

SUPPORTING INFORMATION

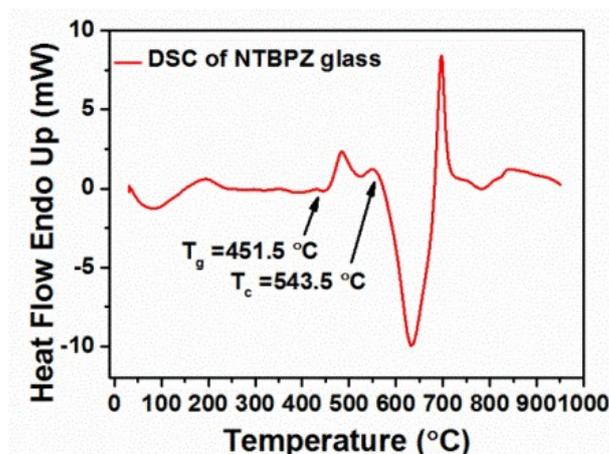


Fig. S1 DSC curve of the different ratio NTBPPZ glass

Differential scanning calorimetry (DSC) (Fig. S1) shows that the glass transition temperature (T_g) and the crystallization temperature (T_c) are 451.5 °C and 543.5 °C, respectively. A part of NTBPPZ glass phase can transform into $\text{NaTi}_2(\text{PO}_4)_3$ crystals, when the heat-treat temperature beyond over 451.5 °C. The nucleus can be formed with the heat-treat temperature between 515 °C and 520 °C. Subsequently, a pure crystalline phase of the $\text{NaTi}_2(\text{PO}_4)_3$ can be formed by reducing the heat-treat temperature between 500 °C to 515 °C,

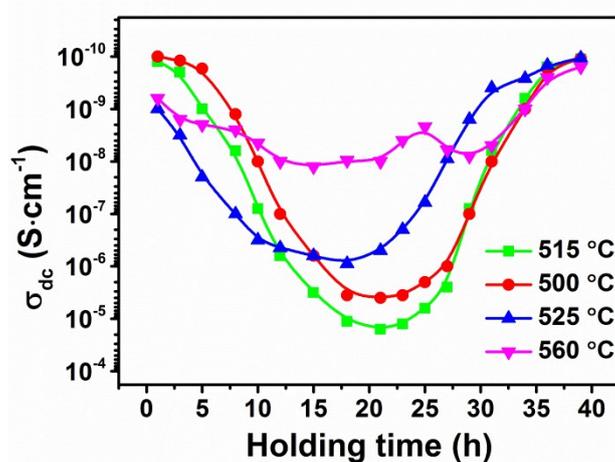


Fig. S2 The change of the sodium-ion conductivity with holding time under different heat-treat temperature.

Fig. S2 shows controlling the heat-treat temperature and the holding time is the key to improve the sodium-ion conductivity. The result shows that the heat-treat temperature and the holding time are two important factors affecting the grain size and uniformity, then affected the ionic conductivity. Consequently, the best sodium-ion conductivity of the NTBPPZ glass-ceramic can be gained with holding time of 20 h under 515 °C.

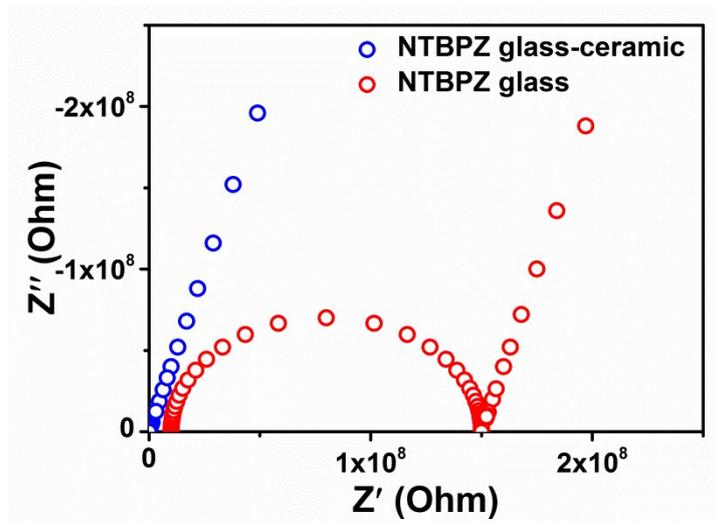


Fig. S3 Complex impedance plots for the NTBZ glass and glass-ceramic at 25 °C after cold pressing at 32 MPa

The impedance plots of the glass pellet exhibit a big semicircle and a spike in the low-frequency region, suggesting that the NTBZ glass behaves as large resistances, which includes the bulk-grain and grain-boundary resistances. The conductivity of the NTBZ glass is only $2 \times 10^{-9} \text{ S} \cdot \text{cm}^{-1}$, which is determined from the cross-sectional resistance between the semicircle and the spike on the x axis (Fig. S3).

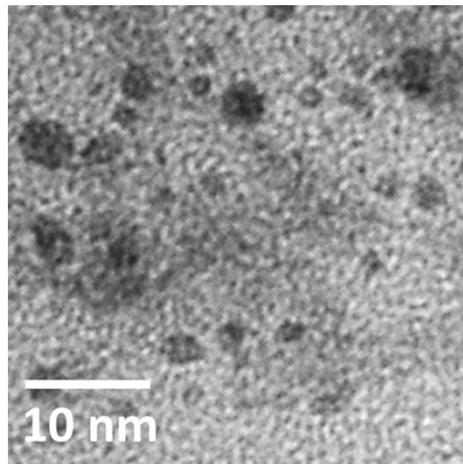


Fig. S4 TEM image of the NTBZ glass-ceramic.

Fig. S4 shows a lot of nanocrystal distribute in NTBZ glass-ceramic homogeneously.

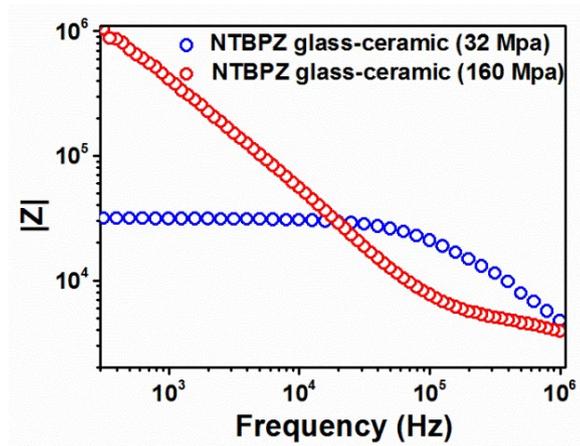


Fig. S5 Bode plots of the pellets of the NTBPZ glass-ceramic at 25 °C after cold pressing at 160 MPa and 32 MPa, respectively

Fig. S5 shows the absolute values of impedance $|Z|$ as a function of frequency of NTBPZ glass-ceramic at 32 MPa behave completely differently from the NTBPZ glass-ceramic at 160 MPa. The NTBPZ glass-ceramic at 160 MPa has smaller impedance than NTBPZ glass-ceramic at 32 MPa in the high-frequency range from 10^3 to 10^6 Hz.