We employed first-principles density functional theory calculations guided by group-theoretical analysis and demonstrated the control of insulator-metal-insulator transition, polarization and two sublattice magnetization in (LaFeO₃)₁/(CaFeO₃)₁ superlattice via. multi structural mode coupling i.e., 'multimode coupling'. We have discovered a polar A-type charge disproportionation mode, Q_{ACD} (analogous to the A-type antiferromagnetic ordering), and found that it couples with the trilinear coupling, Q_{Tri} mode (common in Pnma perovskite oxides and involves three structural modes), and lowers the symmetry further. By tuning the strength of the coupling between the participating modes, the polar metallic phase, polar zero bandgap semiconducting, and polar insulating phases can be obtained. Here, Q_{Tri} switches the polarization direction, whereas, Q_{ACD} can trigger insulator-metal-insulator transition along with the polarization switching. The mechanism is true for any transition metal superlattices constituted with Pnma building blocks and with partially filled e₉ or t₂g electron(s) at the transition metal sites.

Mode coupling in real materials not only drives structural phase transition but also drives functional properties into the low symmetry phase. The ABO₃ perovskite oxides are among the most studied systems owing to their functional properties such as ferroelectricity, weak ferromagnetism, linear magnetoelectricity and many other, primarily driven by structural distortions [1–5]. In Pnma ABO₃ oxides, the trilinear coupling, Q_{Tri} ∼ Q_T ⊗ Q_{R'} ⊗ Q_{AFE,A}, between tilt (Q_T) and in phase rotation (Q_{R'}) of BO₆ octahedra and anti-ferroelectric A-site displacement (Q_{AFE,A}) mode is responsible for driving the phase transition. By employing layered ordering at the A-site, i.e., by constructing AO and A'O layer, the anti-ferroelectricity can be tuned into ferroelectricity leading to finite polarization into the system. Here, Q_T and Q_{R'} drive weak ferromagnetism and linear magnetoelectricity, respectively, into the system and the polarization is induced by the trilinear coupling [6, 7]. This is known as the hybrid improper ferroelectric (HIF) mechanism [5] which is one of the most successful paradigms in designing multiferroic materials where more than one ferroic property can coexist and cross coupled [6–12].

Apart from common distortions a certain type of structural distortion, termed as a charge disproportionation mode (Q_{CD}) has a deterministic role in obtaining insulator-to-metal transition (IMT) [13]. The Q_{CD} mode is mainly observed in systems those contain charge orderings at the B-sublattice [13–18], e.g., perovskite CaFeO₃ [14, 19]. In CaFeO₃, electronic phase separation is associated with a charge disproportionation, 2d^{4+} → d^{3+} + d^{3+}, which is responsible for the band gap opening[14, 19]. Similar mechanism follows for other IMT based materials. In this context, it is proposed that the charge disproportionation and hence the IMT transition can be driven by the intermixing of transition metal ions at the oxide interface and that also can happen in the presence of the polar distortion [20]. Further, perturbation, like strain, tunes the local bonding environment leading to the modification of the band structure at the Fermi level [21].

In this paper, within (LaFeO₃)₁/(CaFeO₃)₁ superlattice (SL) with C-type magnetic configuration, we report a new type of polar charge disproportionation mode Q_{ACD}, as here, the charge disproportionation has A-type ordering (in analogy with A-type magnetic orderings). We show a multimode coupling, Q_M ∼ Q_{Tri} ⊗ Q_{ACD} exists between Q_{Tri} and Q_{ACD}, which lowers the energy with a lower space group (Pc) as compared to the trilinear coupling, Q_{Tri}, in perovskite SLs (i.e., Pmc2₁) [22]. The electric polarization (P), magnetization (M) and IMT show strong correlation and can be tuned via. strain by modifying the strength of the coupling leading to polar metallic, polar zero bandgap semiconducting, and polar insulating phases. Interestingly, the Q_{ACD} is found to switch the direction of polarization of the system through an insulator-metal-insulator path and orbital ordering plays a pivotal role. Finally, we demonstrated that beyond conventional understanding, the mode coupling at the interface and emergence of associate multifunctionality is applicable for any layered (ABO₃)₁/(A'B'O₃)₁ SLs of transition metal oxides (TMOs) with Pnma symmetry and with unpaired e₉ or t₂g electrons.

Density functional theory (DFT) [23] calculations are performed for total energy, geometry optimization and electric polarization using the Berry phase method [24] as implemented VASP [25]. The K-integration in the Brillouin zone is performed using Γ-centered 6 x 6 x 4 points using 500.0 eV energy cut-off. We considered the generalized gradient approximation (GGA) augmented by the Hubbard-U corrections (GGA+U) [26, 27] to describe exchange-correlation effects. To consider d-d Coulomb interactions, we employed U parameters of 5.0, 3.5, 3.0,
arrangement of charge disproportionated mode reflects in FeO$_6$ octahedra which is in analogy with the A-type antiferromagnetic configuration and is shown in Figure 1(f). The Q$_{ACD}$ mode appeared as imaginary frequency and alone exhibited a double well with small depth. Only coupling with the Q$_{Tr}$ leads to a considerable double well indicating energy gain and strong coupling with Q$_{Tr}$, as shown in Figure 2(a).

We then examined how the charge disproportionation modes (i.e., Q$_{GCD}$, Q$_{ACD}$) which are individually responsible for the IMT are coupled to the other dominating distortions. As shown in Figure 2(b), among all the modes couplings, we have found that the coupling between Q$_{Tr}$ and Q$_{ACD}$, i.e.; Q$_M$ $\sim$ Q$_{Tr}$ $\otimes$ Q$_{ACD}$ offers a polar P space group and ensures the lowest energy structure (30 meV/f.u. lower than Pmc2$_1$). Here, Q$_M$ represents a multimode coupling term [9]. We have also considered a similar coupling between Q$_{Tr}$ and Q$_{GCD}$ and after geometry relaxation, it turned out that coupling between Q$_{GCD}$ and Q$_{Tr}$ is not stable. Here, to mention as shown in Figure 2(b), both Q$_{Tr}$ and Q$_{ACD}$ can lead to the respective non-centrosymmetric space groups.

In the presence of Q$_{Tr}$, Pnma LaFeO$_3$ is an antiferromagnetic (G-type) insulator (d$^3$) and Pnma CaFeO$_3$ is a ferromagnetic metal (d$^4$) (Supplementary Note: I). The magnetic ground state of (LaFeO$_3$)$_1$/(CaFeO$_3$)$_1$ superlattice within Pmc2$_1$ symmetry (i.e., in the presence of Q$_{Tr}$) is found to be C-type antiferromagnetic ordering with local magnetic moment on individual Fe is 3.81 $\mu_B$ indicating that Fe is in +4 charge state with 4.0 eV for the Fe-d, Cr-d, Ru-d, Nb-d respectively, and 4.0 eV for Mo-d and Mn-d electrons, while the intra-atomic Hund’s exchange parameter J is kept as 1.0 eV [9]. The exchange-correlation part is estimated by PBEsol functional [28]. The total energy and Hellman-Feynman force are converged to 0.01 meV and 1 meV/A, respectively.

We have performed phonon calculations on high symmetry $P4/mmm$ structure of (LaFeO$_3$)$_1$/(CaFeO$_3$)$_1$ SL to get insights into stable and unstable structural modes (see Supplementary Note: I and II for more details). The participating modes that drive the HIF are shown in Figure 1 at the top panel. The in-phase rotation $\mathbf{Q}_R^+$ ($a^0_b^0c^0$) and tilt $\mathbf{Q}_T$ ($a^-a^-c^0$) are as shown in Figure 1(a) and (b), respectively. The third structural distortion, i.e., anti-ferroelectric A-site displacement mode is shown in Figure 1(c). In addition to the HIF modes, we found other three important structural modes. These are out-of-phase rotation $\mathbf{Q}_R^- (a^0_b^0c^+)$ and tilt $\mathbf{Q}_T$ ($a^-a^-c^0$) where the in-plane oxygen atoms of FeO$_6$ octahedra in the two successive layers are rotating in the opposite directions as is shown in Figure 1(d). The charge disproportionation mode analogous to the G-type antiferromagnetic configuration (hereafter Q$_{GCD}$) as shown is Figure 1(e). The charge disproportionation mode is analogous to the A-type antiferromagnetic configuration (hereafter Q$_{ACD}$) which is in analogy with the A-type antiferromagnetic configuration and is shown in Figure 1(f).
below the $E_F$ and the system emerged as a semiconductor within space group $Pc$, as illustrated in Figure 3(c) (Supplementary Note: II for more details).

The question is now, how to modulate $Q_M$? One possible way to "switch on" the modulation is to apply strain. Upon tensile and compressive strain, (LaFeO$_3$)$_1$/(CaFeO$_3$)$_1$ SL experiences a IMT. In the compressive region beyond 2.5% strain, the system is metallic while right from compressive 2.5% strain to tensile strain region the system behaves as a semiconductor, as shown in Figure 3(d). At compressive 2.5% strain, it shows a zero-band gap semiconducting phase, as shown in Figure 3(e). The electronic phase separation under strain is found to be a change in volume effect of the FeO$_6$ octahedra of the SL and the reconfiguration of strain is found to be a change in volume effect of the FeO$_6$ octahedra analogous to ref.[14] and is shown in Figure 3(f).

We fitted the Landau expansion [7, 13, 30], for the energy and obtained energy surface contour as a function of $Q_{Tri}$ and $Q_{ACD}$ (Supplementary Note: III for more details).

$$f(Q_{Tri}, Q_{ACD}) = a_1 Q_{Tri}^2 + a_2 Q_{ACD}^2 + a_3 Q_{Tri}^2 Q_{ACD}^2 + a_4 Q_{Tri}^2 + a_5 Q_{ACD}^2 + a_6 Q_{Tri}^2 + a_7 Q_{ACD}^2 + a_8 Q_{ACD}^2 + a_9 Q_{Tri}^2 Q_{ACD} + a_{10} Q_{Tri}^2 + a_{11} Q_{ACD}^2 + a_{12} Q_{Tri}^2 Q_{ACD}^2 + a_{13} Q_{Tri}^2 Q_{ACD}^2$$

(1)

We found four equivalent minima with respect to the high symmetry $P4/mmm$ structure. The most energy gain is found when the amplitudes of both the modes are around $\sim 0.5 \text{ Å}$ as shown in Figure 4(a). The coupling between $Q_{Tri}$ and $Q_{ACD}$ lowers the symmetry from metallic $Pmc2_1$ to insulating $Pc$. The question is now how the coupling between $Q_{Tri}$ and $Q_{ACD}$ influences the polarization, magnetization, and density of states (DOS) at the $E_F$.

In Figure 4(b), utilizing the same expansion we have shown the variation of density of states at Fermi Level, i.e., DOS@$E_F$ as a function of ($Q_{Tri}$, $Q_{ACD}$). The coupling between $Q_{Tri}$ and $Q_{ACD}$ gives rise to insulating and metallic regions. If we consider $Q_{Tri}$ is fixed and switch the $Q_{ACD}$ distortion in the opposite sense, i.e., from $-Q_{ACD} \rightarrow (Q_{ACD} = 0) \rightarrow +Q_{ACD}$, we can guide the system from insulating to metallic to again insulating phase. Contrarily, if one goes via $Q_{Tri}$ mode, it is an insulating phase if $Q_{ACD}$ gives an insulating solution and it is metal if $Q_{ACD}$ is giving a metallic solution. The $Q_{ACD}$ mode triggers the charge disproportionation which in turn makes the local magnetic moments on Fe atoms distinguishable by creating two different sublattices. In Figure 4(c), we have shown the difference in the magnetization i.e., $\Delta M$, between $+3 \text{ (}d^3\text{)}$ and $+4 \text{ (}d^4\text{)}$ sublattices, as a function of $Q_{Tri}$ and $Q_{ACD}$. The $Q_{ACD}$ mode can reverse the sign of $\Delta M$ i.e., the two magnetic sublattices can be interchanged. The $\Delta M$ can be as large as $1.2 \mu_B$ per f.u. depending on the strength of $Q_{ACD}$. When optimized to low symmetry $Pc$ phase, the $\Delta M$ is found to be $0.58 \mu_B$ per f.u. Considering Figure 4(b) and (c), a clear correlation between DOS@$E_F$ and $\Delta M$ can be observed.

The $Q_{AFEA}$ mode give rise to the finite polarization $P$ when La/Ca layered ordering has been established within $Q_M \sim Q_{Tri} \otimes Q_{ACD}$ and $Q_{ACD}$ ensures an insulating phase. While varying the $Q_{Tri}$, we have first fixed the $Q_{AFEA}$ at various magnitudes and by selective dynamics, $Q_T$ and $Q_R^+$ distortions are allowed to relax. This establishes the fact that $Q_{AFEA}$ (or $Q_{P}$) $\sim Q_{Tri}$. In
Figure 4(d) we have shown the variation of $\Delta V$ of the FeO$_6$ octahedra.

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The change in volume, $\Delta V$ of the FeO$_6$ octahedra.

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be observed. Interestingly, through $Q_{ACD}$ system undergoes insulator-metal-insulator transition along with the polarization switching.

Table I. Bandgap (B.G), polarization (P), and change in magnetization $\Delta M$ for 3d-4d (LaBO$_3$)$_1$/CaB'O$_3$ superlattices (SL). Here, M indicates metallic phase.

| (LaBO$_3$)$_1$/CaB'O$_3$$_1$ | B.G (eV) | P ($\mu$C/cm$^2$) | $\Delta M$ ($\mu_B$) |
|-----------------------------|---------|-----------------|-----------------|
| Cr/Nb                       | $M$     | $M$             | 1.71            |
| Cr/Mo                       | 1.52    | 23.74           | 1.01            |
| Cr/Ru                       | 1.40    | 26.60           | 1.16            |
| Mn/Nb                       | $M$     | $M$             | 2.62            |
| Mn/Mo                       | 0.98    | 22.62           | 1.81            |
| Mn/Ru                       | 0.03    | 27.39           | 2.01            |
| Fe/Nb                       | $M$     | $M$             | 3.30            |
| Fe/Mo                       | 1.20    | 21.15           | 2.25            |
| Fe/Ru                       | 0.78    | 24.40           | 2.49            |

(LaFeO$_3$)$_1$/FeFeO$_3$$_1$ 0.28 36.38 0.58
universal coupling between $Q_{Tr_i}$ and $Q_{ACD}$. The properties of $(LaBO_3)_1/(CaB'O_3)_1$ SLs are tabulated in Table I. All the Nb-based compounds are metallic whereas all the Mo- and Ru-based compounds are found to be insulating with with band gap ranging from 0.03 eV - 1.52 eV, with maximum for $(LaCrO_3)_1/(CaMoO_3)_1$. Thus, we have identified both polar-metal and polar insulators with large ferroelectric (or, 'ferroelectric like' in the case of metals [20]) distortion. The change in $\Delta M$ follows a linear trend for a fixed 4$d$ and for $(LaFeO_3)_1/(CaNbO_3)_1$ the value of $\Delta M$ is maximum as $3.5 \mu_B$. Total polarization values are found to be within the range of 21.5 - 27.39 $\mu C/cm^2$ and largest for $(LaMnO_3)_1/(CaRuO_3)_1$ heterostructure (polar vector Figure S7).

To conclude, we have proposed a mechanism of multimode coupling through which functional properties such as metal-to-insulator transition, polarisation and magnetization can be engineered at the $(LaFeO_3)_1/(CaFeO_3)_1$ oxide interface. The polarization is driven into the system by trilinear coupling $Q_{Tr_i}$, via, $Q_{AFE}$A. The $Q_{ACD}$ mode drives metal-to-insulator transition and polarization. By tuning the coupling between $Q_{Tr_i}$ and $Q_{ACD}$, polar metallic phase, polar zero band gap semiconducting, and polar insulating phases can be obtained. The in-plane and out-of-plane polarization is induced into the system via, $Q_{AFE}$A and $Q_{ACD}$ distortions, respectively. Through $Q_{ACD}$ path, the system undergoes insulator-metal-insulator transition along the polarization switching. The coupling mechanism between $Q_{Tr_i}$ and $Q_{ACD}$ and emergence of associated properties can be obtained for other superlattices with $Pnma$ building block and partially filled $e_g$ or $t_{2g}$ electron(s) at the B or B' sites.

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[1] W. Eerenstein, N. Mathur, and J. F. Scott, nature 442, 759 (2006).
[2] E. Bousquet, M. Dawber, N. Stucki, C. Lichtensteiger, P. Hermet, S. Gariglio, J.-M. Triscone, and P. Ghosez, Nature 452, 732 (2008).
[3] H. L. Boström, M. S. Senn, and A. L. Goodwin, Nature communications 9, 1 (2018).
[4] M. J. Pitcher, P. Mandal, M. S. Dyer, J. Alaria, P. Borisov, H. Niu, J. B. Claridge, and M. J. Rosseinsky, Science 347, 420 (2015).
[5] N. A. Benedek and C. J. Fennie, Phys. Rev. Lett. 106, 107204 (2011).
[6] S. Ghosh, H. Das, and C. J. Fennie, Phys. Rev. B 92, 184112 (2015).
[7] M. Shaikh, M. Karmakar, and S. Ghosh, Phys. Rev. B 101, 054101 (2020).
[8] J. M. Rondinelli and C. J. Fennie, Advanced Materials 24, 1918 (2012).
[9] M. Shaikh, A. Fathima, M. Swamynadhan, H. Das, and S. Ghosh, Chemistry of Materials 33, 1594 (2021).
[10] Y. S. Oh, X. Luo, F.-T. Huang, W. Yang, and S.-W. Cheong, Nature materials 14, 407 (2015).
[11] F. Pan, C. Attig, N. C. Brustow, A. A. Mostofi, C. Won, S.-W. Cheong, and M. S. Senn, Phys. Rev. B 102, 014101 (2020).
[12] G. Clarke, C. Attig, J. Daniels, S. Checchia, and M. S. Senn, Journal of applied crystallography 54 (2021), 10.1107/S160057672001096.
[13] A. Mercy, J. Biedner, J. Íñiguez, and P. Ghosez, Nature communications 8, 1 (2017).
[14] L. Jiang, D. Saldana-Greco, J. T. Schick, and A. M. Rappe, Phys. Rev. B 89, 235106 (2014).
[15] P. C. Rogge, R. U. Chandrasena, A. Cammarata, R. J. Green, P. Shafer, B. M. Leifer, A. Huon, A. Arab, E. Arenholz, H. N. Lee, T.-L. Lee, S. Nemšik, J. M. Rondinelli, A. X. Gray, and S. J. May, Phys. Rev. Materials 2, 015002 (2018).
[16] G. M. Dalpian, Q. Liu, J. Varignon, M. Biber, and A. Zunger, Phys. Rev. B 98, 075135 (2018).
[17] D. Preziosi, L. Lopez-Mir, X. Li, T. Cornelissen, J. H. Lee, F. Trier, K. Bouzehouane, S. Valencia, A. Gloter, A. Barthélémy, et al., Nano letters 18, 2226 (2018).
[18] C. Dominguez, A. B. Georgescu, B. Mundet, Y. Zhang, J. Fowlie, A. Mercy, A. Waelchli, S. Catalano, D. T. Alexander, P. Ghosez, et al., Nature Materials 19, 1182 (2020).
[19] Y. Zhang, M. M. Schmitt, A. Mercy, J. Wang, and P. Ghosez, Phys. Rev. B 98, 081108 (2018).
[20] S. Ghosh, A. Y. Borisevich, and T. S. Pantelides, Phys. Rev. Lett. 119, 175603 (2017).
[21] P. C. Rogge, R. J. Green, P. Shafer, G. Fabbris, A. M. Barboun, B. M. Leifer, E. Arenholz, M. P. M. Dean, and S. J. May, Phys. Rev. B 98, 201115 (2018).
[22] M. Shaikh, M. Karmakar, and S. Ghosh, Physical Review B 101, 054101 (2020).
[23] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
[24] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B 47, 1651 (1993).
[25] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[26] V. I. Anisimov, F. Aryasetiawan, and A. Lichtenstein, Journal of Physics: Condensed Matter 9, 767 (1997).
[27] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
[28] J. P. Perdew, A. Ruzsinszky, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, O. K. Gunnarsson, and K. Burke, Phys. Rev. Lett. 100, 136406 (2008).
[29] E. Cho, K. Klyukin, S. Ning, J. Li, R. Conin, R. J. Green, B. Yildiz, and C. A. Ross, Physical Review Materials 5, 094413 (2021).
[30] N. Sivadas, P. Doak, and P. Ganesh, arXiv preprint arXiv:2106.08783 (2021).