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Thermoanalytical studies of silver and lead jarosites and their solid solutions

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作者

Ray L. Frost¹ , Sara J. Palmer¹, János Kristóf², Erzsébet Horváth³

¹Queensland University of Technology Inorganic Materials Research Program, School of Physical and Chemical Sciences 2 George Street GPO Box 2434 Brisbane QLD 4001 Australia

²University of Pannonia Department of Analytical Chemistry PO Box 158 8201 Veszprém Hungary

³University of Pannonia Department of Environmental Engineering and Chemical Technology PO Box 158 8201 Veszprém Hungary

摘要

Abstract

Dynamic and controlled rate thermal analysis has been used to characterise synthesised jarosites of formula $[M(Fe)_3(SO_4)_2(OH)_6]$ where M is Pb, Ag or Pb-Ag mixtures. Thermal decomposition occurs in a series of steps. (a) dehydration, (b) well defined dehydroxylation and (c) desulphation. CRTA offers a better resolution and a more detailed interpretation of water formation processes via approaching equilibrium conditions of decomposition through the elimination of the slow transfer of heat to the sample as a controlling parameter on the process of decomposition. Constant-rate decomposition processes of water formation reveal the subtle nature of dehydration and dehydroxylation. CRTA offers a better resolution and a more detailed interpretation of the decomposition processes via approaching equilibrium conditions of decomposition through the elimination of the slow transfer of heat to the sample as a controlling parameter on the process of decomposition. Constant-rate decomposition processes of non-isothermal nature reveal separation of the dehydroxylation steps, since in these cases a higher energy (higher temperature) is needed to drive out gaseous decomposition products through a decreasing space at a constant, pre-set rate.

Keywords

Jarosite, Thermal analysis, Controlled rate thermal analysis, Thermogravimetry

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Ray L. Frost · Sara L. Palmer · János Kristóf ·
Erzsébet Csevács

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Abstract Dynamic and controlled rate thermal analysis has been used to characterise synthesised jarosites of formula $M(\text{Fe}_2(\text{SO}_4)_2(\text{OH})_6)$ where M is Pb, Ag or Pb–Ag mixtures. Thermal decomposition occurs in a series of steps. (a) dehydration, (b) well defined dehydroxylation and (c) desulphation. CRTA offers a better resolution and a more detailed interpretation of water formation processes via approaching equilibrium conditions of decomposition through the elimination of the slow transfer of heat to the sample as a controlling parameter on the process of decomposition. Constant-rate decomposition processes of water formation reveal the subtle nature of dehydration and dehydroxylation. CRTA offers a better resolution and a more detailed interpretation of the decomposition processes via approaching equilibrium conditions of decomposition through the elimination of the slow transfer of heat to the sample as a controlling parameter on the process of decomposition. Constant-rate decomposition processes of non-isothermal nature reveal separation of the

dehydroxylation steps, since in these cases a higher energy (higher temperature) is needed to drive out gaseous decomposition products through a decreasing space at a constant, pre-set rate.

Keywords Jarosite · Thermal analysis ·
Controlled rate thermal analysis · Thermogravimetry

Introduction

Argentojarosite ($\text{AgFe}_2^{+1}(\text{SO}_4)_2(\text{OH})_6$) was first identified in 1923 from the Titanic Standard mine at Dividend, Utah, USA [1]. It has since been identified in at least 14 other US sites. The mineral in some localities is of sufficient abundance as to be a silver bearing ore [2]. Argentojarosite was exploited at Rio Tinto, Spain, from Roman or even pre-Roman times [3]. Argentojarosites had an important influence on the wealth of both Europe and South America [4]. Lead jarosite also known as plumbojarosite ($\text{PbFe}_6(\text{SO}_4)_4(\text{OH})_{12}$) was identified in relation to jarosite in 1902 [5]. Plumbojarosite is often found in cationic mixed jarosites [6–9]. Such minerals are of importance in medieval and archaeological science [10, 11] and are also found in mine drainage sites both ancient and modern [9, 11, 12]. Such formation of jarosites has been occurring since the Bronze Age [13]. The importance of jarosite formation and its decomposition depends upon its presence in soils, sediments and evaporate deposits [14]. These types of deposits have formed in acid soils where the pH is less than 3.0 pH units [15]. Such acidification results from the oxidation of pyrite which may be from bacterial action or through air-oxidation.

The thermal decomposition of jarosites has been studied for some considerable time [16–20]. However no thermal

R. L. Frost (✉) · S. L. Palmer
Inorganic Materials Research Program, School of Physical and
Chemical Sciences, Queensland University of Technology, 2
George Street, GPO Box 2434, Brisbane, QLD 4001, Australia
e-mail: r.frost@qut.edu.au

J. Kristóf
Department of Analytical Chemistry, University of Pannonia,
PO Box 158, 8201 Veszprém, Hungary

E. Horváth
Department of Environmental Engineering and Chemical
Technology, University of Pannonia, PO Box 158, 8201
Veszprém, Hungary



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Akadémiai Kiadó

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