New Tolerance Factor to Predict the Stability of Perovskite Oxides and Halides

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Predicting the stability of the perovskite structure remains a longstanding challenge for the discovery of new functional materials for photovoltaics, fuel cells, and many other applications. Using a novel data analytics approach based on SISSO (sure independence screening and sparsifying operator), an accurate, physically interpretable, and one-dimensional tolerance factor, τ, is developed that correctly classifies 92% of compounds as perovskite or nonperovskite for an experimental dataset containing 576 ABX₃ materials (X = O²⁻, F⁻, Cl⁻, Br⁻, I⁻). In comparison, the widely used Goldschmidt tolerance factor, t, achieves a maximum accuracy of only 74% for the same set of materials. In addition to providing physical insights into the stability of the perovskite structure, classification by τ is monotonic and yields a meaningful probability estimate for a given compound as a stable perovskite. τ is applied to identify more than a thousand inorganic (Cs₂BB'Cl₆) and hybrid organic-inorganic (MA₂BB'Br₆) double perovskites that are predicted to be stable.

Predicting crystal structure from chemical composition continues as a persistent challenge to accelerated materials discovery.¹,² Most approaches capable of addressing this challenge require several computationally demanding electronic-structure calculations for each material composition, limiting their use to a small set of materials.³,⁴,⁵,⁶ Alternatively, descriptor-based approaches enable high-throughput screening applications because they provide rapid estimates of material properties.⁷ Notably, the Goldschmidt tolerance factor,⁹ t, has been used extensively to predict the stability of the perovskite structure based only on the chemical formula, ABX₃, and the ionic radii, ri, of each ion (A, B, X):

\[ t = \frac{r_A + r_X}{\sqrt{2(r_B + r_X)}}. \]  

Fig. 1a, contains A-site cations at the body-centered positions, B-site cations at the cube corners, and X-site anions at the face-center positions, where the cations (A and B) can span the periodic table and the anion, X, is typically a chalcogenide or halide. Distortions from the cubic structure can arise from size-mismatch of the cations and anion, which results in additional perovskite structures and nonperovskite structures, where the perovskite structure is defined as any ABX₃ compound with a network of corner-sharing BX₆ octahedra. The B cation can also be replaced by two different ions, resulting in the double perovskite formula, A₂BB'X₆ (Fig. 1b). Single and double perovskite materials possess exceptional properties for a variety of applications such as electrocatalysis,¹⁰ proton conduction,¹¹ ferroelectrics (using oxides, X = O²⁻), battery materials (using fluorides, X = F⁻), as well as photovoltaics and optoelectronics (using the heavier halides, X = Cl⁻, Br⁻, I⁻).
In this work, we present a new technique for predicting perovskite stability using a machine learned model. We perform a systematic empirical assessment of interatomic distances for 77 elements, with 49 elements appearing at the A site, 67 at the B site, and 5 at the X site. The first step in designing new perovskites for these applications is typically the assessment of stability using $t$, which has informed the design of perovskites for more than 90 years. However, as reported in recent studies, its accuracy is often insufficient.\textsuperscript{19} For example, considering 576 $ABX_3$ solids experimentally characterized at ambient conditions and reported in Refs. \textsuperscript{16, 17, 18}, we find that $t$ correctly distinguishes between perovskite and nonperovskite for only 74\% of materials and performs considerably worse for compounds containing heavier halides (chlorides – 51\% accuracy, bromides – 56\%, and iodides – 33\%) than for oxides (83\%) and fluorides (83\%) (Fig. 2a, Fig. S1, Table S1). This deficiency in generalization to halide perovskites severely limits the applicability of $t$ for materials discovery. In this work, we present a new tolerance factor, $\tau$, which has the form:

$$\tau = \frac{r_x}{r_B} - n_A \left( \frac{r_A}{r_B} \right)$$

where $n_A$ is the oxidation state of A and $r_i$ is the ionic radius of ion $i$. A high overall accuracy of 92\% (94\% on a randomly chosen test set of 116 compounds) and nearly uniform performance across the five anions evaluated (oxides – 92\% accuracy, fluorides – 92\%, chlorides – 90\%, bromides – 93\%, iodides – 91\%) is achieved with $\tau$ (Fig. 2b, Fig. S1, Table S1). Like $t$, the prediction of perovskite stability using $\tau$ requires only the chemical composition, allowing the descriptor to be agnostic to the many structures which are considered perovskite. In addition to predicting if a material is stable as perovskite, $\tau$ also provides a monotonic estimate of the probability that a material is stable in the perovskite structure. The accurate and probabilistic nature of $\tau$ as well as its generalizability over a broad range of compounds allows for new physical insights into the stability of the perovskite structure and the prediction of thousands of new stable inorganic and hybrid organic-inorganic double perovskite halides.

**Finding an improved tolerance factor to predict perovskite stability**

One key aspect of the performance of $t$ is how well the sum of ionic radii estimates the interatomic bond distances for a given structure. Shannon’s revised effective ionic radii,\textsuperscript{20} based on a systematic empirical assessment of interatomic distances in nearly 1,000 compounds, are the typical choice for radii because they provide ionic radius as a function of ion, oxidation state, and coordination number for the majority of elements. Most efforts to improve $t$ have focused on refining the input radii\textsuperscript{16, 18, 21, 22} or increasing the dimensionality of the descriptor either through two-dimensional structure maps\textsuperscript{17, 23, 24} or high-dimensional machine learned models.\textsuperscript{25, 26} However, all hitherto applied approaches for improving the Goldschmidt tolerance factor have only been shown to be effective over a limited range of $ABX_3$ compositions. Despite its modest classification accuracy, $t$ remains the primary descriptor used by experimentalists and theorists to predict the stability of perovskites.
Fig. 2 Assessing the performance of the improved tolerance factor, \( \tau \). a) A decision tree classifier determines that the optimal bounds for perovskite formability using the Goldschmidt tolerance factor, \( t \), are 0.825 < \( t \) < 1.059, which yields a classification accuracy of 74% for 576 experimentally characterized \( \text{ABX}_3 \) solids. b) The improved tolerance factor \( \tau \), developed using SISSO, achieves 92% classification accuracy on the set of 576 \( \text{ABX}_3 \) solids based on perovskite classification for \( \tau < 4.18 \). All classifications made by \( t \) and \( \tau \) on the experimental dataset are provided in Table S1. The largest value of \( \tau \) in the experimental set of 576 compounds is 181.5, however, all points with \( \tau > 13 \) are correctly labeled as nonperovskite and not shown to highlight the decision boundary. c) A comparison of Platt-scaled classification probabilities of \( \tau (\varphi) \) versus \( t \). \( \text{LaAlO}_3 \) and \( \text{NaBeCl}_3 \) are labeled because they are referenced in the text to highlight the variation in \( \varphi \) at nearly constant \( t \). d) A comparison between \( \varphi \) and the decomposition enthalpy (\( \Delta H_{\text{dec}} \)) for 36 double perovskite halides calculated using the Perdew-Burke-Ernzerhof functional (PBE) within density functional theory (DFT) in the \( \text{Fm\textit{3}m} \) structure in Ref. 27, and 37 single and double perovskite chalcogenides and halides in the \( \text{Pm\textit{3}m} \) structure in Ref. 28. The legend corresponds with the anion, \( X \). Positive decomposition enthalpy (\( \Delta H_{\text{dec}} > 0 \)) indicates the structure is stable with respect to decomposition into competing compounds. The green and white shaded regions correspond with agreement and disagreement between the calculated \( \Delta H_{\text{dec}} \) and the classification by \( \tau \). Points of disagreement are outlined in red. \( \text{CaZrO}_3 \) and \( \text{CaHFO}_3 \) are labeled because they are known to be stable in the perovskite structure, although they are unstable in the cubic structure.29, 30 For this reason, the best fit line for the chalcogenides (\( X = \text{O}^-, \text{S}^2-, \text{Se}^2- \)) excludes these two points.

The SISSO (sure independence screening and sparsifying operator) approach\(^1\) is used to identify an improved tolerance factor for predicting whether a given compound will be stable as perovskite. Several alternative atomic properties were considered as candidate features and, among them, SISSO determined that the best performing factor, \( \tau \) (Equation 2, Fig. 2b) depends only on oxidation states and Shannon ionic radii. See Methods for an explanation of the approach used for descriptor identification and a discussion of alternative approaches. For the set of 576 \( \text{ABX}_3 \) compositions, \( \tau \) correctly labels 94% of the perovskites and 89% of the nonperovskites compared with 94% and 49%, respectively, using \( t \). While the classification by \( \tau \) disagrees with the experimental label for 8% of the 576 compounds, the agreement increases to 99% outside the range \( 3.31 < \tau < 5.92 \) (200 compounds in this range) and 100% outside the range \( 3.31 < \tau < 12.08 \) (152 compounds). The experimental dataset may also be imperfect as compounds can manifest different crystal structures as a function of the synthesis conditions due to, for example, defects in the experimental samples (impurities, vacancies, etc.). These considerations emphasize the usefulness of \( \tau \)-derived probabilities, in addition to the binary classification of perovskite/nonperovskite, which address these uncertainties in the experimental data and corresponding classification by \( \tau \).

Beyond the improved accuracy, a significant advantage of \( \tau \) is the monotonic (continuous) dependence of perovskite stability on \( \tau \). As \( \tau \) decreases, the probability of being perovskite (\( \varphi \)) increases, where perovskites are expected for an empirically determined range of \( \tau < 4.18 \) (Fig. 2b, Methods for details). Probabilities are obtained using Platt’s scaling,\(^32\) where the binary classification of perovskite/nonperovskite is transformed into a continuous probability estimate of perovskite...
stability, \( \varphi(t) \), by training a logistic regression model on the \( t \)-derived binary classification. Probabilities cannot similarly be obtained with \( t \) because the stability of the perovskite structure does not increase or decrease monotonically with \( t \), where \( 0.825 < t < 1.059 \) results in a classification as perovskite.

The monotonic nature of \( t \) enables a straightforward understanding of the key aspects that influence the probability of forming stable perovskites. While \( \varphi \) is sigmoidal with respect to \( t \) because of the logistic fit (Fig. S2), a bell-shaped behavior of \( \varphi \) with respect to \( t \) is observed because of the multiple decision boundaries required for \( t \) (Fig. 2c). This relationship leads to an increase in \( \varphi \) (i.e., probability of perovskite stability using \( t \)) with an increase in \( t \) until a value of \( t \approx 0.9 \). Beyond this range, the probabilities level out or decrease as \( t \) increases further. The disparity between \( \varphi \) and the assignment by \( t \) can be significant, especially in the range where \( t \) predicts a stable perovskite (0.825 < \( t \) < 1.059). For example, at nearly constant \( t \), \( \varphi \) varies from < 10% (e.g., the nonperovskite NaBeCl\(_4\) with \( t = 1.00 \) and \( t = 5.76 \)) to > 97% (e.g., the perovskite LaAlO\(_3\) with \( t = 1.01 \) and \( t = 1.79 \)). For NaBeCl\(_3\), instability in the perovskite structure arises from an insufficiently large Be\(^{3+}\) cation on the \( B \)-site, which leads to unstable BeCl\(_6\) octahedra. This contribution to perovskite stability is accounted for in the first term of \( t \) (Equation 2, \( r_0/r_B = \mu^{-1} \), where \( \mu \) is the octahedral factor). Note that \( \mu \) is the typical choice for a second feature used in combination with \( t \),\(^{17,18,23} \) which leads to an 85% classification accuracy for the dataset used in this study (Fig. S3). In contrast to this two-dimensional descriptor (\( t, \mu \)), \( t \) incorporates \( \mu \) as a one-dimensional descriptor and achieves a higher accuracy of 92%.

Comparing \( t \) to calculated perovskite stabilities

Double perovskite halides are a particularly intriguing and emerging class of semiconductors that offer a lead-free alternative to traditional perovskite photoabsorbers.\(^{19,33} \) Since 2016, at least nine compounds of this type have been synthesized in the perovskite structure,\(^{34,35,36,37,38,39,40,41} \) all of which are predicted to be stable by \( t \). Still, the experimentally realized composition space of double perovskite halides is relatively unexplored compared with the number of possible \( A, B, B' \), and \( X \) combinations that can form \( A_2BB'X_6 \) compounds. The precise and probabilistic nature of \( t \), as well as its simple functional form – depending only on widely available Shannon radii (and the oxidation states required to determine the radii) – enables the rapid search across composition space for stable perovskite materials. Prior to attempting synthesis, it is common for new materials to be examined using computational approaches, therefore it is useful to compare the predictions from \( t \) with those obtained using density functional theory (DFT).

The stability and optical properties of 36 double perovskite halides with the \( A_2BB'X_6 \) composition (K, Rb, Cs)\(_2\)(Cu, Ag)\(_2\)(Ga, In)\(_2\)(Cl, Br, I)\(_6\) were recently examined with the Perdew-Burke-Ernzerhof\(^{42} \) exchange-correlation functional (PBE).\(^{27} \) In comparison to these results, a two-dimensional structure map using \( t \) and \( \mu \) agrees with the calculated stability of the rock salt structure for only 25 of 36 calculated compounds using the range specified in Ref. 27; in contrast, our \( t \) factor agrees with the calculated stability for 31 of 36 materials. Significantly, the probabilities resulting from classification with \( t \) linearly correlate with calculated decomposition enthalpies, demonstrating the value of the monotonic behavior of \( t \) and \( \varphi \) (Fig. 2d). Although \( t \) appears to disagree with PBE calculations for five of these double perovskite halides, these compounds are all near the decision boundaries (\( \varphi = 0.5 \), PBE-computed decomposition enthalpy = 0 meV/atom), suggesting that they cannot be confidently classified as stable or unstable perovskites using \( t \) or PBE calculations of the cubic structure.

A subsequent study found that the PBE-computed decomposition enthalpy of cubic perovskites can trend with \( t, \mu \), and the estimated packing fraction, \( \eta \).\(^{28} \) The 37 calculated decomposition enthalpies provided in Ref. 28 are included in Fig. 2d along with the double perovskite halides from Ref. 27. Among this set, \( t \) agrees with the predictions from PBE for 33 of the 37 single and double perovskite chalcogenides and halides. Of the four disagreements, CaZrO\(_3\) and CaHfO\(_3\) reveal the power of \( t \) compared with PBE calculations of the cubic structure as these two oxides are known to be isostructural with the orthorhombic perovskite CaTiO\(_3\), from which the name perovskite originates.\(^{29,30} \) The PBE calculations predict decomposition enthalpies of \(< -90 \) meV/atom for these two compounds in the cubic structure, indicating they are nonperovskites. In contrast, \( t \) predicts both compounds to be stable perovskites with \(-65\%\) probability, which agrees with experiment. These results indicate that a key challenge in the prediction of perovskite stability from quantum chemical calculations is the requirement of a specific structure as an input as there are more than 20 unique structures classified as perovskite (i.e., those having corner-sharing \( BX_6 \) octahedra). Because \( t \) is structure-agnostic and dependent only on the composition, the stability of all perovskite structures is implicitly considered by this factor. Classification probabilities for all materials shown in Fig. 2d are available in Table S2.

Stabilities of thousands of new inorganic and hybrid double perovskite halides

Motivated by the promise of double perovskites for photovoltaic applications, we used \( t \) to predict the formability of 259,296 \( A_2BB'X_6 \) perovskites, of which 57,542 are predicted to be stable in the perovskite structure. Two particularly attractive classes of materials within this set are: \( A = \text{Cs}^+ \), \( X = \text{Cl}^- \) and \( A = (\text{CH}_3\text{NH}_3)^+ \) (methylammonium, MA\(^+\)), \( X = \text{Br}^- \) double
Considering 72 inorganic cations for the $B$ and $B'$ sites (those with likely oxidation states of $1^+$, $2^+$, or $3^+$), 2,556 compounds with the formula $\text{Cs}_2\text{BB}'\text{Cl}_6$ are enumerated. Of these, $\tau$ predicts 833 stable perovskites, with 328 compounds identified that have a greater probability of perovskite formation than the recently synthesized perovskite, $\text{Cs}_2\text{AgBiCl}_6$ ($\phi = 69.6\%$). A map of probabilities for charge-balanced $\text{Cs}_2\text{BB}'\text{Cl}_6$ compounds is shown in Fig. 3 (lower triangle). Within this set of 328 probable perovskites, a general trend for perovskite stability is realized by combining $B = \text{Ag}$ with any of 33 inorganic cations for the $B'$-site cation including: Bi and In (which have been synthesized) as well as Au, Ce, La, Mo, Nb, Sb, Sc, Ta, and Y. Besides Ag, other common $B$-site cations within this set of 328 compounds include Au (25 highly probable perovskites above 69.6%), Sn (18), Mn (17), and Ti (17). For MA$^+$ double perovskite bromides, 860 compositions are predicted to be stable in the perovskite structure with 583 having probability greater than that of $\text{Cs}_2\text{AgBiCl}_6$. As with Cs$^+$ on the $A$-site, Ag and Au as $B$-site cations are responsible for a large fraction of the highly probable double perovskites when MA$^+$ is the $A$-site cation, consisting of 31 and 54 of the 583 high probability perovskites, respectively (Fig. 3 upper triangle). Although the $\text{Cs}_2\text{BB}'\text{Cl}_6$ and (MA)$_2\text{BB}'\text{Br}_6$ maps are qualitatively similar, the $A = \text{MA}^+$ double perovskites exhibit enhanced stability with alkali metals at $B$ and $B'$ sites. This result is rationalized by the functional form of $\tau$ (Equation 2) in which the stability of the perovskite structure increases as $r_A/r_B$ increases from 1 to $e$; thus, increasing the size of the $A$-site cation leads to increased stabilities for $r_A/r_B \leq e$. For this analysis, the effective ionic radius of MA$^+$, $r_{\text{MA}^+}$, was taken to be 2.17 Å. The sensitivity of the predictions from $\tau$ was assessed as a function of $r_{\text{MA}^+}$ and found to be robust to small changes in the radius (±10%). Because MA$^+$ is significantly larger than inorganic $B$ cations, a further increase of $r_{\text{MA}^+}$ by 10% results in the identical classification for all 2,556 (MA)$_2\text{BB}'\text{Br}_6$ compounds evaluated. Reducing $r_{\text{MA}^+}$ by 10% changes the classification of ~3% of compounds from perovskite to nonperovskite as the larger $B$ cations now approach $r_{\text{MA}^+}$, which leads to instability in the context of $\tau$. An additional consideration when using $\tau$ or $\phi$ is the averaging of the $B$ and $B'$ radii into an effective radius, $r_{\text{B,eff}}$, as this approach does not separately consider the individual radii of $B$ and $B'$. Classification probabilities for all $A_2\text{BB}'X_6$ compositions presented in Fig. 3 are available in Table S3.

**Fig. 3.** Map of predicted inorganic and hybrid organic-inorganic double perovskite halides. Lower triangle: the probability of forming a stable perovskite with the formula $\text{Cs}_2\text{BB}'\text{Cl}_6$ as predicted by $\tau$. Upper triangle: the probability of forming a stable perovskite with the formula (CH$_3$NH$_2$)$_2\text{BB}'\text{Br}_6$ as predicted by $\tau$. White spaces indicate $B/B'$ combinations that do not result in charge-balanced compounds with $r_A > r_{\text{B,eff}}$. The colors indicate the Platt-scaled classification probabilities of $\tau$ ($\phi$), with higher $\phi$ indicating a higher probability of forming a stable perovskite.
Compositional mapping of perovskite stability

In addition to enabling the rapid exploration of stoichiometric perovskite compositions, \( \tau \) provides the probability of perovskite stability for an arbitrary combination of \( n_A, r_A, r_B, \) and \( r_X \), which is shown in Fig. 4. The form of \( \tau \) (Equation 2) suggests that as \( n_A \) increases above 2\(^+\), the stability of the perovskite structure should increase. This trend is observed for \( X = O^{2-} \) with decreasing \( n_A \) (top row of Fig. 4, from left to right), which combined with the smaller radius of \( O^{2-} \) compared with the halides, enables a wider range of stable \( r_A \) and \( r_B \) values than any of the halides. As \( r_X \) increases, \( r_B \) must similarly increase to enable the formation of stable \( BX_6 \) octahedra. This effect is noticeable when separately comparing compounds containing \( Cl^- \) (left), \( Br^- \) (center), and \( I^- \) (right) (bottom row of Fig. 4), where the range of allowed cation radii decreases as the anion radius increases. Interestingly, this inverse relationship of allowed cation radii with increasing anion radius is not limited to only the \( B \)-site cations but affects the allowed radii of \( A \)-site cations for stable perovskites, which can be seen to decrease significantly for iodides relative to chlorides.

For each grouping shown in Fig. 4, experimentally realized perovskites and nonperovskites are shown as single points to compare with the range of values in the predictions made from \( \tau \). Doping at various concentrations presents a nearly infinite number of potential \( AA'BB'(XX')_6 \) compositions that allows for the tuning of technologically useful properties. \( \tau \) can suggest the size and concentration of dopants on the \( A, B, \) or \( X \) sites that should lead to improved stability in the perovskite structure. For instance, \( Cs_2AgInCl_6 \) becomes more stable as a perovskite if \( r_A \) or \( r_B \) is increased slightly (e.g., by the isovalent substitution of \( In^{3+} \) with \( Y^{3+} \)).

![Fig. 4. The effects of radii and oxidation states on the stability of single, double, and hybrid perovskite oxides and halides. Top row: \( X = O^{2-} \) (left to right – \( n_A = 3^+, 2^+, 1^+ \)). Bottom row: \( n_A = 1^+ \) (left to right – \( X = Cl^- \), \( Br^- \), \( I^- \)). The experimentally realized perovskites \( LaGaO_3, \) \( Sr_2FeMoO_6, \) \( AgNbO_3, \) \( Cs_2AgInCl_6, \) \( (MA)_2AgBrI_3, \) and \( MAPbI_3 \) are shown as open circles in the corresponding plot, which are all predicted to be stable by \( \tau \). The experimentally realized nonperovskites \( InGaO_3, \) \( CoMnO_3, \) \( LiBiO_3, \) \( LiMgCl_3, \) \( CsNiBr_3, \) and \( RhPbI_3 \) are shown as open triangles and predicted to be unstable in the perovskite structure by \( \tau \). The gray region where \( r_B > r_A \) is not classified because when this occurs, \( A \) becomes \( B \) and vice versa based on our selection rule \( r_A > r_B \).](image-url)

### Conclusions

We report a new tolerance factor, \( \tau \), which enables the prediction of perovskite stability significantly better than the widely used Goldschmidt tolerance factor, \( t \), and the two-dimensional structure map using \( t \) and the octahedral factor, \( \mu \). The deficiency of \( t \) was found to arise from the functional form and not the input features (i.e., composition, oxidation states, and Shannon ionic radii) as the calculation of \( \tau \) requires the same inputs as \( t \). Thus, \( \tau \) enables a superior prediction of new perovskite materials with negligible computational cost. The monotonic nature of \( \tau \) allows for the determination of perovskite probability as a continuous function of the radii and oxidation states of \( A, B, \) and \( X \), which clarifies how chemical substitutions at each of the sites modulate the tendency for perovskite formation. Using \( \tau \), we predict the probability of inorganic and organic-inorganic double perovskite formation for thousands of unexplored compounds, resulting in a library of stable perovskites for use in various applications, including photovoltaics. Due to the simplicity and accuracy of \( \tau \), we expect its use to accelerate the discovery and design of perovskites for applications ranging from optoelectronics to electrocatalysis.
Methods

To develop a descriptor that takes as input the chemical composition and outputs a prediction of perovskite stability, the features which comprise the descriptor must also be specified based only on the composition. Yet it is not known a priori which cation will occupy the A-site or B-site given only a chemical composition, \(CC'X_3\) (\(C\) and \(C'\) being cations). To determine which cation is A or B, a list of allowed oxidation states (based on Shannon’s radii\(^{29}\)) is defined for each cation. Next, all pairs of oxidation states for \(C\) and \(C'\) that charge-balance \(X_3\) are considered. If more than one charge-balanced pair exists, a single pair is chosen based on the electronegativity ratio of the two cations (\(\chi_C/\chi_{C'}\)). If \(0.9 < \chi_C/\chi_{C'} < 1.1\), the pair that minimizes \(|n_C - n_{C'}|\) is chosen. Otherwise, the pair that maximizes \(|n_C - n_{C'}|\) is chosen with the oxidation states of \(C\) and \(C'\) assigned, the values of the radii for the cations occupying the A and B sites are chosen to be closest to the coordination number of twelve and six, which are consistent with the coordination environments of the A and B cations in the perovskite structure. Finally, the radii of the C and C’ cations are compared and the larger cation is assigned as the A–site cation. This strategy reproduces the assignment of the A and B cations for 100% of 313 experimentally labeled perovskites. Further benchmarking of the \(\chi_C/\chi_{C'}\) criteria for oxidation-state assignments will be reserved for subsequent studies.

For the discovery of \(\tau\), the oxidation states \(\{n_A, n_B, n_X\}\), ionic radii \(\{r_A, r_B, r_X\}\), and radii ratios \(\{r_{AB}, r_{AX}, r_{BX}\}\) comprise the primary features, \(\Phi_0\), where \(\Phi_0\) refers to the descriptor-space with \(n\) iterations of complexity as defined in Ref. 31. For example, \(\Phi_1\) refers to the primary features \(\Phi_0\) together with one iteration of algebraic/functional operations applied to each feature in \(\Phi_0\). \(\Phi_2\) then refers to the application of algebraic/functional operations to all potential descriptors in \(\Phi_1\), and so forth. Note that \(\Phi_n\) contains all potential primary features within \(\Phi_{n-1}\) with a filter to remove redundant potential descriptors. For the discovery of \(\tau\), complexity up to \(\Phi_3\) is considered, yielding \(3 \times 10^9\) potential descriptors. An alternative would be to exclude the radii ratios from \(\Phi_0\) and construct potential descriptors with complexity up to \(\Phi_2\). However, given the minimal \(\Phi_0 = \{n_A, n_B, n_X, r_A, r_B, r_X, r_{AB}, r_{AX}, r_{BX}\}\), there are \(~1 \times 10^{10}\) potential descriptors in \(\Phi_3\), so \(~1 \times 10^{10}\) potential descriptors would be expected in \(\Phi_n\) (based on \(~1 \times 10^2\) being present in \(\Phi_1\) and \(~1 \times 10^2\) in \(\Phi_2\)), and this number is impractical to screen using available computing resources.

The dataset of 576 \(ABX_3\) compositions was partitioned randomly into an 80% training set for identifying candidate descriptors and a 20% test set for analyzing the predictive ability of each descriptor. The top 100,000 potential descriptors most applicable to the perovskite classification problem were identified using one iteration of SISSO with a subspace size of 100,000. Each descriptor in the set of \(~3 \times 10^9\) was ranked according to domain overlap, as described in Ouyang et al.\(^{31}\) To identify a decision boundary for classification, a decision tree classifier with a max depth of two was fit to the top 100,000 candidate descriptors ranked based on domain overlap. Domain overlap (and not decision tree performance) is used as the SISSO ranking metric because of the significantly lower computational expense associated with applying this metric. Notably, \(\tau\) was the 14,467\(^{th}\) highest ranked descriptor by SISSO using the domain overlap metric and, as such, this defines the minimum subspace required to identify \(\tau\) using this approach. Without evaluating a decision tree model for each descriptor in the set of \(~3 \times 10^9\) potential descriptors, we cannot be certain that a subspace size of 100,000 is sufficient to find the best descriptor. However, the identification of \(\tau\) within a subspace as small as 15,000 suggests that a subspace size of 100,000 is sufficiently large to efficiently screen the much larger descriptor space. We have also conducted a test on this primary feature space \(\Phi_0 = \{n_A, n_B, n_X, r_A, r_B, r_X, \chi_{AB}, \chi_{AX}, \chi_{BX}\}\) with a subspace size of 500,000. Even after increasing the subspace size by 5\(\times\), \(\tau\) remains the highest performing descriptor (classification accuracy of 92% on the 576 compound set). An important distinction between the SISSO approach described here and by Ouyang et al. in Ref. 31 is the choice of sparsifying operator (SO). In this work, domain overlap is used to rank the features in SISSO, but a decision tree with max depth of two is used as the SO (instead of domain overlap) to identify the best descriptor of those selected by SISSO. This alternative SO is used to decrease the leverage of individual data points as the experimental labeling of perovskite/nonperovskite is prone to some ambiguity based on synthesis conditions, defects, and other experimental considerations.

The benefit of including the radii ratios in \(\Phi_0\) is made clear by comparing the performance of \(\tau\) to the best descriptor obtained using the minimal primary feature space with \(\Phi_0 = \{n_A, n_B, n_X, r_A, r_B, r_X\}\). Repeating the procedure used to identify \(\tau\) yields a \(\Phi_3\) with \(~1 \times 10^8\) potential descriptors. The best 1D descriptor was found to be \(\frac{r_B}{n_A(r_A-r_B)} + \frac{r_B}{r_A} - \frac{r_B}{r} \) with classification accuracy of 89%.

We also consider the effects of including properties outside of those required to compute \(t\) or \(\tau\). Beginning with \(\Phi_0 = \{n_A, n_B, n_X, r_A, r_B, r_X, \chi_{AB}, \chi_{AX}, \chi_{BX}, \chi_{i}, \chi_{j}\}\), where \(\chi_{i}\) is the empirical covalent radius of neutral element \(i\), \(\chi_{j}\) is the empirical first ionization energy of neutral element \(i\), and \(\chi_i\) is the Pauling electronegativity of element \(i\), all taken from WebElements,\(^{52}\) an aggregation of a number of references which are available within. Repeating the procedure used to identify \(\tau\) results in \(~6 \times 10^{10}\) potential descriptors in \(\Phi_3\). The best performing 1D descriptor was found to be \(\frac{r_{A}r_{X} - \chi_{A} - \chi_{X}}{\gamma_{COV,A}/r_B - \gamma_{COV,A}/r_X} \) with classification accuracy of 90%, lower than \(\tau\) which makes use of only the oxidation states and ionic radii, and only slightly higher than the accuracy of the descriptor obtained using the minimal feature set.
To assess the performance of descriptors with increased dimensionality, following the approach to higher dimensional descriptor identification using SISSO described in Ref. 31, the residuals from classification by $\tau$ (those misclassified by the decision tree, Fig. 2b) are used as the target property in the search for a second dimension to include with $\tau$. From the same set of $\sim 3 \times 10^9$ potential descriptors constructed to identify $\tau$, the 100,000 1D descriptors that best classify the 41 training set compounds misclassified by $\tau$ are identified based on domain overlap. Each of these 100,000 descriptors are paired with $\tau$ and the performance of each 2D descriptor was assessed using a decision tree with max depth of two. The best performing 2D descriptor was found to be

$$\tau \left(\frac{|r_{A'B'}/r_B^2 - n_B r_A/r_B|}{|r_{A'B'}/r_B^2 - r_A/r_B + n_B|}\right)$$

with a classification accuracy of 95% on the 576 compound set. Improvements are expected to diminish as the dimensionality increases further due to the iterative nature of SISSO and the higher order residuals used for subspace selection. Although the second dimension leads to slightly improved classification performance on the experimental set compared with $\tau$, the simplicity and monotonicity of $\tau$, which enables physical interpretation and the extraction of meaningful probabilities, support its selection instead of the more complex 2D descriptor. The benefits and capabilities of having a meaningfully probabilistic one-dimensional tolerance factor, such as $\tau$, are described in detail within the main text.

SISSO was performed using Fortran 90. Platt’s scaling $^{32}$ was used to extract classification probabilities for $\tau$ by fitting a logistic regression model on the decision tree classifications using 3-fold cross-validation. Decision tree fitting and Platt scaling were performed within the Python package, scikit-learn. Data visualizations were generated within the Python packages matplotlib and seaborn.

**Data availability**

A repository containing all files necessary for classifying $ABX_3$ and $AA'BB'(XX')_6$ compositions as perovskite or nonperovskite using $\tau$ is available at https://github.com/CJBartel/perovskite-stability.
References


52. webelements.com

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Author Contributions
MS and CJB conceived the idea. CJB, CS and BRG designed the studies. CJB performed the studies. CJB, CS, and BRG analyzed the results and wrote the manuscript. RO provided the SISSO algorithm and facilitated its implementation. CBM, LMG and MS supervised the project. All the authors discussed the results and implications and edited the manuscript.

Additional Information
The supporting information contains a list of all 576 $ABX_3$ used for training and testing of $\tau$, a performance comparison of $\tau$ and $\rho$ by composition, probabilities of perovskite stability as a function of $\tau$, and a $(\tau, \mu)$ structure map for the 576 $ABX_3$ solids. Associated information with Fig. 2d and Fig. 3 is also provided.

Competing Financial Interests
The authors declare no competing financial interests.
Supplementary information for
New Tolerance Factor to Predict the Stability of Perovskite Oxides and Halides

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Table S1. 576 ABX₃ used for training and testing τ (see TableS1.csv).
Within this table – exp_label = 1 corresponds with experimentally labeled perovskites and exp_label = −1, nonperovskites; is_train = 1 corresponds with a training set compound and is_train = −1 a test set compound; τ is provided as tau, classification using τ as tau_pred, classification using t as t_pred, and τ-derived probabilities, φ as tau_prob. A, B, X, n_A, n_B, n_X, r_A, r_B, r_X, and t are also provided and named as they are in the text.

Figure S1. Comparing the performance of t and τ by composition. Classification accuracy on the full set of 576 experimentally characterized ABX₃ solids (all) and by compounds containing X = O, F, Cl, Br, I. The number appearing above each pair of columns corresponds with the number of compounds evaluated within each set.

Figure S2. Sigmoidal relationship between φ and τ. A comparison of Platt-scaled classification probabilities of τ (φ) versus τ for the 576 experimentally characterized ABX₃ solids. The outlying compounds at τ > 10 which are labeled perovskite yet have small φ are PuVO₃, AmVO₃, and PuCrO₃, which may indicate poorly defined radii or experimental characterization.
Figure S3. \((t, \mu)\) structure map for 576 ABX\(_3\) solids. A decision tree trained on all compounds finds the optimal bounds for perovskite stability to occur for \(t > 0.830\) and \(\mu > 0.426\), which results in a classification accuracy of 85%.

Table S2. Additional information associated with Fig. 2d (see Table S2.csv).
Columns are named as described for Table S1 with the additional columns: source – corresponding with the DOI from which the DFT decomposition enthalpy was obtained and \(dH_{\text{dec}} \text{ (meV/atom)}\) – the PBE-computed decomposition enthalpy of the cubic structure.

Table S3. Additional information associated with Fig. 3 (see Table S3.csv).
Columns are named as described for Table S1 and Table S2.