



## Thermal stability of ionic solids: A melting points survey

Leslie Glasser

Curtin Institute for Computation, Discipline of Chemistry Curtin University, GPO Box U1987, Perth, WA 6845, Australia



### A B S T R A C T

While predictive correlations of the melting points of organic solids are well-established and reliable, the melting points of ionic solids are less understood. We provide a comprehensive survey of the related literature for ionic solids which shows that the primary factors to consider are the ambient temperature values of the formation enthalpies and the distances among the ions as enshrined in their crystal structures. These conclusions from standard thermodynamic analyses are supported by an independent current machine-learning program.

This result contrasts with the common belief that lattice energies are a leading factor in melting. This basic idea is confounded by the irrelevant (but generally overwhelming) inclusion of the formation energy of gaseous ions in the evaluation of lattice energies through thermochemical cycles.

The melting points of simple metal halides are correlated with their formation enthalpies per halide ion and distances among ions as determined by their crystal structures rather than their lattice energies. As the formula units of ionic solids increase in chemical and structural complexity the relations also become more complex.

### Introduction

Melting temperatures of ionic materials are of interest with regard to their applications. At one extreme, they comprise the high-temperature refractory materials from which furnaces are constructed [1] while, at the other extreme, low-temperature melting materials are useful for environmentally-friendly ceramics used, for example, in construction of passive components of communication devices [2]. Ionic liquids, [3] which contain bulky charged organic anions, will not be considered in the present context.

The factors which influence the melting temperatures of *molecular solids* (whether organic, such as CH<sub>4</sub>, or inorganic, such as GeX<sub>4</sub> and PbCl<sub>4</sub>) are reasonably well understood: [4] these factors include (i) molecular mass; (ii) symmetry and structure – linear, branched, or cyclic; and (iii) interactions among the molecules such as hydrogen bonding, polar interactions, or van der Waals forces [5–9]. The energy to separate materials into their free *gaseous molecules or atoms* is termed the cohesive energy, and can be found by experiment since the properties of the independent atoms are well-established [10].

Šima has provided a comprehensive discussion [5] of the melting of inorganic solids, drawing attention to the distinction between molecular compounds such as GeX<sub>4</sub> and extended (so-called “polymeric”) inorganic solids. The author notes the lack of a comprehensive treatment of factors influencing melting in *extended ionic solids* which are not so obvious as in organic materials. Certainly, coulombic forces between ions are paramount with their strengths dependent upon the ion charges and their distances apart, as determined by the crystal structures. One measure of the interactive forces is the formation energy (or enthalpy,  $\Delta_f H$ ) of the ionic material from its elements. An alternative energetic measure of these forces is the lattice energy,  $U_{POT}$  (or lattice enthalpy), which is

the energy required to convert a condensed ionic material into its independent *gaseous ions* [11,12] and which thereby takes account of both the charge interactions and their distances in the solid.

By contrast with cohesive energies, lattice energies cannot be measured experimentally since independent gaseous ions cannot be prepared. Instead, lattice energy for a particular ionic material may be found as closing a Born-Haber-Fajans thermochemical cycle [12] involving that ionic material, or may be directly computed for a particular ionic material based on quantum methods, [13,14] or by use of the standard Born-Mayer (or Born-Landé) equation, [12,15] summing coulombic attraction and London repulsion terms for a binary charge system, or by a generalisation of the Kapustinskii equation [16,17] from binary charge systems to systems of any complexity [18,19]

$$U_{POT} = 2I \left( \frac{\alpha}{V_m^{1/3}} + \beta \right) \quad (1)$$

with separate constants  $\alpha$  and  $\beta$  for each group of ionic materials such as MX, MX<sub>2</sub>, M<sub>2</sub>X, M<sub>2</sub>X<sub>2</sub>, etc., with a corresponding formula volume,  $V_m$ , individual integer charges,  $z_i$ , and ionic strength factor,  $I$ , where

$$I = \sum_{i>j}^n z_i z_j = -\frac{1}{2} \sum_k^t n_k z_k^2 \quad (2)$$

A general *limiting lattice energy equation*, applicable beyond ~5 000 kJ mol<sup>-1</sup> and having no adjustable coefficients, has also been developed [11]

$$U_{POT} = AI \left( \frac{2I}{V_m} \right)^{1/3} \quad (3)$$

where  $A$  is a standard electrostatic term with value 121.39 kJ mol<sup>-1</sup> nm. The  $\alpha$  constants are similar in value to the constant  $A$ .

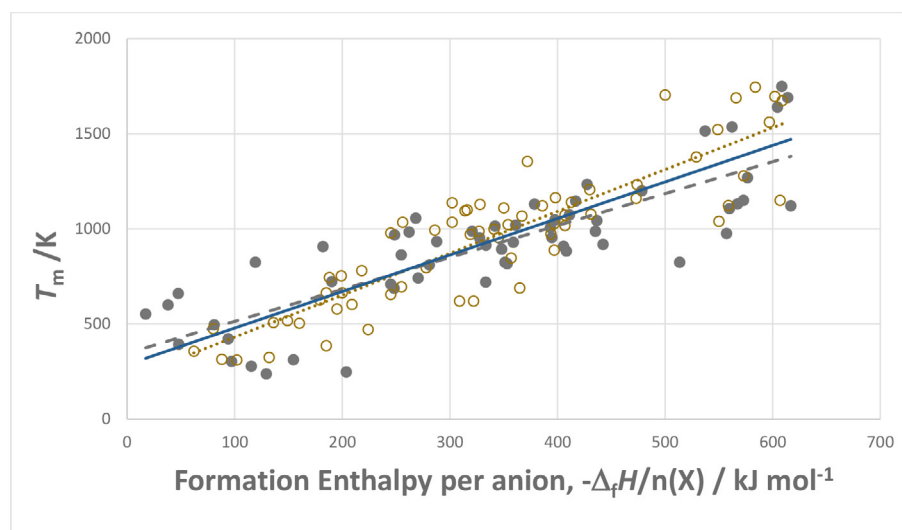
E-mail address: [l.glasser@curtin.edu.au](mailto:l.glasser@curtin.edu.au)

<https://doi.org/10.1016/j.ctta.2022.100092>

Received 5 September 2022; Received in revised form 15 October 2022; Accepted 31 October 2022

2667-3126/© 2022 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>)



**Fig. 1.** Melting temperature,  $T_m / K$ , for metal halides,  $MX$ ,  $MX_2$ ,  $MX_3$  and  $MX_4$  plotted against their formation enthalpies per anion,  $-\Delta_f H/n(X)$ . The data for the open circles have been read with “Plot Digitizer” software [34] from Turkdogan [35] and are listed in the accompanying Supplementary file together with our collected data for the filled circles. Linear equations for the 65 Turkdogan data (dotted line) are  $T_m / K = -2.20 (\pm 0.15)\Delta_f H/n(X) + 212 (\pm 54)$  with  $R^2 = 0.78$  and for the 58 Supplementary data (dashed line)  $T_m / K = -1.68 (\pm 0.15)\Delta_f H/n(X) + 347 (\pm 57)$  with  $R^2 = 0.69$ . The standard errors of the estimates of  $T_m$  are 172 K and 190 K, respectively. The linear fit for the combined metal halides (solid line) yields  $T_m / K = -1.92 (\pm 0.11)\Delta_f H/n(X) + 269 (\pm 39)$  with  $R^2 = 0.73$  and with a standard error of the estimate of  $T_m$  at 185 K for the 123 data items. The 95% confidence interval of the slope for the combined data set is  $\pm 0.21$ . The statistical data were obtained using the Regression function of the Excel data analysis software. Although Fig. 1 displays a difference in slope between the digitized Turkdogan data and those collected here, this difference lies

within their 95% confidence intervals and simply results from the use of slightly different sets of data.

In the following, we examine melting temperatures of ionic materials with widely-differing crystal structures in order to consider the applicability of correlations which have been proposed.

#### Data mining: collection of structural information and melting points

It is commonly believed [1,5,20,21] that the melting points of inorganic materials are related to their lattice energies and thus to their crystal structures - which provide the distances between the constituent ions. There are many sources of data for inorganic materials, such as the annual *Handbook of Chemistry and Physics* [22,23] and Barin’s *Thermochemical Data of Pure Substances*, [24] but they lack suitable classification into groups of structurally similar materials which is relevant to differences in their melting processes. Therefore, in addition to such general data sources, we have obtained data from purpose-specific publications, such as Wolf and Jeanloz [25] and Greis [26] for some complex fluorides, Fujiwara [27] for  $MXO_n$  solids, and Galasso [28] and Poirier [29] for perovskite-type materials. Melting point and related data is also reported by Šima [5]

Our groups of similarly-structured ionic solids comprise the alkali metal halides,  $MX$ , being the simplest and best-studied, the alkaline-earth halides,  $MX_2$ ; binary oxides, selenides and sulfides,  $M_2O$  and  $M_2S$ ; fluorides; non-fluoride perovskites,  $ABO_3$ ; miscellaneous “hard metals” such as VN; complex oxides; and apatites; listed in order of increasing ionic strength in the attached Supplementary file.

#### Inorganic Melting Point Relations

Van Uitert has considered melting point relations for simple halides and oxides [30]. Fujiwara has developed a reasonably extensive melting point relation [27] for inorganic compounds of type  $MXO_n$  as a function of the ionic radius and the polarizability of the ions  $M^+$  and of  $X^{(2n-1)+}$  in the anion  $XO_n^-$ , such as nitrate,  $NO_3^-$ .

The most frequently considered method for melting point determination of inorganic systems was developed by Lindemann [31] in 1910 with many subsequent attempts at improvement [32]. It is based upon the Debye temperature of the material and assumes that the amplitudes of vibration become sufficiently great as temperature increases so that the solid “shakes itself to pieces” [33] and melting occurs. The Lindemann rule as applied to mineral systems has been considered by Wolf

and Jeanloz [25] who regard it as speculative at best, and also its extensions and refinements as applied to perovskite minerals by Galasso [28] and by Poirier [29]

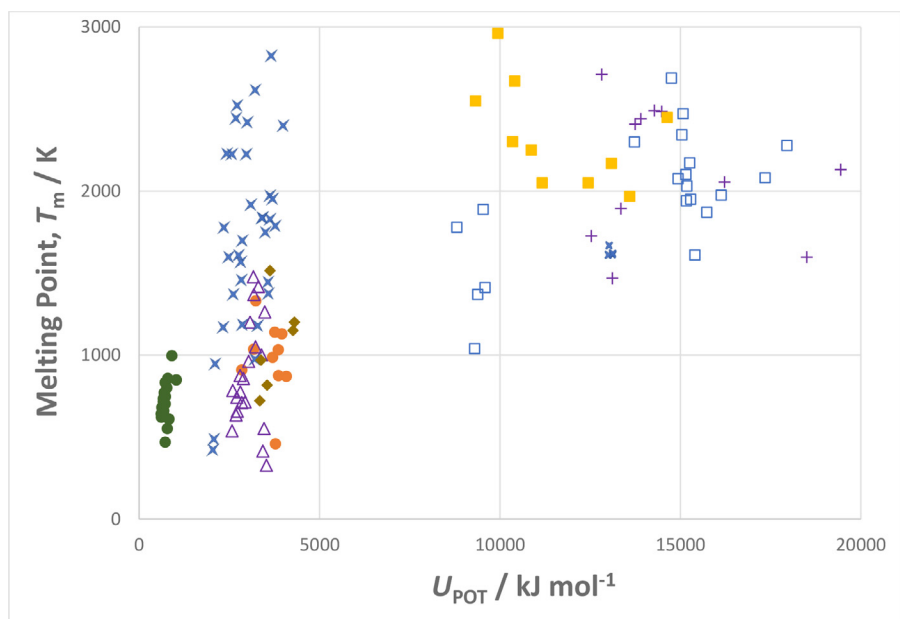
Turkdogan, in an extensive graphical compilation (whose data could be read using “Plot Digitizer” software [34]) related melting points of inorganic compounds,  $M_pX_q$ , to their formation enthalpies per anion number,  $\Delta_f H/q(X)$  [35]. Fig. 1 is a plot of such data for metal halides both from Turkdogan and from data compiled in the supplied Supplementary file. Most recently, Qin, et al., [2] have developed a machine-learning algorithm particularly directed at the detection of low-melting point oxides for ceramic applications.

#### Discussion: correlation of melting points to energy of the ionic material

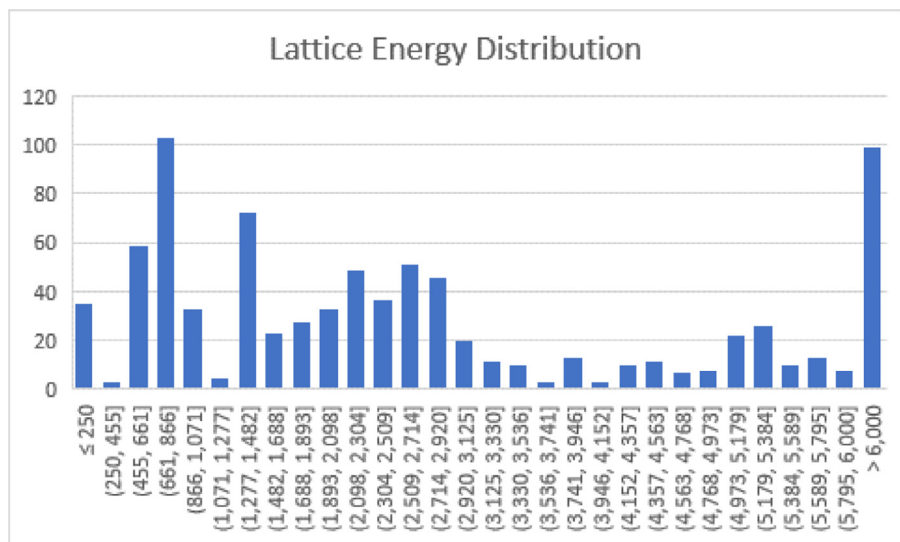
Turkdogan has comprehensively demonstrated [35] a correlation between melting points and formation enthalpies of ionic materials. This supersedes the generally assumed connection with lattice energies [1,5,20] which, in their thermochemical cycles, include the irrelevant confusion of the much larger component of formation of gaseous ions. Fig. 2 demonstrates the very limited relation between melting point and lattice energy.

An obvious feature in Fig. 2 is the absence of data points in the range of lattice energies from about 4 000 to 8 000  $\text{kJ mol}^{-1}$ . This arises because lattice energy is strongly dependent upon ionic strength Eq. (2) which, in turn, is dependent on the square of ionic charge,  $z$ , with the resulting large gap in  $z^2$  values between 9 and 16. Similar gaps in lattice energy which might have been expected between larger values of  $z$  are filled by the variations in formula volumes contributing to the lattice energies of these more complex ionic materials. This contention is supported by Fig. 3 which is a histogram of lattice energies of more than 800 ionic materials, which shows a reduced presence of values in the range 3 000 to 5 000  $\text{kJ mol}^{-1}$ .

Generic studies of melting points of inorganic solids have now been complemented by a machine-learning analysis of about 3 600 inorganic materials by Qin, et al. [2] Their root mean square error of the fit to the melting points is 247 K. The authors have identified the principal factors in controlling melting points as being formation energy per atom and density together with the number of atoms as a more nebulous contributor (a “recessive gene” in their terms). Both of the latter terms are, it



**Fig. 2.** Plot of melting points,  $T_m / K$ , versus lattice energy,  $U_{POT} / kJ mol^{-1}$ , which separate into groups according to their ionic strengths,  $I$ , with alkali metal halides,  $MX$ , being the simplest (ionic strength  $I = 1$ , green circles); followed by the alkaline-earth halides,  $MX_2$  (ionic strength  $I = 3$ , open purple triangles); alkali metal and alkaline earth oxides, sulfides and selenides,  $MO$ ,  $M_2O$ ,  $MS$  and  $MSe$  (ionic strength  $I = 3$ , blue stars); fluorides (ionic strength  $I = 3-5$ , orange circles);  $MX_3$  (ionic strength  $I = 6$ , brown diamonds); non-fluoride perovskites (ionic strength  $I = 11-16$ , open blue squares); miscellaneous “hard metals” [36] (ionic strength  $I = 9-12$ , filled orange squares); complex oxides (ionic strength  $I = 12-19$ , pluses); and apatites (ionic strength  $I = 24$ , cluster of three small stars).



**Fig. 3.** Histogram of the frequency of lattice energies over the range 0 to 6 000  $kJ mol^{-1}$  from a database of 829 ionic materials [23] demonstrating a broad minimum in frequency over the range 3 000 to 5 000  $kJ mol^{-1}$ .

seems, simply surrogates for the ion distance-defining crystal structures as contained in other analyses [5,35].

## Conclusion

The melting points of simple ionic solids such as the metal halides are correlated with their formation enthalpies as demonstrated by Turkdogan but the relations become increasingly complex as the formula units increase in complexity. The machine learning program of Qin, et al., confirms that the important factors in melting are both their formation energies and their crystal structures while lattice energies are of little value since their data values are confounded by the inclusion of the overwhelming formation energies of gaseous ions in lattice energy thermochemical cycle calculations which are clearly irrelevant to melting.

The conclusion must be that melting point correlations may be established within a group of related materials as for the halides and oxides, [30] or for the other correlations of Turkdogan, [35] or for  $MXO_n$  solids as Fujiwara has demonstrated [27]. It appears that specific melting points cannot currently be reliably predicted and need to be determined experimentally.

## Supplementary Information

A Supplementary Melt Thermodynamics.xls file contains melting point, lattice energy and ambient formation enthalpy data for 131 inorganic materials, collected from a variety of referenced sources, together with data read from the Turkdogan graphical plots. The file also collects and plots the data for Fig. 1, and provides separate plots for each of the halide groups  $MX$ ,  $MX_2$ ,  $MX_3$  and  $MX_4$ , comparing the Turkdogan digitised values against those now collected. The linear equations fitted to each data group are included.

## Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Supplementary File supplied File included

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ctta.2022.100092.

## References

- [1] J.D. Smith, W.G. Fahrenholtz, Refractory Oxides J.F. Shackelford, R.H. Doremus (Eds.), *Ceramic and Glass Materials: Structure, Properties and Processing* (2008) 87–110.
- [2] J. Qin, Z. Liu, M. Ma, Y. Li, Machine Learning-Assisted Materials Design and Discovery of Low-Melting-Point Inorganic Oxides for Low-Temperature Cofired Ceramic Applications, *ACS Sustain. Chem. Eng.* 10 (2022) 1554–1564.
- [3] L. Chen, V.S. Bryantsev, A density functional theory based approach for predicting melting points of ionic liquids, *Phys. Chem. Chem. Phys.* 19 (2017) 4114–4124.
- [4] A.R. Katritzky, R. Jain, A. Lomaka, R. Petrukhin, U. Maran, M. Karelson, Perspective on the Relationship between Melting Points and Chemical Structure, *Cryst. Growth Des.* 1 (2001) 261–265.
- [5] J. Šima, Structure-related melting and boiling points of inorganic compounds, *Found. Chem.* 18 (2016) 67–79.
- [6] J.F. Krzyżaniak, P.B. Myrdal, P. Simamora, S.H. Yalkowsky, Boiling Point and Melting Point Prediction for Aliphatic, Non-Hydrogen-Bonding Compounds, *Ind. Eng. Chem. Res.* 34 (1995) 2530–2535.
- [7] P. Simamora, S.H. Yalkowsky, Group Contribution Methods for Predicting the Melting Points and Boiling Points of Aromatic Compounds, *Ind. Eng. Chem. Res.* 33 (1994) 1405–1409.
- [8] S.H. Yalkowsky, D. Alantary, Estimation of Melting Points of Organics, *J. Pharm. Sci.* 107 (2018) 1211–1227.
- [9] F.D. Stacey, R.D. Irvine, Theory of Melting: Thermodynamic Basis of Lindemann's Law, *Australian J. Phys.* 30 (1977) 631–640.
- [10] L. Glasser, D.A. Sheppard, Cohesive Energies and Enthalpies: Complexities, Confusions, and Corrections, *Inorg. Chem.* 55 (2016) 7103–7110.
- [11] L. Glasser, H.D.B. Jenkins, Lattice energies and unit cell volumes of complex ionic solids, *J. Am. Chem. Soc.* 122 (2000) 632–638.
- [12] L. Glasser, L. von Szentpaly, Born-Haber-Fajans cycle generalized: Linear energy relation between molecules, crystals, and metals, *J. Am. Chem. Soc.* 128 (2006) 12314–12321.
- [13] K. Latimer, S. Dwaraknath, K. Mathew, D. Winston, K.A. Persson, Evaluation of thermodynamic equations of state across chemistry and structure in the materials project, *NPJ Comput. Mater.* 4 (2018) 40.
- [14] A. Jain, S.P. Ong, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson, The Materials Project: A materials genome approach to accelerating materials innovation, *APL Materials* 1 (2013) 011002.
- [15] H.D.B. Jenkins, Thermodynamics of the Relationship between Lattice Energy and Lattice Enthalpy, *J. Chem. Educ.* 82 (2005) 950–952.
- [16] A.F. Kapustinskii, General formula for the lattice of crystals of arbitrary structure, *Z. Phys. Chem. B* 22 (1933) 257–260.
- [17] A.F. Kapustinskii, Lattice energy of ionic crystals, *Quart. Rev. Chem. Soc.* 10 (1956) 283–294.
- [18] L. Glasser, Lattice Energies of Crystals with Multiple Ions - a Generalised Kapustinskii Equation, *Inorg. Chem.* 34 (1995) 4935–4936.
- [19] L. Glasser, The Equivalence of the Charge Interaction Sum and the Ionic Strength, *Chem. Thermodyn. Therm. Anal.* 6 (2022) 100059.
- [20] Quora How is lattice energy related to melting point? <https://www.quora.com/How-is-lattice-energy-related-to-melting-point> (accessed August, 2022).
- [21] J. Shanker, M. Kumar, Studies on Melting of Alkali Halides, *Physica Status Solidi (B)* 158 (1990) 11–49.
- [22] J.R. Rumble, (Editor-in-Chief), *CRC Handbook of Chemistry and Physics*, 102nd ed., Taylor and Francis Group, Routledge, 2022.
- [23] H.D.B. Jenkins, H.K. Roobottom, Lattice Energies, in: W.M. Haynes (Ed.), *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 2015 Editor-in-Chief.
- [24] I. Barin, *Thermochemical Data of Pure Substances*, 2nd ed., VCH, Weinheim, 1993.
- [25] G.H. Wolf, R. Jeanloz, Lindemann melting law - anharmonic correction and test of its validity for minerals, *J. Geophys. Res.* 89 (1984) 7821–7835.
- [26] O. Greis, M.S.R. Cader, Polymorphism of high-purity rare earth trifluorides, *Thermochim. Acta* 87 (1985) 145–150.
- [27] S. Fujiwara, Formula for the Melting Points of Inorganic Compounds of Type  $MXO_n$ , *Bull. Chem. Soc. Jpn.* 25 (1952) 347–351.
- [28] F.S. Galasso, *Structure, Properties and Preparation of Perovskite Type Compounds*, Pergamon Press, Oxford, 1969.
- [29] J.P. Poirier, Lindemann law and the melting temperature of perovskites, *Phys. Earth Planet. Interiors* 54 (1989) 364–369.
- [30] L.G. Van Uitert, Melting-Point Relations for Simple Halides and Oxides, *J. Am. Ceram. Soc.* 64 (1981) 544–548.
- [31] F.A. Lindemann, Über die Berechnung molekularer Eigenfrequenzen, *Phys. Z.* (1910) 11.
- [32] M.M. Vopson, N. Rogers, I. Hepburn, The generalized Lindemann melting coefficient, *Solid State Commun.* 318 (2020) 113977.
- [33] F.C. Frank, N.V. Sidgwick, Melting as a disorder phenomenon, *Proc. R. Soc. Ldn. Series A. Math. Phys. Sci.* 170 (1939) 182–189.
- [34] Huwaldt, J. A. Plot Digitizer. <http://plotdigitizer.sourceforge.net/> (accessed August, 2022).
- [35] E.T. Turkdogan, Thermodynamic and Kinetic Properties of Elements and Inorganic Compounds Relating to their Melting and Boiling Point Temperatures, *Can. Metall. Quart.* 41 (2002) 151–162.
- [36] *International Journal of Refractory Metals and Hard Materials*. <https://www.sciencedirect.com/journal/international-journal-of-refractory-metals-and-hard-materials> (accessed August, 2022).

## Further reading

- [1] C Talbot, L Yap, The relationship between lattice enthalpy and melting point in magnesium and aluminium oxides, *School Science Review* 94 (2013) 9–11.