Heats of Crystallization of Some Amorphous Oxides

M. NATARAJAN, G. V. CHANDRASHEKHAR, and C. N. R. RAO[1]
Department of Chemistry, Indian Institute of Technology, Kanpur, India

Heats associated with the exothermic crystallization reactions of amorphous Al_2O_3, Cr_2O_3, Fe_2O_3, and TiO_2 have been determined.

EXOTHERMIC crystallization reactions associated with large heats have been observed in the differential thermal analysis curves of amorphous ferric oxide and chromia (*1*, *7*), titania (*11*), and alumina (*2*). After the exothermic reactions these oxides show high crystallinity as evidenced by x-ray analysis. An examination of the literature indicated that there was little information on the quantitative aspects of crystallization reactions, and it was considered worthwhile to examine the crystallization reactions in a few oxides. Such a study would be of importance in surface chemistry as well as solid-state chemistry. Further, these studies could be of value in the understanding of the pseudo-crystallization (disorder-order) reactions in oxides (*8*, *10*).

EXPERIMENTAL

The crystallization reactions of Al_2O_3, Cr_2O_3, Fe_2O_3, and TiO_2 have been studied by quantitative differential thermal analysis (DTA) employing the phase transformations of lithium sulfate (monoclinic → cubic; 590° C.; ΔH, 6.9 kcal. mole^{-1}), potassium sulfate (orthorhombic → hexagonal; 579° C.; ΔH, 2.1 kcal. mole^{-1}) and potassium nitrate (II → I; 136° C.; ΔH, 1.2 kcal. mole^{-1}) as external standards (*9*). The values of the ΔH_{cryst} reported here are based on three independent measurements of the DTA peak areas with respect to all the three standards; the ΔH_{cryst} values from the three standards agreed well with each other. In this laboratory, the applicability and limitations of the DTA to the study of the quantitative energy aspects of phase transformations have been examined in detail (*9*). Since the crystallization reactions are associated with large heats, the technique is considered to be suitable to provide fairly reliable values for the heats of crystallization.

The DTA curves were recorded by employing an Aminco Thermoanalyzer fitted with a voltage stabilizer, deviation amplifier, programmed furnace, and an *XY* recorder. The uncertainty in the ΔH_{cryst} values is ~10%. The values of the energy of activation, E_a, calculated from the procedure of Borchardt and Daniels (*3*) are, however, likely to be associated with larger uncertainties (*9*).

Amorphous alumina was prepared by ammoniacal hydrolysis of $AlCl_3$ followed by drying in vacuum at ~100° C. Fe_2O_3 and Cr_2O_3 were prepared by the ammoniacal hydrolysis of the nitrates followed by drying in an air-oven at ~120° C. Titanium peroxide was prepared by the procedure reported in the literature (*5*, *6*); the crystallization peak of TiO_2 appears after the endothermic peak owing to the decomposition of the peroxide (*11*). Thermogravimetric analysis showed that there was no mass loss in the temperature range of the exothermic crystallization reactions in the case of Fe_2O_3, Cr_2O_3, and TiO_2; mass loss was negligible in the case of Al_2O_3. All the oxides were crystalline after the exothermic reactions as found by x-ray analysis. Cr_2O_3 and Fe_2O_3 had the rhombohedral structures, while Al_2O_3 was in the γ-form. TiO_2 had the anatase structure.

RESULTS AND DISCUSSION

Table I. Heats of Crystallization of Oxides[a]

	Cryst. Temp., ° C.		Kcal. Mole^{-1}	
	Initial	Peak	$-\Delta H_{\text{cryst}}$	E_a
Al_2O_3	170	265	14	12
Cr_2O_3	390	410	12	40
Fe_2O_3	260	335	32	20
TiO_2^b	250	305	15	18

[a] The data are for freshly prepared samples. [b] Freshly prepared TiO_2(anatase) gives a single exothermic peak at ~305° C. With aging, another peak appears at ~230° C. If the area under the latter peak is also considered, the ΔH_{cryst} becomes much larger. The final product after crystallization is anatase in both the cases.

The temperatures corresponding to the initiation and the peak in the DTA curves for the crystallizations reactions are listed with the enthalpies and energies of activation in Table I. All the ΔH_{cryst} values are large. The ΔH_{cryst} for Fe_2O_3 found in this study agrees with that of Frieke and Klenk (*4*), who estimated the lower limit for the heat of crystallization to be 13 kcal. mole^{-1} by measurements of heats of solution in HF.

The ΔH_{cryst} values reported here should be of value, since there seems to be no other data or estimates available in the literature; further, it is difficult to measure the heats of solutions of crystalline oxides owing to their high insolubility even in very strong acids. The E_a values for the crystallization reactions are not very high in comparison with the activation energies for phase transformations in solids (*9*), indicating that crystallization of amorphous oxides takes place with relative ease.

The description of the initial states of the oxides as amorphous is not decisive or exact, since many amorphous states may be possible with different energies and therefore different heats of crystallization. The present study, however, shows that the low-temperature removal of water from hydroxides or oxygen from peroxides leaves the oxides in "relic" structures which will then crystallize at higher temperatures releasing energy. The data reported here should clearly indicate the magnitude of the heats of such crystallization reactions.

LITERATURE CITED

(1) Bhattacharyya, S.K., Ramachandran, V.S., Ghosh, J.C., *Advn. Catalysis* **9**, 114 (1957).
(2) Bhattacharyya, S.K., Srinivasan, G., Ganguli, N.D., *J. Indian Chem. Soc.* **41**, 233 (1964).
(3) Borchardt, H.J., Daniels, F., *J. Am. Chem. Soc.* **79**, 41 (1957).
(4) Frieke, R., Klenk, J., *Z. Electrochem.* **41**, 617 (1935).
(5) Jere, G.V., Patel, C.C., *Z. Anorg. Allgem. Chem.* **319**, 176 (1962).
(6) Kharkar, D.P., Patel, C.C., *Current Sci. (India)* **24**, 413 (1955).
(7) Rao, C.N.R., Hoffman, C.W.W., *J. Sci. Ind. Res. (India)* **15B**, 663 (1956).
(8) Rao, C.N.R., Pitzer, K.S., *J. Phys. Chem.* **64**, 282 (1960).
(9) Rao, C.N.R., Rao, K.J., *J. Mater. Sci.* **1**, 238 (1966).
(10) Rao, C.N.R., Yoganarasimhan, S.R., Lewis, M.P., *Can. J. Chem.* **38**, 2359 (1960).
(11) Yoganarasimhan, S.R., Rao, C.N.R., *Trans. Faraday Soc.* **58**, 1579 (1962).

RECEIVED for review May 21, 1967. Accepted December 21, 1967. Work sponsored by the U. S. National Bureau of Standards by a grant of research project (G-51) through their Special International Program.

---

[1] Present address: Visiting Professor of Chemistry (1967–68), Purdue University, Lafayette, Ind. 47907