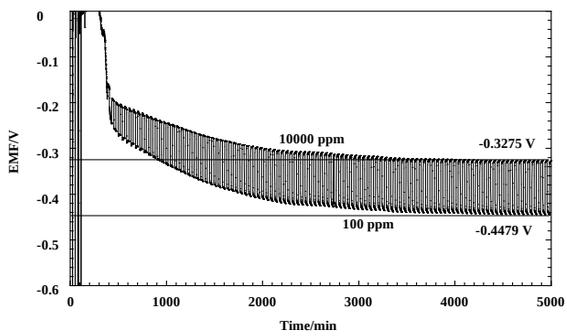

Fig.2 EMF response observed at 460 ^oC