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Thermal Expansion of CaZnSO

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Abstract—The temperature stability range of the zinc calcium oxysulfide CaZnSO has been determined in an inert atmosphere using high-temperature x-ray diffraction, thermogravimetry, and x-ray microanalysis. The lattice parameters and thermal expansion coefficients of CaZnSO have been measured in the range 298–1170 K and have been represented by best fit equations.

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INTRODUCTION

Calcium-containing oxysulfides belong to a poorly explored class of compounds forming on heating of sulfides with calcium oxide [1–4]. According to Igiehon et al. [3], CaZnSO has a hexagonal structure. Petrova et al. [5] refined the lattice parameters and determined the space group of this zinc calcium oxysulfide using the Rietveld profile analysis method. CaZnSO was shown to possess hexagonal symmetry (sp. gr. $P6_3mc$) with lattice parameters a = 0.37547(1) nm and c = 1.14014(5) nm (V = 0.1392 nm^3, Z = 2). Its x-ray density is 3.66 g/cm^3. The atoms in CaZnSO form layers stacked in the [001] direction. Its structure can be thought of as made up of alternating corrugated Zn–S and Ca–O bilayers [5]. Data on the thermal stability of CaZnSO and the temperature variation of its lattice parameters are not available in the literature.

The purpose of this work was to assess the thermal stability of CaZnSO in an inert atmosphere, to measure its lattice parameters at temperatures of up to 1170 K, and to determine its thermal expansion coefficient.

EXPERIMENTAL

The thermal stability of CaZnSO was studied using a Mettler-Toledo thermal analyzer (DTA + TG). The sample was heated to 1670 K at a rate of 10 K/min in flowing argon (50 ml/min).

High-temperature x-ray diffraction (XRD) measurements were made on a DRON-2.0 automated diffractometer (CoK_α or CuK_α radiation, graphite monochromator) equipped with a UVD-2000 attachment. The internal standard used was single-crystal semiconductor-grade silicon (a = 0.543106 nm). The sample was heated to 970 K in flowing helium (p_{O_2} = 10^3 Pa). Lattice parameters were determined by a standard procedure [6, 7] with an accuracy of ±0.0001 in a and ±0.0002 nm in c.

The elemental composition of the phases present was determined on a CAMEBAX x-ray microanalyzer. In thermodynamic calculations, we used the HSC-5.1 program.

The zinc calcium oxysulfide sample for this investigation was synthesized by heating a 1 : 1 mixture of reagent-grade calcium oxide precalcined at 1270 K and pure-grade zinc sulfide (for luminophors) to 1370 K in flowing helium over a period of 3 h. After grinding the sample to a particle size under 0.063 mm, the excess calcium oxide was removed by washing with 3% acetic acid. After filtration and drying, the zinc calcium oxysulfide powder contained (all in wt %) Ca, 24.6; Zn, 40.9; and S, 19.8. The content of impurity phases (starting reagents) was within 3% as determined by XRD.

RESULTS AND DISCUSSION

The TG curve of CaZnSO (Fig. 1) shows a slight weight loss below 1370 K, due to the decomposition of the calcium hydroxide and calcium carbonate formed during chemical purification of the sample. Starting at 1370 K, the sample weight decreases substantially, and the weight loss reaches 13% at 1670 K, which is due to zinc sulfide sublimation. The DTA curve shows an endothermic peak at 1554 K, independent of the heating rate, attributable to the melting of the oxysulfide. The second heating at a rate of 10 K/min results in an additional endotherm, with an onset temperature of 1500 K and a peak temperature of 1520 K, due to the melting of the eutectic [1] resulting from partial CaZnSO decomposition.

The XRD data for the CaZnSO sample after heating at 10 K/min to 1020, 1270, and 1560 K (Fig. 2) indicate that, up to 1270 K, the oxysulfide is stable and the extent of the reaction

$$\mathrm{CaZnSO} \longleftrightarrow \mathrm{ZnS} + \mathrm{CaO} \qquad (1)$$

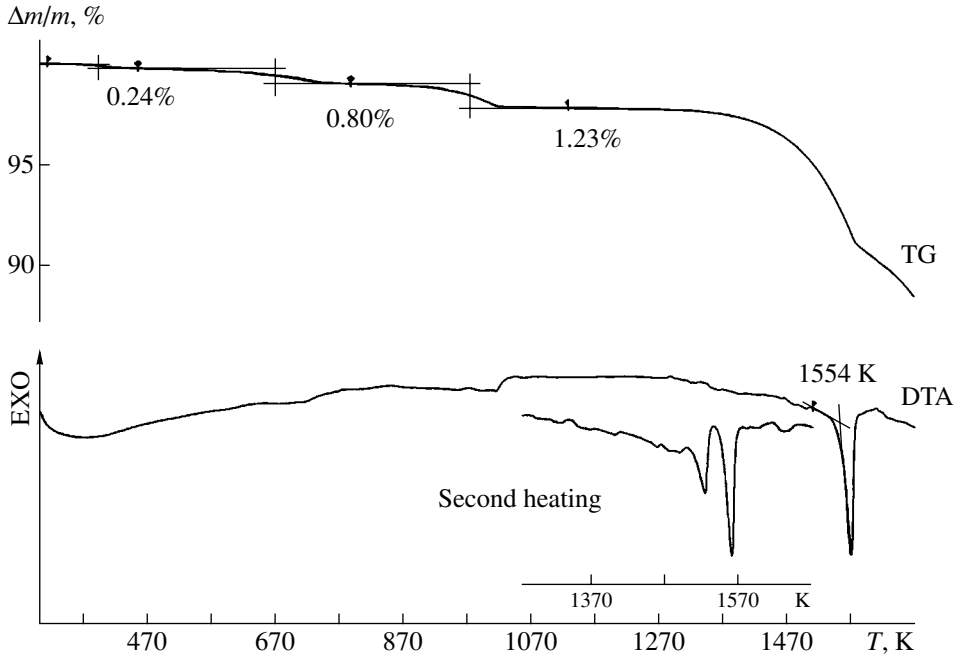

Fig. 1. Thermal analysis of CaZnSO in flowing argon at a heating rate of 10 K/min.

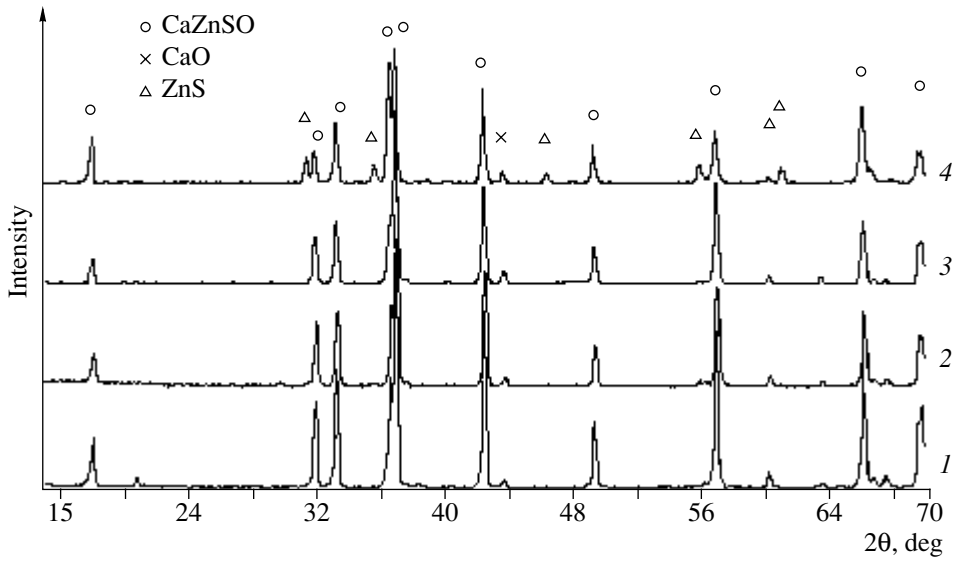

Fig. 2. XRD patterns (CoK_α radiation) of zinc calcium oxysulfide: (*1*) as-prepared and (*2–4*) after heating to 970, 1270, and 1560 K, respectively.

is insignificant. Only after heating to 1560 K and melting of the oxysulfide did the XRD pattern of the cooled sample show reflections from ZnS and CaO. The exchange reaction

$$ZnS + CaO = ZnO + CaS \quad (2)$$

is thermodynamically implausible in the temperature range under consideration, as supported by the positive values of the Gibbs energy (J):

$$\Delta G^0 = 12036.6 - 1.84T. \quad (3)$$

X-ray microanalysis data for melted CaZnSO (1560 K) also indicate the formation of ZnS and CaO inclusions (Fig. 3). The oxysulfide phase consists of elongated crystallites about 10 μm in width, whose areal proportion is up to 70%. According to x-ray microanalysis data, zinc calcium oxysulfide contained (all in wt %) Ca, 25.5; Zn, 43.4; S, 21.5; and the balance, O.

High-temperature XRD measurements (CuK_α radiation) demonstrate that the lattice parameters of the

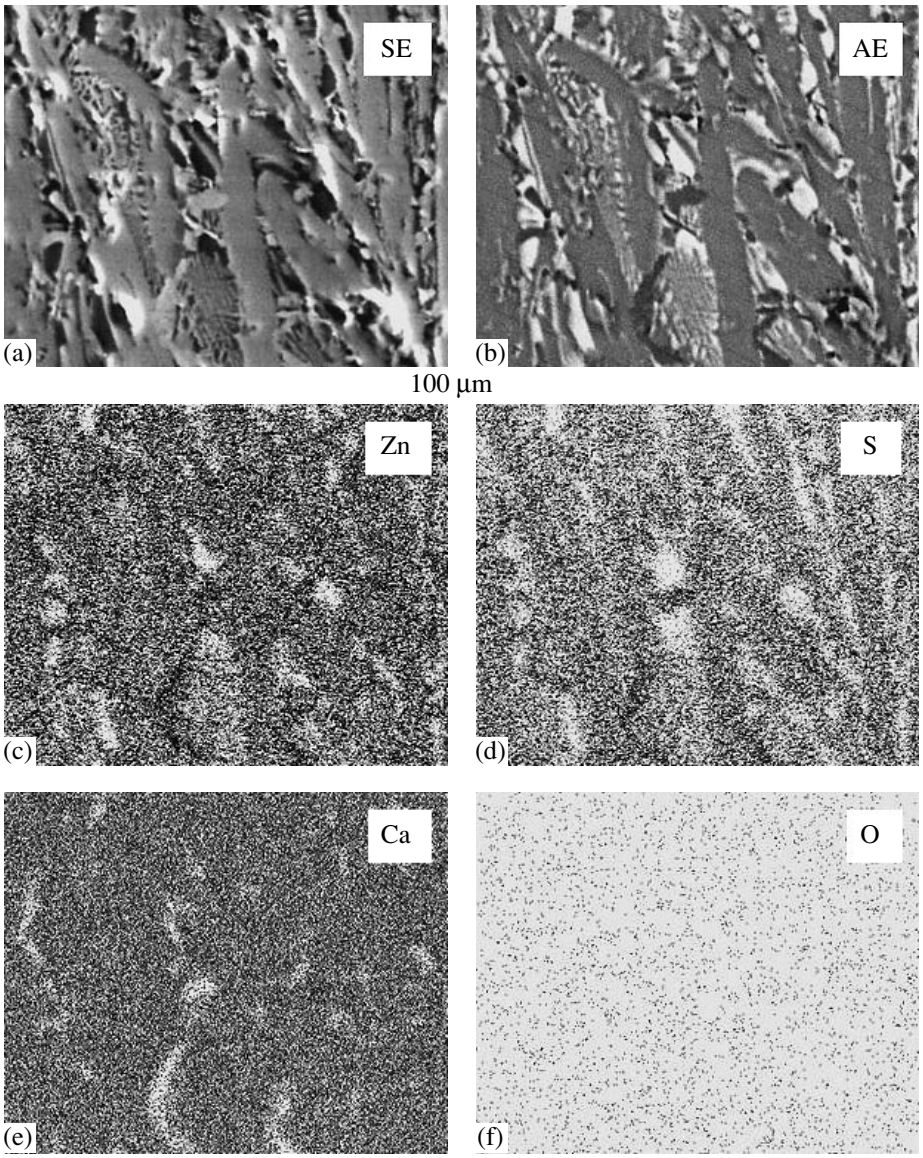

Fig. 3. Microstructure of the zinc calcium oxysulfide sample: (a) secondary-electron image, (b) specimen-current image, and (c–f) x-ray maps.

oxysulfide (Fig. 4) are linear functions of temperature up to 970 K, as represented by

$$a = 0.3742 + 4.57 \times 10^{-6}\ T, \quad (4)$$

$$c = 1.1351 + 15.13 \times 10^{-6}\ T, \quad (5)$$

$$V = 0.1376 + 5.34 \times 10^{-6}\ T \quad (6)$$

with high accuracy (R^2 = 0.997, 0.993, and 0.994 for Eqs. (4), (5), and (6), respectively).

The thermal expansion coefficients of CaZnSO, evaluated as [7]

$$\alpha_{a(c)} = (a,\ c)_1^{-1}[(a,\ c)_2 - (a,\ c)_1]/(T_2 - T_1), \quad (7)$$

are $\alpha_a = 1.26 \times 10^{-5}$ K^{-1} and $\alpha_c = 1.30 \times 10^{-5}$ K^{-1}. These values indicate that the thermal expansion of the CaZnSO lattice is almost isotropic. The *c*/*a* ratio is constant at 3.035 over the entire temperature range studied. The thermal expansion coefficients of CaZnSO are substantially larger than those of wurtzite (ZnS): $\alpha_a = 6.54 \times 10^{-6}$ K^{-1} and $\alpha_c = 4.59 \times 10^{-6}$ K^{-1} [7]. Comparison of the lattice parameters of the isostructural oxysulfides CaZnSO and CaFeSO [8] demonstrates that these compounds are close in *a*, whereas the *c* and *V* of zinc calcium oxysulfide exceed those of iron calcium oxysulfide, which seems to be due to the larger ionic radius of Zn^{2+} compared to Fe^{2+} [9].

Heating CaZnSO to above 970 K at p_{O_2} = 10 Pa leads to the formation of CaS. Raising the temperature to 1170 K results in the reduction of the oxysulfide, zinc

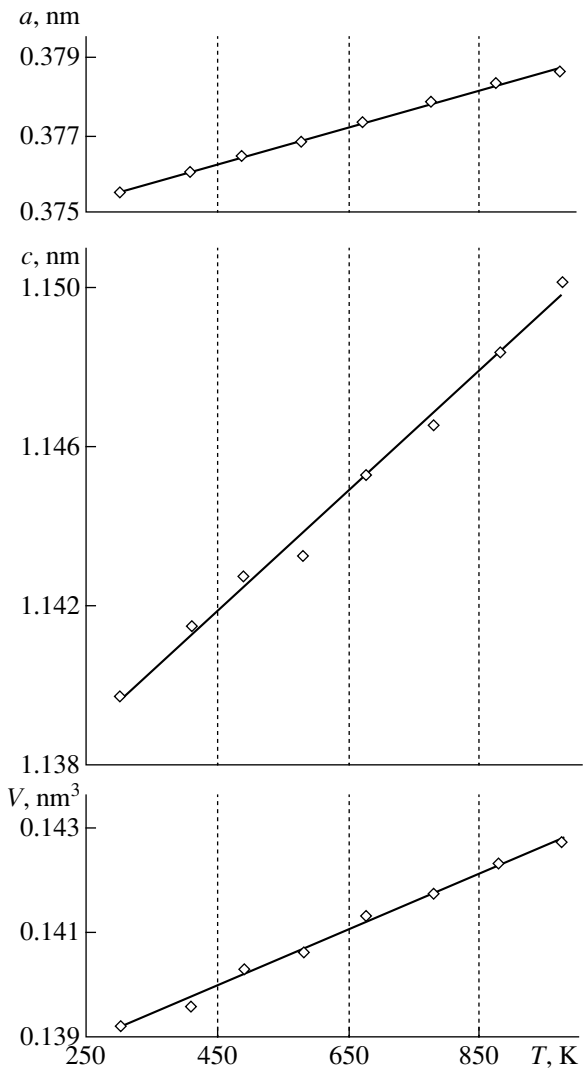

Fig. 4. Lattice parameters as functions of temperature for CaZnSO during heating in helium.

vaporization [9], and the formation of phase-pure calcium sulfide:

$$CaZnSO = CaS + Zn\uparrow + 0.5O_2. \quad (8)$$

The forming CaS has a cubic structure with a = 0.5697 nm at 298 K. During heating from 970 to 1170 K, the lattice parameters of CaS increase linearly, with a thermal expansion coefficient $\alpha = 1.69 \times 10^{-5}$ K^{-1}. The stability field of CaZnSO in the $\log(p_{CO_2}/p_{CO})$–T phase diagram was only inferred from thermodynamic calculations [10]. The present results suggest that the effect of p_{O_2} on the thermal stability of zinc calcium oxysulfide must be assessed more accurately.

CONCLUSIONS

The zinc calcium oxysulfide CaZnSO is stable in an inert atmosphere up to 1370 K. At higher temperatures, CaZnSO partially decomposes. The hexagonal cell parameters of CaZnSO increase linearly with temperature, and its thermal expansion is almost isotropic.

ACKNOWLEDGMENTS

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