The Route to Resource-Efficient Novel Materials

by

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Combining the efforts of physicists, materials scientists, economists and resource-strategy researchers opens up an interdisciplinary route enabling the substitution of rare elements by more abundant ones, serving as a guideline for the development of novel materials.

Scarcity and possible future shortages of key elements used in modern technology has come into the focus of public interest and was the topic of a recent special issue of *Nature Materials*[1]. It is one of the most imminent challenges of modern materials science to develop new materials that enable replacement of rare elements by more abundant ones that have comparable or better functionalities than those currently used[2,3]. So far most scientists developing new functional materials are accustomed to using materials parameters as sole guidance in their research. It is equally important, however, to judge the economic merits and resource availability too. Incorporation of these interdisciplinary aspects at an early stage of the research has to be a key priority in future materials research and development.

To illustrate this multidisciplinary approach, we apply it to the prototypical example of materials with extremely high dielectric constants of 10^3 or above. These materials could pave the way for a new generation of electronic components, for example as capacitors with outstanding energy-storage capabilities that could replace batteries[4–6]. Here, we demonstrate the prospects of several such materials from the perspective of materials science, resource strategy and resource management, providing three filters that the material has to pass through to be suitable for application. Criteria for the materials science filter are based only on technically relevant properties whereas the criticality of materials is considered in the resource strategy filter. The final filter deals with economic aspects of the resources and of the processing techniques. Combining these filters and estimating the time-dependent criticality of the resources and economic aspects then enables the selection of a specific material for the defined application.

The interdisciplinary approach we present here can serve as a valuable methodology in the future development and applications of advanced functional materials.

Recently, the discovery of new materials showing a very high, so-called colossal dielectric constant (CDC) has triggered significant research activity[6]. The dielectric constant is the primary parameter determining the performance of capacitors. Capacitors are ubiquitous in electronic circuits and can also be considered for energy storage, for example to recuperate the braking energy in hybrid cars. So far, capacitors using CDC materials are mostly based on ferroelectrics, which are materials with ordered electric dipoles. These ferroelectrics have been used for decades[7], and more than one trillion units of ferroelectric-based multilayer ceramic capacitors (MLCC)[8] were fabricated in 2010. Dozens are included in every smartphone. $BaTiO_3$ (BTO), doped with rare earths, is the most suitable material for such devices at present[9]. The recent shortage of rare earths is expected to have a dramatic influence on the MLCC market in the near future, which can be verified through an economic risk analysis. Here, we describe a case study for developing alternative materials for MLCCs. We compare the materials currently used to newly developed ceramics, applying the threefold-filter approach discussed above.

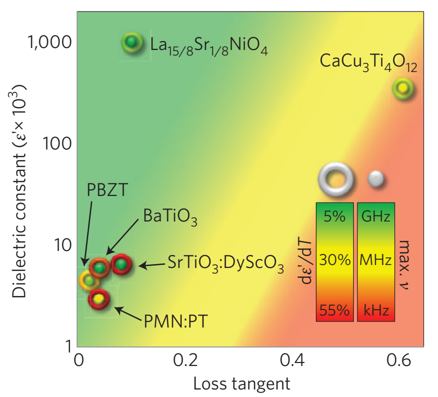

Figure 1 | Comparison of several compounds including CDCs regarding their suitability as capacitors: CDC materials $La_{15/8}Sr_{1/8}NiO_4$ (ref. 12) and $CaCu_3Ti_4O_{12}$ (refs 4,6), ferroelectrics $BaTiO_3$ (ref. 14) and barium-doped lead zirconate titanate (PBZT)[13], ferroelectric $SrTiO_3$:$DyScO_3$ multilayers[16], and the so-called relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN:PT)[15]. Four materials parameters are compared: dielectric constant and loss tangent at frequencies of 1 kHz, capacitance variation between −30°C and 65°C (outer ring, colour coded) and upper frequency limit of the applied a.c. voltage (inner circle, colour coded).

Materials science aspects

The most relevant materials parameters of capacitors are the dielectric constant, the loss tangent, the temperature stability of the dielectric constant and the maximum frequency of a.c. voltage that can be applied. The dielectric constant should be large to enhance the capacitance of the MLCC and to increase the charge-storage efficiency, which is a prerequisite for further device miniaturization. The loss tangent must be minimized to reduce dissipation of stored energy into heat and to avoid draining of the stored charge.

The high dielectric constant in the range 10^3–10^4 of the currently used BTO arises from the ferroelectric ordering of Ti ions. Unfortunately, this effect is strongly temperature-dependent and thus ferroelectric MLCCs are hampered by the poor temperature stability of their capacitance. Recently, a number of new materials with nearly temperature-independent CDCs have been discovered that have been considered as potentially useful capacitor materials[10]. A prominent example is $CaCu_3Ti_4O_{12}$ (CCTO; ref. 4) with a temperature-independent dielectric constant of 10^4 near room temperature. Other transition-metal oxides with CDCs near room temperature[6], including $La_{2-x}Sr_xNiO_4$ (x = 1/3 or 1/8)[11,12] are also viable.

The properties of several conventional as well as new CDC materials[12–16] are compared in Fig. 1. As the plot shows, the properties of CCTO generally surpass those of the more conventional materials but its high loss severely hampers applications. In contrast, from a materials science perspective alone, $La_{15/8}Sr_{1/8}NiO_4$ (LSNO) is superior in all respects. In the following, we focus on LSNO, CCTO and BTO as a test study to illustrate the approach and discuss them from the viewpoints of resource strategy and management.

Resource strategy

The resource strategy assesses raw materials based on various economical, ecological, socio-cultural and political indicators accounting for the whole life period of a specific technology[17,18]. First, data is collected on deposits, reserves and annual production. Industrial manufacturing of BTO, CCTO or LSNO requires specific raw materials containing barium, titanium, lanthanum and so on, typically in the form of oxides or salts such as carbonates, nitrates or sulphates. For example, barium is commonly extracted from barite, $BaSO_4$. Lanthanum is mainly extracted from monazite and bastnäsite. In Fig. 2, worldwide allocations of the most important barium and titanium mineral deposits are shown, and the proportions of global reserves and annual production are compared for the most prominent nations holding many of the raw materials[19]. For various elements, the supply depends critically on only a few countries.

The supply risk is estimated by considering the current reserves-to-production ratio (RPR; expressed in years), the market concentration of deposits, reserves and production sites, the political stability of the supplying nations, and the ecological impact of extracting ores[17]. Factors such as additional demand arising from emerging technologies as well as the potential for recycling are also considered. In most cases, these criteria can be quantified by indices[17] such as the Herfindahl–Hirschmann index[20,21] that defines market concentration by the sum of the squared fractional shares of the largest producers.

For the elements considered here, strontium is the most critical in the short-term due to its rather low RPR of about 16 years (see Fig. 2 for reserves and annual production). In light of the present discussions regarding shortages of rare earths, lanthanum currently has an astonishingly high RPR of ~850 years. However, owing to growing demand this value has decreased dramatically over the past 15 years. If, in addition, the market-concentration criterion is taken into account, rare earths can also be considered critical. Based on a resource-strategy using all the criteria mentioned above, CCTO is the best among the considered materials for our test case.

Resource management

The third filter assesses the implementation of alternative capacitor materials from a producer's point of view. It uses the discounted-cash-flow method involving the calculation of the net present value (NPV)[22], which is the sum of cash

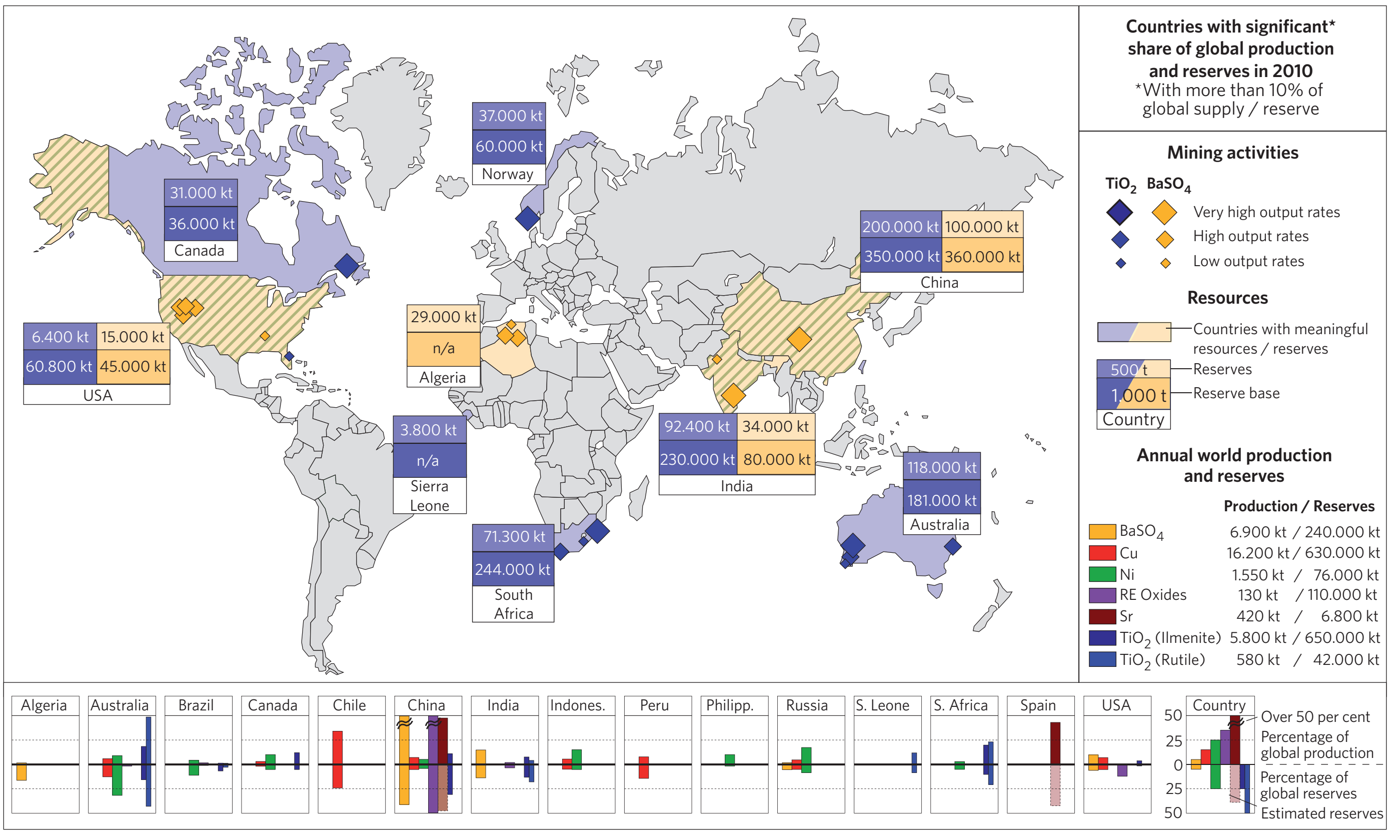

Figure 2 | World map of mineral deposits and reserves of TiO_2 and $BaSO_4$. Upper numbers in the boxes denote the currently and economically available reserves. The lower numbers include reserves that have reasonable potential for becoming economically available in the future. For various other raw materials, the lower charts provide information on the proportions of global reserves and annual productions for the most prominent nations[19].

flows for a company resulting from the implementation of a new technique/product, in this example, for a 10-year period. It includes initial investments (such as machinery), future cash inflows (revenues) and outflows (expenses such as operational costs). Future cash is of less value than present cash. Thus, the present value R_p of any future cash flow R_t (t: year) has to be adjusted with a discount rate i, leading to $R_p = R_t / (1+i)^t$.

As an approximate discount rate, the typical weighted average cost of capital (wacc) of a company within the electronic semiconductor industry (11.5%) can be used[23]. The wacc is the rate of return expected by different investors, weighted by their proportion of the total capital. In our example, for practical reasons we assume the production procedure is cost-equal for the considered materials. Then the relevant parameters are the prices and quantities of the respective materials. When comparing economic merits of alternative materials, the difference of the investment alternatives' net present value can be taken as a decision criterion. For the examples of BTO and LSNO this is expressed by:

$$\Delta E_{\mathrm{NPV}} = \sum_{t=t_0}^{t_n} \frac{\mathrm{price}_{\mathrm{BTO}}(t_0) \times \mathrm{amount}_{\mathrm{BTO}}(t_0)}{(1+\mathrm{wacc})^t} - \sum_{t=t_0}^{t_n} \frac{\mathrm{price}_{\mathrm{LSNO}}(t_0) \times \mathrm{amount}_{\mathrm{LSNO}}(t_0)}{(1+\mathrm{wacc})^t}$$

In the case of equal amounts per MLCC, the less expensive material would be preferred.

Next, a risk analysis of the investment alternatives is performed. This involves a statistical time series analysis of the past price developments of raw materials, including a determination of expected value and standard deviation, which enables an extrapolation to estimate future cash outflows[24]. These are used as input parameters for the discounted-cash-flow method. Finally, some additional value can be assigned to the ability of a company to react to future developments, for example by switching to an alternative material if the price of a currently inexpensive material increases[23].

For the present example, assuming a replacement of one quarter of the current annual production of MLCCs, we arrive at ΔE_{NPV} = -\$1.1 billion for CCTO and +\$0.6 billion for LSNO (both compared to BTO). From an economic viewpoint, LSNO is clearly preferable, even if we neglect its better materials properties, which should lead to even higher NPVs. Keeping the option to reconvert production to the less risky, but more expensive BTO is worth \$29 million. A further interesting outcome of our analysis is that the risk of fluctuations in raw material costs (barite for example) is negligible because they only marginally influence the overall price.

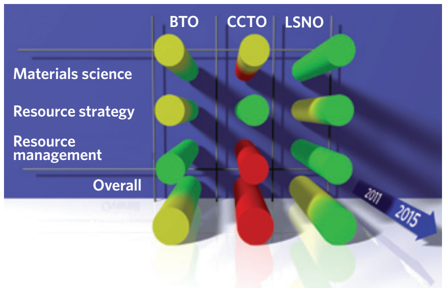

Figure 3 | Time-development prospects of three CDC materials from the perspectives of materials science, resource strategy and resource management, including an extrapolation up to the year 2015. In the bottom row, the overall suitabilities are indicated. The different colours denote the merits of the respective material; green, yellow and red signifying high, medium and poor suitability, respectively.

Conclusions

The suitability of the considered materials for capacitor production is presented in Fig. 3 from the viewpoint of the three disciplines, including an extrapolation to 2015. The time development of the materials science criteria mirrors the fact that sticking to BTO will make it difficult to follow Moore's law of continuous device miniaturization. This will lead to a slight degradation of the overall suitability for this material in the future (bottom row in Fig. 3). CCTO is critically hampered by its high loss; however future developments may reduce this value. Irrespective of this, the overall performance of CCTO is poor, mainly due to its negative ΔE_{NPV}. For LSNO the rather low RPR of strontium represents no major problem on the timescale of Fig. 3. For the rare-earth lanthanum the current RPR is not yet critical. Only a complete delivery failure would represent a major problem and thus, due to the high market concentration, LSNO has to be judged potentially critical in the future. However, if the current rare-earths situation can be resolved by the opening of new mines[25], LSNO will clearly be competitive among the materials considered in this case study.

The example presented here demonstrates the interdisciplinary approach required to assess the suitability of new materials for a given application. Its importance is exemplified by the conclusion that the highly rated CCTO, whose investigation was mostly motivated by its application prospects, is far less suitable as new capacitor material than commonly thought, if applying the three filters introduced in this Commentary. We are convinced that this approach can serve as a useful guide for future research aiming at the development of novel functional materials for commercially viable applications. ❐

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References

1. *Nature Mater.* **10,** 157 (2011).
2. Nakamura, E. & Sato, K. *Nature Mater.* **10**, 158-161 (2011).
3. Service, R. F. *Science* **327**, 1596-1597 (2010).
4. Homes, C. C., Vogt, T., Shapiro, S. M., Wakimoto, S. & Ramirez, A. P. *Science* **293**, 673-676 (2001).
5. Sinclair, D. C., Adams, T. B., Morrison, F. D. & West, A. R. *Appl. Phys. Lett.* **80**, 2153-2155 (2002).
6. Lunkenheimer, P. *et al. Eur. Phys. J. Special Topics* **180**, 61-89 (2010).
7. Haertling, G. H. *J. Am. Ceram. Soc.* **82**, 797-818 (1999).
8. Pan, M-J. & Randall, C. A. *IEEE Electr. Insul. Mag.* **26**, 44-50 (2010).
9. Kishi, H., Mizuno, Y. & Chazono, H. *Jpn. J. Appl. Phys.* **42**, 1-15 (2003).
10. Adams, T. B., Sinclair, D. C. & West, A. R. *Adv. Mater.* **14**, 1321-1323 (2002).
11. Park, T. *et al. Phys. Rev. Lett.* **94**, 017002 (2005).
12. Krohns, S. *et al. Appl. Phys. Lett.* **94**, 122903 (2009).
13. Kanai, H., Furukawa, O., Abe, H. & Yamashita, Y. *J. Am. Ceram. Soc.* **77**, 2620-2624 (1994).
14. Hirose, N. & West, A. R. *J. Am. Ceram. Soc.* **79**, 1633-1641 (1996).
15. Choi, S. W., Shrout, R. T. R., Jang, S. J. & Bhalla, A. S. *Ferroelectrics* **100**, 29-38 (1989).
16. Haeni, J. H. *et al. Nature* **430**, 758-761 (2004).
17. Ad-hoc Working Group on Defining Critical Raw Materials *Critical raw materials for the EU* (European Commission, June 2010).
18. Reller, A. *et al. Gaia* **18**, 127-135 (2009).
19. *United Geological Survey (USGS): Mineral Commodity Summaries 1995-2011* (US Department of the Interior, 2011).
20. Herfindahl, O. C. *Concentration in the US Steel Industry* PhD thesis, Columbia Univ. (1950).
21. Hirschmann, A. O. *National Power and the Structure of Foreign Trade* (Univ. California Press,1945).
22. Huang, C. & Litzenberger, R. *Foundations for Financial Economics* (Pearson, 1988).
23. Copeland, T. E. *et al. Financial Theory and Corporate Policy* (Addison Wesley, 2006).
24. Hamilton, J. D. *Time Series Analysis* (Princeton Univ. Press, 1994).
25. Kato, Y. *et al. Nature Geosci.* **4,** 535-539 (2011).

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