High-pressure synthesis of novel lithium niobate-type oxides

To cite this article: Yoshiyuki Inaguma et al 2010 J. Phys.: Conf. Ser. 215 012131

View the article online for updates and enhancements.

Related content
- High-pressure synthesis, crystal chemistry and physics of perovskites with small cations at the A site
  Alexei A Belik and Wei Yi
- Progressive pressure-induced transformation from isolated MnX₄ (Td) to exchange-coupled MnX₆ (OH) systems in A₂MnX₄ (X: Cl, Br) crystals
  L'Nataf, Y Rodriguez-Lazcano, F Aguado et al.
- ESR study of transition metal ions in magnesium titanate
  A F M Y Hader and A Edgar

Recent citations
- Ferroelectricity in corundum derivatives
  Meng Ye and David Vanderbilt
- Lithium Niobate-Type Oxides as Visible Light Photovoltaic Materials
  Jiangang He et al
- Phase stability of the SrMnO₃ hexagonal perovskite system at high pressure and temperature
  Morten Bormann Nielsen et al
High-pressure synthesis of novel lithium niobate-type oxides

Yoshiyuki Inaguma, Masashi Yoshida, Takeshi Tsuchiya, Akihisa Aimi, Kie Tanaka, Tetsuhiro Katsumata, Daisuke Mori

Department of Chemistry, Faculty of Science, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo, 171-8588, Japan

E-mail: yoshiyuki.inaguma@gakushuin.ac.jp

Abstract. We found that two lithium niobate-type oxides, CdPbO$_3$ and PbNiO$_3$ were synthesized by high-pressure as metastable low-pressure perovskite-type phases. We then discussed the stability of lithium niobate-type and perovskite-type oxides relative to oxides with other structure for $ABO_3$ compounds. Consequently, the tolerance factor of perovskite is not the only predominant one to determine the stability and the crystal field effects of 3$d$ transition metal ions are also important.

1. Introduction

Much attention has been paid to perovskite-type oxides in the field of material science due to their functional properties. In contrast, though lithium niobate-type structure is much related to perovskite-type one, studies on functional lithium niobate-type oxides have been limited because there are only two lithium niobate-type oxides which are synthesized under ambient pressure, LiNbO$_3$ and LiTaO$_3$. On the other hand, in the field of earth science, lithium niobate phase is considered to be unquenchable high pressure perovskite-phase, and several lithium niobate phases have been reported as meta-stable quenched phases [1]. To date, lithium niobate-type oxides such as MnMoO$_3$ ($M$ = Ti[2-5], Sn[6, 7]), FeMoO$_3$ ($M$ = Ti[3, 7-9], Ge[10]), MgMoO$_3$ ($M$ = Ti[11], Ge[3, 12, 13]), ZnGeO$_3$[13, 14], garnet[15] and CuTaO$_3$[16] have been stabilized by high-pressure and high-temperature heat treatment. Among them, Syono et al.[2, 6] and Sleight et al.[16] have first paid attention to functional properties of lithium niobate-type oxides. Following them, it is anticipated that many functional lithium niobate-type oxides will be synthesized under high-pressure. Recently, we found that lithium niobate-type ZnSnO$_3$ can be synthesized under high-pressure, which is a polar oxide with a non-cetrosymmetric space group $R3c$ [17]. The knowledge in earth science indicates that the search for candidate perovskite phases is useful for candidate lithium niobate phases. It is therefore vital to predict the stability of perovskite and/or lithium niobate phase in search for novel functional compounds.

In this paper, we report the high-pressure synthesis of novel lithium niobate-type oxides, CdPbO$_3$ and PbNiO$_3$ together with ZnSnO$_3$, and discuss the predominant factors to determine the stability of lithium niobate and perovskite phases.

2. Experimental procedure

Polycrystalline samples were synthesized by a solid-state reaction under high pressure at elevated temperature. The mixture of starting materials was sealed in a gold capsule (0.2 mm in thickness, 3 mm in inner diameter, and 3 mm in depth). A pyrophyllite cube block (13 mm in side length) was used as a pressure medium. A cylindrical graphite heater was placed in the cube block. The capsule put in
the NaCl sleeve was placed in the heater. The mixture of starting materials was allowed to react in a TRY cubic multianvil-type high pressure apparatus (NAMO 2001) at 3-7 GPa and 650-1200ºC, and then was quenched to room temperature. The starting materials, pressure and temperature conditions are listed in Table 1. The phase was identified by the X-ray powder diffraction (XRD) method. The crystal structure was refined by the Rietveld analysis program, RIETAN 2000[18] using the XRD data.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Starting materials</th>
<th>Pressure</th>
<th>Temperature, keeping time</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSnO₃</td>
<td>ZnO, SnO₂</td>
<td>7 GPa</td>
<td>1000ºC, 30 min</td>
<td>6</td>
</tr>
<tr>
<td>CdPbO₃</td>
<td>CdO, PbO₂</td>
<td>7 GPa</td>
<td>650 – 1200ºC, 30 min</td>
<td>this work</td>
</tr>
<tr>
<td>PbNiO₃</td>
<td>PbO₂, NiO</td>
<td>3-7 GPa</td>
<td>750 – 1200ºC, 30 min-2 h</td>
<td>this work</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Phase identification of ZnSnO₃, CdPbO₃, PbNiO₃

Kudo et al.[19] and Yamamoto et al.[20] have reported that a perovskite phase of CdPbO₃ was synthesized under 7.5 GPa at 700ºC for 30 min and 5 - 6.5 GPa, respectively. In our experiments, observed phases in CdPbO₃ quenched sample depend on heating temperature. Figure 1 shows the X-ray diffraction patterns for CdPbO₃ synthesized under a pressure of 7 GPa at various heating temperature for 30 min. As seen in Figure 1, a perovskite phase is a main one at the heating temperature of 750ºC the same as Kudo et al.[19] and Yamamoto et al.[20] have reported. However, perovskite and lithium niobate phases coexist at 750 - 1000ºC, and a lithium niobate-type phase is a main one at 1200 and 1300ºC. This may be due to the difference in pressure release related to the shrinkage of volume when the temperature decreases. On the other hand, though quenched PbNiO₃ first exhibited orthorhombic perovskite structure, the structure easily changes from perovskite to lithium niobate-type one by a heat treatment at 400 - 500 K under ambient pressure. According to the bond valence sum estimated using the inter-atomic distances, the valences of Pb and Ni are +4 and +2, respectively. This is supported by the fact that Ishiwata et al.[21] have found the valence pair +4-+2 for A-B in a perovskite (Bi₀.₈Pb₀.₂)NiO₃.

Figure 1. X-ray diffraction patterns for CdPbO₃ synthesized under a pressure of 7 GPa at various heating temperature for 30 min.
Figure 2 shows the X-ray diffraction patterns for lithium niobate-type ZnSnO₃, CdPbO₃, and PbNiO₃. All the lithium niobate-type compounds possess hexagonal structure with the non-centrosymmetric space group R₃c. The lattice parameters of ZnSnO₃, PbNiO₃, and CdPbO₃ are listed in Table 2. As seen in Table 2, the lattice volume of perovskite phase is smaller than that of lithium niobate-type phase. This implies that perovskite phases are the high-pressure phases of lithium niobate. Both of lithium niobate-type CdPbO₃ and PbNiO₃ then exhibit semiconducting behavior with small temperature dependence, and PbNiO₃ exhibits the anti-ferromagnetic anomaly in the vicinity of 205 K. The detailed structures, physical properties and their relationship will be reported elsewhere.

![Figure 2. X-ray diffraction patterns for lithium niobate-type ZnSnO₃, PbNiO₃, and CdPbO₃.](image)

Table 2. Lattice parameters for ZnSnO₃, CdPbO₃, and PbNiO₃

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Phase</th>
<th>Symmetry</th>
<th>a / Å</th>
<th>b / Å</th>
<th>c / Å</th>
<th>Volume per formula unit / Å³</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSnO₃</td>
<td>LiNbO₃-type</td>
<td>hexagonal</td>
<td>5.2622(1)</td>
<td>5.2622(1)</td>
<td>14.0026(2)</td>
<td>56.0</td>
<td>ref. 6</td>
</tr>
<tr>
<td>CdPbO₃</td>
<td>LiNbO₃-type</td>
<td>hexagonal</td>
<td>5.681(2)</td>
<td>5.681(2)</td>
<td>14.640(4)</td>
<td>68.2</td>
<td>this work</td>
</tr>
<tr>
<td>CdPbO₃</td>
<td>perovskite</td>
<td>orthorhombic</td>
<td>5.887(3)</td>
<td>8.061(5)</td>
<td>5.676(8)</td>
<td>67.3</td>
<td>this work</td>
</tr>
<tr>
<td>PbNiO₃</td>
<td>LiNbO₃-type</td>
<td>hexagonal</td>
<td>5.362(2)</td>
<td>5.362(2)</td>
<td>14.089(4)</td>
<td>58.5</td>
<td>ref. 20</td>
</tr>
<tr>
<td>PbNiO₃</td>
<td>perovskite</td>
<td>orthorhombic</td>
<td>5.463(1)</td>
<td>7.705(2)</td>
<td>5.358(1)</td>
<td>56.4</td>
<td>this work</td>
</tr>
</tbody>
</table>

3.2. Predominant factors of occurrence of perovskite and lithium niobate-type phase

Figure 3 shows Goldschmit diagram for selected compounds [1, 7]. Here, “A” is the cation radius in six-fold coordination, “B” is the cation radius in six-fold coordination. Dotted lines indicate perovskite tolerance factor, \( t = (r_A + r_O) / \sqrt{2(r_B + r_O)} \), where \( r_A \) and \( r_O \) denote the ionic radii in six-fold coordination of \( A^- \), \( B^- \)-cation and oxide ion after Shannon[22], respectively. There is a boundary between perovskite and lithium niobate phase in the vicinity of \( t = 0.85 \). This trend of tolerance factor predicts that MgTiO₃, CoTiO₃ and NiTiO₃ ilmenites could change to the perovskites under high-
pressure which revert to lithium niobate phases during pressure release. In fact, though MgTiO$_3$ is formed into a lithium niobate phase, CoTiO$_3$ and NiTiO$_3$ perovskites or lithium niobate phases cannot be stabilized but NaCl-type MO and α-PbO$_2$-relateds denser TiO$_2$ are stabilized under high-pressure [3], indicating that the tolerance factor is not only predominant factor stabilizing the perovskite or lithium niobate phases. The findings are related to crystal-field effects of transition ions [3, 23, 24, 25]. Number of $d$ electrons, ionic radius with six-fold coordination [22], octahedral crystal–field splitting, $\Delta_o$, crystal-field stabilization energy (CFSE) of divalent ion, $M^{2+}$ with high-spin configuration, and perovskite or lithium niobate phases including $M^{2+}$ ion are listed in Table 3. Here, the CFS in the case that the corresponding ligand is aqua, H$_2$O, is adopted as the referring value of CFS. Though CFS is varied between 8500 - 10400 cm$^{-1}$ for Mn$^{2+}$ to Fe$^{2+}$ ions, the octahedral CFSE of Co$^{2+}$ and Ni$^{2+}$ ions are greater than those for other transition metal ions even if considering the difference in the degree of CFS. This indicates that Co$^{2+}$ and Ni$^{2+}$ ions prefer to octahedral coordination. The site preference of Co$^{2+}$ and Ni$^{2+}$ ions based on CF effects is attributed to the stability of ilmenite with six-fold coordination or the decomposition into NaCl-type MO with six-fold coordination and α-PbO$_2$-related denser dioxides [3]. On the other hand, the occurrence of perovskite or lithium niobate phase in MnMO$_3$ seem to be due to zero octahedral CFSE, indicating that Mn$^{2+}$ ion exhibits no site-preference and flexibility to place in various coordinated sites. Furthermore, in PbNiO$_3$, the valence pair of Pb and Ni is +4 - +2 and Ni$^{2+}$ ion is placed in octahedral site. This is attributed to the strong octahedral CFSE of Ni$^{2+}$ ions.

![Figure 3. Goldschmit diagram for selected compounds [1, 7]. “A” is the cation radius in six-fold coordination, “B” is the cation radius in six-fold coordination. Dotted lines are contours of the perovskite tolerance factor, which is calculated from the ionic radii in six-fold coordination. Filled squares: perovskite-forming compounds. Blue filled circles: lithium niobate quenched products. Green triangle: ilmenite compounds.](image)

<table>
<thead>
<tr>
<th>Divalent ion $M^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Mn$^{2+}$</th>
<th>Fe$^{2+}$</th>
<th>Co$^{2+}$</th>
<th>Ni$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Zn$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of $d$ electrons</td>
<td>0</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>$M^{2+}$/Å</td>
<td>0.72</td>
<td>0.83</td>
<td>0.78</td>
<td>0.75</td>
<td>0.69</td>
<td>0.73</td>
<td>0.74</td>
</tr>
<tr>
<td>CFS $\Delta_o$</td>
<td>-</td>
<td>8500</td>
<td>10400</td>
<td>9500</td>
<td>8500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CFSE</td>
<td>-</td>
<td>2/5$\Delta_o$</td>
<td>4/5$\Delta_o$</td>
<td>6/5$\Delta_o$</td>
<td>3/5$\Delta_o$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>perovskite or lithium niobate phase</td>
<td>MgSiO$_3$</td>
<td>MnVO$_3$</td>
<td>MnTiO$_3$</td>
<td>FeTiO$_3$</td>
<td>Pb$^{4+}$NiO$_3$</td>
<td>ZnGeO$_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MgGeO$_3$</td>
<td>MnGeO$_3$</td>
<td>FeGeO$_3$</td>
<td>-</td>
<td>ZnSnO$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MgTiO$_3$</td>
<td>MnSnO$_3$</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Octahedral crystal–field splitting, $\Delta_o$, crystal-field stabilization energy (CFSE) of divalent ion, $M^{2+}$ with high-spin configuration, and perovskite or lithium niobate phases including $M^{2+}$ ion.
4. Summary
Two novel lithium niobate-type oxides, CdPbO$_3$ and PbNiO$_3$ were synthesized by high-pressure and high temperature heat treatment as metastable low-pressure perovskite-type phases. In contrast, in ZnSnO$_3$, the perovskite phase has not been observed. The confirmation of perovkite phase by in-situ X-ray diffraction experiment under high-pressure will be a future work. The tolerance factor of perovskite is not only predominant one to determine the stability of perovskite/lithium niobate phase and the octahedral crystal field stabilization energy of 3$d$ transition metal ions should be also taken into account. The $ABO_3$ compounds with Ni$^{2+}$ or Co$^{2+}$ ion in the octahedral $B$-ion site are candidate perovskite or lithium niobate ones

Acknowledgements
The authors thank Dr. H. Kojitani and Prof. M. Akaogi for valuable information and experimental support, Mr. M. Nakasima and Mr. H. Nakagawa for their help of experiments, Dr. K. Hiraki and Prof. T. Takahashi for their help of magnetic susceptibility measurement. This work was partially supported by the Grant-in-Aid for Scientific Research (B) (No. 21360325) of Japan Society for the Promotion of Science and the Promotional Project for Development of Strategic Research base for Private Universities: matching fund subsidy from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References