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PLASTIC CRYSTALS AND THEIR POTENTIAL USE IN NEW TECHNOLOGIES
Some necessary comments

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The paper gives some comments about the potential use of plastic crystals in energy storage. The main point deals with the possibilities of binary solid solution formation. Three binary phase diagrams in the pentaerythritol series are commented on.

Introduction

A review article entitled 'Les cristaux plastiques en vue d'applications thermiques dans les technologies nouvelles' recently appeared in this journal [1]. This paper gives partial and even sometimes erroneous information about plastic crystals. The complete absence of bibliographic references must be emphasized.

The author chose the pentaerythritol series, i.e. pentaerythritol (PE), pentaglycerin (PG), neopentylglycol (NPG) and their solid solutions to illustrate the potential applications of plastic crystals.

One must express regret for not finding the actual state of the art in this paper, whose title suggests a general scope. The included results are only partial. A critical examination of the already abundant scientific literature

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would be necessary because some discrepancies are currently observed [2–15]. Apart from this kind of oversight, numerous imprecise or wrong statements may lead to the reader to erroneous conclusions.

One point may concern the preparation of 'mixtures' using water recrystallization procedures. PG and NPG are hygroscopic materials, and it is even possible to form hydrates NPG·$6H_2O$ [15], PG·$4H_2O$ [8] and PG·xH_2O (x varying from 1 to 20) [17], which will not be easily and completely destroyed in the vacuum evaporation steps.

The main point concerns the possibilities of binary solid solution formation. No correct statement can be made if the phase diagrams are unknown (or not taken into account). For the chosen series this necessity is particularly important, due to the diversity of the phase diagrams for PG-PE [6], NPG-PG [10] and NPG-PE [8, 9, 11, 12]. It is the solid-solid transition (crystal-plastic crystal) of either pure components or solid solutions which is concerned in view of applications for energy storage. In the case of solid solutions, the storage is no longer isothermal, but takes place in a temperature range which goes from the inferior solvus to the superior one (crossing of the two solid phases domain).

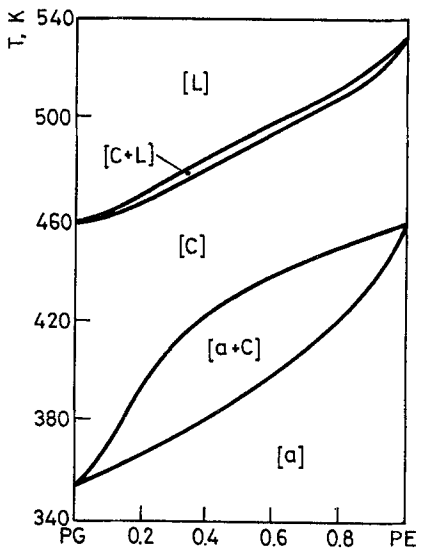

Fig. 1 PG-PE phase diagram (Ref. 6); a: tetragonal; C: face centered cubic; L: liquid

PG-PE (Fig. 1) is the only binary system which shows complete miscibility in the two kinds of solid states, i.e. the only one which permits the

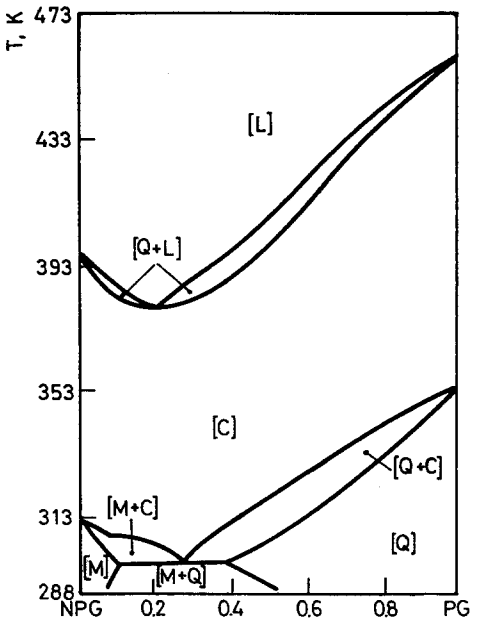

Fig. 2 NPG-PG phase diagram (Ref. 10); M: monoclinic; Q: tetragonal; C: face centered cubic; L: liquid

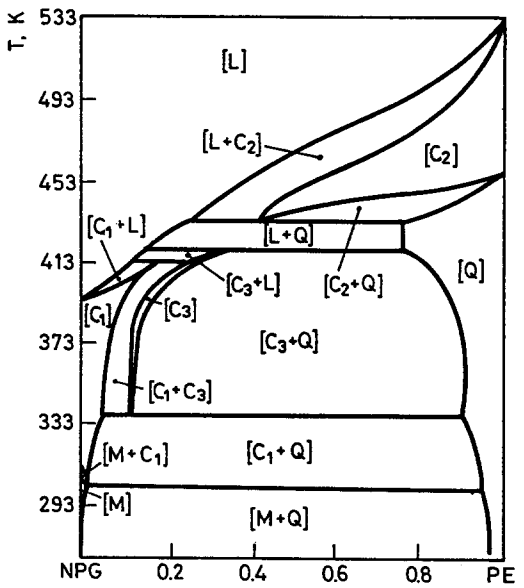

Fig. 3 NPG-PE phase diagram (Ref. 12); M: monoclinic; Q: tetragonal; C_1, C_2, C_3: face centered cubic; L: liquid

obtaining of phase change materials whatever the composition is. However, the temperature range for storage may extend over 40 deg or more.

The two other systems are far more complicated. The possibility of obtaining solid solutions suitable for energy storage is restricted for NPG-PG (Fig. 2) and nearly non-existent for NPG-PE (Fig. 3).

Moreover, practical applications will then have to deal with kinetic problems, such as the very common 'subcooling' of plastic cubic phases, and the handling of readily subliming materials. These problems are not mentioned in reference [1].

In conclusion, in spite of the above remarks, it remains true that these materials (if suitably selected) present important potentialities for energy storage applications. The purpose of the present contribution is to point out that a presentation as simplistic as the concerned paper [1] may lead to erroneous conclusions. The binary phase diagrams have necessarily to be examined and carefully understood.

References

1 L. Elegant, J. Thermal Anal., 35 (1989) 1795.
2 J. Timmermans, J. Phys. Chem. Solids, 18 (1961) 1.
3 L. A. K. Staveley, J. Phys. Chem. Solids, 18 (1961) 46.
4 E. Murrill and L. Breed, Thermochim. Acta, 1 (1970) 239.
5 D. K. Benson, R. W. Burrows and J. D. Weeb, Solar Energy Materials, 13 (1986) 133.
6 M. Barrio, J. Font, J. Muntasell, J. LI. Tamarit, N. B. Chanh and Y. Haget, J. Chim. Phys., 87 (1990) 255.
7 J. LI. Tamarit, Tesis Doctoral, Universitat de Barcelona, 1988.
8 M. Teisseire, Thèse de Doctorat, Université de Nice, 1989.
9 D. O. Lopez, Tesis Doctoral, Universitat Autònoma de Barcelona, 1990.
10 M. Barrio, J. Font, D. O. Lopez, J. Muntasell, J. LI. Tamarit, N. B. Chanh and Y. Haget, J. Chim. Phys., 87 (1991) 1835.
11 M. Teisseire, N. B. Chanh, M. A. Cuevas Diarte, J. Guion, Y. Haget, D. O. Lopez and J. Muntasell, Thermochim. Acta, 181 (1991) 1.
12 M. Barrio, J. Font, D. O. Lopez, J. Muntasell, J. LI. Tamarit, N. B. Chanh and Y. Haget, J. Phys. Chem. Solids, 52 (1991) 665.
13 D. Mayer, Thèse de Doctorat, E. N. S. Mines de Paris, Sophia Antipolis, 1987.
14 V. H. Peter Franck, K. Krzemicki and H. Vollenke, Chem. Z., 97 (1973) 206.
15 J. F. Wilmet, Thèse de Doctorat, Université de Nice, 1990.
16 J. B. Ott, J. R. Goates, E. M. Wooley and J. G. Priest, J. Chem. Thermodyn., 14 (1982) 1077.
17 D. K. Benson and R. W. Burrows, U.S. pat., 4, 702, 853, 27 (October 1987).

Zusammenfassung — Es werden einige Bemerkungen über die potentielle Verwendung von Plast-Kristallen in der Energiespeicherung gemacht. Dabei geht es hauptsächlich um die Möglichkeit der Bildung binärer fester Lösungen. Drei binäre Phasendiagramme der Pentaerythrit-reihe wurden diskutiert.