Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 163–168

KINETICS OF ISOTHERMAL DECOMPOSITION OF $ZnSeO_3$ AND $CdSeO_3$

L. T. Vlaev[*], *V. G. Georgieva and G. G. Gospodinov*

Department of Physical Chemistry, Assen Zlatarov University, Bourgas 8010, Bulgaria

The kinetics of decomposition of $ZnSeO_3$ and $CdSeO_3$ was studied under isothermal heating on a derivatograph. The values of activation energy, pre-exponential factor in Arrhenius equation and change of entropy were calculated for the formation of the activated complex by the reagent. The dependencies observed are interpreted according to the generalized perturbation theory of chemical reactivity.

Keywords: *cadmium selenite, isothermal decomposition, kinetics parameters, zinc selenite*

Introduction

The synthesis and studies of $ZnSeO_3$ and $CdSeO_3$ are connected with their use as pigments in glass and ceramics industries, as luminophors or precursors for preparation of the corresponding selenides, which possess interesting semi-conductor properties [1–4]. Different methods for preparation [1, 5–9], crystalline structure [10–13] and a number of other physico-chemical characteristics have already been reported [5, 14–22]. It is well known that $ZnSeO_3$ melts at 893–895 K [20, 23] while $CdSeO_3$ – at 943 K [1, 5, 6]; their decomposition starts below these temperatures by formation of the corresponding oxides accompanied by sublimation of SeO_2.

The kinetics of decomposition of these selenites, however, has not been reported by now [24] although it is very important, since under heating in reduction medium (H_2 or CO) the selenites are reduced to the corresponding selenides, which possess valuable semi-conductor properties.

The aim of the present work is to find the values of the parameters characterizing the kinetics of cadmium and zinc selenites decomposition under isothermal heating.

Experimental

Synthesis

The anhydrous selenites of zinc and cadmium were prepared by hydrothermal synthesis at 373 K and autogenous pressure for 30 days, using a mixture of $Zn(OH)_2$ or CdO with aqueous solution of H_2SeO_3 [25, 26]. After filtration and washing with distilled water, the solid phase was dried in air at 373 K for 6 h. According to the data from X-ray powder diffraction analysis and IR-spectroscopy, the crystals obtained were $ZnSeO_3$ and $CdSeO_3$, respectively.

Thermal measurements

The thermogravimetric measurements were performed on a derivatograph system Paulik–Paulik–Erdey (MOM, Hungary) in nitrogen flow ($25\ cm^3\ min^{-1}$) under isothermal heating in the temperature interval 823–998 K. For this purpose, 100 mg finely ground sample was placed in platinum crucible (7 mm diameter and 14 mm height). α–Alumina, calcined at 1173 K was used as a standard reference material. The sample mass was measured continuously for 15–120 min with accuracy of ±1 mg. The temperature was kept constant within the interval ±2 K and the reaction progress (α) was from 0.03 to 0.96.

Mathematical background

The basic kinetic equation was used:

$$\frac{d\alpha}{dT} = kf(\alpha) \tag{1}$$

where k – rate constant and the function $f(\alpha)$ involves the decomposition progress α at moment t calculated by the formula:

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \tag{2}$$

where W_0, W and W_f are the initial, actual and final sample mass. According to Šesták [27], the function $f(\alpha)$ can be written in a general form:

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[*] Author for correspondence: vlaev@btu.bg

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

$$f(\alpha)=\alpha^{\mathrm{m}}(1-\alpha)^{\mathrm{n}}[-\ln(1-\alpha)]^{\mathrm{p}} \tag{3}$$

with respect to its correspondence to the models derived for homogeneous reactions, nucleation-growth process, surface process, diffusion or random nucleation, where n, m and p are empirically obtained exponent factors, one of them always being zero.

Depending on the specific kinetic model of the process, the form of the function $f(\alpha)$ would be different. The algebraic expressions of the functions most often used in [28–30] are presented in Table 1 in differential and integral form.

The integral form of the function $g(\alpha)$

$$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=kt \tag{4}$$

at T=const. represents a linear dependence, the slope of which is used to calculate the rate constant k at certain temperature. The dependence of the rate constant on the temperature is usually described by the Arrhenius equation:

$$k=A\exp\left(-\frac{E}{RT}\right) \tag{5}$$

where A – pre-exponential factor, E – activation energy, R – gas constant and T – temperature.

Taking the logarithm of Eq. (5) gives:

$$\ln k=\ln A-\frac{E}{RT} \tag{6}$$

The value of E is calculated from the slope of the straight line and A – from the cut-off from the ordinate. Using the equation of Eyring [31] from the theory of the activated complex (transition state):

$$k=\frac{\mathrm{e}\chi k_{\mathrm{B}}T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{E}{RT}\right) \tag{7}$$

where e=2.7183 is the Neper number, χ is a transmission coefficient, which is unity for monomolecular reactions, k_{B} is the Boltzmann constant, h is the Plank constant and $\Delta S^{\neq}$ is the change of entropy for the acti-

Table 1 Algebraic expressions of $f(\alpha)$ and $g(\alpha)$ for the kinetic models of thermal decomposition, considered in this work

Symbol	$f(\alpha)=\alpha^{\mathrm{m}}(1-\alpha)^{\mathrm{n}}[-\ln(1-\alpha]^{\mathrm{p}}$	$g(\alpha)=\int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)}=\mathrm{kt}$	Reaction model
1. Chemical decomposition process or mechanism non-invoking equations			
$F_{3/2}$	$(1-\alpha)^{3/2}$	$2[(1-\alpha)^{-1/2}-1]$	Three-halves order kinetics
F_2	$(1-\alpha)^2$	$\alpha/(1-\alpha)$	Second-order kinetics
F_n	$(1-\alpha)^{\mathrm{n}}$	$[1-(1-\alpha)^{1-\mathrm{n}}]/(1-n)$	$n^{-\mathrm{th}}$ order kinetics ($n\neq1$)
2. Acceleratory rate equations			
$P_{3/2}$	$\alpha^{-1/2}$	$(2/3)\alpha^{3/2}$	Power law ($\alpha=kt^{2/3}$)
P_2	$\alpha^{1/2}$	$2\alpha^{1/2}$	Power law ($\alpha=kt^2$)
P_3	$\alpha^{2/3}$	$3\alpha^{1/3}$	Power law ($\alpha=kt^3$)
P_4	$\alpha^{3/4}$	$4\alpha^{1/4}$	Power law ($\alpha=kt^4$)
P_5	α	$\ln\alpha$	Exponential law ($\alpha=1-\exp(-kt)$)
3. Sigmoid rate equations or random nucleation and subsequent growth			
A_1, F_1	$1-\alpha$	$-\ln(1-\alpha)$	Random nucleation or first order kinetics
$A_{3/2}$	$(1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$(3/2)[-\ln(1-\alpha)]^{2/3}$	Avrami–Erofeev equation (n=1.5)
A_2	$(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$2[-\ln(1-\alpha)]^{1/2}$	Avrami–Erofeev equation (n=2)
A_3	$(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$3[-\ln(1-\alpha)]^{1/3}$	Avrami–Erofeev equation (n=3)
A_4	$(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$4[-\ln(1-\alpha)]^{1/4}$	Avrami–Erofeev equation (n=4)
A_u	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$	Prout–Tompkins equation
4. Deceleratory rate equations			
4.1. Phase boundary reaction			
R_1, P_1, F_0	$(1-\alpha)^0$	α	One dimensional advance of the reaction interface, power law ($\alpha=kt$) or zero order kinetics
R_2, $F_{1/2}$	$(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$	Contracting area (cylindrical symmetry) or one-half order kinetics
R_3, $F_{2/3}$	$(1-\alpha)^{2/3}$	$3[1-(1-\alpha)^{1/3}]$	Contracting volume (spherical symmetry) or two-thirds order kinetics
4.2. Based on the diffusion mechanism			
D_1	$1/\alpha$	$\alpha^2/2$	One dimensional diffusion or parabolic law ($\alpha=kt^{1/2}$)
D_2	$1/-\ln(1-\alpha)$	$\alpha+(1-\alpha)\ln(1-\alpha)$	Two dimensional diffusion (Valensi equation)
D_3	$(1-\alpha)^{2/3}/1-(1-\alpha)^{1/3}$	$(3/2)[1-(1-\alpha)^{1/3}]^2$	Three dimensional diffusion (Jander equation)
D_4	$(1-\alpha)^{1/3}/1-(1-\alpha)^{1/3}$	$(3/2)[1-(2/3)\alpha-(1-\alpha)^{2/3}]$	Three dimensional diffusion (Gins.–Brouns. eq.)
D_5	$(1-\alpha)^{5/3}/1-(1-\alpha)^{1/3}$	$(3/2)[(1-\alpha)^{-1/3}-1]^2$	Zuravlev–Lesokhin–Tempelman equation
D_6	$(1+\alpha)^{2/3}/[(1+\alpha)^{1/3}-1]$	$(3/2)[(1+\alpha)^{1/3}-1]^2$	Komatsu–Uemura or anti-Jander equations

vated complex formation from the reagent. The comparison the equations of Arrhenius (Eq. (5)) and Eyring (Eq. (7)) gives:

$$A=\frac{e\chi k_B T}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right) \tag{8}$$

The change of entropy $\Delta S^{\neq}$ for the formation of the reagent activated complex can be calculated by the formula:

$$\Delta S^{\neq}=R\ln\frac{Ah}{e\chi k_B T} \tag{9}$$

The existence of a linear dependence between ln$A$ and E in reactions of the same type described by the equation:

$$\ln A=\ln k_{\text{iso}}+\frac{E}{RT_{\text{iso}}} \tag{10}$$

is often discussed in [32–37]. This dependence is known as kinetic compensation effect, isokinetic effect or θ rule. T_{iso} is the temperature at which the decomposition of substances proceeding along the same mechanism is characterized by the same rate constant k_{iso}. At temperatures higher than T_{iso}, the decomposition of the substance with higher activation energy continues at a rate higher than that of the substance with lower value of E.

Various hypotheses have been put forward to elucidate the compensation effect [33]. Two of these hypotheses may be useful for elucidation of Eq. (10) for some reactions of thermal dissociation. According to one of them, the course of the reaction involves an electron or proton transfer by means of the tunnel effect. The other hypothesis is based on the assumption that the compensation effect results from occurrences of reactions acting on active centers of different activation energies, according to the exponential distribution.

Results and discussion

Figure 1 shows only 4 of the α–t curves of decomposition of $ZnSeO_3$ and $CdSeO_3$; the other were omitted for clarity.

Curves 1 and 2 characterize the thermal decomposition of the solid phases of $ZnSeO_3$ and $CdSeO_3$, respectively, while curves 3 and 4 are for their melts. Since the curves characterizing the decomposition of $CdSeO_3$ at certain temperature lie below these of $ZnSeO_3$ at the same temperature, then the decomposition of $CdSeO_3$ was considered to proceed at lower rate. Using the algebraic expressions of the function $g(\alpha)$ presented in Table 1, calculations were made with all the temperatures of the kinetic experiment to find the function which would produce the highest correlation coefficient of linear regression R^2. It was found that the experimental data best delineated a straight line when mechanism non-invoking equations (type F) with different values of n were used. It turned out that the kinetics of decomposition of $ZnSeO_3$ and $CdSeO_3$ solid phases can be best described with values of n close to unity, while the decomposition of the corresponding melts – with values of n close to 0.75. These observations are illustrated in Fig. 2 where the kinetic straight lines are plotted in co-ordinates $g(\alpha)$ *vs.* t.

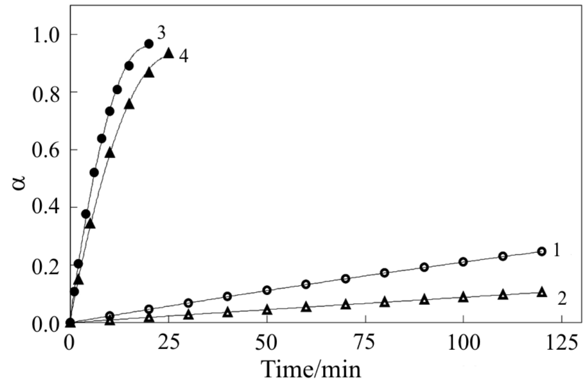

Fig. 1 α–t curves of isothermal decomposition of 1, 3 – $ZnSeO_3$ and 2, 4 – $CdSeO_3$ at: 1, 2 – 848 K and 3, 4 – 973 K

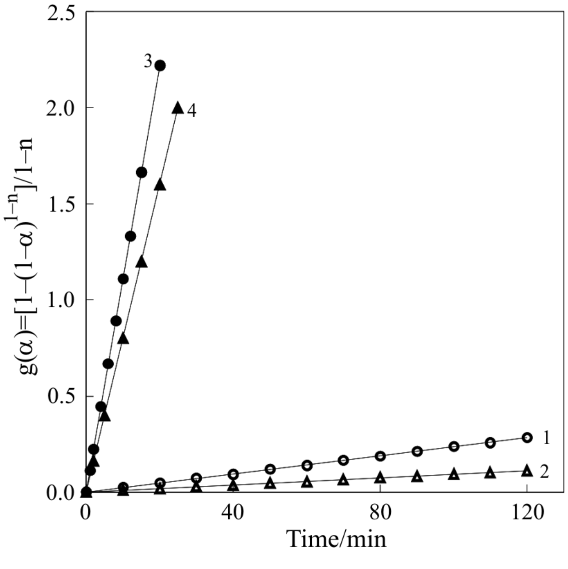

Fig. 2 Plots of $g(\alpha)$ *vs.* t. Designation as in Fig.1

Table 2 shows the values of the rate constants of decomposition of the selenites studied at different temperatures. Using these values and Eq. (6), Arrhenius plots for $ZnSeO_3$ and $CdSeO_3$ thermal decomposition were drawn and are presented in Fig. 3.

As can be seen from Fig. 3, both curves ln$k$ *vs.* $1/T$ have two linear sections. The first ones (A_1B_1 and A_2B_2) are more steep and represent the decomposition of the

Table 2 Dependence of the rate constant of thermal decomposition of $ZnSeO_3$ and $CdSeO_3$ on temperature

Temperature/K	k/min^{-1}	
	$ZnSeO_3$	$CdSeO_3$
823	$8.3\cdot10^{-4}$	–
848	$2.3\cdot10^{-3}$	$9.2\cdot10^{-4}$
873	$6.3\cdot10^{-3}$	$2.6\cdot10^{-3}$
898	$1.5\cdot10^{-2}$	$7.0\cdot10^{-3}$
923	$3.1\cdot10^{-2}$	$1.8\cdot10^{-2}$
948	$5.9\cdot10^{-2}$	$4.2\cdot10^{-2}$
973	$1.1\cdot10^{-1}$	$8.0\cdot10^{-2}$
998	–	$1.5\cdot10^{-1}$
1023	–	$2.7\cdot10^{-1}$

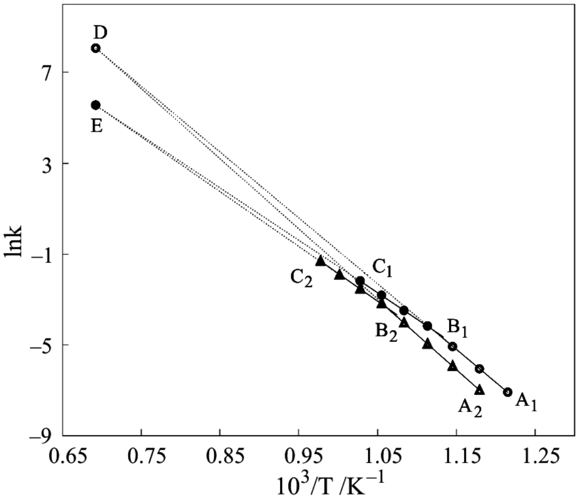

Fig. 3 Arrhenius plot for thermal decomposition of: 1 – $ZnSeO_3$ and 2 – $CdSeO_3$

solid phases of $ZnSeO_3$ and $CdSeO_3$, respectively. The second ones (B_1C_1 and B_2C_2) are less steep and correspond to the decomposition of the melts of $ZnSeO_3$ and $CdSeO_3$. The different slopes of the two groups showed that the decomposition of the solid phases would occur at higher activation energies compared to the corresponding melts. Besides, $CdSeO_3$ (solid or melt) decomposed at higher activation energy than $ZnSeO_3$. The finding of the coefficients of the corresponding empiric linear equations provides a possibility to locate the co-ordinates of the intersection points B_1 and B_2, which turned out to be at the melting temperatures of both selenites, ±2 K. This observation lead us to the conclusion that the decomposition of the melts is connected with lower values of the activation energy (higher rate constants) due to the greater dynamics in the liquid phase and its higher lability. This was confirmed also by reports by other authors (Bakeeva *et al.* [6]) who studied the dependence of SeO_2 vapor pressure on the heating temperature of $CdSeO_3$ and found that the linear curve $\ln p$ *vs.* $1/T$ was bent at a temperature corresponding to the melting point of $CdSeO_3$. Besides, they observed that the temperature coefficient of the vapor pressure ($d\ln p/dT$) was higher for the decomposition of the melt than for the solid phase. It means that the decomposition of the melt was kinetically easier. Furthermore, our studies showed that the extrapolation of the straight lines gives the intersection points D and E, which have the same value of $1/T$, respectively T. This temperature was considered to be the isokinetic temperature of the decomposition of both selenites studied (T_{iso}=1465 K). The value of the isokinetic temperature showed also that the decomposition of $CdSeO_3$ at temperatures higher than T_{iso} would proceed at a rate higher than that of $ZnSeO_3$. All the values characterizing the kinetic parameters of thermal decomposition of the two selenites are summarized in Table 3.

As can be seen from Table 3, the values of the activation energy of decomposition of $CdSeO_3$ were higher than these of $ZnSeO_3$ despite the state of aggregation of these compounds. As it has already been reported [38], there is a direct relationship between the cation radius of the selenite and its thermal stability and activation energy of thermal decomposition. Similar tendency was observed for the decomposition of some perchlorates [39, 40], carbonates and sulfates [41]. A common conclusion is that the reason for this is the different degree of the effect of counterpolarization in the oxoanion under the effect of the different polarization ability of the cation. We, however, prefer to explain the tendency observed using the generalized perturbation theory of chemical reactivity developed by Klopman and Hud-

Table 3 Kinetic characteristics of the isothermal decomposition of $ZnSeO_3$ and $CdSeO_3$

Parameters	$ZnSeO_3$		$CdSeO_3$	
	solid	melt	solid	melt
r_{cat}/Å	0.83		1.03	
R^2	0.9793	0.9882	0.9886	0.9761
n	0.97	0.73	1.04	0.76
E/kJ mol^{-1}	241.4	192.2	256.8	200.3
A/min^{-1}	$1.7\cdot10^{12}$	$2.3\cdot10^{9}$	$6.1\cdot10^{12}$	$4.5\cdot10^{9}$
$-\Delta S^{\neq}$/J mol^{-1} K^{-1}	61.8	117.9	51.2	112.3

son [42]. According to this theory, interactions occur predominantly between 'hard' ions resulting in formation of ionic bonds or between 'soft' ions resulting in covalent bonds in the molecule. Taking into account the nucleophilicity and electrophilicity orders reported in [42], SeO_3^{2-} is a 'soft' ion, Zn^{2+} is a 'hard' ion due to its smaller ionic radius and Cd^{2+} is again 'soft' ion due to its bigger ionic radius. Therefore, when selenites are formed from the corresponding ions in the solution, the bonds in $CdSeO_3$ molecule would be more covalent (and, respectively, stronger) compared to these in $ZnSeO_3$. Hence, higher temperature would be necessary to break these bonds, which means that the thermal decomposition of $CdSeO_3$ should occur at higher activation energy. This is confirmed by the higher melting temperature of $CdSeO_3$ compared to $ZnSeO_3$ [1, 6].

It is well known that the pre-exponential factors for solid-phase reaction are expected to have a wide range of values (six or seven orders of magnitude). Empirical first order pre-experimental factors may vary from 10^5 to 10^{16} min^{-1} [43–45]. The low factors will often indicate a surface reaction, but if the reactions are not dependent on surface area, the low factor may indicate a 'tight' complex. The high factors will usually indicate a 'loose' complex. In case of bulk decomposition any molecule is as likely to react as any others; and no preference is shown toward corners, edges, surface, defects or sites of previous decomposition. There are four special cases, which will indicate the range in values for the pre-exponential factors for the rate constants. In case I ($A \approx 10^{14}$ min^{-1}) there is no change in degree of the rotational excitation between the reactions and the complex. There will be two subcases – completely free rotation and completely restricted rotation. The first one probably can only refer to unimolecular reactions. In case II ($A \approx 10^{15}$ min^{-1}) the complex has a 'freer' condition than the reagents. This may be most likely to occur on a surface where the complex might extend itself from the surface and perhaps rotate parallel to the surface. The reactant is assumed to be completely restricted. In case III ($A \approx 10^{11}$ min^{-1}) the complex is highly restricted in rotation. For the unimolecular reaction the complex would be expanded in size and hence interact more strongly with its neighbors. In case IV ($A \approx 10^5$ min^{-1}) the reagents are in equilibrium with a surface adsorbed layer. The adsorbed species on the surface then react via the activated complex to give products. In conclusion of the activated complex has freer rotation than the reactant; the first order pre-exponential factor is high.

When solid-state reactions of the same type occur, it was found that large values of A correspond to large values of E. The large E values are usually connected with the higher strength of the chemical bond (bonds) which is to be broken. At the same time, according to the Eq. (8) large values of A should be accompanied by substantial values of $\Delta S^{\neq}$. It is well known that $\Delta S^{\neq}$ can be less, equal or higher than zero. In the cases when $\Delta S^{\neq}<0$, the reactions are classified as 'slow' and when $\Delta S^{\neq}>0$ – as 'fast' [46]. The negative values of $\Delta S^{\neq}$ indicate that the activated complex is 'more organized' than the initial reagent. We found [38] for the thermal decomposition of selenites of the same group of the Periodic table (for instance, $Al_2(SeO_3)_3$, $Ga_2(SeO_3)_3$, $In_2(SeO_3)_3$) that the thermal stability, the values of E and A increase from top to bottom of the group and the values of $\Delta S^{\neq}$ become less negative. According to GPT, a strong bond between the ions is formed when both cation and anion behave either as 'soft' or 'hard', since minimal rearrangement of the ionic orbitals (maximum adaptability) is necessary in both cases. According to our interpretation, in these cases the bonds would be strong (large values of E) but only slight rearrangement would be necessary (small absolute values of $\Delta S^{\neq}$) to break them for the formation of the activated complex of the reagent.

According to [46] the negative values of $\Delta S^{\neq}$ indicated that the activated complex has a more ordered structure than the reactant, and the reaction is slower than normal. In our case, the higher absolute values of $\Delta S^{\neq}$ observed for the decomposition of the melts show that their decomposition is accompanied by higher change of the entropy for the formation of the activated complex, since the liquid aggregate state (higher temperature) is characterized by higher values of entropy. On the other hand, the higher values of $\Delta S^{\neq}$ observed for $ZnSeO_3$ were higher than these for $CdSeO_3$, which is due to the necessity of more significant 'rearrangement' in the $ZnSeO_3$ structure because the bond between the cation and the anion is predominantly ionic. The same tendency was observed at the isothermal decomposition of aluminum, gallium and indium selenites [38].

Conclusions

It can be stated in conclusion that the thermal stability of the selenites is a function of their cation radius and polarizability, which reflects on the nature of the chemical bond formed. In interactions taking place under charge control, the chemical bond is ionic while for interactions with orbital control the bond is covalent. The first type of interactions occurred, mainly between ions with small radii (strongly hydrated) and the second type – between large ions (weakly hydrated). It can be concluded, therefore, that the dependencies observed for the thermal stability of selenites result from the perturbation of the molecular orbitals of the anion (donor) and cation (acceptor) occurring during the formation of the corresponding selenite.

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Received: March 2, 2004
In revised form: May 12, 2004