High pressure-high temperature synthesis of lithium-rich $\text{Li}_3\text{O}(\text{Cl}, \text{Br})$ and $\text{Li}_{3-x}\text{Ca}_{x/2}\text{OCl}$ anti-perovskite halides

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ABSTRACT

In this work, we investigated the systems of $(\text{Li}, \text{Ca}) - \text{O} - (\text{Cl}, \text{Br})$ under high pressure and temperature for the synthesis of lithium-rich anti-perovskite (LiRAP) halides. We successfully synthesized $\text{Li}_{3-x}\text{Ca}_{x/2}\text{OCl}$ anti-perovskite with $x = 0.0, 0.1, 0.2$ near 0.5 GPa and temperatures of 400-425 K and Li_3OBr anti-perovskite at 3.0 GPa and 450 K. Different from the synthetic route previously reported at ambient pressure, $\text{LiA} + 2\text{LiOH} \rightarrow \text{Li}_3\text{OA} + \text{H}_2\text{O}$, the LiRAP halides under high P - T conditions are formed by dehydration of end-member and Ca-doped halide hydrates with a general formula of $\text{Li}_{2x+1}\text{A}(\text{OH})_{2y}$, where A can be Cl or Br and x must be equal to y . This proposed formula predicts several new halide hydrates including $\text{Li}_3\text{Cl}(\text{OH})_2$, $\text{Li}_5\text{Cl}(\text{OH})_4$, $\text{Li}_3\text{Br}(\text{OH})_2$, and $\text{Li}_5\text{Br}(\text{OH})_4$, indicating that halide hydrates are structurally flexible to accommodate a range of lithium and hydroxide occupancies in the puckered layers of $[\text{Li}_{2x+1}(\text{OH})_{2y}]^+$.

Electrolyte is a key element in the electric energy storage applications and has often been used as ionic transfer medium in batteries, capacitors, and fuel cells. Among currently available battery technologies, Lithium-ion technology is most promising thanks to its high energy density, 210 Wh kg^{-1} or 650 Wh l^{-1} [1]. Although good ionic conductors, the commonly used liquid electrolytes impose a number of limitations [2] including low electronic conduction, relatively low potential difference due to limited electrochemical window, electrolyte degradation by redox interaction with anode and cathode, and safety and environmental concerns due to their acidic, toxic, or flammable nature. Li-ion batteries utilizing solid-state electrolytes offer attractive solutions to many of these problems and can also potentially provide higher energy density [3].

One material displaying superionic conductivity in its solid state, is NaMgF_3 perovskite [4]. In this material the structural instability due to phonon softening at elevated temperatures is responsible for the superionic transition [5]. At high temperatures, thermally activated fluorine anions (F) vibrate enormously in an ellipsoidal path, which promotes the transport of F ions *via* the vacancy hopping mechanisms. In addition, only F atoms migrate in the crystal lattice of NaMgF_3 perovskite. Inspired by superionic conductivity of NaMgF_3 perovskite, we recently formulated a series of "electronically-inverted" lithium anti-perovskites (LiRAP) with high Li concentrations and a generalized formula $\text{Li}_{3-x}\text{M}_{x/2}\text{OA}_{1-z}\text{A}'_z$ [6], where M can be alkaline earth metals of Ca, Ba, and Sr and A and A' are distinct halogens (Cl, Br, I). The cubic or nearly cubic perovskite structure is preserved in these inverted perovskites [6], which in principle allows lithium superionic conductivity in a way very similar to fluorine superionic conductivity in NaMgF_3 perovskite.

This work is further motivated by the observations that ionic conductivity can be enhanced up to four orders of magnitude through the replacement of Li^+ by a higher valent cation in a conventional ABO_3 perovskite structure [7-9]. This is primarily because the vacancies created due to charge difference facilitate Li^+ hopping in the crystal lattice. In a LiRAP, the replacement of one Li^+ by one Ca^{2+} in Li_3OCl , for example, introduces a vacancy in the crystal lattice to form a solid-solution series of $\text{Li}_{3-x}\text{Ca}_{x/2}\text{OCl}$. By analog with previous findings in the conventional ABO_3 perovskite, we expect that such doping would significantly improve the ionic conductivity. Indeed, our recent impedance measurements show that the ionic conductivity in

$\text{Li}_{2.9}\text{Ca}_{0.05}\text{OCl}$ anti-perovskite is more than one order of magnitude higher than that in the Li_3OCl end-member [6]. As part of the efforts to further explore synthetic routes for anti-perovskite $\text{Li}_{3-x}\text{M}_{x/2}\text{OA}_{1-z}\text{A}'_z$, we carried out synthesis experiments under high-pressure (P) – high-temperature (T) conditions for the end-member Li_3OBr and a solid solution series $\text{Li}_{3-x}\text{Ca}_{x/2}\text{OCl}$ with $x = 0.0, 0.1, \text{ and } 0.2$. We unveiled an alternate reaction path for the synthesis of LiRAP through the dehydration of two new hydrates, $\text{Li}_3\text{Cl}(\text{OH})_2$ and $\text{Li}_5\text{Br}(\text{OH})_4$.

For the preparation of end-member and Ca-doped LiRAP halides, high purity powders of Li_2O , CaO , LiCl , and BrCl were first weighed in desired molar ratios, as summarized in **Table 1**, and mechanically mixed. To ensure homogeneity in the starting reagents, each mixture was then grounded in a stainless crucible by a high-energy ball mill, 3h for Li_3OBr and 2h for all other compositions. Before brought to the experimental facility, each of the resultant powders was enclosed in a sample bottle sealed by high-performance Scotch® tape. All these procedures were carried out at ambient conditions in a glove box filled with inert gas of Ar.

Table 1 Summary of starting materials for preparation of Li-based anhydrous anti-perovskite halides

Starting mixture	Weight in gram	Molar ratio	Target sample
# 1 Li_2O and LiCl	0.413 g Li_2O ; 0.587 g LiCl	$\text{Li}_2\text{O}:\text{LiCl} = 1:1$	Li_3OCl
# 2 Li_2O , CaO , and LiCl	0.386 g Li_2O ; 0.038 g CaO ; 0.576 g LiCl	$\text{Li}_2\text{O}:\text{CaO}:\text{LiCl} = 0.95:0.05:1$	$\text{Ca}_{0.05}\text{Li}_{2.9}\text{OCl}$
# 3 Li_2O , CaO , and LiCl	0.359 g Li_2O ; 0.075 g CaO ; 0.566 g LiCl	$\text{Li}_2\text{O}:\text{CaO}:\text{LiCl} = 0.90:0.1:1$	$\text{Ca}_{0.1}\text{Li}_{2.8}\text{OCl}$
# 4 Li_2O and LiBr	0.512 g Li_2O ; 0.744 g LiBr	$\text{Li}_2\text{O}:\text{LiBr} = 2:1$	Li_3OBr

The formation process of anti-perovskite halides was monitored by *in-situ* and *real-time* synchrotron x-ray diffraction under high P - T conditions. The experiments were conducted using a cubic anvil apparatus at beamline X17B2 of the National Synchrotron Light Source, Brookhaven National Laboratory [10]. An energy-dispersive x-ray method was employed with

diffracted x-rays collected at fixed Bragg angles of $2\theta = 6.621^\circ$. In all experiments reported here, a cubic mixture of amorphous boron and epoxy resin was used as pressure-transmitting medium, and amorphous carbon was used as heating element. The starting mixtures and NaCl powders were packed, in a volume ratio of approximately 1:1, into a cylindrical container of hexagonal boron nitride (BN), 1.0mm inner diameter and 2.0mm length. A thin disk of BN was placed between the two layers to prevent the powder mixture from reacting with the NaCl powder.

NaCl was used as an internal pressure standard and temperatures were measured by a W/Re25%-W/Re3% thermocouple. The temperature variations over the entire length of sample container at 1500 K were of the order of 20 K, and the radial temperature gradients were less than 20 K at this condition. X-ray diffraction patterns were obtained for both samples and NaCl in close proximity to the thermocouple junction; errors in temperature measurements were thus estimated to be approximately 10 K. Pressures were calculated from Decker's equation of state [11] for NaCl using lattice parameters determined from x-ray diffraction profiles at each experimental condition. Five NaCl diffraction lines, 111, 200, 220, 222 and 420, were usually used for determination of pressure. Within the accuracy of the Decker scale, the uncertainty in pressure measurements is mainly attributed to statistical variation in the position of diffraction lines and is typically less than 2% of measured values in the P - T range of this study.

For each of the experiments reported in this work, the sample was loaded into a pressure cell in a glove box filled with Ar gas. To isolate the sample powders from atmospheric moisture, all air pathways on the pressure cell was sealed by Duco® cement. The pressure cell was then sealed into a plastic tube before it was taken out of the glove box. Typically, it takes 15-20 minutes to set up a pressure cell into the hydraulic press and to pump it up to the pressure under which the sample cell is isolated from room air. The starting powders were first compressed at room temperature to 0.5 GPa for starting mixtures #1-3 and to 3.0 GPa for mixture #4, followed by stepwise heating to the maximum temperature of 573 K and subsequent cooling to room temperature. Along these experimental P - T paths, diffraction data were collected for both sample and NaCl under selected conditions. For samples recovered at ambient conditions, we collected 2-3 diffraction patterns at different sample positions to examine their homogeneity.

Figure 1 shows the diffraction patterns collected at ambient conditions for the starting mixtures with a 1:1 molar ratio of $\text{Li}_2\text{O}:\text{LiCl}$ and a 2:1 molar ratio of $\text{Li}_2\text{O}:\text{LiBr}$. In both profiles, the diffraction lines associated with Li_2O or LiOH , LiCl , and LiBr are not observed. On the other hand, they can be fit quite nicely using the Le Bail method to the known hydrates of $\text{Li}_4\text{Cl}(\text{OH})_3$ and $\text{Li}_4\text{Br}(\text{OH})_3$ [12, 13], both of which possess a monoclinic structure with space group $p21/m$ and are formed by the reaction

where A can be either Cl or Br. Given the starting compositions for mixtures 1 and 4 and phase-pure reaction products revealed in **Figure 1**, the observed hydrates are formed by the reactions

These findings indicate that, although caution has been taken at all experimental steps to isolate starting powders from room air, they react with atmospheric moisture at ambient conditions to form hydrates. In reactions (2) and (3), $\text{Li}_3\text{Cl}(\text{OH})_2$ and $\text{Li}_5\text{Br}(\text{OH})_4$ represent new hydrates in the systems Li-Cl-O-H and Li-Br-O-H, respectively.

Most interestingly, the diffraction patterns for both $\text{Li}_3\text{Cl}(\text{OH})_2$ and $\text{Li}_5\text{Br}(\text{OH})_4$ can be indexed by the known structure for $\text{Li}_4\text{Br}(\text{OH})_3$ despite their differences in stoichiometric composition. As illustrated in **Figure 1**, the monoclinic $p21/m$ structure in $\text{Li}_4\text{Cl}(\text{OH})_3$ and $\text{Li}_4\text{Br}(\text{OH})_3$ contains puckered layers of $[\text{Li}_4(\text{OH})_3]^+$ connected by chlorine ions. The fact that all four hydrates of different stoichiometry adopt the same crystal structure indicates that the monoclinic $p21/m$ crystal lattice is structurally flexible for accommodating a range of lithium and hydroxide occupancies. It is also noted in **Figure 1** that the unit cell parameters for $\text{Li}_3\text{Cl}(\text{OH})_2$ and $\text{Li}_5\text{Br}(\text{OH})_4$ do not show notable variations with respect to $\text{Li}_4\text{Cl}(\text{OH})_3$ and $\text{Li}_4\text{Br}(\text{OH})_3$. This is not entirely unexpected because the three-dimensional crystal lattice is mainly “straighten” by chlorine ions, which are substantially larger than H^+ and Li^+ . Based on reactions (1) - (3), the formation of lithium halide hydrates can be generalized by the reaction

where A is a halogen and x must be equal to y. For A = Cl and Br, the generalized formula, $\text{Li}_{2x+1}\text{A}(\text{OH})_{2y}$, predicts two additional new hydrates of $\text{Li}_3\text{Br}(\text{OH})_2$ and $\text{Li}_5\text{Cl}(\text{OH})_4$. The reaction (4) can further be extended to $\text{Li}_2\text{Cl}(\text{OH})$ and $\text{Li}_2\text{Br}(\text{OH})$ with $x = y = 0.5$ in $\text{Li}_{2x+1}\text{A}(\text{OH})_{2y}$. Both hydrates, however, are known and possess a cubic $Pm-3m$ (221) structure [14], indicating that the monoclinic $\text{Li}_{2x+1}\text{A}(\text{OH})_{2y}$ hydrates are limited to $1 \leq x \leq 2$ and $1 \leq y \leq 2$ with $x = y$. In the system Li-I-O-H, $\text{Li}_4\text{I}(\text{OH})_3$ has previously been reported to have an orthorhombic symmetry and space group $Pmmn$ [13], suggesting that the monoclinic $p21/m$ structure for $\text{Li}_{2x+1}\text{A}(\text{OH})_{2y}$ can only be applied to A = Cl and Br. For starting mixtures #2 and #3 in **Table 1** the diffraction patterns collected at ambient conditions are essentially identical to those shown in **Figure 1**, indicating that reaction (4) can also be applied to the Ca-doped systems for Li.

Figure 2 shows the formation processes of Li_3OCl and Li_3OBr anti-perovskite under high P - T conditions, monitored by *in-situ* and *real-time* synchrotron x-ray diffraction. For starting mixture with a 1:1 molar ratio of $\text{Li}_2\text{O}:\text{LiCl}$ (*i.e.*, mixture #1 in **Table 1**), the diffraction pattern becomes simplified considerably when $\text{Li}_3\text{Cl}(\text{OH})_2$ was heated from 375 K to 425 K at a pressure of 0.6 GPa (*left panel*). At temperatures above 425 K, the observed diffraction lines can mostly be indexed by a cubic $Pm-3m$ (221) structure, indicating that Li_3OCl anti-perovskite is formed by the dehydration reaction

In the Ca-doped systems (*i.e.*, starting mixtures # 2 and 3 in **Table 1**), the anti-perovskite $\text{Li}_{3-x}\text{Ca}_x\text{OCl}$ was observed at 423 and 398 K, respectively, for $x = 0.1$ and $x = 0.2$ upon heating at ~ 0.5 GPa. Similar to reaction (5), they are formed by the dehydration of $\text{Li}_{3-x}\text{Ca}_{x/2}\text{Cl}(\text{OH})_3$.

It is evident in **Figure 2** that the pattern collected at 0.6 GPa and 455 K is not phase-pure for Li_3OCl anti-perovskite. Some of the impure diffraction lines are from hexagonal BN, which was used as the sample container and also for separating the sample from NaCl pressure standard. However, there are still a few weak diffraction lines that cannot be accounted for by either $Pm-3m$ Li_3OCl or hexagonal BN. While we cannot be conclusive about their origin due to the limited

number of reflections, the un-indexed diffraction peaks do not match any of the known lines for Li_2O , LiOH , and LiCl (as well as CaO or Ca metal in the case of $\text{Li}_{3-x}\text{Ca}_{x/2}\text{OCl}$). Strictly speaking, the indexed Miller indices for $\text{Li}_{3-x}\text{Ca}_{x/2}\text{OCl}$ correspond to the pseudocubic structure. This is because the calculated tolerance factor, $t = (r_{\text{Cl}} + r_{\text{Li}})/\sqrt{2}(r_{\text{O}} + r_{\text{Li}})$, where r is the ionic radius of the respective ions, shows that Li_3OCl should be distorted to a lower symmetry, primarily due to the small Cl anions at A site of the $\text{A}^{-1}\text{B}^{-2}\text{Li}^{+1}_3$ system. Such structural distortions are also typical of many perovskite compounds. Future high-resolution diffraction studies are needed to resolve the crystal structure of Li_3OCl anti-perovskite and the lattice distortion caused by the Ca doping.

For starting mixture with a 2:1 molar ratio of $\text{Li}_2\text{O}:\text{LiBr}$ (*i.e.*, the starting composition # 4 in **Table 1**), the $Pm\text{-}3m$ Li_3OBr anti-perovskite was observed in two independent experiments, one upon heating from 423 K to 459 K at 3.5 GPa (**Figure 2, right-panel**) and the other from 425 K to 458 K at 2.95 GPa. Evidently, it is formed by the following dehydration reaction

However, additional diffraction lines observed in the patterns cannot be indexed by the known tetragonal LiOH , suggesting that LiOH may undergo a pressure-induced phase transition under the present experimental conditions. It is worthwhile to mention that the starting composition with 2:1 molar ratio of $\text{Li}_2\text{O}:\text{LiBr}$ is purposely used to explore the hydration process of the starting mixture; it is not an ideal composition for producing phase-pure anti-perovskite. For both reactions (5) and (6) the dehydration process is endothermic, which is inferred by the observed drop in temperature of $\sim 5 - 10$ K at constant heating power. For comparison, in the lack of chemical reactions, the temperatures are typically stable within 1-2 K at the present experimental conditions (*i.e.*, 400 – 500 K).

At ambient pressure, anti-perovskite halides are formed by the reaction $\text{LiA} + 2\text{LiOH} \rightarrow \text{Li}_3\text{OA} + \text{H}_2\text{O}$ (ref 6), where A can be either Cl or (Cl, Br) solid solution. In this earlier study, the experimental procedures involved continuous heating in a quartz tube over the range 600–630 K (*i.e.*, above the melting temperature of 555 K for Li_3OCl) and removal of water under high vacuum to drive the chemical equilibrium toward the formation of the Li_3OA product. In this

regard, the dehydration of $\text{Li}_{2x+1}\text{A}(\text{OH})_{2y}$ (reactions 5 and 6) presents a new and an alternate reaction path for the synthesis of LiRAP. For both ambient and high pressure synthesis, the reaction products are hygroscopic and sensitive to atmospheric moisture.

Table 2 summarizes the onset pressure and temperature conditions observed for the formation of Li_3OCl , Li_3OBr , and $\text{Li}_{3-x}\text{Ca}_{x/2}\text{OCl}$ anti-perovskite through dehydration reactions of (5) and (6). All these phases can be quenched to ambient conditions for property-functionality characterization. Based on our impedance measurements on the recovered samples [6], Li_3OCl and Li_3OBr anti-perovskites exhibit superionic conductivity of $\sigma > 10^{-3} \text{ S/cm}$ at room temperature. As temperature approaches the melting point, the ionic conductivities show significant jumps and reach advanced superionic conductivity of $\sigma > 10^{-2} \text{ S/cm}$.

Table 2 The onset pressure and temperature conditions observed for dehydration of end-member and Ca-doped $\text{Li}_{2x+1}\text{Cl}(\text{OH})_{2y}$ hydrates to form Li_3OBr and $\text{Li}_{3-x}\text{Ca}_{x/2}\text{OCl}$ anti-perovskite. For lattice parameters, the values in bold are the averages of 2-3 measurements on the recovered samples at different samples positions, which are listed below the average values.

Starting mixture	Anti-perovskite	Pressure GPa	Temperature K	Ambient lattice parameter, Å
# 1	Li_3OCl	0.64	423	3.9084 3.9090(1) 3.9078(1)
# 2	$\text{Li}_{2.9} \text{Ca}_{0.05}\text{OCl}$	0.40	423	3.9056 3.9045(1) 3.9063(2) 3.9060(1)
# 3	$\text{Li}_{2.8} \text{Ca}_{0.1}\text{OCl}$	0.47	398	3.9044

				3.9039(2) 3.9048(1)
# 4	Li ₃ OBr	2.95	458	4.0507 4.0456(1) 4.0538(1) 4.0527(1)

Table 2 also shows the lattice parameters measured on the recovered samples at different sample positions; all anti-perovskite samples are fairly homogeneous given the resolution of energy-dispersive XRD. Within the mutual error bars, the lattice constants of Ca-doped Li₃OCl anti-perovskite are slightly smaller than those of Ca-free end member. This is not unexpected because the replacement of one Li⁺ ion by one Ca²⁺ cation would introduce one vacancy in the anti-perovskite crystal lattice. In a number of nonstoichiometric materials, the introduction of vacancies leads to the reduction of lattice volume [15-17]. Consistent with this trend of variation, the lattice constants observed in this work decreases slightly with increasing vacancy concentration in Li_{3-x}Ca_{x/2}OCl (**Table 2**).

In summary, we investigated the synthetic concept and routes for anti-perovskite Li_{3-x}M_{x/2}OA_{1-z}A'_z. With applications of high pressure and temperature in systems (Li, Ca) – O – (Cl, Br), we successfully synthesized Li_{3-x}Ca_{x/2}OCl anti-perovskite with x = 0.0, 0.1, 0.2 near 0.5 GPa and temperatures of 400-425 K and Li₃OBr anti-perovskite at 3.0 GPa and 450 K. We also propose a general formula, Li_{2x+1}A(OH)_{2y}, for lithium hydrate halides, which predicts several new compounds in the systems Li-Cl-O-H and Li-Br-O-H.

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References

- [1] J. M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.
- [2] K. Xu, *Chem. Rev.* 104 (2004) 4303–4418.
- [3] C.S. Sunandana, P.S. Kumar, *Bull. Mater. Sci.* 27 (2004) 1–17.
- [4] M. O'keeffe, J.O. Bovi, *Science* 206 (1979) 599–600.
- [5] Y. Zhao, D.J. Weidner, J.C. Parise, D. Cox, *Phys. Earth Planet. Inter.* 76 (1993) 1–16 and 17–34.
- [6] Y. Zhao, L.L. Daemen, L. L. *J. of Am. Chem. Soc.* 134 (2012) 15042–15047.
- [7] A.G. Belous, G.N. Novitsukaya, S.V. Polyanetskaya, Y.I. Gornikov, *Izv. Akad. Nauk. SSSR Neorg. Mater.* 23 (1987) 470–472.
- [8] Y. Inagumi, C. Liqun, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta, W. Wakihara, *Solid State Commun.* 86 (1993) 689–693.
- [9] H. Kawai, J. Kuwano, *J. Electrochem. Soc.* 141 (1994) L78–79.
- [10] D.J. Weidner, M.T. Vaughan, J. Ko, Y. Wang, X. Liu, A. Yeganeh-haeri, R.E. Pacalo, R. Y. Zhao, In Y. Syono and M.H. Manghnani (ed.) *High-Pressure Research: Application to Earth and Planetary Sciences*. AGU, Washington DC, **1992**, pp. 13–17.
- [11] D.L. Decker, *J. Appl. Phys.* 42 (1971) 3239–3244.
- [12] H. Barlage, H. Jacobs, *Zeitschrift fuer Anorganische und Allgemeine Chemie* 620 (1994) 471–474.

- [13] A. Hoennerscheid, J. Nuss, C. Muehle, M. Jansen, *Zeitschrift fuer Anorganische und Allgemeine Chemie* 629 (2003) 317–320.
- [14] K. Friese, A. Hoennerscheid, M. Jansen, *Zeitschrift fuer Kristallographie* 218 (2003) 536–541.
- [15] R.M. Hazen, R. Jeanloz, *R. Rev. Geophys. Space Phys.* 22 (1984) 37–46.
- [16] B. Simons, *Carnegie Institute of Washington Yearbook* 79 (1980) 376–380.
- [17] J. Zhang, *Phys. Rev. Lett.* 84 (2000) 507–510.

Figure 1 The ambient diffraction patterns for starting mixtures with a 1:1 molar ratio of $\text{Li}_2\text{O}:\text{LiCl}$ (top) and a 2:1 ratio of $\text{Li}_2\text{O}:\text{LiBr}$ (bottom). Shown in the middle is a monoclinic $p21/m$ structure reported for $\text{Li}_4\text{Cl}(\text{OH})_3$ and $\text{Li}_4\text{Br}(\text{OH})_3$. The calculated profiles are based on the Le Bail fits and are shown in red. The green tick marks denote the positions of allowed reflections for the known monoclinic $p21/m$ structure. The blue diamond symbols indicate the main diffraction lines for the hexagonal boron nitride (BN). Similar patterns were obtained at ambient conditions for starting mixtures #2 and 3 listed in Table 1.

Figure 2 *In-situ* and *real-time* observations of the formation of Li_3OCl (left panel) and Li_3OBr (right panel) anti-perovskite under high P - T conditions using synchrotron x-ray diffraction. The powder mixtures # 1 and #4 in Table 1 were used as starting materials, respectively, for Li_3OCl and Li_3OBr . Asterisks denote major diffraction lines of hexagonal boron nitride.