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## Introduction

## Neutron diffraction

Extremely rapid (or “pulse power”) energy conversion has become a critical technique due to its numerous applications as compact devices in mining, renewable energy industries.

The pressure-driven depolarization behavior in ferroelectric materials enables the fast conversion of mechanical energy to electrical energy for applications, which have driven extensive research in this field for many years. Nb doped Pb(Zr<sub>0.95</sub>Ti<sub>0.05</sub>)O<sub>3</sub> (PZT 95/5) has dominated this area for more than half a century. However, the toxicity of lead and increasing environmental regulation will limit its applications in the future. There is thus an urgent current need for the discovery of lead-free FE materials to replace PZT 95/5.

In this work, lead-free (Ag<sub>0.935</sub>K<sub>0.065</sub>)NbO<sub>3</sub> (AKN) ferroelectric materials are designed and synthesized for explosive energy conversion applications. This material not only possesses a record-high energy storage density, but also exhibits excellent temperature stability. An in-situ neutron diffraction technique and phenomenological theory are used to elucidate the structure evolution under pressure. A device has also been fabricated and high performance demonstrated.

## Pressure induced depolarization

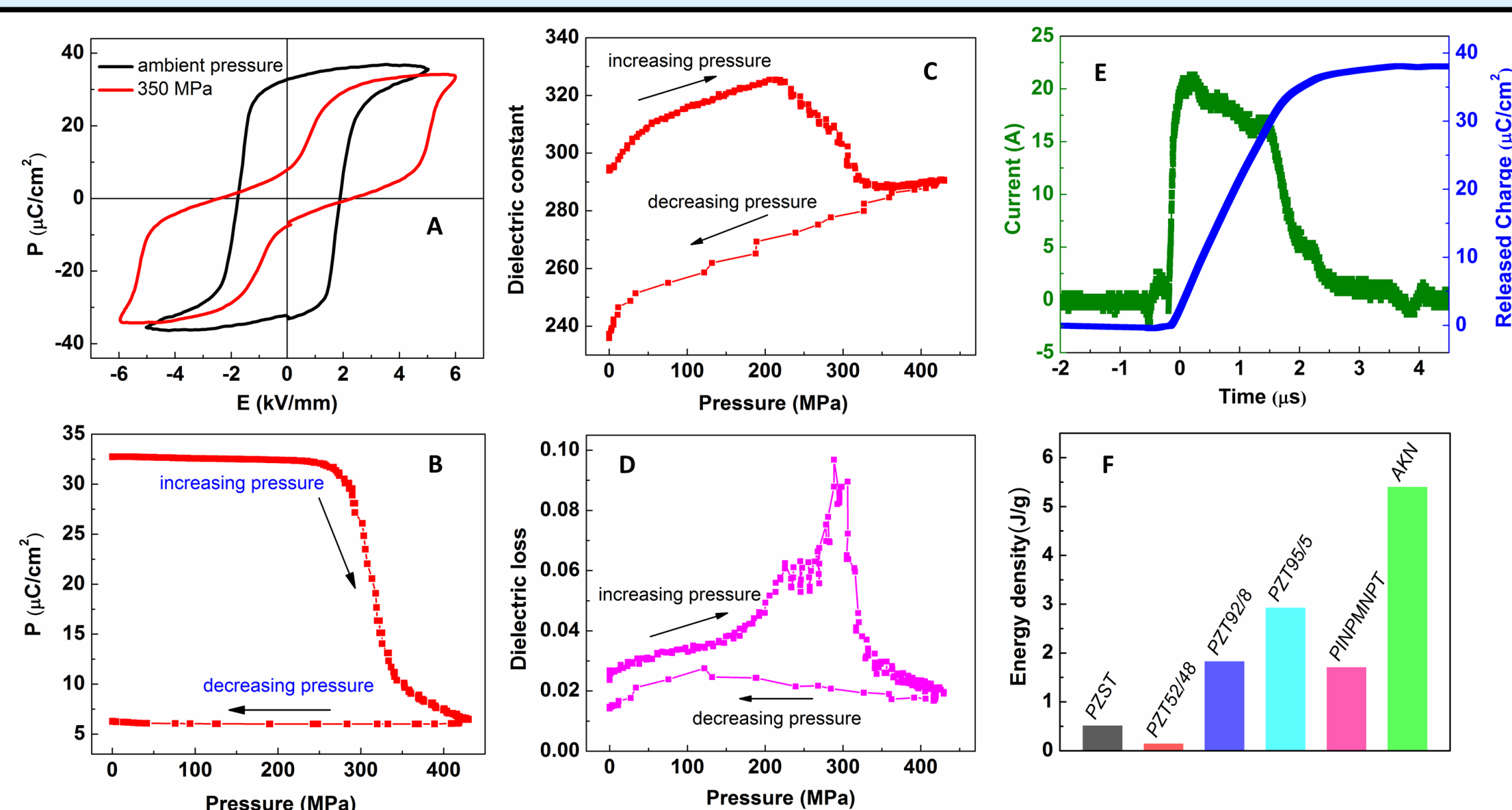


Fig. 1 (A) The pressure dependent P-E loops of AKN FE ceramics, (B), The in-situ depolarization curve of pre-poled AKN ceramics (C) and (D), The hydrostatic pressure dependent dielectric constant and dielectric loss of poled AKN ceramics at room temperature. (E) Practical dynamic discharging response of assembled AKN FE ceramic devices. (F) A comparison of the energy storage densities per unit of weight of the AKN ceramics and other FE materials

- The AKN ceramics experience change from single loop-featured FE character at ambient pressure to double loop-featured, AFE character at 350 MPa.
- The pressure driven depolarization curve of poled AKN ceramics shows the remnant polarization remains almost unchanged up to 240 MPa, while experiences sharp decrease at around 300 MPa.
- The dielectric constant and loss of poled AKN show sharp change at around phase transition pressure.
- An Ferroelectric energy storage device is fabricated and 38  $\mu\text{C}/\text{cm}^2$  is released within 1.8 microseconds. According to the following calculation equation:  $W = P_r^2 / (2(\epsilon_0 \cdot \epsilon_r \cdot \rho))$ , the energy storage density per unit of weight of AKN is much higher than other FE materials.

## Temperature stability

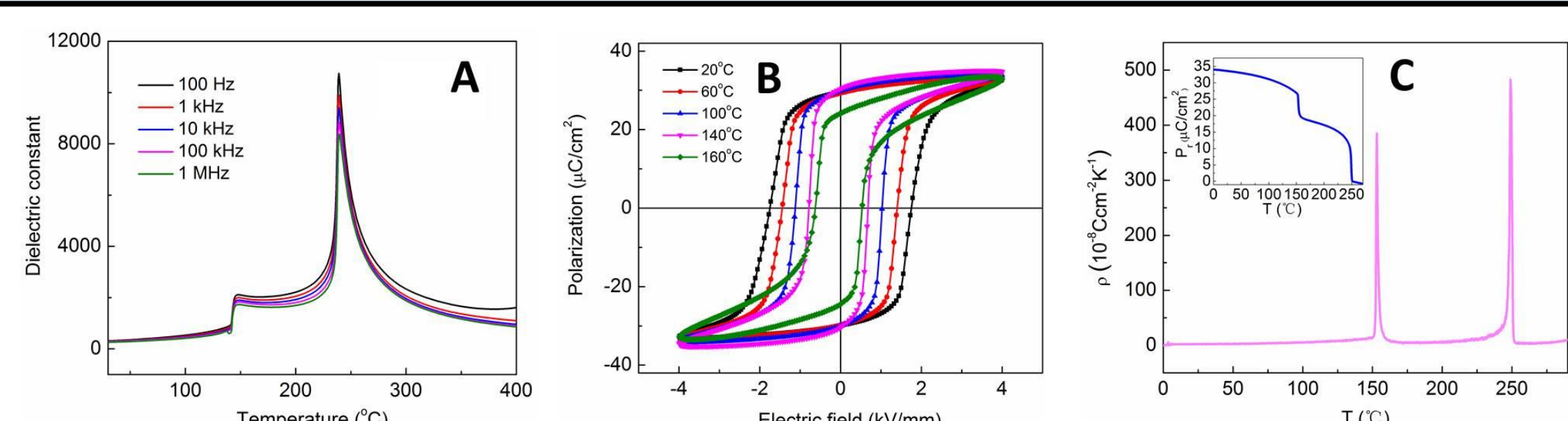


Fig 2. The temperature dependent dielectric, ferroelectric and pyroelectric of AKN ceramics. (A and C: poled samples)

The AKN ceramics experience no disruptive phase transition until a FE-FE phase transition occurs at 150 °C, indicating excellent temperature stability. This is another advantage over PZT95/5, where a similar FE-FE phase transition leads to polarization loss at 41-70 °C.

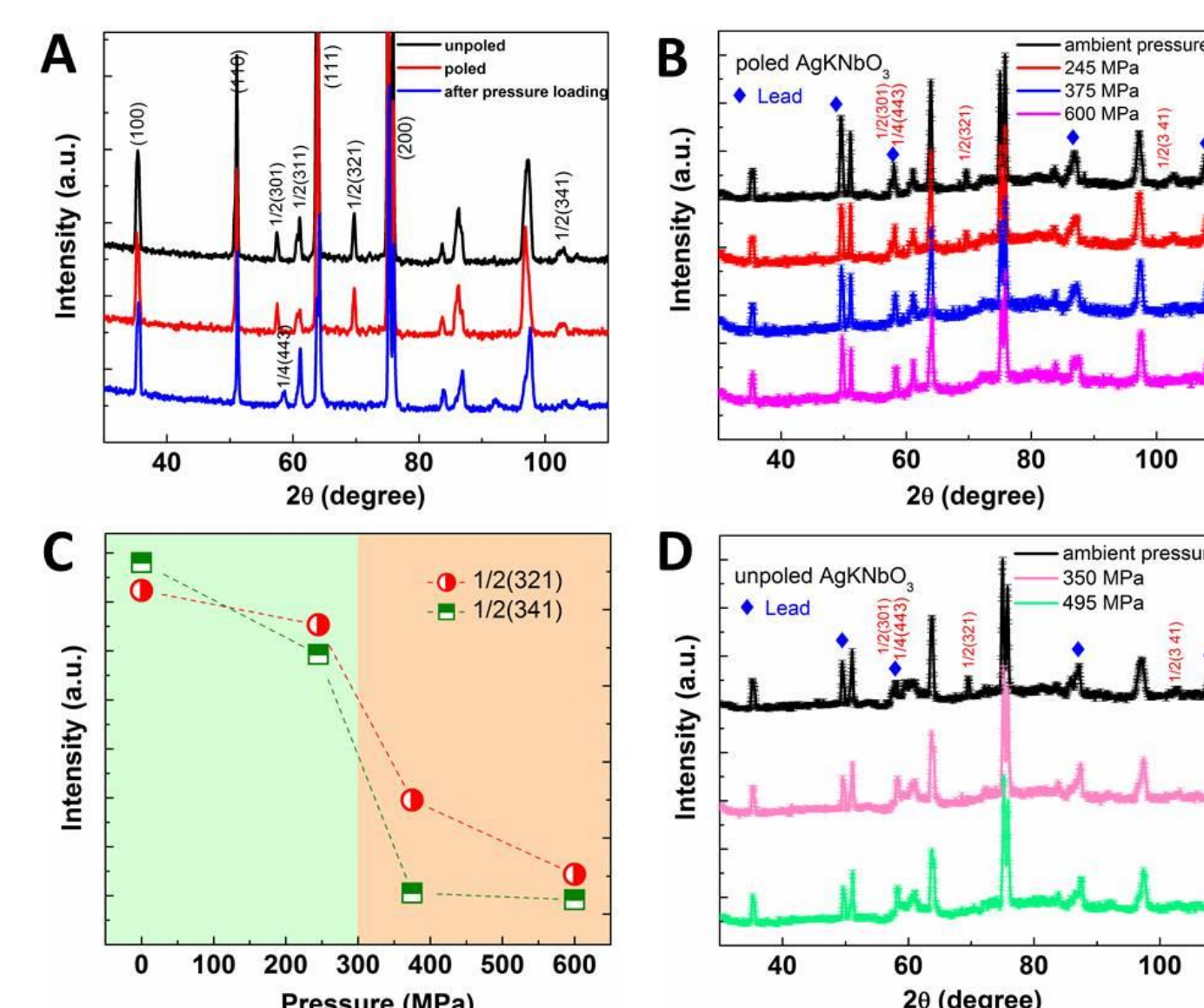


Fig. 3 (A). NDPs of an unpoled AKN ceramic sample, a poled AKN ceramic sample and a poled AKN ceramic after experiencing 600 MPa hydrostatic pressure. In-situ NDPs of AKN ceramics of (B) poled samples and (D) unpoled samples. (C) The integrated area of the 1/2(321) and 1/2(341) peaks for poled samples.

- The FE phase is characterized by  $\frac{1}{2}(301)_p$ ,  $\frac{1}{2}(311)_p$ ,  $\frac{1}{2}(321)_p$  and  $\frac{1}{2}(341)_p$  reflections, arising from  $a^-a^+c^+$  octahedral tilting. While the AFE phase is reflected by  $\frac{1}{4}(443)_p$  and  $\frac{1}{4}(229)_p$ , associated with the  $a^-a^+c^-/a^-a^+c^+$  tilt system.
- According to the emergence and disappearance of characteristic satellites, the AKN ceramics undergo a FE-AFE phase transition with increasing pressure no matter whether they were pre-poled or not.
- The AKN sample remains AFE after the removal of the pressure condition, indicating the pressure induced FE-AFE phase transition is irreversible.

## Theory modelling

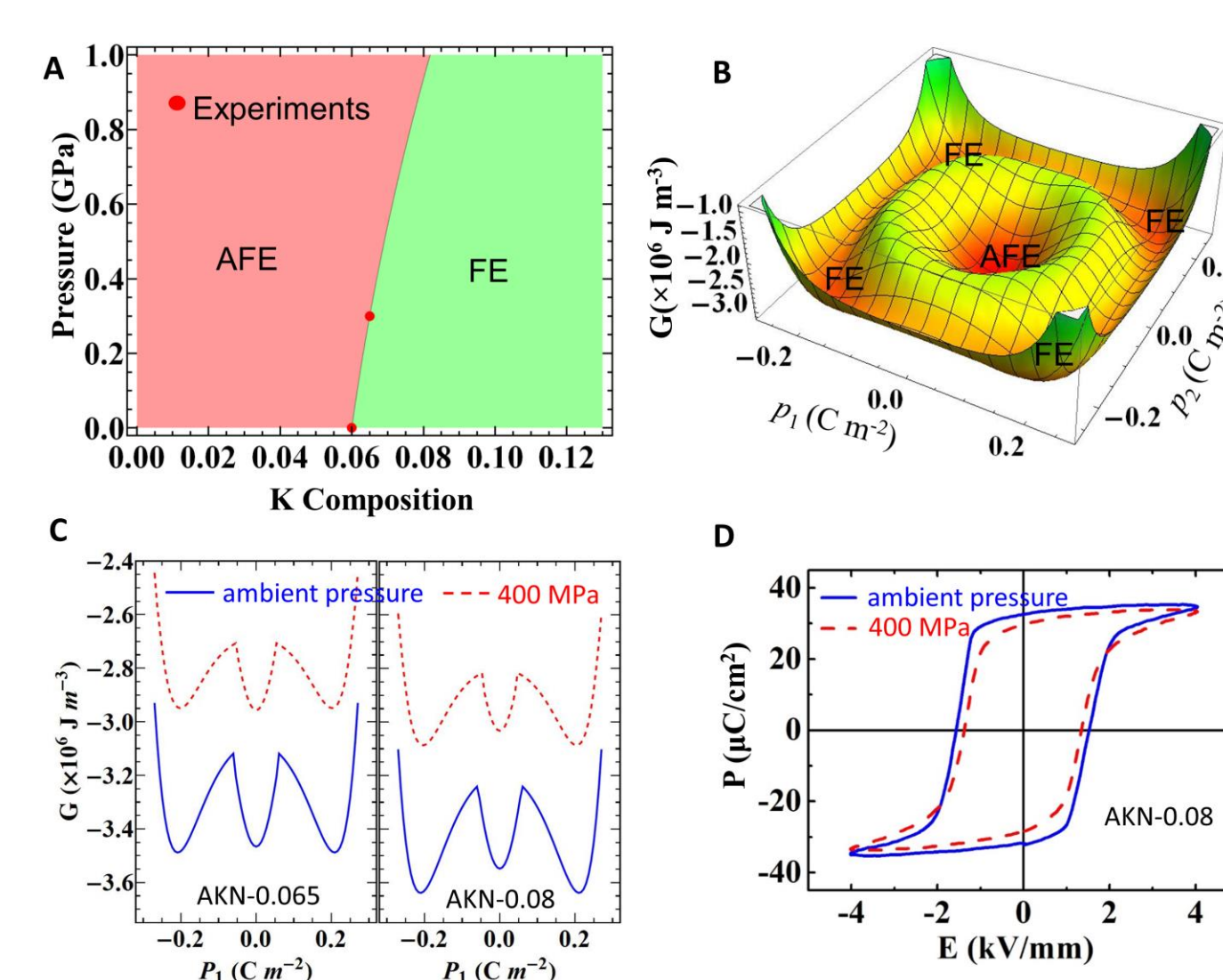


Fig. 4. (A) Pressure-composition phase diagram of the AKN system. (B) Energy contours as a function of  $p_1$  and  $p_2$ . (C) The energy profiles of (Ag<sub>0.935</sub>K<sub>0.065</sub>)NbO<sub>3</sub> and (Ag<sub>0.92</sub>K<sub>0.08</sub>)NbO<sub>3</sub> under different hydrostatic pressures. (D) The P-E loops of (Ag<sub>0.92</sub>K<sub>0.08</sub>)NbO<sub>3</sub> under different hydrostatic pressures.

- A pressure-composition phase diagram for AKN is calculated based on energy minimization.
- Although pressure suppresses the stabilities of both the FE and AFE phases, the FE phase is more sensitive to the applied pressure.
- The difference between the energy minima of the FE and AFE phases under ambient pressure of (Ag<sub>0.935</sub>K<sub>0.065</sub>)NbO<sub>3</sub> is small, while for (Ag<sub>0.92</sub>K<sub>0.08</sub>)NbO<sub>3</sub>, this difference is increased. Thus, it is more difficult to drive the FE-AFE phase transition for (Ag<sub>0.92</sub>K<sub>0.08</sub>)NbO<sub>3</sub>.

## Conclusion

- A lead-free, high performance, (Ag<sub>0.935</sub>K<sub>0.065</sub>)NbO<sub>3</sub> FE material has been discovered that shows outstanding potential (large polarization, low volume density, lead-free, high energy density, fast charge releasing) for next-generation, energy conversion applications.
- The FE-AFE phase transition upon increasing pressure forms the basis of the pressure driven depolarization of AKN, which is demonstrated from both macroscopic properties and neutron diffraction analysis.
- The FE-AFE phase transition is associated with the change of space group from  $Pmc2_1$  to  $Pbcm$ , with the accompanying oxygen octahedral tilt system changing from  $a^-a^+c^+$  to  $a^-a^+c^-/a^-a^+c^+$ .
- A proposed phenomenological theory has been used to further confirm our experimental results.

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