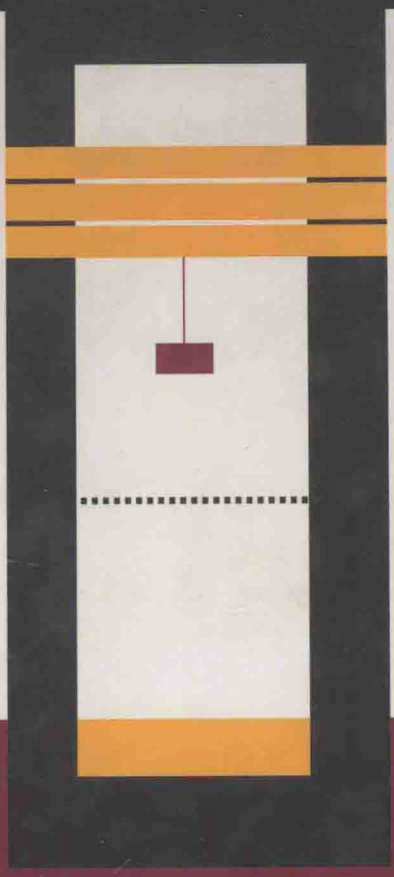
The Proceedings of the Seventh International Symposium on Hydrothermal Reactions



Hydrothermal Reactions and Techniques

S H Feng • J S Chen • Z Shi

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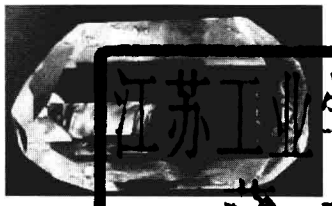
Changchun, China 14 – 18 December 2003



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World Scientific
NEW JERSEY • LONDON • SINGAPORE • SHANGHAI • HONG KONG • TAIPEI • BANGALORE

Published by

World Scientific Publishing Co. Pte. Ltd.

5 Toh Tuck Link, Singapore 596224

USA office: Suite 202, 1060 Main Street, River Edge, NJ 07661

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

HYDROTHERMAL REACTIONS AND TECHNIQUES
Proceedings of the Seventh International Symposium

ISBN 981-238-675-0

Printed by FuIsland Offset Printing (S) Pte Ltd, Singapore

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Preface

Hydrothermal techniques have been widely applied in the synthesis of conventional and advanced materials, treatment of wastes and preparation and extraction of special chemicals. These techniques have also been investigated for mimicking geothermal processes. Nowadays, hydrothermal techniques and sciences play a very important role both in industry and in academia.

These proceedings include contributions to the Seventh International Symposium on Hydrothermal Reactions (ISHR–7) from chemists and chemical engineering scientists worldwide who are active in the field of hydrothermal reactions and techniques. The previous six international symposia on hydrothermal reactions were held in Japan (1982), USA (1985), Russia (1989), France (1993), USA (1997) and Japan (2000), respectively. And this year sees the seventh one of this series to be held in Changchun, China. The aim of the symposium is to offer an opportunity for researchers all over the world to exchange advanced ideas and to promote the basic and applied aspects on hydrothermal and solvothermal reactions. This symposium continues to stress the science and technology related to hydrothermal and solvothermal systems. On the basis of about 200 abstracts submitted to ISHR–7, full papers were subsequently contributed, and after scientific review, 67 of the contributed full papers were selected for inclusion in these proceedings.

There are five parts in these proceedings with each part representing a unique sub-area of hydrothermal and/or solvothermal science and technology. The first part of the proceedings covers topics of hydrothermal and solvothermal chemistry; the second part deals with supercritical fluids, supercritical water oxidation process and waste treatment, and the third part involves growth of single crystals, thin films, nanomaterials and oriented organization from hydrothermal/solvothermal systems. In the fourth part, inorganic-organic hybrid materials are addressed whereas the fifth part of the proceedings is concerned with new techniques, theory and modeling related with hydrothermal/solvothermal reactions.

We are grateful to our colleagues, both in China and abroad, for their kind support and help during the organization of the symposium. Most of the colleagues serve as a member of the advisory board and the organizing committee. Thanks are also due to the authors of both the abstracts and the full papers who spared no efforts to make contributions to the symposium and to these proceedings. Finally, we would like to express our gratitude to the World Scientific Publishing Co. Pte. Ltd. for the publication of these proceedings.

Editors
Shou-Hua Feng
Jie-Sheng Chen
Zhan Shi

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Part I

Hydrothermal and Solvothermal Chemistry

DIRECT HYDROTHERMAL SYNTHESIS OF MULTI-COMPONENT OXIDES BY HIGH TEMPERATURE MIXING METHOD

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A high temperature mixing method has been developed to prepare multi-component oxides directly without formation of intermediate compounds under hydrothermal conditions. In this method, starting solutions are mixed under hydrothermal conditions to get a desired compound. When a calcium nitrate solution was mixed with an ammonium phosphate solution at 200°C, larger hydroxyapatite crystals were obtained in comparison with those prepared by the same hydrothermal treatment of the precipitate formed by mixing two solutions at room temperature. Xonotlite fibrous crystals were prepared in a very short time by mixing a silica solution and a calcium hydroxide solution at 250°C.

1 Introduction

Hydrothermal technique is an attractive method to prepare ceramic powders [1] due to low temperature processing, possibility of particle morphology control, and production of sinterable powders. The hydrothermal reaction usually proceeds by dissolution and precipitation of the reactants, which are heated to a hydrothermal condition from room temperature to get a desired compound. If stable compounds exist at low temperatures, these compounds are first formed during heating, and transformed to compounds which are stable at high temperatures. In the case of hydrothermal preparation of multi-component oxides, the reaction process is much complicated because the compositions of the desired compounds stable at high temperatures are usually different from those stable at low temperatures. We have developed a new hydrothermal method for direct preparation of multi-component oxides by mixing each starting solution at high temperatures under hydrothermal conditions.

In this paper, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) and xonotlite ($Ca_6Si_6O_{17}(OH)_2$) crystals were prepared using the high temperature mixing method. Hydroxyapatite is the main inorganic constituent in bone and tooth enamel, and is the interesting bioactive material. When hydroxyapatite is prepared from phosphate and calcium salt solutions, amorphous calcium phosphate is first precipitated [2] by mixing starting solutions at room temperature, and transformed to crystalline hydroxyapatite by aging or hydrothermal treatment. Hydroxyapatite crystals thus formed are rather small.

Xonotlite is an important binder for heat insulating materials, building materials and artificial wood, because of its high stability at high temperatures and fibrous crystal form. It is usually prepared hydrothermally from a suspension of silica and calcium hydroxide at temperatures over 180 °C. It takes a very long time to prepare xonotlite, because CSH gel

and tobermorite are formed at low temperatures [3]. If xonotlite is formed directly without formation of intermediate compounds, it is expected to decrease the reaction time.

2 Methods

2.1 Preparation of Hydroxyapatite [4]

Starting materials were aqueous solutions of 0.167M $Ca(NO_3)_2$ and 0.1M $(NH_4)_2HPO_4$. After adjusting pH to 10.0 with an ammonia solution, they (7ml each) were separately placed in each chamber of the multi-chamber autoclave made of the stainless steal with a liner of Teflon. The total inner volume of the autoclave was 50 ml and the each chamber had 12.5 ml volume. The autoclave was fixed on a rotation shaft in an oven. Two methods, low temperature and high temperature mixing method, were employed to prepare hydroxyapatite. In the low temperature mixing method, the autoclave was rotated with 20 rpm at room temperature to mix two solutions in the autoclave, and then heated to 200°C. On the other hand, the autoclave was heated to 200°C without rotation to heat the two solutions separately in the high temperature mixing method, and it was rotated after the temperature of the solutions reached to 200°C. In both cases, the hydrothermal treatment was conducted at 200°C for 24 hours.

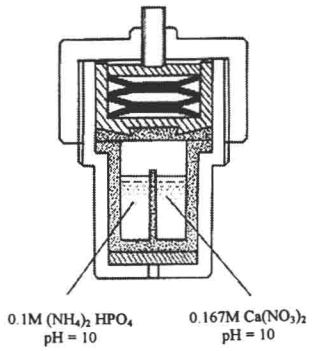

Figure 1. Multi-chamber autoclave for preparation of hydroxyapatite.

2.2 Preparation of Xonotlite [5]

In order to prepare xonotlite directly without formation of intermediate compounds, starting materials were dissolved in water or an alkaline solution and two solutions including calcium and silica were mixed under hydrothermal conditions where xonotlite was stable. Figure 2 shows a hydrothermal apparatus for preparation of xonotlite. It consisted of 2 pumps, a fine long tube (1 mm in inner diameter, 100 m in length) to decrease pressure, and 5 autoclaves for dissolution of silica (a) and calcium hydroxide (b), reaction chamber (c), separation of the solid products from suspension (d), and sampling of the product (e). The inner volume of each autoclave was 220, 200, 500, 550, and 20 cm^3, respectively. The long tube to decrease the pressure was cooled with water to stabilize the inner pressure.

In this study, a silica solution (590 ppm in 0.01M NaOH solution) and a calcium hydroxide solution (560 ppm) were prepared beforehand using the autoclave (a) and (b),