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DECISION
of 25 July 2003

Case Number: T 0671/98 - 3.3.5

Application Number: 92112158.8

Publication Number: 0523696

IPC: C04B 35/50

Language of the proceedings: EN

Title of invention:

Mixed ionic conductors and the preparation thereof

Applicant:

MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.

Opponent:

-

Headword:

Ionic conductors/MATSUSHITA

Relevant legal provisions:

EPC Art. 84, 56, 111(1)

Keyword:

"Clarity objection - overcome"

"Novelty - yes"

"Remittal to first instance for further prosecution"

Decisions cited:

-

Catchword:

-



Case Number: T 0671/98 - 3.3.5

D E C I S I O N
of the Technical Board of Appeal 3.3.5
of 25 July 2003

Appellant:
(Applicant)

MATSUSHITA ELECTRIC INDUSTRIAL CO., LTD.
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Representative:

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Decision under appeal:

Decision of the Examining Division of the
European Patent Office posted 21 January 1998
refusing European application No. 92112158.8
pursuant to Article 97(1) EPC.

Composition of the Board:

Chairman: R. K. Spangenberg
Members: B. P. Czech
M. B. Günzel

Summary of Facts and Submissions

- I. The appeal is from the decision of the examining division to refuse the European patent application No. 92 112 158.8.
- II. The contested decision was taken on the basis of a set of claims amended during the substantive examination of the application. The amended claims 1, 3 and 4 had the following wording:

"1. A mixed ionic conductor which comprises an ion conductive oxide represented by the formula:



wherein M is a rare earth element selected from the group consisting of Y, Nd, Sm, Gd, Tb, Dy, Ho and Er and wherein α is defined by $1.5 > \alpha > 0$ and x is defined by

0.25 > x > 0.17 when M is Y,
0.22 > x > 0.12 when M is Nd,
0.21 > x > 0.13 when M is Sm,
0.23 > x > 0.16 when M is Gd,
0.25 > x > 0.17 when M is Tb,
0.25 > x > 0.17 when M is Dy,
0.26 > x > 0.18 when M is Ho, and
0.26 > x > 0.17 when M is Er;

and wherein said oxide exhibits at least proton conductivity and comprises a distorted orthorhombic perovskite crystal structure having crystal constants a, b and c defined by $a > b > c$, wherein the lattice constant ratio b/c is greater than 1.010 and exhibits a peak value resulting from the adjustment of the amount of M."

"3. The ionic conductor of claim 1, wherein said oxide is in a form selected from the group consisting of a perovskite system, a sintered system and a polycrystal system represented by the formula $BaCe_{1-x}Gd_xO_{3-\alpha}$, wherein x is defined by $0.23 > x > 0.16$ and wherein the oxide exhibits proton conductivity and oxide cation conductivity at a temperature ranging from 400 to 1000°C."

"4. The ionic conductor of claim 3, which comprises an oxide represented by the formula $BaCe_{1-x}Gd_xO_{3-\alpha}$, wherein $x = 0.2$."

III. During the examination of the case, the examining division considered the following prior art documents:

D1: Journal of the Electrochemical Society, 135, February 1988, No. 2, pages 529 to 533; H. Iwahara et al., "Proton Conduction in Sintered Oxides Based on $BaCeO_3$ ".

D2: Solid State Ionics, vol. 46, May/June 1991, No. 1/2, pages 111 to 115; R.C.T. Slade et al., "Systematic examination of hydrogen ion conduction in rare-earth doped barium cerate ceramics"

D3: Solid State Ionics, vol. 35, July/August 1989, No. 1/2, pages 179 to 188; N. Bonanos et al., "Ionic conductivity of gadolinium-doped barium cerate perovskites"

D4: GB-A-2 206 571

The following prior art document was only mentioned in the search report:

D5: Journal of the American Ceramic Society, 64, August 1981, No. 8, pages 479 to 485; I. Riess et al., "Density and Ionic Conductivity of sintered $(\text{CeO}_2)_{0.82}(\text{GdO}_{1.5})_{0.18}$ "

The examining division also considered

D6: a declaration by Noboru Taniguchi, and

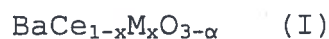
D7: a copy of a letter to the USPTO dated 13 December 1993.

- IV. The examining division held that the subject-matter of the claims was unclear since claim 3 contained subject-matter beyond the scope of claim 1, on which the former depended. More particularly, by virtue of part of the elevated temperatures mentioned therein, claim 3 was considered to refer to products having a cubic crystal structure, in contrast to the orthorhombic crystal structure required by claim 1. Moreover, the examining division argued that the compounds of claims 3 and 4 lacked novelty at temperatures of from 800 to 1000°C since D3 also disclosed cubic BaCeO_3 doped with 0.20 moles Gd per unit formula.
- V. With its statement of the grounds of appeal, the appellant (applicant) submitted an amended set of claims and addressed the objections that had led to the refusal of the application.

VI. In a communication dated 18 July 2002, the board indicated that it did not intend to maintain the clarity objection of the examining division, but raised several other such objections against the claims on file, *inter alia* against the use of the expression "oxide cation". Concerning the novelty of the claimed subject-matter over D3 and D4, it *inter alia* pointed out that it remained to be seen whether D3/D4 clearly and unambiguously disclosed oxides with a b/c ratio > 1.010. The board also indicated that it would probably remit the case to the first instance.

VII. In reply to this communication, the appellant filed a further amended set of claims 1 to 6, claims 1 and 3 thereof having the following wording:

"1. An ionic conductor mainly consisting of an ion conductive oxide represented by the formula:



wherein M is a rare earth element selected from the group consisting of Y, Nd, Sm, Gd, Tb, Dy, Ho and Er and wherein α is defined by $1.5 > \alpha > 0$ and x is defined by

- 0.25 > x > 0.17 when M is Y,
- 0.22 > x > 0.12 when M is Nd,
- 0.21 > x > 0.13 when M is Sm,
- 0.23 > x > 0.16 when M is Gd,
- 0.25 > x > 0.17 when M is Tb,
- 0.25 > x > 0.17 when M is Dy,
- 0.26 > x > 0.18 when M is Ho, and
- 0.26 > x > 0.17 when M is Er;

and wherein said oxide exhibits proton conductivity and oxide cation conductivity at an elevated temperature and comprises an orthorhombic perovskite crystal structure having crystal constants a , b and c defined by $a > b > c$, wherein the lattice constant ratio b/c is greater than 1.010".

"3. The ionic conductor of claim 1, wherein said oxide is in the form of a sintered and polycrystal system represented by the formula $BaCe_{1-x}Gd_xO_{3-\alpha}$, wherein x is defined by $0.23 > x > 0.16$ and wherein the elevated temperature is in the range of from 600 to 1000°C."

The appellant also filed copies of the following documents, which are mentioned in D7:

D8: Solid State Ionics, vol. 53 to 56, 1992, pages 998 to 1003; Noboru Taniguchi et al., "Proton conductive properties of gadolinium-doped barium cerates at high temperatures", and

D9: 60th Electrochemical Spring Meeting on April 1, 1993; Reference 2J17; N. Taniguchi et al., "Stability of $BaCe_{0.8}Gd_{0.2}O_{3-\alpha}$ Electrolyte for Fuel Cell" (document in Japanese)

VIII. The essential arguments of the appellant can be summarised as follows:

It submitted that the "oxide cation" designated the negatively charged O^{2-} ion. It argued that it was evident that the crystal structure as stated in claim 1 related to normal conditions, i.e. to room temperature, where the conductor was orthorhombic. Referring to the

contents of D6, where the differences between the processes used for the preparation of the ionic conductors according to the present application and D3/D4, respectively, are emphasised, it argued that the conductor material claimed had a crystal structure and properties different from the ones of the materials disclosed in D3 and D4, despite their stoichiometrically identical chemical composition.

- IX. The appellant requested that the contested decision be set aside and that a patent be granted on the basis of the claims 1 to 6 filed with its letter dated 28 January 2003.

Reasons for the Decision

The only points at issue in the present appeal are the clarity of the claims and the novelty of their subject-matter.

1. *Clarity*

- 1.1 The application in suit, the applicant's own declaration, as well as the prior art, all refer to the "O²⁻ ion" in connection with the "oxide ion" conductivity of oxides, see the present application as filed, page 6, line 19, D6, page 8, line 9 and figures 3(a)(b)(c), D2, page 115, the half-sentence bridging the two columns, and D5, page 479, line 3 of the abstract. The board is also convinced that generally, a person skilled in the art would consider the expression "oxide ion" to stand for the "O²⁻ ion",

which is an ion bearing negative charges, ie an anion and not a cation.

1.2 The board thus holds that the expression "oxide cation" as used throughout the application as filed as well as in present claim 1 is obviously erroneous in the sense of Rule 88 EPC and should in fact read "oxide ion" or "oxide anion". Hence, for the purpose of the present decision, the board considers this expression to stand for the expression "oxide ion" in the generally recognised sense, ie for the O^{2-} anion. Nevertheless the board considers it necessary to amend said expression upon further prosecution of the case.

1.3 Present claim 1 specifies that the oxide making up the claimed conductor has an orthorhombic perovskite crystal structure as defined by the conditions " $a > b > c$ " and " b/c greater than 0.010".

1.3.1 Since the measurements necessary for characterising a crystalline material in terms of its crystal constants a , b and c are not necessarily carried out at elevated temperatures, the board can accept that, in the absence of any indications to the contrary, the description of a crystal structure as given in claim 1 and, by means of the back-reference to claim 1, in claim 3, has to be understood as relating to the crystal structure at normal conditions, ie at ambient temperature. Hence, it is clear that the doped oxides referred to in claims 1 and 3 are defined as being of orthorhombic crystal structure at ambient temperature.

1.3.2 According to the claims, the doped oxides must exhibit the inherent property of being both proton and oxide ion conductive at elevated temperatures. Even if claim 3 was specifically directed to an oxide **at** an elevated temperature, which is not the case, this oxide would still need to have, at ambient temperature, the crystal structure indicated in claim 1. Whether the orthorhombic crystal structure turns into a cubic one at specific elevated temperatures, as alleged by the applicant (see eg D7, page 3, right-hand column, second paragraph) subsequently to the filing of the application, and whether a particular type of conductivity is actually due to this change in structure, is thus not relevant with respect to the clarity of present claims 1 and 3.

1.3.3 Hence, the board is of the opinion that claim 3 does not contain subject-matter beyond the scope of claim 1, and that the claims are not, therefore, unclear.

2. *Novelty over D3 and D4*

2.1 Documents D3 and D4 are both by the same authors and relate to the preparation of gadolinium-doped barium cerate. D3 is the more recent document, as can be seen from comparing the filing date of D4 (July 1987) with the date at which the article D3 was received by the publisher (August 1988). D3 refers to D4 concerning preparation details (see D3, page 180, right-hand column, the end of the second paragraph).

2.1.1 D3 and D4 apparently describe a same set of experiments for the preparation of oxides of perovskite structure and of formula $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-x/2}$. Both documents explicitly

mention oxides prepared by reacting the starting compounds of Ba, Ce and Gd in the amounts necessary for obtaining oxides wherein x is 0.05, 0.10, 0.15, 0.20 or 0.30. Among these specific oxides, the one wherein x is 0.2 can possibly fall under the scope of present claim 1 ($0.16 < x < 0.23$ for Gd). Moreover, D4 discloses a preferred range with x being from 0.01 to 30 atom fraction, and preferably from 0.10 to 0.20 atom fraction. See D3, pages 180 to 182, sections 2.1, 2.2, 3.1, page 183 to 184, section 3.2.2, table 2, and figures 3 and 4, and D4, page 3, line 1 to page 8, line 13, and page 11, table 5.

2.1.2 From the quoted passages it can be gathered that the preparation method according to both D3 and D4 involves grinding a mixture of BaCO_3 , CeO_2 and Gd_2O_3 , heating it in air to 1100°C , grinding the powders so formed and heating them in air at about 1400°C for an extended period. A solid electrolyte is then formed from the material obtained by re-grinding and sieving to below $40\ \mu\text{m}$, pressing the powders obtained to pellets with glycol as binder, and sintering for 10 hours at 1475°C in an atmosphere of 5% hydrogen in nitrogen.

2.1.3 According to the general description of the preparation method as given in D4, the powders obtained after the second heating stage at 1400°C show a pure BaCeO_3 phase according to X-ray powder diffraction measurements (see page 6, lines 13 to 15). According to D3, the powders obtained at this stage are qualified as homogeneous (see page 181, left-hand column, lines 4 to 6). However, the board notes that according to D3, ie the more recent document, the analysis of X-ray powder diffraction patterns shows that the preparation method

therein disclosed leads to polyphasic products when the respective amounts of starting materials are such as to lead to x values greater than 0.15, and that an additional BaGd_2O_4 phase appears for Gd amounts corresponding to $0.20 \leq x \leq 0.40$. See in particular page 182, left-hand column, second paragraph, last sentence, and page 184, Figure 3, where the dashed line starting at $x = 0.15$ corresponds to polyphasic material.

2.1.4 As far as they concern the structure of the materials prepared, the experimental data reported in D3 (see page 182, section 3.1) and D4 (see pages 7 to 8, section 2.1), such as d -spacings and the corresponding peak heights concern the product wherein x is 0.1. According to D4, the same d -spacings are found for all the prepared oxides, in varying degrees of sharpness. According to D3, the line splitting appears to be indicative of a cubic unit cell, the widths of the peaks increasing with increasing values of x up to $x = 0.15$, and above this value the BaCeO_3 -related peaks broadening further. The b/c ratio of the crystalline oxides is not expressly indicated in D3 and D4.

2.2 As repeatedly emphasised by the appellant, the preparation method described in D3 and D4 differs from the one used according to the application in suit, leading to products having a different crystal structure. The respective solid state reaction processes differ *inter alia* by virtue of the barium starting material used, the temperatures applied and the particle size distribution before the final sintering, see eg D6, page 10, table 2, first row. The application is also silent about the formation of a polyphasic product in the case of $x = 0.2$. In the

absence of any evidence that the crystal structure of the products does not depend on the method of preparation, the board accepts the appellant's submission that the said differences between the preparation processes may lead to materials having different crystal structures and, consequently, different physical properties.

2.2.1 In D6, page 1, the appellant states that irrespective of whether the experimental d-spacing data indicated in table 1 of D4 for a compound wherein $x = 0.1$ are considered to correspond to ("indexed as") an orthorhombic or to a cubic crystal structure, the lattice constant ratio b/c as computed with these data is never greater than 1,010. The appellant also pointed out the finding of D4 (see page 7, lines 18 to 20 and 22 to 24), according to which the d-spacings do not substantially vary with the Gd amount (see D6, page 2, lines 13 to 14). Moreover, according to page 4, lines 15 to 20 of D6, samples obtained by reproducing the preparation method of D4, showed that the products obtained had a b/c value smaller than 1.009, even if Gd was added in an amount corresponding to $x = 0.2$. Although it is not clear on which experimental facts these assertions are based, the board has no evidence to challenge the results submitted.

2.2.2 Moreover, the comparative experimental data presented in table 1 of D6, first and fourth columns, show that even in the case of $x = 0.1$, the relative peak heights of some of the d-spacing values indicated differ substantially from each other, depending on whether the preparation method of D3 or the one described in the application in suit was used. It can also be gathered

from this table that for products prepared according to the applicant's method, the d-spacing values vary depending on the amount of Gd.

- 2.3 In the absence of evidence pointing to the contrary, the board accepts the findings of the appellant submitted by means of the declaration D6. Consequently, based on the available experimental data, it cannot be assumed that a value of b/c greater than 1.010 was implicitly disclosed by those products referred to in D3 and D4 which were obtained by using an amount of Gd corresponding to $x = 0.2$.

Moreover, the board considers that the formation of a further phase at values of x greater than 0.15 as addressed in D3 implies that the method used does not lead to the full incorporation of the corresponding amount of Gd into the barium cerate. This raises doubts concerning the validity of the formula $BaCe_{1-x}Gd_xO_{3-x/2}$ for describing the products obtained according to D3 or D4 using such amounts of Gd.

- 2.4 Since D3 and D4 do not clearly and unambiguously disclose an orthorhombic Gd-doped barium cerate perovskite of formula $BaCe_{1-x}Gd_xO_{3-\alpha}$ which at least implicitly meets the compositional **and** structural definition given in present claim 1, the subject-matter of present claim 1, and consequently of present claims 2 to 6 dependent thereon, is novel in view of the disclosures of documents D3 and D4.

3. The board is also convinced that the subject-matter of the present claims is novel over the other prior art documents cited in the search report. More particularly,

D1 and D2, although relating to rare-earth doped oxides of formula $BaCe_{1-x}M_xO_{3-\alpha}$, do not disclose x-values greater than 0.1. D5 relates to Gd-doped CeO_2 but not to doped $BaCeO_3$.

4. The objections that led to the refusal of the application were thus overcome by arguments and amendments. However, considering the nature of some of the other objections raised during the substantive examination, as well as the diverging assessments of the available data concerning the types of conductivities occurring in the products according to the application and the prior art, respectively, the board considers it appropriate to remit the case to the first instance for its further prosecution pursuant to Article 111(1) EPC.

Order

For these reasons it is decided that:

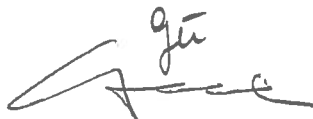
1. The decision under appeal is set aside.
2. The case is remitted to the first instance for further prosecution.

The Registrar:

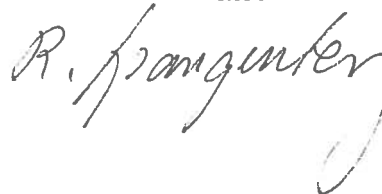


U. Bultmann

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The Chairman:



R. Spangenberg