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(54) **MAGNETOCALORIC MATERIAL AND PROCESS FOR PRODUCING IT**

MAGNETOKALORISCHES MATERIAL UND VERFAHREN UM ES HERZUSTELLEN

MATÉRIAU MAGNÉTOCALORIQUE ET PROCEDE DE SA PRODUCTION

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Description

[0001] The invention relates to polycrystalline magnetocaloric materials, to processes for their production and to their use in coolers, heat exchangers or generators, in particular in refrigerators.

[0002] Thermomagnetic materials, also referred to as magnetocaloric materials, can be used for cooling, for example in refrigerators or air conditioning units, in heat pumps or for direct generation of power from heat without intermediate connection of a conversion to mechanical energy.

[0003] Such materials are known in principle and are described, for example, in WO 2004/068512. Magnetic cooling techniques are based on the magnetocaloric effect (MCE) and may constitute an alternative to the known vapor circulation cooling methods. In a material which exhibits a magnetocaloric effect, the alignment of randomly aligned magnetic moments by an external magnetic field leads to heating of the material. This heat can be removed from the MCE material to the surrounding atmosphere by a heat transfer. When the magnetic field is then switched off or removed, the magnetic moments revert back to a random arrangement, which leads to cooling of the material below ambient temperature. This effect can be exploited for cooling purposes, but also for heating. Typically, a heat transfer medium such as water is used for heat removal from the magnetocaloric material.

[0004] The materials used in thermomagnetic generators are likewise based on the magnetocaloric effect. In a material which exhibits a magnetocaloric effect, a small change in temperature can lead to a big change in magnetization. Magnetized by an external magnetic field, when the material is heated, a big change in the induction flow through a coil and thus an electromotive force are generated. Cooling the material below the critical temperature leads again to the occurrence of an electromotive force. This effect can be exploited for conversion of heat to electrical energy.

[0005] The magnetocaloric generation of electrical energy is associated with magnetic heating and cooling. At the time of first conception, the process for energy generation was described as pyromagnetic energy generation. Compared to devices of the Peltier or Seebeck type, these magnetocaloric devices can have a significantly higher energy efficiency.

[0006] The research into this physical phenomenon began in the late 19th century, when two scientists, Tesla and Edison, filed a patent on pyromagnetic generators. In 1984, Kirol described numerous possible applications and conducted thermodynamic analyses thereof. At that time, gadolinium was considered to be a potential material for applications close to room temperature.

[0007] A pyromagnetoelectric generator is described, for example, by N. Tesla in US 428,057. It is stated that the magnetic properties of iron or other magnetic substances can be destroyed partially or entirely or can disappear as a result of heating to a particular temperature. In the course of cooling, the magnetic properties are re-established and return to the starting state. This effect can be exploited to generate electrical power. When an electrical conductor is exposed to a varying magnetic field, the changes in the magnetic field lead to the induction of an electrical current in the conductor. When, for example, the magnetic material is surrounded by a coil and is then heated in a permanent magnetic field and then cooled, an electrical current is induced in the coil in the course of heating and cooling in each case. This allows thermal energy to be converted to electrical energy, without an intermediate conversion to mechanical work. In the process described by Tesla, iron, as the magnetic substance, is heated by means of an oven or a closed fireplace and then cooled again.

[0008] For the thermomagnetic or magnetocaloric applications, the material should permit efficient heat exchange in order to be able to achieve high efficiencies. Both in the course of cooling and in the course of power generation, the thermomagnetic material is used in a heat exchanger.

[0009] US 2006/0117758 and WO 2009/133049 disclose magnetocaloric materials of the general formula MnFe($P_wGe_xSi_z$). Preferred materials are $MnFeP_{0.45-0.70}Ge_{0.55-0.30}$ or $MnFeP_{0.5-0.70}(Si/Ge)_{0.5-0.30}$. In each case, the example compositions comprise proportions of Ge. These substances still do not have a sufficiently great magnetocaloric effect for all applications.

[0010] EP patent application 10 150 411.6 entitled "Magnetocaloric materials", which was filed on January 11, 2010 and was yet to be published at the priority date of the present application, describes magnetocaloric materials of the general formula

$$(Mn_xFe_{1-x})_{2+z}P_{1-y}Si_y$$

where

$$0.55 \leq x < 1$$

$$0.4 \leq y \leq 0.8$$

$$-0.1 \leq z \leq 0.1.$$

[0011] Can Thanh et al. JOURNAL OF APPLIED PHYSICS 103, 07B318 (2008) describe structure, magnetism, and magnetocaloric properties of certain $MnFeP_{1-x}Si_x$ compounds.

[0012] DINH THI C PRO AM THANH: "Magnetocalorics and Magnetism in MnFe (P,Si,Ge) materials" (ph. D. thesis, Universiteit van Amsterdam, NL, 21 April 2009, ISBN: 978-90-5776-188-1) describes MnFe(P,Si,Ge) explores MnFe (P,Si,Ge) materials for magnetic cooling applications, especially certain $MnFeP_{1-x}Si_x$ compounds.

[0013] It is an object of the present invention to provide magnetocaloric materials having a large magnetocaloric effect, low thermal hysteresis and a working temperature in the range from 0 to 150°C.

[0014] The object is achieved in accordance with the invention by the magnetocaloric material defined by claim 1.

[0015] Preferably, $0.25 \leq x \leq 0.35$. x preferably has a minimum value of 0.28, more preferably of 0.3. The maximum value of x is preferably 0.34, in particular 0.33. More preferably $0.28 \leq x \leq 0.34$, in particular $0.30 \leq x \leq 0.33$.

[0016] y preferably has a minimum value of 0.4. The maximum value of y is preferably 0.6, more preferably 0.44. More preferably $0.4 \leq y \leq 0.6$, in particular $0.4 \leq y \leq 0.44$.

[0017] z may differ from 0 by small values. Preferably $-0.05 \leq z \leq 0.05$, in particular $-0.02 \leq z \leq 0.02$, especially $z = 0$.

[0018] The inventive magnetocaloric materials preferably have a hexagonal structure of the Fe_2P type.

[0019] It has been found in accordance with the invention that especially an Mn/Fe element ratio of less than 0.54, especially in the range from 0.5/1.5 to 0.7/1.3, leads to magnetocaloric materials with stabilized phase formation and low thermal hysteresis. The inventive materials allow a working temperature in application in the range from 0°C to + 150°C.

[0020] The magnetocaloric effect of the inventive materials is comparable to the magnetocaloric effect of what are known as giant magnetocaloric materials such as $MnFeP_xAs_{1-x}$, $Gd_5(Si, Ge)_4$ or $La(Fe, Si)_{13}$.

[0021] The thermal hysteresis, determined in a magnetic field of 1 T with a sweep rate of 1°C/min, is preferably < 5°C, more preferably < 2°C, due to the balanced Mn/Fe and P Si ratios.

[0022] The inventive materials additionally have the advantage that they are formed from elements which are available in large amounts and are generally classified as nontoxic.

[0023] The thermomagnetic materials used in accordance with the invention can be produced in any suitable manner.

[0024] The inventive magnetocaloric materials can be produced by the process of claim 6.

[0025] The thermomagnetic materials are produced, for example, by solid phase reaction of the starting elements or starting alloys for the material in a ball mill, subsequent pressing, sintering and heat treatment under inert gas atmosphere and subsequent cooling, for example slow cooling, to room temperature. Such a process is described, for example, in J. Appl. Phys. 99, 2006, 08Q107.

[0026] For example, suitable amounts of Mn, Fe, P and Si in element form or in the form of preliminary alloys such as Mn_2P or Fe_2P can be ground in a ball mill. The powders are pressed and sintered at temperatures in the range from 900 to 1300°C, preferably of about 1100°C, for a suitable time, preferably 1 to 5 hours, especially about 2 hours, and then heat treated at temperatures in the range from 700 to 1000°C, preferably about 850°C, for suitable periods, for example 1 to 100 hours, more preferably 10 to 30 hours, especially about 20 hours, under a protective gas atmosphere.

[0027] Alternatively, the element powders or preliminary alloy powders can be melted together in an induction oven. It is then possible in turn to perform a heat treatment as specified above.

[0028] Processing via melt spinning is also possible. This makes possible a more homogeneous element distribution which leads to an improved magnetocaloric effect; cf. Rare Metals, Vol. 25, October 2006, pages 544 to 549. In the process described there, the starting elements are first induction-melted in an argon gas atmosphere and then sprayed in the molten state through a nozzle onto a rotating copper roller. There follows sintering at 1000°C and slow cooling to room temperature. In addition, reference may be made to WO 2004/068512 and WO 2009/133049 which however do not form part of the present invention.

[0029] Also disclosed is a process for producing the thermomagnetic materials, comprising the following steps:

a) converting chemical elements and/or alloys in a stoichiometry which corresponds to the magnetocaloric material in the solid and/or liquid phase,

b) optionally converting the reaction product from stage a) to a solid,

c) sintering and/or heat treating the solid from stage a) or b),

d) quenching the sintered and/or heat treated solid from stage c) at a cooling rate of at least 100 K/s.

[0030] The thermal hysteresis can be reduced significantly and a large magnetocaloric effect can be achieved when the magnetocaloric materials are not cooled slowing to ambient temperature after the sintering and/or heat treatment, but rather are quenched at a high cooling rate. This cooling rate is at least 100 K/s. The cooling rate is preferably from 100 to 10 000 K/s, more preferably from 200 to 1300 K/s. Especially preferred cooling rates are from 300 to 1000 K/s.

[0031] The quenching can be achieved by any suitable cooling processes, for example by quenching the solid with water or aqueous liquids, for example cooled water or ice/water mixtures. The solids can, for example, be allowed to fall into ice-cooled water. It is also possible to quench the solids with subcooled gases such as liquid nitrogen. Further processes for quenching are known to those skilled in the art. What is advantageous here is controlled and rapid cooling.

[0032] The rest of the production of the magnetocaloric/thermomagnetic materials is less critical, provided that the last step comprises the quenching of the sintered and/or heat treated solid at the inventive cooling rate. The process may be applied to the production of any suitable thermomagnetic materials, as described above.

[0033] In step (a) of the process, the elements and/or alloys which are present in the later thermomagnetic material are converted in a stoichiometry which corresponds to the thermomagnetic material in the solid or liquid phase.

[0034] Preference is given to performing the reaction in stage a) by combined heating of the elements and/or alloys in a closed vessel or in an extruder, or by solid phase reaction in a ball mill. Particular preference is given to performing a solid phase reaction, which is effected especially in a ball mill. Such a reaction is known in principle; cf. the documents cited above. Typically, powders of the individual elements or powders of alloys of two or more of the individual elements which are present in the later thermomagnetic material are mixed in pulverulent form in suitable proportions by weight. If necessary, the mixture can additionally be ground in order to obtain a microcrystalline powder mixture. This powder mixture is preferably heated in a ball mill, which leads to further comminution and also good mixing, and to a solid phase reaction in the powder mixture. Alternatively, the individual elements are mixed as a powder in the selected stoichiometry and then melted.

[0035] The combined heating in a closed vessel allows the fixing of volatile elements and control of the stoichiometry. Specifically in the case of use of phosphorus, this would evaporate easily in an open system.

[0036] The reaction is followed by sintering and/or heat treatment of the solid, for which one or more intermediate steps can be provided. For example, the solid obtained in stage a) can be subjected to shaping before it is sintered and/or heat treated.

[0037] Alternatively, it is possible to send the solid obtained from the ball mill to a melt-spinning process. Melt-spinning processes are known per se and are described, for example, in Rare Metals, Vol. 25, October 2006, pages 544 to 549, and also in WO 2004/068512 and WO 2009/133049, which however do not form part of the present invention.

[0038] In these processes, the composition obtained in stage a) is melted and sprayed onto a rotating cold metal roller. This spraying can be achieved by means of elevated pressure upstream of the spray nozzle or reduced pressure downstream of the spray nozzle. Typically, a rotating copper drum or roller is used, which can additionally optionally be cooled. The copper drum preferably rotates at a surface speed of from 10 to 40 m/s, especially from 20 to 30 m/s. On the copper drum, the liquid composition is cooled at a rate of preferably from 10^2 to 10^7 K/s, more preferably at a rate of at least 10^4 K/s, especially with a rate of from 0.5 to 2 x 10^6 K/s.

[0039] The melt-spinning, like the reaction in stage a) too, can be performed under reduced pressure or under an inert gas atmosphere.

[0040] The melt-spinning achieves a high processing rate, since the subsequent sintering and heat treatment can be shortened. Specifically on the industrial scale, the production of the thermomagnetic materials thus becomes significantly more economically viable. Spray-drying also leads to a high processing rate. Particular preference is given to performing melt spinning.

[0041] Alternatively, in stage b), spray cooling can be carried out, in which a melt of the composition from stage a) is sprayed into a spray tower. The spray tower may, for example, additionally be cooled. In spray towers, cooling rates in the range from 10^3 to 10^5 K/s, especially about 10^4 K/s, are frequently achieved.

[0042] The sintering and/or heat treatment of the solid is effected in stage c) as described above.

[0043] In the case of use of the melt-spinning process, the period for sintering or heat treatment can be shortened significantly, for example to periods of from 5 minutes to 5 hours, preferably from 10 minutes to 1 hour. Compared to the otherwise customary values of 10 hours for sintering and 50 hours for heat treatment, this results in a major time advantage.

The sintering/heat treatment results in partial melting of the particle boundaries, such that the material is compacted further.

[0044] The melting and rapid cooling in stage b) thus allows the duration of stage c) to be reduced considerably. This also allows continuous production of the thermomagnetic materials.

[0045] The inventive magnetocaloric materials can be used in any suitable applications. For example, they are used in coolers, heat exchangers or generators. Particular preference is given to use in refrigerators.

[0046] The invention is illustrated in detail by examples.

Examples

Preparation of the magnetocaloric materials

[0047] 15 g of a mixture of Mn flakes, Si flakes and Fe_2P powder with a nominal stoichiometry of $Mn_{0.6}Fe_{1.4}P_{0.6}Si_{0.4}$ were ground in a planetary ball mill with a BPR (ball to powder weight ratio) of 4 for 10 hours. The powder obtained in the grinding was then pressed into cylinder form and sealed in an ampoule under 200 mbar of argon gas. This was followed by a sintering step at 1100°C for 2 hours and a heat treatment at 850°C for 20 hours. The sample was removed after the furnace had been cooled down.

[0048] Samples with the nominal composition $Mn_{0.66}Fe_{1.34}P_{0.58}Si_{0.42}$, $Mn_{0.62}Fe_{1.38}P_{0.58}Si_{0.42}$ and $Mn_{0.66}Fe_{1.34}P_{0.56}Si_{0.44}$ were prepared in the same way.

Magnetic properties

[0049] The magnetic properties of the samples thus prepared were determined in a Quantum Design MPMSXL SQUID magnetometer.

Figure 1 shows the temperature dependence of the magnetization $M(Am^2kg^{-1})$, determined with a sweep rate of 1 K/min in a magnetic field of 1 T. The temperature dependence between the heating and cooling curves at the transition shows the thermal hysteresis of the first-order magnetic transition for these samples. The value depends on the particular sample, but is always less than 2 K in the samples studied. The significant change in magnetization in the region of about 70 Am^2kg^{-1} as a result of the sharp magnetic transition shows a large magnetocaloric effect.

Figure 2 shows the change in magnetic entropy $-\Delta S_n(J/kg\ K)$ as a function of temperature for these samples. The change in magnetic entropy was derived from the magnetic isotherms, measured at different temperatures close to the transition, using the Maxwell equation. The values obtained for the change in magnetic entropy are comparable to corresponding values for the so-called GMCEs (giant magnetocaloric effect materials).

[0050] The unfilled symbols relate to a field change of 0-1 T. The filled symbols represent a field change for 0-2 T.

Claims

1. A magnetocaloric material of the general formula

$$(Mn_xFe_{1-x})_{2+z}P_{1-y}Si_y$$

where

$$0.20 \leq x \leq 0.40$$

$$0.4 \leq y \leq 0.8$$

$$-0.1 \leq z \leq 0.1.$$

2. The magnetocaloric material according to claim 1 , wherein $0.25 \leq x \leq 0.35$.

3. The magnetocaloric material according to claim 1 or 2, wherein $0.4 \leq y \leq 0.6$.

4. The magnetocaloric material according to any of claims 1 to 3, wherein $-0.05 \leq z \leq 0.05$.

5. The magnetocaloric material according to any of claims 1 to 4, which has a hexagonal structure of the Fe_2P type.

6. A process for producing the magnetocaloric materials according to any of claims 1 to 5 by solid phase conversion

or liquid phase conversion of the starting elements or starting alloys for the material, optionally cooling, then pressing, sintering and heat treating under inert gas atmosphere and subsequently cooling to room temperature, or by melt spinning of a melt of the starting elements or starting alloys.

7. Use of the magnetocaloric materials according to any of claims 1 to 5 coolers, heat exchangers or generators.

8. The use according to claim 7 in refrigerators.

Patentansprüche

1. Magnetokalorische Materialien der allgemeinen Formel

$$(Mn_xFe_{1-x})_{2+z}P_{1-y}Si_y$$

mit der Bedeutung

$$0,20 \leq x \leq 0,40$$

$$0,4 \leq y \leq 0,8$$

$$-0,1 \leq z \leq 0,1.$$

2. Magnetokalorische Materialien nach Anspruch 1, wobei $0,25 \leq x \leq 0,35$ ist.

3. Magnetokalorische Materialien nach Anspruch 1 oder 2, wobei $0,4 \leq y \leq 0,6$ ist.

4. Magnetokalorische Materialien nach einem der Ansprüche 1 bis 3, wobei $-0,05 \leq z \leq 0,05$ ist.

5. Magnetokalorische Materialien nach einem der Ansprüche 1 bis 4, wobei sie eine hexagonale Struktur des Fe_2P-Typs aufweisen.

6. Verfahren zur Herstellung der magnetokalorischen Materialien nach einem der Ansprüche 1 bis 5 durch Festphasenumsetzung oder Flüssigphasenumsetzung der Ausgangselemente oder Ausgangslegierungen für das Material, gegebenenfalls Abkühlen, nachfolgendes Verpressen, Sintern und Tempern unter Inertgasatmosphäre und nachfolgendes Abkühlen auf Raumtemperatur, oder durch Schmelzspinnen einer Schmelze der Ausgangselemente oder Ausgangslegierungen.

7. Verwendung der magnetokalorischen Materialien nach einem der Ansprüche 1 bis 5 in Kühlern, Wärmetauschern oder Generatoren.

8. Verwendung nach Anspruch 7 in Kühlschränken.

Revendications

1. Matériau magnétocalorique de la formule générale

$$(Mn_xFe_{1-x})_{2+z}P_{1-y}Si_y$$

où

$$0,20 \leq x \leq 0,40,$$

$$0,4 \leq y \leq 0,8,$$

$$-0,1 \leq z \leq 0,1.$$

2. Matériau magnétocalorique selon la revendication 1, dans lequel $0,25 \leq x \leq 0,35$.

3. Matériau magnétocalorique selon la revendication 1 ou 2, dans lequel $0,4 \leq y \leq 0,6$.

4. Matériau magnétocalorique selon l'une quelconque des revendications 1 à 3, dans lequel $-0,05 \leq z \leq 0,05$.

5. Matériau magnétocalorique selon l'une quelconque des revendications 1 à 4, qui a une structure hexagonale du type Fe_2P.

6. Procédé de production des matériaux magnétocaloriques selon l'une quelconque des revendications 1 à 5 par conversion en phase solide ou conversion en phase liquide des éléments de départ ou d'alliages de départ pour le matériau, éventuellement refroidissement, puis pressage, frittage et traitement thermique sous atmosphère gazeuse inerte et par la suite refroidissement jusqu'à la température ambiante, ou par filage à chaud d'une masse fondue des éléments de départ ou d'alliages de départ.

7. Utilisation des matériaux magnétocaloriques selon l'une quelconque des revendications 1 à 5 dans des refroidisseurs, des échangeurs de chaleur ou des générateurs.

8. Utilisation selon la revendication 7 dans des réfrigérateurs.

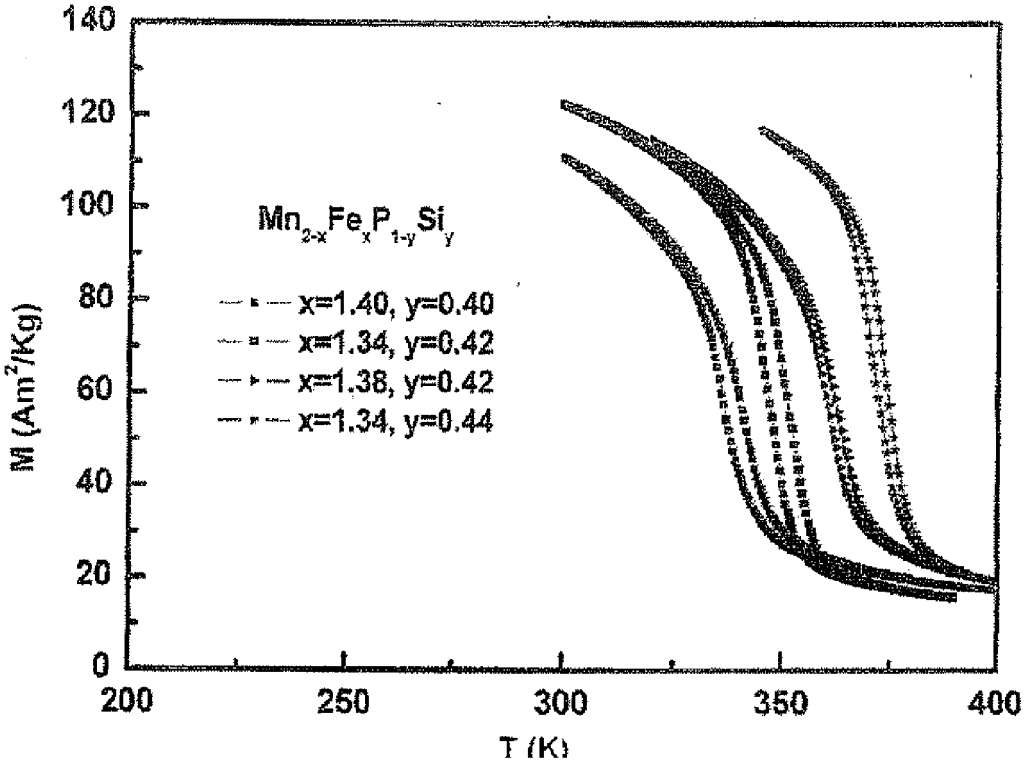

140
120
100
80
60
40
20
0
M (Am²/Kg)
200
250
300
350
400
T (K)
Mn2-xFexP1-ySiy
x=1.40, y=0.40
x=1.34, y=0.42
x=1.38, y=0.42
x=1.34, y=0.44

Fig. 1

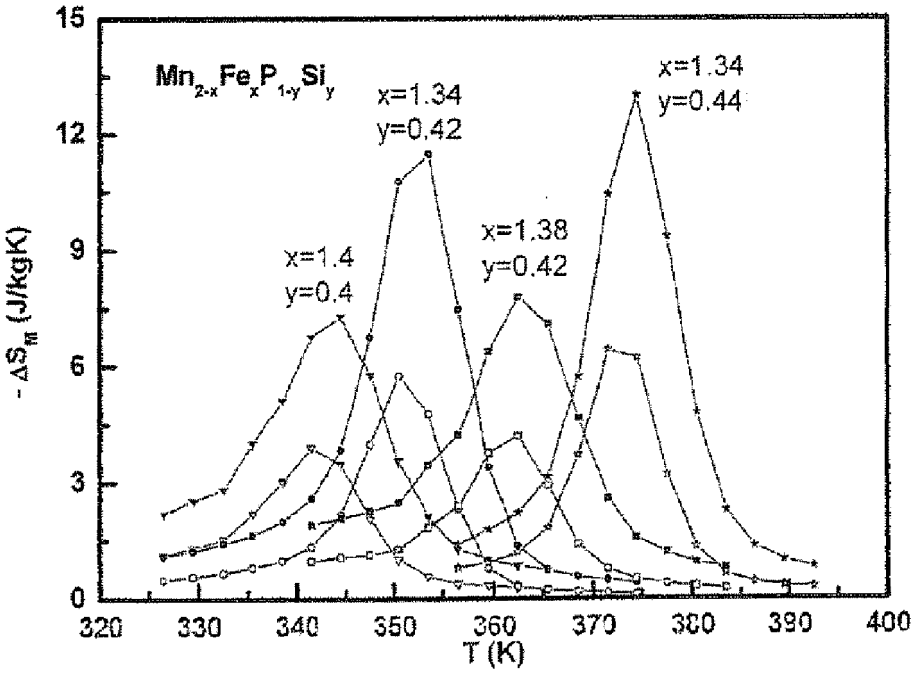

Mn2-xFexP1-ySiy
x=1.34
y=0.42
x=1.34
y=0.44
x=1.38
y=0.42
x=1.4
y=0.4
- ΔSm (J/KgK)
T (K)
0
3
6
9
12
15
320
330
340
350
360
370
380
390
400

Fig. 2

REFERENCES CITED IN THE DESCRIPTION

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