Photo-sensitizing thin-film ferroelectric oxides using materials databases and high-throughput calculations

Jose J. Plata,1 Javier Amaya Suárez,1 Santiago Cuesta-López,2 Antonio M. Márquez,1 and Javier Fdez. Sanz1
1Departamento de Química Física, Universidad de Sevilla, Seville, Spain∗
2Fundación ICAMCYL, International Center for Advanced Materials and Raw Materials of Castilla y León, León, Spain
(Dated: March 18, 2019)

Conventional solar cell efficiency is usually limited by the Shockley-Queisser limit. This is not the case, however, for ferroelectric materials, which present a spontaneous electric polarization that is responsible for their bulk photovoltaic effect. Even so, most ferroelectric oxides exhibit large band gaps, reducing the amount of solar energy that can be harvested. In this work, a high-throughput approach to tune the electronic properties of thin-film ferroelectric oxides is presented. Materials databases were systematically used to find substrates for the epitaxial growth of KNbO3 thin-films, using topological and stability filters. Interface models were built and their electronic and optical properties were predicted. Strain and substrate-thin-film band interaction effects were examined in detail, in order to understand the interaction between both materials. We found substrates that significantly reduce the KNbO3 band gap, maintain KNbO3 polarization, and potentially present the right band alignment, favoring the electron injection in the substrate/electrode. This methodology can be easily applied to other ferroelectric oxides, optimizing their band gaps and accelerating the development of new ferroelectric-based solar cells.

I. INTRODUCTION

Solar energy is the most abundant source of clean and renewable energy with photovoltaics, PV, being the most promising technology for the coming decades. However, to make this technology competitive, significant improvements must be made in the efficiency of the solar cells and manufacturing costs must be reduced. PV device performance depends on three main features: i) efficient light absorption, ii) effective charge separation and iii) fast transport and charge extraction. Conventional solar cells based on p – n junctions and other new solar cell generations are good light harvesters, but they are limited by the Shockley-Queisser limit, because carriers are separated by the internal electric field at the p – n junction [1]. This is not the case for ferroelectric materials, which present a spontaneous electric polarization, providing an alternative way to separate excited carriers [2]. This charge separation due to the polarization in the bulk of the material is called bulk photovoltaic effect, BPVE [3, 4], and has attracted the attention of the scientific community to ferroelectric materials as candidates to design new and more efficient PV devices [5, 6].

Oxide perovskites, organic-inorganic perovskites — also known as hybrid halide perovskites — and, more recently, chalcohalides are the ferroelectric materials used for solar energy conversion [7]. Hybrid perovskite thin-films such as CH3NH3PbI3, MAPbI3, have changed the solar cell paradigm in the last decade because of their low cost and high efficiency [8–10]. However, there is some debate about their ferroelectric nature [11, 12]. Chalcohalides such as SbSI are abundant and also good solar absorbers [13], but they usually have a small enthalpy difference between the ferroelectric and paraelectric phases, and smaller polarization than many oxide perovskites [7]. Ferroelectric oxide perovskites, ABO3, combine a strong spontaneous electric polarization with a wide range of thermal, chemical and mechanical stability [14, 15]. Moreover, the availability of low-cost methods for their synthesis and device fabrication makes them very attractive from an economic point of view, too. This is the reason why the power conversion efficiency, PCE, of solar cells based on these materials, has rapidly grown from 0.28% to 8.1% in less than seven years [16, 17].

Ferroelectric oxide perovskites also present hindrances that should be overcome to design efficient PV devices. The wide band gap of these materials remains as the main obstacle to achieve higher PCE. Reducing the band gap from 2 eV–3 eV to 1.5 eV, the maximum emission of the solar spectrum, is the main goal. Different strategies have been proposed to tune the electronic properties of these oxides [18]. For instance, perovskite band gaps are reduced as much as 1.2 eV via polarization rotation through the rhombohedral-to-tetragonal structural transition [19]. Doping of the A and B sites has also been identified as a valid approach to modify the gap of oxide perovskites [20–27]. As an alternative to chemical modifications, strain effects on ferroelectric thin-films have been proposed as an effective method to customize their properties [28].

Strain engineering of thin-films is a frequently applied route to enhance material properties. Systems under strain have demonstrated that it is even possible to combine, in principle, incompatible properties such as ferroelectricity and band topology [29]. In the case of perovskites thin-film, the strain is usually controlled through its epitaxial growth on a substrate with a specific lattice-mismatch [30]. Then, substrates play a dual role in solar cells: i) tuning the electronic properties of the ferroelectric material, and ii) acting as one of the electrodes of the solar cell. Although some encouraging results have been obtained during recent years [31, 32] and new techniques

∗ jplata@us.es
have been introduced to modify the strain of ferroelectric materials [33–36], the limited number of available substrates hampers the tunability of ferroelectric thin-films. Moreover, the search for an optimal substrate for a specific ferroelectric thin-film requires the analysis of not only structural but also electronic properties of both materials at their interface. This time- and resource-consuming task cannot be tackled by experimental trial-and-error approaches, so data-driven and theory-driven frameworks need to be developed to accelerate this device design. In this article, we propose a novel high-throughput search of substrates for oxide perovskites thin-films in order to design ferroelectric-based solar cell devices. One of the most studied oxide perovskites, KNbO₃ [14, 21, 23, 37–40], was selected as proof of concept due to its simple and low-cost synthesis in epitaxial thin-films [41–45]. Material databases are automatically screened for potential substrates for the epitaxial growth of KNbO₃ thin-films is possible. Then, the electronic properties of the interfaces, including band bending models, are explored to evaluate band gap modifications of KNbO₃ and its interaction with the electrode.

II. METHODOLOGY

A. High-throughput substrate search

The Materials Project, MP, database was used to find potential substrates for the epitaxial growth of KNbO₃ through its Materials Application Programming Interface, MAPI [46]. This search includes semiconductors and insulators that belong to different structural prototypes such as diamond, zincblende, rock salt, fluorite, wurtzite, and anatase. Energy above the hull, E_{hull}, of each material was used as a descriptor of their thermodynamic stability and synthesizability, considering only materials whose E_{hull} < 0.1 eV/atom. Slab models were built taking into account the most stable planes and the Wulff construction of each prototype (Table 1).

<table>
<thead>
<tr>
<th>Prototype</th>
<th>Formula</th>
<th>Pearson</th>
<th>S.G. #</th>
<th>Planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>A</td>
<td>cF8</td>
<td>227</td>
<td>(1 0 0), (1 1 1), (0 0 1) [47, 48]</td>
</tr>
<tr>
<td>Rock salt</td>
<td>AB</td>
<td>cF8</td>
<td>225</td>
<td>(1 0 0), (1 1 1), (1 1 0) [49]</td>
</tr>
<tr>
<td>Fluorite</td>
<td>AB₂</td>
<td>cF12</td>
<td>225</td>
<td>(1 0 0), (1 1 0), (0 0 1) [50, 51]</td>
</tr>
<tr>
<td>Zincblende</td>
<td>AB</td>
<td>cF8</td>
<td>216</td>
<td>(1 1 0) [52, 53]</td>
</tr>
<tr>
<td>Wurtzite</td>
<td>AB</td>
<td>hP4</td>
<td>186</td>
<td>(1 1 0) [54]</td>
</tr>
<tr>
<td>Anatase</td>
<td>AB₂</td>
<td>tI12</td>
<td>141</td>
<td>(1 0 1), (0 0 1) [55]</td>
</tr>
</tbody>
</table>

B. Lattice mismatch and surface models

The lattice mismatch between two surfaces was measured using an algorithm based on the Zur and McGill approach [56]. This algorithm is available in New Materials Lab repository at GitHub and Zenodo [57]. The primitive surface cells of the substrate and the thin-film are the only required inputs to evaluate their commensurability. In order to determine if 2D lattices match, we have to find if each of them possesses a superlattice where their area, A, surface lattice vectors, a – b, and surface angle between a and b, α, are the same. If the substrate and the thin-film have primitive surface cell areas A_{sub} and A_{tf} respectively, their superlattice surface areas are n_{sub}A_{sub} and n_{tf}A_{tf} where n_{sub} and n_{tf} are integer numbers. When both superlattices present the same area, 

\[
\frac{n_{sub}}{n_{tf}} = \frac{A_{tf}}{A_{sub}}. \tag{1}
\]

However, it is very unlikely that both lattices will match exactly. A user parameter defining the maximum percentage error between both areas, ε_A, has been included to limit the search of n_{sub} and n_{tf} pairs,

\[
ε_A = \left| \frac{n_{sub}A_{sub} - n_{tf}A_{tf}}{n_{sub}A_{sub}} \right| \cdot 100. \tag{2}
\]

Similarly, an upper limit on the possible n_{sub} and n_{tf} values is introduced to limit the size of the interface models. This maximum area, A_{max} is defined as,

\[
A_{max} > n_{sub}A_{sub}, \tag{3}
\]

and

\[
A_{max} > n_{tf}A_{tf}. \tag{4}
\]

Once a list of compatible n_{sub} and n_{tf} pairs, that fulfill Eqs. 2-4, is created, all possible superlattice surfaces with an area of n_{sub}A_{sub} and n_{tf}A_{tf} are compared. The primitive surface vectors, a and b, are transformed in the superlattice surface vectors, u and v, using transformation matrices [58],

\[
\begin{pmatrix}
u \\ v
\end{pmatrix} = \begin{pmatrix} i & j \\ 0 & m \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix}, \tag{5}
\]

where i, j and m are integers, and

\[
i \cdot m = n, \tag{6}
\]

\[
i, m > 0, \tag{7}
\]

\[
0 \leq j \leq m - 1. \tag{8}
\]

The superlattice surface vectors of both surfaces are compared, selecting only the interfaces in which the mismatch between vectors and angles are below the thresholds defined by the user. The error associated with the vector misfit is defined as,

\[
ε_u = \left| \frac{u_{sub} - u_{tf}}{u_{sub}} \right| \cdot 100, \tag{9}
\]
and for the angle misfit is defined as,

$$\epsilon_\alpha = \left| \frac{\alpha_{\text{sub}} - \alpha_{\text{tf}}}{\alpha_{\text{sub}}} \right| \cdot 100,$$

(10)

where $u = |\mathbf{u}|$ and $\cos \alpha = \frac{|\mathbf{u} \cdot \mathbf{v}|}{|\mathbf{u}||\mathbf{v}|}$. Because more than one superlattice combination can fulfill all the conditions, only the system with the minimal coincident interface area, MCIA [59], is selected to build an atomistic model.

Ferroelectric oxides are brittle and tend to crack with low compressive or tensile strains [60, 61]. However, their thin-films present much better mechanical strength. Interfaces such as BiFeO$_3$/YAlO$_3$ have been reported with biaxial strains up to 6% [62, 63]. That is why all the interfaces presented in this work have been built considering moderate misfits between the slabs ($\epsilon_A < 15\%$, $\epsilon_u < 5\%$, $\epsilon_\alpha < 5\%$) and reducing the atomic models below 250 atoms ($A_{\text{max}} = 100 \AA^2$).

C. Computational details

All structures were relaxed using the VASP code [64–66] with the projector-augmented wave, PAW, method [67, 68]. Energies were obtained using the generalized gradient approximation, GGA, proposed by Perdew et al. [69] and a plane-wave basis set with a cutoff of 500 eV. The number of valence electrons and the Hubbard-like parameter ($U$) of the K$^{+}$/Nb$^{3+}$ and O$_{2-}$ ions were set to 10 and 1 eV, respectively. Geometries were considered optimized when the frequency-dependent dielectric function, $\varepsilon(\omega)$, as proposed by Gajdoš et al. [75]. Polarization perpendicular to the surface, $P_z$, was calculated in the KNbO$_3$ film as [76–78],

$$P_z = \frac{q_e}{\Omega} \sum_{i=1}^{N} Z_{i,z}^* \delta z_i,$$

(11)

where $\Omega$ is the volume of the KNbO$_3$ film, $N$ is the number of cations in the film and $\delta z_i$ is the relative displacement in $z$ between the cations, K/Nb, and the anions, O, located in the same plane parallel to the surface. $Z_{i,z}^*$ is the component of the Born effective charges perpendicular to the surface plane using density-functional perturbation theory [75, 79]. This approach only considers the polarization due to atom displacements with respect to their centrosymmetric positions, but it is accurate enough to predict the KNbO$_3$ bulk $P$, 35 $\mu$C cm$^{-2}$, compared to experimental values, 37–41 $\mu$C cm$^{-2}$ [37, 80, 81].

III. RESULTS

Strain effects. The modifications on the electronic structure of KNbO$_3$ bulk and surfaces by mechanical strain were studied before building models with the substrate-thin-film interface. Using this approach, it is possible to differentiate the effects that stem from the substrate-thin-film interactions, or only from the strain. Different exchange-correlation functionals were used previously in the study of tetragonal KNbO$_3$ [20, 82, 83] (Table S1). While all of them describe reasonably well the lattice parameters, there are quantitative differences between the predicted band gaps. LDA predicts a indirect band gap, $E_g$, around 1.40 eV and 1.50 eV [20, 82], however, experimental values are reported between 3.08 eV and 3.30 eV [84, 85]. The use of hybrid functionals does not guarantee systematic improvements. For instance, there is a 0.68 eV difference between the gap predicted with HSE06 using a 30% of exact exchange (3.23 eV) [83] and standard HSE06 (2.55 eV) [20]. We have opted for a PBE+U functional that improves the band gap values obtained with LDA, but it is not as computationally demanding as hybrid functionals. Band gap values for strained bulk structures are depicted in Figure 1 between -5% and 5% misfit with respect to the equilibrium lattice parameter, $a$. The band gap is modified in a range of 0.46 eV from 1.85 eV at -5% strain to 1.39 eV at 5% strain. A very similar trend was found for the 2 layers KNbO$_3$ thin-film, where $E_g$ ranges between 1.68 eV at -5% strain and 1.40 eV at 5% strain. This band gap value corresponds to $M, A \rightarrow \Gamma$ indirect transition (Figure S1) which is in agreement with previous experimental reports [85]. When a negative strain is applied to the bulk (or in the case of the thin-film), the energies of the $\Gamma$ and $Z$ points become degenerated at the edge of the conduction band (Figure S1). In light of these results, substrates that produce a positive strain on KNbO$_3$ thin-films are particularly interesting. Positive strains do not only reduce the band gap of this ferroelectric material, but they also reportedly increase their polarization [20, 86] which is indicative of a stronger BPVE.

Substrates. A high-throughput search was performed to find insulators and semiconductors that can be used as potential substrates for the KNbO$_3$ epitaxial growth. The list of substrates is included in the supplementary information (Table S2) and the misfits for surfaces vectors, $\epsilon_u$ and $\epsilon_\alpha$, are depicted in Figure 2a. Most of the points in the Figure 2a diagonal correspond to substrate (100) surfaces and the other series of points where $\epsilon_u \neq \epsilon_\alpha$ mainly correspond to substrate (110) surfaces. A total of
of both materials controls the band gap, which is also important because the substrate acts as electrode. Indeed, band alignment optimization is known to be crucial in increasing solar cell device efficiency, promoting the dissociation between photo-excited electrons and holes before recombination processes occur [90–93]. As a first step, the interfaces have been classified into three types of heterojunctions (Figure 3a). Type I heterojunctions correspond to straddling gaps and Type II to staggered gaps. Different labels are used to highlight if the bottom edge of the conduction band corresponds to states projected on the KNbO₃ thin-film or on the substrate. When the edge...
of the conduction band is mainly populated by states localized on the KNbO$_3$ thin-film, “tf” label is used. On the other hand, “sub” label means that the edge of the conduction band corresponds to states localized on the substrate. Type III heterojunctions are broken gap systems which behave as metals. This classification (Figure 3a) has been performed calculating the projected DOS for each atom of the system (Figure 3b) and using band bending models (Figure 3c). For these models, thin-film and substrates were initially placed in cells with approximately 20 Å of separation between each other, which guarantees no interaction between the slabs. The distance between the slabs was reduced in different steps, relaxing the position of the atoms and calculating the projected DOS in each of them (Figure 3c). KNbO$_3$/NaCl interface is used as an example in Figures 3b,c. This interface is type I$_{f}$ because the states below the Fermi energy and at the bottom edge of the conduction band are localized on the the KNbO$_3$. The high ionization potential of NaCl and its more ionic character compared to the KNbO$_3$ make its valence band lower in energy and narrower than KNbO$_3$ valence band (Figure 3b). The band bending model (Figure 3c) shows that the total band gap does not suffer significant changes during the approach of the slabs but there is a gradual shift to higher (lower) energies of the NaCl valence (conduction) band due to the interaction between the slabs when they get closer.

There are many systems presenting a band gap lower than the isolated and strained KNbO$_3$ thin-film, but not all fulfill the conditions to be considered potential candidates. Photons are collected by the KNbO$_3$ thin-film so electron excitations to the conduction band are more likely if the higher states of the valence band around the Fermi level belong to the KNbO$_3$ film. This requirement reduces the list of candidates to heterojunctions I$_{f}$ and II$_{sub}$. Nine systems with heterojunctions I$_{f}$ were found and all of them correspond to rock salt and fluorite structural prototypes. KNbO$_3$/AgCl is the interface I$_{f}$ with the lowest band gap, 1.61 eV, being approximately 0.1 eV lower than KNbO$_3$ bulk band gap value. Interestingly, AgCl is the substrate with the lower band gap, 2.05 eV, compared to the other eight substrates. That is why the relationship between isolated substrate surface band gaps, $E_g^{subs}$, and KNbO$_3$/substrate band gap, $E_g^{KNO/subs}$, is explored (Figure S3). It appears there is a direct correlation between $E_g^{subs}$ and $E_g^{KNO/subs}$ which explains why a lower interface band gap is obtained for AgCl. Most importantly, KNbO$_3$ is a p-type absorber [94], where minority carriers are electrons excited into the conduction band. Thus, electron injection from KNbO$_3$ thin-film conduction band to the substrate/electrode conduction band determines the efficiency of the solar cell. While the excited electrons have to overcome a barrier to be transferred to the substrate in heterojunctions I$_{f}$, there is not such a barrier in heterojunctions II$_{sub}$. Only one system was found with this type of band alignment, KNbO$_3$/CdS.

KNbO$_3$/CdS. The band gap predicted for the KNbO$_3$/CdS is 1.35 eV (Figure 4a), which represents a reduction of 0.4 eV with respect to the non-strained KNbO$_3$ bulk band gap value. Moreover, the gap between the edge of the valence band and the first states of the conduction band localized on the KNbO$_3$ slab is 1.40 eV. This value is consistent with the band gap values obtained for KNbO$_3$ thin-films with similar strains to the CdS lattice parameter. Density of states, DOS, was also calculated with the HSE functional [95, 96] because the use of more than one $U$ parameter, $U_{eff}^{Cd}$ = 2.1 eV and $U_{eff}^{Nb}$ = 2.1 eV, combined with the known GGA band gap understimation could lead to artificial band alignments [97]. As expected, HSE band gap (2.22 eV) is higher than PBE+U value (Figure 4b) but it is still lower than the HSE bulk band gap value (2.66-3.23 eV) [20, 83]. Few other changes are found in the HSE electronic structure compared to PBE+U calculations. While most of states around the Fermi energy are localized in the KNbO$_3$ for the PBE+U DOS, the density of states localized in the CdS around the Fermi energy clearly increases for the HSE DOS. However, the bottom edge of the conduction band remains the same, with CdS being the main contributor.

The relative positions between the KNbO$_3$ and CdS bands play a key role in understanding the efficiency of the device. However, no information about the electron injection is extracted from them. To shed some light on this point, optical spectra were simulated using the imaginary part of the frequency-dependent dielectric function, $\epsilon_2(\omega)$, (Figure 4c). An important shoulder below 3 eV appears in the KNbO$_3$/CdS spectra (green line) that is not shown in the unstrained KNbO$_3$ thin-film spectra (dashed orange line). Thus, this shoulder may be connected with the presence of the substrate. The spectra of both fragments, CdS surface (blue line) and strained KNbO$_3$ thin-film (orange line), are also included in Figure 4c. A 0.42 eV shift to lower energies is observed when the unstrained and strained KNbO$_3$ thin-films spectra are compared, which is consistent with the band gap reduction previously mentioned. Moreover, the shoulder below 3 eV seems to be mainly related to CdS-CdS transitions. The summation of both fragment spectra (dashed black line) is also depicted to elucidate the electron injection mechanism between the thin film and the electrode. This procedure has been successfully used before to discern between direct and indirect injection mechanisms in quantum dots, QD, solar cells [98, 99]. In QDs solar cells, the injection mechanism is described as mainly direct (indirect) if QD absorption peak changes (does not change) its position with respect to the isolated QD when adsorbed on the semiconductor. The intensity of the KNbO$_3$/CdS is slightly higher than the summation of both fragment spectra between 1.5 eV and 2.0 eV. This difference could be assigned to transitions from the top of the valence band that are localized on the KNbO$_3$ system and the bottom of the conduction band localized on the CdS following a direct mechanism. There are also some small changes between 2.5 eV and 3.5 eV where the KNbO$_3$/CdS spectra is lower in intensity compared to the summation of the fragment spectra. However, both spectra match very well
such as BaTiO$_3$ which have been proposed for photovoltaic applications. Of experimental values obtained for KNbO$_3$, the values predicted for the bulk, but it is in the range was found. This is around a 50% reduction compared to the KNbO$_3$ thin-film, a $P_z$ of 14 $\mu$C cm$^{-2}$ was found. This is around a 50% reduction compared to the values predicted for the bulk, but it is in the range of experimental values obtained for KNbO$_3$ thin films, 6-42 $\mu$C cm$^{-2}$ [100, 101] and other ferroelectric materials which have been proposed for photovoltaic applications such as BaTiO$_3$ [102], 26 $\mu$C cm$^{-2}$, SbSI [102], 25 $\mu$C cm$^{-2}$, or CuPbSbS$_3$ [103], 1.83 $\mu$C cm$^{-2}$.

in most of the energy range. This supports the idea that most of the transitions in the spectra are CdS-CdS and KNbO$_3$-KNbO$_3$, with an indirect mechanism being the main channel for the electron injection. The same trend is found when the HSE functional is used to compute the dielectric function, finding only a shift to higher energies of the simulated spectra but keeping the same features (Figure S4). Finally, polarization, $P_z$, was calculated for the KNbO$_3$ thin-film, on top of the CdS substrate to ensure that the bulk spontaneous polarization does not disappear. For the KNbO$_3$ thin-film, a $P_z$ of 14 $\mu$C cm$^{-2}$ was calculated for the KNbO$_3$/NaCl system. Valence bands (bottom rectangles) and conduction bands (upper bands) are always aligned placing vacuum level at $E = 0$ eV.

IV. CONCLUSIONS

The main goal of this work has been providing a new approach to accelerate the design of new solar cells based on thin-film ferroelectric oxides. Computational materials databases have been combined with a high-throughput mismatch calculator to identify potential substrates for the epitaxial growth of KNbO$_3$ thin-films. These substrates were used to build interface models which have been studied by means of density functional theory. The influence of lattice mismatch and band alignment were analyzed to optimize the band gap and reduce KNbO$_3$ band gap.

FIG. 3. a) Heterojunction classification based on KNbO$_3$ thin-film (orange) and substrate (blue) bands alignment. Fermi energy is depicted with gray horizontal lines and band gaps with gray double head arrows. b) Density of states, DOS, for the KNbO$_3$/NaCl interface. Total DOS is shown with solid black line and KNbO$_3$ and NaCl DOS projections are coloured on orange and blue areas respectively. c) Band bending model for the KNbO$_3$/NaCl system. Valence bands (bottom rectangles) and conduction bands (upper bands) are always aligned placing vacuum level at $E = 0$ eV.
bands enhances a fast-charge transport from the KnBO$_3$ to the CdS conduction bands avoiding electron-hole recombination. A indirect injection seems to be the main mechanism when simulated absorption spectra are analyzed in detail. This study is a good example of how computational materials databases combined with first principles calculations are excellent tools in spurring the development of new solar cell devices, thus reducing the variables that need to be explored experimentally.

V. ACKNOWLEDGMENTS

This work was funded by the Ministerio de Economía y Competitividad (CTQ2015-64669-P), Junta de Andalucía (FQM-132) and European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement HT-PHOTO-DB No 752608. The authors thankfully acknowledge the computer resources at Magerit and the technical support provided by Supercomputing and Visualisation Center of Madrid, CeSViMa (QCM-2018-1-0012). SCL acknowledges Junta de Castilla y León and the project ExploreMat 02.22.467B01.780.82.0.


J. Lombardi, F. Pearsall, W. Li, and S. O Brien, *Synthesis and dielectric properties of nanocrystalline oxide perovskites, $\text{[KNbO}_3\delta$]$_{1-\delta}$/$\text{BaNb}_{0.5}\text{Nb}_{0.5}\text{O}_{3-\delta}$, derived from potassium niobate $\text{KNbO}_3$ by gel collection*, J. Mater. Chem. C **4**, 7989–7998 (2016).


