Mixed Polyanion Glass Cathodes: Mixed Alkali Effect

A. K. Kercher, a,∗ A. S. Chapel, b J. A. Kolopus, a and L. A. Boatner a

a Materials Science & Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
b University of Tennessee, Knoxville, Tennessee 37996, USA

In lithium-ion batteries, mixed polyanion glass cathodes have demonstrated high capacities (200–500 mAh/g) by undergoing conversion and intercalation reactions. Mixed polyanion glasses typically have the same fundamental issues as other conversion cathodes, i.e.: large hysteresis, capacity fade, and 1st-cycle irreversible loss. A key advantage of glass cathodes is the ability to tailor their composition to optimize the desired physical properties and electrochemical performance. The strong dependence of glass physical properties (e.g., ionic diffusivity, electrical conductivity, and chemical durability) on the composition of alkali mixtures in a glass is well known and has been named the mixed alkali effect. The mixed alkali effect on battery electrochemical properties is reported here for the first time. Depending on glass composition, the mixed alkali effect is shown to improve capacity retention during cycling (from 39% to 50% after 50 cycle test), to reduce the 1st-cycle irreversible loss (from 41% to 22%), and improve the high power (500 mAh/g) capacity (from 50% to 67% of slow discharge capacity).

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.188171jes] All rights reserved.

Manuscript submitted June 23, 2017; revised manuscript received August 28, 2017. Published September 13, 2017.

Most researched cathode materials for Li ion batteries are crystalline. Glass (amorphous) cathode materials have received relatively little attention.1 The most explored class of polyanion glass cathodes is vanadates glasses, which typically demonstrate 100–300 mAh/g capacities when not discharged below 1 V (vs. Li).2,3 Phosphate glass cathodes have also been demonstrated in thin film batteries with a LiPON electrolyte.5 Typically, polyanion glass cathodes have substantial capacity fade during tens of cycles.

Mixed polyanion glasses, which contain mixtures of polyanions such as phosphate, borate, vanadate, and molybdate, are high-capacity cathode materials (200–500 mAh/g) that can undergo conversion and intercalation reactions.4 Phosphovanadate glasses with Ag, Cu, Co, Fe, and Ni cations have previously been demonstrated to be electrochemically active.6 Mixed polyanion glasses, however, typically have the same fundamental electrochemical problems as other conversion cathodes i.e.: large hysteresis (typical ~55% cycling efficiency), capacity fade during 10’s of cycles, and a large 1st-cycle irreversible loss (~25%). Nevertheless, a key advantage of glass cathodes is the ability to tailor the composition and thereby change the physical properties and electrochemical performance. For example, previous work has demonstrated the ability to improve the cycling efficiency (as high as 67% efficiency), capacity retention, and/or 1st-cycle irreversible loss (as low as 6% loss) by adding lithium and borate to copper phosphovanadate glasses.7 Aoyagi, et al.8 demonstrated high capacity (~300 mAh/g) and reasonably good capacity retention (66% after 100 cycles) from Li-Fe-P-V-O glass and glass-ceramic cathodes. Yamauchi, et al.19 demonstrated a tin-based mixed polyanion anode, which cycles well for tens of cycles. Additionally, Suman, et al.10 demonstrated cycling of a mixed polyanion glass-ceramic in a Na-ion battery.

In polyanion glasses, a mixture of alkali cations is well known to have a particularly strong effect on the physical properties of a glass, which is commonly referred to as the mixed alkali effect. For a fixed total alkali content, many glass physical properties often exhibit a maxima or minima as a function of an alkali fraction (e.g., Na fraction for a Na xLa1−x containing glass).12 The mixed alkali effect is stronger when the size difference between the alkali cations is larger. The mixed alkali effect can be particularly strong for the case of electrical conductivity (often reduced by 2–6 orders of magnitude), the alkali diffusion coefficient (often reduced by 2–4 orders of magnitude), and chemical durability (alkali extraction reduced by 4–6 times).13 Transition metal cations in a glass can affect the intensity of a mixed alkali effect; Na/K iron phosphate glasses have shown a negligible mixed alkali effect on conductivity, density, and dissolution rate (<10% property change),15 while Na/K phosphate glasses with zinc16 or vanadium17 have shown a significant mixed alkali effects on conductivity. As discussed here, we found that the mixed alkali effect also has a significant influence on the electrochemical properties of glass cathodes, i.e., an influence that is likely due to these key physical property changes.

The mixed alkali effect on glass cathodes in lithium ion batteries would be perforce complex, because the alkali content of the glass changes during the charge and discharge processes. For example, a Na-Li glass would have a higher alkali content and a lower Na fraction during the discharge process. As the alkali mixture and total alkali content change, the physical properties of the glass would change dramatically during electrochemical cycling. This manuscript represents an initial examination of the electrochemical impact of a mixed alkali effect for Na, K, Rb, Cs, Na-Li, and K-Li bearing glass cathodes. All compositions studied herein were based on copper metaphosphate metavanadate (CuPV) glasses. CuPV glass compositions were chosen, because their conversion reactions occur at relatively high voltages (2.3–2.5 V discharge plateau) and our previous work has studied the effect of polyanion content in similar compositions.10

Experimental

Glass processing.—The CuPV glasses characterized herein had different alkali contents where the formula can be written as AnBx Cu (1/2 PO3 • 1/2 VO3)2+x+y where A & B are alkali cations. In the following text, the names of these glasses will be written in the form AnCuPV (if only one alkali is present) or as A,B CuPV. A list of all of the characterized glasses is shown in Table I (compositions based on dry precursor weights). The glasses were produced by melting the glass precursors in air at 1225–1250 °C (except for Li Cu (1/2 PO3 • 1/2 VO3)2 that was melted at 1050 °C) and then splat quenching the glass melt between cold copper plates. The copper plates were 1.5 cm thick and 15 cm in diameter and were chilled in liquid nitrogen before use. Glass splats were typically about 5–8 cm diameter and approximately 1 mm thick. The precursors were: copper (II) pyrophosphate hydrate, copper (II) oxide, vanadium (V) oxide, ammonium dihydrogen phosphate, lithium dihydrogen phosphate, sodium carbonate, potassium carbonate, rubidium carbonate, and cesium carbonate.

Glass powders were produced by crushing the glass splats with a Sepor jaw crusher, dry milling the crushed pieces using a Spex 8000M mixer mill with 10 mm zirconia media for 10 minutes, and further milling in ethanol using 3 mm zirconia media for 30 minutes. Powder X-ray diffraction (Cu-Kα source, 10–70° 2θ) was used to characterize powder from each glass splat; all reported materials exhibited XRD patterns with broad humps and without any observed crystalline peaks (representative XRD patterns of glass powders shown in Figure 1).

* Electrochemical Society Member.

E-mail: kercherak@ornl.gov
While this type of XRD pattern is consistent with a pure glass phase, XRD analysis could not detect the presence of small quantities (<5 wt%) of a crystalline phase.

**Cell fabrication & testing.**—Cathode tapes were produced by casting slurries of glass powder, graphite (Timcal C-Nergy KS 6L), carbon black (Timcal Super C65), and polyvinylidene fluoride (Kynar Powerflex LG) (6/2/1/1 by weight, respectively) in n-methyl-2-pyrrolidone using a square-frame tape caster (178 or 203 μm gap) on a 23 μm de-passivated aluminum current collector using an MTI Corporation automatic thick-film coater (MSK-AFA-III). The cathode tapes were vacuum dried overnight at ~80 °C and calendered to a 50 μm gap with an MTI Corporation MR-100A electric precision width rolling press. Cathode disks were then produced with a 1.11 cm hole punch.

Coin cells (CR2032, 316L stainless steel, polypropylene gasket) were assembled inside an argon-atmosphere glove box using cathode disks, an electrolyte (1.2 M LiPF6 in ethylene carbonate/dimethyl carbonate {3:7 by weight}), two 1.59 cm diameter Celgard 2325 separator disks (25 μm thick micro-porous polypropylene & polyethylene), and a lithium anode (punched from 1 mm thick lithium foil from Alfa-Aesar) hand-pressed onto a stainless steel spacer disk.

Coin cells were electrochemically evaluated on a Maccor series 4000 battery tester. Cycle testing was performed on the coin cells from 4.5 to 1 V at 20 mA/g and 100 mA/g. All voltages in this study were measured vs. Li/Li+. During charging, the cells were charged to 4.5 V and then were held potentiostatically until the current dropped below 10 μA. Specific capacity, 1st-cycle irreversible loss, and cycling efficiency are all reported based on 20 mA/g testing. Capacity retention is reported based on 100 mA/g testing. Because of the 1st-cycle irreversible loss, the cycling efficiency was measured between the 2nd discharge and 1st recharge (discharge energy/recharge energy).

**Results and Discussion**

**Single alkali CuPV glasses.**—The lithium, sodium, and potassium contents of CuPV glasses were varied from zero to 1 alkali per Cu (i.e., AxCu (1/2 PO3 • 1/2 VO3)). Also, rubidium and cesium CuPV glasses (Rb0.05CuPV & Cs0.05CuPV) were produced to further explore the effect of alkali cation size. Alternatively, these alkali-bearing glasses can be considered as cation mixtures with a fixed polyoxoanion content: (AxCuI-x,0.5)PO3.25. The Li,CuPV glasses do not have a mixed alkali content during charge & discharge processes, but the other single alkali CuPV glasses do. Comparing Li,CuPV with the other single alkali CuPV glasses will differentiate the effect of alkali content from a mixed alkali effect.

The first discharge, first recharge, & second discharge results at 20 mA/g (~C/20) and cycling results at 100 mA/g (~C/4) for single alkali glasses are shown in Figure 2. The high-capacity electrochemical reactions below ~2.5 V are a Cu-based conversion reaction and a vanadium-based intercalation reaction (occurring concurrently or sequentially).9 The plateau voltages of the first discharge curves were similar for all Li,CuPV glasses (Figure 2a); the Li,CuPV glass only had a slightly lower plateau voltage (2.3 V versus 2.4 V). However, Na,CuPV & K,CuPV with x ≥ 0.5 had significantly lower plateau

---

**Table I. Glass compositions (as-batched), theoretical capacity from copper electrochemical reactions, and theoretical capacity associated with an intercalation reaction causing a single valence change in vanadium.**

| Composition | Theo. Cu capacity (mAh/g) | Theo. V single valence capacity (mAh/g) |
|-------------|--------------------------|----------------------------------------|
| CuPV        | 222                      | 111                                    |
| Li0.05CuPV  | 218                      | 112                                    |
| Li0.5CuPV   | 185                      | 116                                    |
| LiCu        | 159                      | 119                                    |
| Na0.05CuPV  | 217                      | 111                                    |
| Na0.5CuPV   | 180                      | 113                                    |
| NaCu        | 152                      | 114                                    |
| K0.05CuPV   | 216                      | 111                                    |
| K0.5CuPV    | 175                      | 110                                    |
| KCu         | 145                      | 109                                    |
| Rb0.05CuPV  | 214                      | 110                                    |
| Cs0.05CuPV  | 212                      | 109                                    |
| Na0.05Li0.95CuPV | 159                  |                                           |
| Na0.5Li0.95CuPV | 155                  |                                           |
| K0.05Li0.95CuPV | 158                  |                                           |
| K0.5Li0.95CuPV | 152                  |                                           |

---

While this type of XRD pattern is consistent with a pure glass phase, XRD analysis could not detect the presence of small quantities (<5 wt%) of a crystalline phase.

**Cell fabrication & testing.**—Cathodes tapes were produced by casting slurries of glass powder, graphite (Timcal C-Nergy KS 6L), carbon black (Timcal Super C65), and polyvinylidene fluoride (Kynar Powerflex LG) (6/2/1/1 by weight, respectively) in n-methyl-2-pyrrolidone using a square-frame tape caster (178 or 203 μm gap) on a 23 μm de-passivated aluminum current collector using an MTI Corporation automatic thick-film coater (MSK-AFA-III). The cathode tapes were vacuum dried overnight at ~80 °C and calendered to a 50 μm gap with an MTI Corporation MR-100A electric precision width rolling press. Cathode disks were then produced with a 1.11 cm hole punch.

Coin cells (CR2032, 316L stainless steel, polypropylene gasket) were assembled inside an argon-atmosphere glove box using cathode disks, an electrolyte (1.2 M LiPF6 in ethylene carbonate/dimethyl carbonate {3:7 by weight}), two 1.59 cm diameter Celgard 2325 separator disks (25 μm thick micro-porous polypropylene & polyethylene), and a lithium anode (punched from 1 mm thick lithium foil from Alfa-Aesar) hand-pressed onto a stainless steel spacer disk.

Coin cells were electrochemically evaluated on a Maccor series 4000 battery tester. Cycle testing was performed on the coin cells from 4.5 to 1 V at 20 mA/g and 100 mA/g. All voltages in this study were measured vs. Li/Li+. During charging, the cells were charged to 4.5 V and then were held potentiostatically until the current dropped below 10 μA. Specific capacity, 1st-cycle irreversible loss, and cycling efficiency are all reported based on 20 mA/g testing. Capacity retention is reported based on 100 mA/g testing. Because of the 1st-cycle irreversible loss, the cycling efficiency was measured between the 2nd discharge and 1st recharge (discharge energy/recharge energy).

**Results and Discussion**

**Single alkali CuPV glasses.**—The lithium, sodium, and potassium contents of CuPV glasses were varied from zero to 1 alkali per Cu (i.e., AxCu (1/2 PO3 • 1/2 VO3)). Also, rubidium and cesium CuPV glasses (Rb0.05CuPV & Cs0.05CuPV) were produced to further explore the effect of alkali cation size. Alternatively, these alkali-bearing glasses can be considered as cation mixtures with a fixed polyoxoanion content: (AxCuI-x,0.5)PO3.25. The Li,CuPV glasses do not have a mixed alkali content during charge & discharge processes, but the other single alkali CuPV glasses do. Comparing Li,CuPV with the other single alkali CuPV glasses will differentiate the effect of alkali content from a mixed alkali effect.

The first discharge, first recharge, & second discharge results at 20 mA/g (~C/20) and cycling results at 100 mA/g (~C/4) for single alkali glasses are shown in Figure 2. The high-capacity electrochemical reactions below ~2.5 V are a Cu-based conversion reaction and a vanadium-based intercalation reaction (occurring concurrently or sequentially).9 The plateau voltages of the first discharge curves were similar for all Li,CuPV glasses (Figure 2a); the Li,CuPV glass only had a slightly lower plateau voltage (2.3 V versus 2.4 V). However, Na,CuPV & K,CuPV with x ≥ 0.5 had significantly lower plateau
voltages (NaCuPV 2.0 V, KCuPV 1.75 V) for the first cycle. This lowered plateau voltage during discharge was likely due to a lower ionic diffusivity and/or lower electronic conductivity in the discharging glass phase associated with a mixed alkali effect. Consistent with these results, the diffusivity/conductivity reduction of a mixed alkali effect would be expected to be more pronounced for increasing amounts of non-Li cations and for larger non-Li cations. The charging curves showed a distinctly different trend with alkali content. The CuPV glass showed a pronounced peak in the charge curve. Additions of small amounts of alkali (x = 0.05) to CuPV greatly reduced or eliminated the peak in the charge curve. Additions of large amounts of alkali (x = 1) appeared to increase the voltage of the charge peak above 4.5 V, which greatly increased the 1st-cycle irreversible loss.

Some electrochemical metrics were primarily affected by the alkali content. Small alkali additions (A0.05) improved the capacity retention of CuPV glasses, but only caused slight improvements in the 1st-cycle irreversible loss and cycling efficiency (Figure 3). Large alkali additions to CuPV glasses caused higher 1st-cycle irreversible loss (as high as 44% for KCuPV) and higher cycling efficiency after the 1st cycle (above 60% for all ACuPV glasses). Increasing the alkali content
Figure 3. 1st-cycle specific capacity (a), 1st-cycle irreversible loss (b), cycling efficiency (c), and 50 cycle capacity retention (d) for single alkali copper phosphate vanadate glasses.

doest decrease the specific capacity, but not beyond what would be expected based solely on composition. If the composition is written in terms of constant polyanion content \((A_xCu_{1-0.5x}P_3O_{12}VO_3)\), then it is readily apparent that alkali addition decreases the Cu available for a conversion reaction. If a full theoretical capacity of the Cu conversion reaction is assumed, then the vanadium-based intercalation reactions in these single alkali glasses would have capacities equivalent to 1.50–1.79 vanadium valence changes (based on Table I).

A distinct mixed alkali effect could also be observed for the capacity retention of glass cathodes. For \(A_{0.05}CuPV\), the capacity retention for the non-Li CuPV glasses (45% Na\(_{0.05}CuPV\), 50% K\(_{0.05}CuPV\), 46% Rb\(_{0.05}CuPV\), and 49% Cs\(_{0.05}CuPV\) exceeds the Li\(_{0.05}CuPV\) value (43%) at 50 cycles. For \(A_1CuPV\), the capacity retention for the non-Li CuPV glasses (25% for K\(_1CuPV\)) were lower than for Li\(_1CuPV\) (41%).

Higher power performance also exhibited evidence of a mixed alkali effect (see Figure 4a). Glass cathodes were cycled at variable rates to determine their rate performance, starting at 20 mA/g (\(\sim C/20\)) and progressing to higher currents (after test completion, a final 20 mA/g discharge was compared to the 2nd 20 mA/g cycle to confirm nearly full capacity retention). The second 20 mA/g cycle was compared to the first subsequent 500 mA/g cycle (\(\sim 1.3C\)), in order to eliminate the effect of 1st-cycle irreversible loss. Li\(_xCuPV\), Rb\(_{0.05}CuPV\), and Cs\(_{0.05}CuPV\) discharged at 500 mA/g all had capacities of 147–153 mAh/g (50% of their 20 mA/g capacities). In general, \(A_1CuPV\) glasses had the worst high power capacities (e.g., 19–31% of their 20 mA/g capacities). For Na\(_xCuPV\) & K\(_xCuPV\), the measured optimum high rate performances (63% & 67% of 20 mA/g values, respectively) occurred at different non-Li contents (50% Na & 5% K). The reason for different optimum compositions for best rate performance is unknown, but the alkali composition necessary to achieve a specific physical property value (such as ionic diffusivity) would be expected to be lower for larger alkali cation sizes based on the mixed alkali effect.

**Mixing two alkali cations.**—A series of CuPV glasses was made with a constant alkali content (Alkali-copper ratio = 1), but with mixtures of alkalis (i.e., \(A_xLi_{1-x}Cu(\frac{1}{2}P_3O_{12}\cdot\frac{1}{2}VO_3)\)). These mixed

Figure 4. A rate comparison between 20 mA/g & 500 mA/g (both after 1st cycle) for (a) single alkali copper phosphate vanadate glasses and (b) mixed alkali copper phosphate vanadate glasses.
alkali glasses exhibited a mixed alkali effect “as made”, but the alkali mixture would change during the charge and discharge processes. The first discharge, first recharge, & second discharge results at 20 mA/g and cycling results at 100 mA/g for mixed alkali glasses are shown in Figure 5. Note that all $A_xLi_{1-x}CuPV$ mixed alkali glasses ($0 < x < 1$) lacked the distinctive charge curve peak found in CuPV glass, but the 1st-cycle irreversible loss was lower than $Li_1CuPV$ glass.

For the mixed alkali glasses, the most pronounced mixed alkali effects were observed for 1st-cycle irreversible loss, the measured voltage for the conversion reaction, and high power performance. Mixtures of alkali cations consistently reduced the 1st-cycle irreversible loss (Figure 5), but the lowest irreversible loss was observed for $Na_{0.05}Li_{0.95}CuPV$ (22%). The measured voltages for the conversion reaction in $Na_{0.05}Li_{0.95}CuPV$, $K_{0.05}Li_{0.95}CuPV$ and $Li_1CuPV$ were very similar (Figure 5), but glasses with a higher fraction of a non-Li alkali had progressively lower voltages in the first cycle (as low as 1.76 V for $K_1CuPV$). The high power performance improved with 5% non-Li substitution (Figure 4), with the greatest effect observed for $Na_{0.05}Li_{0.95}CuPV$ (its 500 mA/g capacity is 42% of its 20 mA/g capacity).

**Conclusions**

The mixed alkali content of a glass is known to strongly affect its physical properties, such as the electrical conductivity, alkali diffusion coefficient, and chemical durability. The electrochemical effects

![Figure 5](image1.png)

**Figure 5.** Discharge-charge-discharge curves & cycling results for: (a) Na-Li copper phosphate vanadate glasses and (b) K-Li copper phosphate vanadate glasses.

![Figure 6](image2.png)

**Figure 6.** 1st-cycle specific capacity (a), 1st-cycle irreversible loss (b), cycling efficiency (c), and 50 cycle capacity retention (d) for mixed alkali copper phosphate vanadate glasses.
of alkali and mixed alkali content on glass cathodes have not been previously reported to our knowledge. Single and mixed alkali copper phosphate vanadate (CuPV) glasses were tested as Li-ion battery cathodes to separately determine the electrochemical effects of alkali content and the mixed alkali content.

The alkali effects on glass cathode performance were:

• Increasing alkali content decreased the 1st-cycle specific capacity due to a reduced amount of Cu available for a conversion reaction (e.g., 396 mAh/g for glass with 0 Li per Cu and 356 mAh/g for glass with 1 Li per Cu).

• Large alkali additions (1 alkali per Cu) caused a higher 1st-cycle irreversible loss (up to 44% irr. loss) and a higher cycling efficiency (> 60% cycling efficiency).

The mixed alkali effects on glass cathode performance were:

• Higher capacity retention after 50 cycles (up to 50%) occurred in glasses containing 0.05 non-Li alkali per Cu (compared to 39% for glass with no alkali).

• In the first cycle, the conversion reaction voltage was lowered in glasses containing 1 non-Li alkali per Cu (to as low as 1.76 V, compared to 2.3–2.4 V for glasses with Li-only or with no alkali).

• 1st-cycle irreversible loss was reduced from 41% to 22% by substituting 5% non-Li content into a glass cathode with 1 Li per Cu.

• Optimum non-Li alkali contents improved the high rate (500 mA/g) capacity from 50% to 67% of slow discharge capacity.

Acknowledgments

Research has been supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U. S. Department of Energy through the Advanced Battery Materials Research (BMR) Program. Shay Chapel’s work was funded through the Higher Education Research Experiences program, which was administered by the Higher Education Research Experiences program, which was administered by the Oak Ridge Institute for Science & Education. Special thanks to: Nancy Dudney, Jagjit Nanda, Jim Kiggans, Joanne Ramey, Cliff Davission, Ashli Clark, Michael Naguib, and Claus Daniel at Oak Ridge National Laboratory.

References

1. C. Julien, Ionics, 2, 169 (1996).
2. N. Machida, R. Fuchida, and T. Minami, Solid State Ionics, 35, 295 (1989).
3. N. Machida, R. Fuchida, and T. Minami, Solid State Ionics, 37, 299 (1990).
4. N. Machida, R. Fuchida, and T. Minami, Solid State Ionics, 40/41, 589 (1990).
5. S. Denis, E. Baudran, M. Touboul, and J.-M. Tarascon, J. Electrochem. Soc., 144(12), 4099 (1997).
6. Y. Piffard, F. Leroux, D. Guyomard, J.-L. Mansot, and M. Tournoux, J. Power Sources, 68, 698 (1997).
7. Y. Sati, S. Saito, H. Hayashi, T. Furuya, and S. Kasanagi, J. Power Sources, 258, 54 (2014).
8. A. K. Kercher, J. O. Ramey, K. J. Carroll, J. O. Kiggans, N. J. Dudney, R. A. Meisner, L. A. Boatner, and G. M. Veith, J. Electrochem. Soc., 161(14), A2210 (2014).
9. A. K. Kercher, J. A. Kolopus, R. L. Sacci, R. E. Ruther, N. C. Gallego, S. L. Stooksbury, L. A. Boatner, and N. J. Dudney, J. Electrochem. Soc., 163(2), A131 (2016).
10. A. K. Kercher, J. A. Kolopus, R. L. Sacci, R. E. Ruther, N. C. Gallego, S. L. Stooksbury, L. A. Boatner, and N. J. Dudney, J. Electrochem. Soc., 164(4), A804 (2017).
11. T. Aoyagi, T. Fujieda, T. Toyama, K. Kono, D. Takamatsu, T. Hirano, T. Naito, Y. Hayashi, and H. Takizawa, J. Non-cryst. Solids, 453, 28 (2016).
12. H. Yamashita, G. Park, T. Nagakane, T. Honma, T. Komatsu, T. Sakai, and A. Sakamoto, J. Electrochem. Soc., 160(10), A1725 (2013).
13. G. Suman, C. S. Rao, P. K. Ojha, M. S. S. Babu, and R. B. Rao, J. Mater. Sci., 52, 5038 (2017).
14. D. E. Day, J. Non-cryst. Solids, 21, 343 (1976).
15. X. Fang, C. S. Ray, G. K. Marasinghe, and D. E. Day, J. Non-cryst. Solids, 263–4, 293 (2000).
16. H. W. Guo, X. F. Wang, Y. X. Gong, and D. N. Gao, J. Non-cryst. Solids, 356, 2109 (2010).
17. G. B. Devidas, T. Sankarappa, B. K. Chougule, and G. Prasad, J. Non-cryst. Solids, 353, 426 (2007).