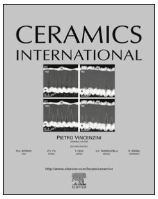
Ceramics International 42 (2016) 16969–16980

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Introduction of novel kinetic approach to calculation of activation energy and its application to the sinter-crystallization of strontian feldspar

Petr Ptáček*, Tomáš Opravil, František Šoukal

Brno University of Technology, Faculty of Chemistry, Centre for Materials Research CZ.1.05/2.1.00/01.0012, Purkyňova 464/118, Brno CZ-612 00, Czech Republic

ARTICLE INFO

Article history:
Received 30 June 2016
Received in revised form
21 July 2016
Accepted 28 July 2016
Available online 29 July 2016

Keywords:
Strontian feldspar
Sr-celsian
Ceramics
Kinetics
Thermodynamics
Activated complex

ABSTRACT

The kinetics, the mechanism and the thermodynamics of activated state of formation of primary strontian feldspar via sinter-crystallization of non-equilibrium melt during the thermal treatment of ceramic body was investigated in this work via differential thermal analysis using isoconversional Kissinger kinetic equation. The process of formation of non-equilibrium melt and subsequent crystallization of primary strontian feldspar requires the activation energy of 631 ± 3 and 664 ± 2 kJ mol^{-1}, respectively. The investigation of mechanism of formation of primary strontian feldspar reveals that the process is driven by the surface nucleation and diffusion controlled growth of the new phase. The nucleation rate decreases with the time of process and non-equilibrium melt can be formed only in metastable equilibrium with activated state of strontian feldspar. Deep consideration of kinetic data leads to the deduction of new kinetic approach that enables single calculation of activation energy and frequency factor of heterogeneous processes as well as the dependence of thermodynamic parameters of activated state on temperature. Further consideration of kinetic data reveals that the activation energy is directly proportional to the function of $\mathrm{csch}\,(z)+1$. For $\boldsymbol{z}=\boldsymbol{e}$, this term enables to derive the value for the parameter $\boldsymbol{B}(\boldsymbol{x})$ in empirical equation for Arrhenius temperature integral $\boldsymbol{p}(\boldsymbol{x})$ proposed by Doyle to be 1.0642.

1. Introduction

Feldspars are intensively studied due to their importance in petrography [1,2], understanding the Earth's geology [2,3], soil sciences, where some clay minerals are produced by weathering of feldspars directly or through intermediate phases [4,5], as well as in the production of ceramics, glass and glass-ceramics [6–9]. Ground rocks of potassium feldspar have also wide efficiency as a fertilizer [10]. The composition of this subclass of silicate minerals, i.e. tectosilicates with Al-Si framework [11], is described by the formula MT_4O_8 (or $M_xT_yO_8$, where $\boldsymbol{y}$ reaches 4 and the parameter $\boldsymbol{x}$ does not fall below 0.975 [12]). Feldspars are the most abundant minerals in the Earth's crust (60–64% by weight) [13,14]. **T**-sites (aluminosilicate framework) are occupied by small strongly charged cations (typically Si^{4+} and Al^{3+}) and **M**-sites (interstices) are occupied by larger, weakly charged cations (Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, …). Feldspars can be characterized by the content of all 92 naturally occurring elements [12]. In Na- and K-feldspars, Si^{4+} and Al^{3+} can be completely replaced by Ga^{3+} and Ge^{3+}[15].

Synthetic strontian feldspar (Sr-celsian, strontium aluminosilicate feldspar, SAS, $SrAl_2Si_2O_8$) is of great technological interest due to low thermal expansion coefficient [16,17]), low and thermally stable dielectric constant, low dielectric losses, high mechanical strength, chemical inertness, and high melting temperature. Therefore they are known as the materials for the matrix of fiber-reinforced ceramic composites, protective coatings, electro-ceramics and refractories [18–25] as well as for the preparation of glass ceramics [26–28] and luminescent pigments of $MAl_2Si_2O_8{:}X^{n+}$; where M=Ca, Sr, Ba and X^{n+} denotes ions of doped element [29–35].

Previous investigation of reaction mechanism, kinetics and thermodynamics of the process of formation of synthetic strontian feldspar via ceramic route [36] revealed that the main reaction pathway is initiated by the thermal decomposition of $SrCO_3$ and continues with the formation of binary oxide intermediates and primary strontian feldspar via the crystallization from non-equilibrium melt. The reactions between intermediates or the reaction of these intermediates with SiO_2 and Al_2O_3 leads to the formation of secondary strontian feldspar. Large plate-like particles of

---

* Corresponding author.
E-mail addresses: ptacek@fch.vutbr.cz (P. Ptáček), opravil@fch.vutbr.cz (T. Opravil), soukal@fch.vutbr.cz (F. Šoukal).

http://dx.doi.org/10.1016/j.ceramint.2016.07.203
0272-8842/

tertiary strontian were formed by recrystallization of primary and secondary strontian feldspar. The formation of strontian within the temperatures over 1150 °C is driven by the kinetics of chemical reaction of 1.5 order and requires the average apparent activation energy of 229.3 kJ mol^{-1}.

This work expands these foundations by detailed investigation of reaction mechanism, kinetics and thermodynamic of the process of formation of synthetic primary strontian feldspar as an essential part of the main reaction pathway. The investigation of kinetic results and thermodynamic data of activated state enables to formulate proper equations to determine the activation energy, the frequency factor as well as the relations describing the dependence of enthalpy, entropy, volume and density of transition state on temperature. Since the synthetic strontian feldspar was sometimes abbreviated as strontian in the text of previous work [36], in order to avoid confusion with the mineral strontianite [37], this abbreviation is not used in this work.

2. Experimental

2.1. Synthesis and analysis of properties of sample

Raw meal for the synthesis of strontian feldspar was prepared by mixing strontium carbonate ($SrCO_3$), alumina (Al_2O_3) and silica (SiO_2) in the mass ratio of 1.45:1:1.18, which corresponds to the stoichiometric composition of $SrAl_2Si_2O_8$ ($SrO \cdot Al_2O_3 \cdot 2SiO_2$). The initial homogenization of raw meal was performed by short milling (5 min) with vibration laboratory mill. The kinetics of formation of primary strontian feldspar during the thermal treatment of raw meal was investigated by TG-DTA (TG-DTA analyzer SDT Q600). 30 mg of sample were heated in the air conditions (100 $cm^3\ min^{-1}$) under the rate from 5 to 20 °C min^{-1}. The other aspects of the process of strontian feldspar synthesis are described in previous work [36].

2.2. Applied kinetic approach

The kinetic triplet of the process includes the information about the activation energy, the frequency factor and the mechanism. The apparent activation energy ($\boldsymbol{E}_a$) and the frequency factor ($\boldsymbol{A}$) of investigated process were evaluated by the mechanism-free maximum rate (peak) method of type B [38] based on the Kissinger kinetic approach [39–41]. The peak temperature ($\boldsymbol{T}_m$), i.e. the temperature at which the rate of investigated process ($d\boldsymbol{\alpha}/d\boldsymbol{t}$) reaches its maximum, is a stationary point where the transformation rate is equal to zero [38,40,42,43]:

$$\frac{d\,\alpha}{d\,t} = f(\alpha)\,k(T) = 0 \tag{1}$$

where α is the fractional conversion, $\boldsymbol{t}$ is the time and $\boldsymbol{k}(\boldsymbol{T})$ is the proportionality factor known as the rate constant at absolute temperature $\boldsymbol{T}$. α (fraction reacted [44]) is readily determined as a fractional change of any physical property associated with the reaction progress, e.g. the mass change during the thermal decomposition of solids [45]:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} = \frac{\Delta m}{m_{total}} \tag{2}$$

where $\boldsymbol{m}_0$, $\boldsymbol{m}_t$ and $\boldsymbol{m}_f$ are initial ($\boldsymbol{t}=0$), measured at time $\boldsymbol{t}$ and final masses.

The particular function $f(\alpha)$ which is proportional to the amount of reactant is known as the "kinetic model" (the concept given by Eq. (1) was introduced by Guldberg and Waage[46–48] as the "law of mass action"). Therefore, the temperature dependence of the reaction rate constant is given by the Arrhenius law [49]:

$$k(T) = A\exp\left[-E_a/RT\right] \tag{3}$$

it can be further derived [41]:

$$\frac{d^2\alpha}{dt^2} = \frac{d\alpha\left[d\alpha/dt\right]}{dt} = \left(\frac{d\,f(\alpha)}{dt}A\ \exp\left[-\frac{E_a}{RT}\right] + A\ f(\alpha)\frac{d\left[\exp(-E_a/RT)\right]}{dt}\right)_{T=T_m} = 0 \tag{4}$$

Assuming that the heating rate is constant but not equal to zero ($\Theta = d\boldsymbol{T}/d\boldsymbol{t} \neq 0$) and the term $d[exp(-\boldsymbol{E}_a/\boldsymbol{RT})]/d\boldsymbol{t} = \boldsymbol{E}_a\Theta/\boldsymbol{RT}^2$ exp $(-\boldsymbol{E}_a/\boldsymbol{RT})$:

$$\frac{d\left[f(\alpha)\right]}{dt} + f(\alpha)\frac{E_a\Theta}{RT^2} = 0 \tag{5}$$

Given the identity $f'(\alpha) = d[f(\alpha)]/d\alpha$ then $d[f(\alpha)]/d\boldsymbol{t} = f'(\alpha)d\alpha/d\boldsymbol{t}$ leads to the equation:

$$A\ \exp\left[-\frac{E_a}{RT_m}\right]f'(\alpha_m)\ \ + \frac{E_a\Theta}{RT_m^2} = 0 \tag{6}$$

where $\alpha_{\boldsymbol{m}}$ is the fractional conversion (or the degree of transformation [41]) reached for the temperature $\boldsymbol{T}_m$ and $\boldsymbol{R}$ is the universal gas constant (8.314 J K^{-1} mol^{-1}). The term $f'(\alpha_m) \equiv df(\alpha)/d\alpha|_{\alpha=\alpha m}$ is assumed as a constant, i.e. is independent of $\boldsymbol{\Theta}$ or $\boldsymbol{T}_m$. Eq. (6) can be solved for $\Theta/\boldsymbol{T}_m^{\,2}$ and expressed via its logarithm form:

$$\ln\left[\frac{\Theta}{T_m^2}\right] = -\frac{E_a}{RT_m} + \ln\left(-\frac{AR}{E_a}f(\alpha_m)\right) \tag{7}$$

For the reaction of first-order ($\boldsymbol{n}=1$), where ($f(\alpha)=1-\alpha$) is $f'(\alpha_m)=-1$ and term $ln\,(-f'(\alpha))=0$, can then be written [41]:

$$\ln\left[\frac{\Theta}{T_m^2}\right] = -\frac{E_a}{RT_m} + \ln\left(\frac{AR}{E_a}\right) \tag{8}$$

A generalized solution of Kissinger equation containing the solution of $f'(\alpha)$ for common forms of $f(\alpha)$, i.e. the reaction mechanism or the kinetic model, and for near equilibrium solid–gas heterogeneous transformations, can be found in works [50–52], respectively.

The combination of the second derivative equation (Eq. (4)) with the kinetic model of Freeman and Carroll [53], where $f(\alpha) = (1-\alpha)^{\mathbf{n}}$, leads to the equation for the reaction of nth-type, which can be written as follows [54,55]:

$$\ln\left[\frac{\Theta}{T_m^2}\right] = \ln\left[\frac{AR}{E_a}n(1-\alpha_m)^{n-1}\right] - \frac{E_a}{RT_m} = const. - \frac{E_a}{RT_m} \tag{9}$$

where term $(1-\alpha_m)$ is the fraction of remaining sample, i.e. not reacted [44], which is the constant for given value of $\boldsymbol{n}$. The points on the plot of $ln\,(\boldsymbol{AR}/\boldsymbol{E}_a)$ versus $\boldsymbol{T}_m^{\,-1}$ were fitted by the straight line with the slope equal to $-\boldsymbol{E}_a/\boldsymbol{R}$, i.e. $\boldsymbol{E}_a = -\boldsymbol{R}\ (\partial(ln\,\Theta/\boldsymbol{T}_m^{\,2})/\partial(1/\boldsymbol{T}_m))$, whereas the intercept yields to the constant term of Eq. (9). For most kinetic models, the percent error in the calculation of the activation energy is below 2% if $\boldsymbol{E}_a/\boldsymbol{RT}_m > 10$ [41,54,56].

The mechanism was estimated from the shape of DTG peak via the value of kinetic exponent ($\boldsymbol{n}$) which is related to the empirical order of reaction [39]. The exponent can be calculated from the equation derived by Augis and Bennet [57,58]:

$$n = \frac{2.5\,R\,T_m^2}{w_{1/2}\,E_a} \tag{10}$$

where $\boldsymbol{w}_{1/2}$ is a half-width (width at a half height) of peak. The value of kinetic exponent is typical for various mechanisms of the