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Size-induced structural transitions in the Cu-O and Ce-O systems

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We have studied the effect of reducing the particle size on the crystal structures of copper oxide and cerium oxide. Below 25 nm, the cubic Cu_2O is found to be more stable than the monoclinic CuO. This confirms an earlier conjecture that the ionic character of a solid tends to increase with a reduction in the particle size. As a result, high-symmetry crystal structures are more likely to be stable at smaller sizes. For cerium oxide, the bulk (cubic) CeO_2 phase remains stable down to 4.8 nm and, as expected, does not undergo a transition to any of the other available structures with lower symmetry.

I. INTRODUCTION

The study of finite-size effects in various classes of small solids has recently acquired great significance since many such systems have important applications, such as in catalysis, sensors, magnetic recording, magnetic fluids, electronic and optical materials, and as precursors for high strength materials. These systems are also very interesting from the point of view of basic physics. From a study of several different categories of nanocrystalline oxides, we have recently proposed the following general rule.[1] In a majority of partially covalent oxides, the unit-cell volume increases with a decrease in particle size and the lattice gets distorted in such a way that the *crystal symmetry tends to increase*. In some cases [such as Fe_2O_3,[2] Al_2O_3,[1] ZrO_2,[3] and $BaTiO_3$ (Ref. 4)], the lattice distortion that occurs with decreasing size is large enough to induce a transition to a more symmetric crystal structure. In most other cases, there is simply a size-induced reduction in an asymmetry parameter. Many important physical properties (such as the transition temperature and the magnitude of the order parameter in cooperative systems) are affected significantly by such changes in the size and symmetry of the crystallographic unit cell. It was earlier argued that the size-induced increase in the crystal symmetry is related to an increasing ionic character of the solid.[1] We now provide a direct confirmation of this conjecture.

In some of the oxides, there is—in addition to the symmetry change—a variation in the oxygen stoichiometry with a reduction in the crystal size. As an example, for the three high-T_c oxides in which finite-size effects have been studied [viz., $La_{1.85}Sr_{0.15}CuO_4$,[5] $YBa_2Cu_3O_{7-\delta}$,[6] and $Bi_2Sr_2CaCu_2O_{8+y}$ (Ref. 6)], the oxygen number decreases monotonically with a reduction in size. Here, we attempt to test the generality of this effect.

In the above context it is interesting to study finite-size effects in CuO, a strongly covalent oxide with a low-symmetry (monoclinic) structure. The other commonly occurring oxide of Cu, Cu_2O has a high-symmetry (cubic) structure and a lower anion/cation ratio. The oxides of Cu are also interesting in their own right. In addition to both CuO and Cu_2O being semiconducting, they provide a relatively simple reference system for the study of the complex cuprates (which include the oxide superconductors). The second system chosen was cerium oxide, which may exist as CeO (cubic), Ce_2O_3 (hexagonal), CeO_2 (cubic), and Ce_6O_{11} (monoclinic). A comparison of the results in these two systems can be expected to clarify the relative importance of changes in lattice symmetry, ionic-covalent character, and oxygen stoichiometry (valence) with a decrease in the crystal size.

II. EXPERIMENTAL

To rule out any process- or precursor-dependent effects, nanoparticulate CuO was synthesized by two different routes: rapid liquid dehydration and precipitation. The liquid dehydration process involves fast nucleation of fine particles from an aqueous solution of copper citrate. Distilled acetone was used as dehydrating agent since it has a high solubility for water but not for copper citrate. The copper citrate precursor thus obtained was calcined to produce copper oxide. Samples with different average sizes were obtained by changing the solution concentration and the calcination condition. The second route involved the precipitation of copper oxalate from a solution of copper acetate at a constant pH of ≈2.0. The oxalate was converted to oxide by heating and the particle size was controlled as before.

Cerium oxide nanoparticles were synthesized by a modified sol-gel method from a solution of $Ce(NO_3)_3\cdot 6H_2O$. A stable suspension (sol) of $Ce(OH)_3$ was gelated using a chemical dehydrating agent together with a surfactant. The gelated material was dried and calcined at different temperatures to obtain different sizes of cerium oxide nanoparticles (ranging in size from 5 nm to about 1 μm).

Chemical phase analysis was carried out by powder x-ray diffraction (XRD) using a Jeol JDX 8030 instrument. The coherently diffracting domain size (d_{XRD}) was calculated from the width of the XRD peaks under the Scherrer approximation[7] (which assumes the small crystallite size to be the only cause of line broadening) after correcting for instrumental broadening. The equivalent spherical diameter (d_{BET}) of the powder samples was calculated from the specific surface area measured by the Brunauer-Emmett-Teller

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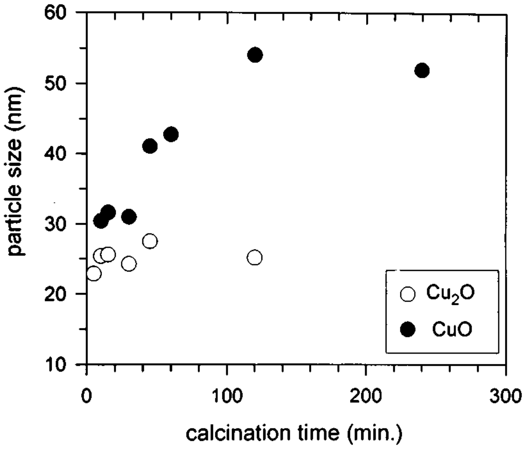

FIG. 1. Dependence of the particle size (coherently diffracting XRD domain size) of CuO and Cu_2O phases on the calcination time of the copper citrate precursor produced by rapid dehydration. All the samples were calcined at 400 °C.

(gas adsorption) technique[8] using a Quantachrome Quantasorb Jr. instrument.

III. RESULTS AND DISCUSSIONS

A. Size effects in copper oxide

Heating the citrate precursor (produced by rapid dehydration) at 250 °C results in a mixture of Cu_2O and CuO. The percentage of Cu_2O in the mixture was found to decrease when either the calcination temperature or the calcination time was increased. We observe, however, that though the particle size of CuO increases gradually (from 30 to 55 nm) with heating time, that of Cu_2O remains approximately constant at $d_{\mathrm{XRD}} \approx 25$ nm (see Fig. 1). The figure refers to samples obtained from the same starting solution concentration (0.5 M) and calcined at 400 °C for different times. The above result possibly indicates the existence of a critical particle size up to which the Cu_2O phase remains stable. Any further growth in size due to thermal aggregation leads to a conversion to CuO.

Transmission electron micrographs give us a direct idea of the particle size and its distribution. Most particles fall in the 12–18 nm range in the sample heated for 10 min at 400 °C [Fig. 2(a)]. The size range is larger (20–50 nm) in the sample heated for 120 min at 400 °C [Fig. 2(b)] due to the presence of small Cu_2O and larger CuO particles. Note that the XRD technique appears to slightly overestimate the particle size in these cases.

The results are essentially similar for copper oxide particles prepared by direct precipitation. Figure 3 shows the XRD patterns of these samples after calcination at 250 °C (15 min) and 350 °C (15 min). The relative enhancement of the Cu_2O phase at low particle sizes is obvious. The formation of Cu_2O, therefore, appears to be a size-induced phenomenon which is independent of the process and the precursor.

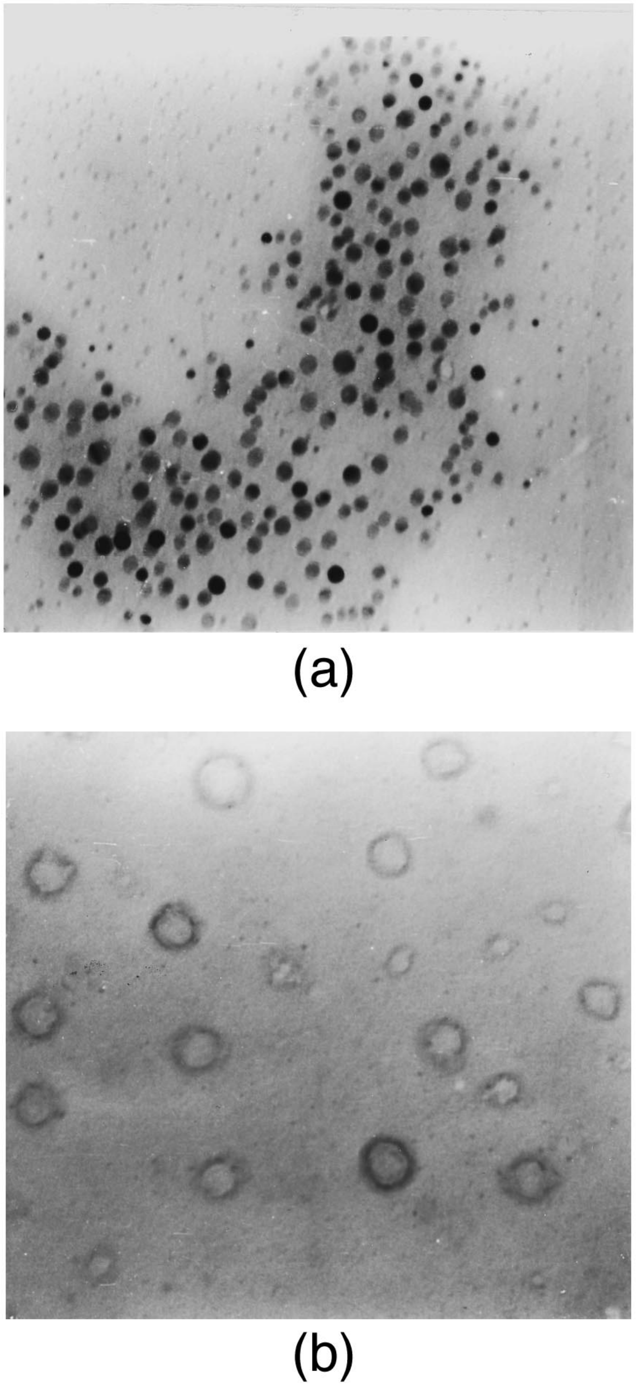

FIG. 2. Transmission electron micrographs of the CuO-Cu_2O system formed by heating the precursor at 400 °C for (a) 10 min and (b) 120 min. The instrumental magnification was ×140 000 in both cases. (Approximate scale: micrograph width=514 nm.)

Figure 4 shows that the size-induced transition from the low-symmetry CuO phase to the high-symmetry Cu_2O phase is accompanied by a sharp increase in the unit-cell volume (calculated per formula unit). We have previously suggested[1] that the increase in crystal symmetry that occurs with reducing size is related to a size-induced *negative* pressure effect (as evidenced by an expansion in the unit-cell volume). High-pressure measurements in transition-metal oxides indicate that the covalence increases with increasing pressure.[9] We therefore postulated that a reduction in particle size should result in an enhancement in the ionic character of the system and a consequent tendency towards structures of comparatively higher symmetry. This argument is directly supported by the present results since Cu_2O—in addition to

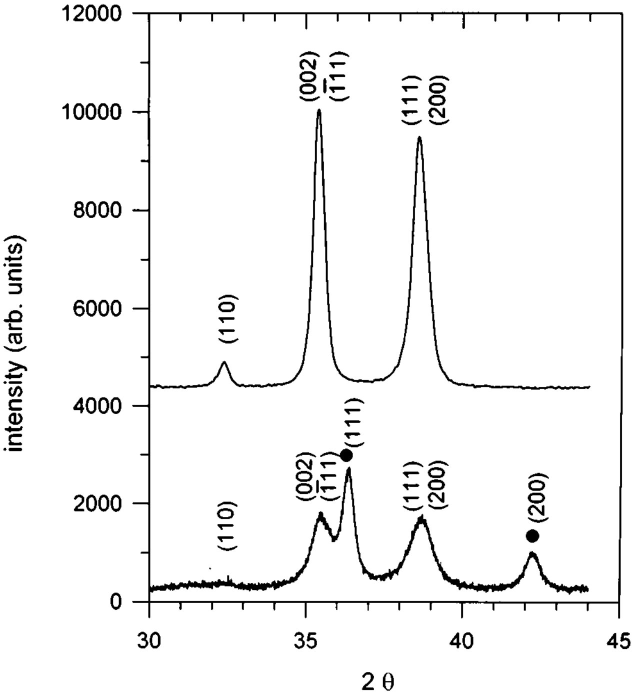

FIG. 3. X-ray diffractograms from samples prepared by the calcination of copper citrate precursors at 250 °C for 15 min (lower curve) and 350 °C for 15 min (upper curve). The upper spectrum shows the characteristic diffraction maxima for CuO only, while the lower one shows lines from CuO as well as Cu_2O (marked with ●).

being more symmetric—is also more ionic than CuO, as can be shown from Fajan's rules of ionic polarizability.[10]

It is probably a coincidence that some of the higher-symmetry structures (including Cu_2O), which are more stable at low particle sizes, are also oxygen deficient compared to the corresponding "bulk" phases. To understand the role of oxygen in such size-induced structural changes, we performed a complementary experiment involving cerium oxide.

B. Size effects in cerium oxide

The stable, "bulk" phase of cerium oxide is cubic CeO_2. If a release of oxygen is a necessary part of the size reduction process, then a size-induced structural transition to either the oxygen-deficient phase Ce_6O_{11} (low-symmetry) or to CeO or Ce_2O_3 (both cubic) could be expected. But if an increase in symmetry is the more important effect of size reduction, then cubic CeO_2 should not undergo a change in its crystal structure with decreasing size. But even a conversion to cubic CeO is unlikely, since its unit-cell volume (0.329 nm^3) is less than that of CeO_2 (0.396 nm^3), and our earlier results[1,2] indicate that the unit-cell volume tends to expand as the particle size is reduced (negative pressure effect).

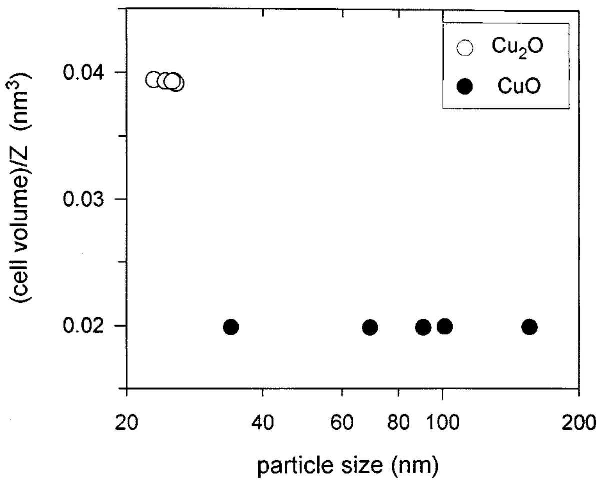

FIG. 4. Variation of the normalized unit-cell volume (per formula unit) with the XRD domain size in the CuO-Cu_2O system.

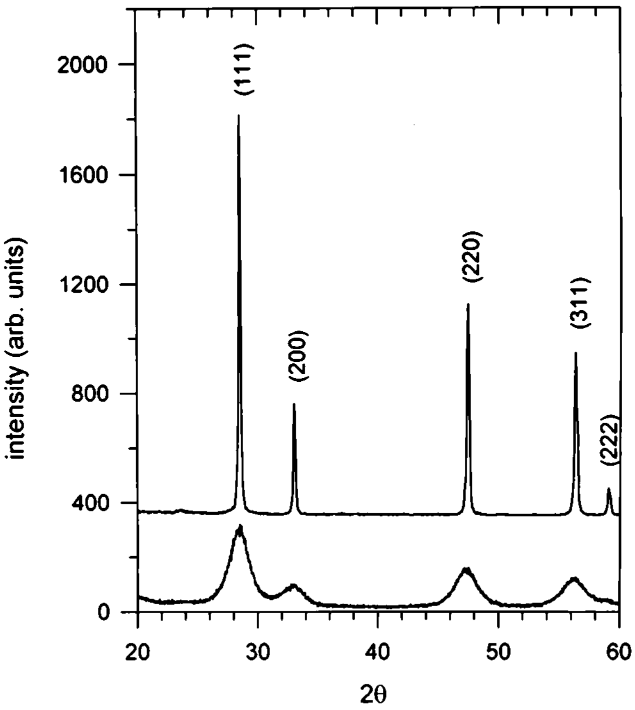

FIG. 5. X-ray diffractograms for CeO_2 samples produced by calcining the precursor at 100 °C for 15 min (lower curve) and at 1000 °C for 10 h (upper curve). The upper spectrum represents single phase, bulk CeO_2 (d_{BET}=684 nm), and there is no observable phase change down to 4.8 nm (d_{BET}) as can be seen from the lower spectrum.

We used the sol-gel technique to produce ultrafine particles of cerium oxide with various average sizes down to 4.8 nm (d_{BET}). Calcining the precursor at 1000 °C for 10 h leads to single phase (bulk) CeO_2 with d_{BET}=684 nm, while calcining at 100 °C for 15 min still leads to completely single phase CeO_2 with d_{BET}=4.8 nm (Fig. 5). Clearly, the high-symmetry cubic phase remains perfectly stable with a decrease in size and does not transform to any of the other known phases with lower oxygen stoichiometry.

IV. CONCLUSION

A size-driven transformation to higher-symmetry structures appears to be quite common in covalent or partially covalent oxides. We have provided experimental evidence to show that the high-symmetry phase that is more stable at lower sizes is less "covalent" than the bulk phase. An enhanced oxygen mobility and a reduction in the oxygen number, on the other hand, does not appear to be a direct result of size reduction.

The possibility of producing a predictable change in the symmetry of a chemical phase has important potential applications, and the synthesis of Cu_2O itself provides an example. The usual method prescribed for the formation of Cu_2O involves thermal reduction of CuO above 1100 °C. Nanoparticle routes could be used as novel alternative techniques for synthesizing Cu_2O at much lower temperatures. This should be made possible by proper optimization of the process conditions so as to maintain the particle size of the calcined sample below the critical size associated with the formation of Cu_2O.

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[1] P. Ayyub, V. R. Palkar, S. Chattopadhyay, and M. S. Multani, Phys. Rev. B **51**, 6135 (1995).

[2] P. Ayyub, M. S. Multani, M. Barma, V. R. Palkar, and R. Vijayaraghavan, J. Phys. C **21**, 2229 (1988).

[3] T. Mitsuhashi, M. Ichihara, and U. Taksuke, J. Am. Ceram. Soc. **57**, 97 (1974).

[4] K. Uchino, E. Sadanaga, and T. Hirose, J. Am. Ceram. Soc. **72**, 1555 (1989).

[5] V. R. Palkar, P. Ayyub, D. R. Nepali, and M. S. Multani, Z. Phys. D **26**, S234 (1993).

[6] M. S. Multani, P. Guptasarma, V. R. Palkar, P. Ayyub, and A. V. Gurjar, Phys. Lett. A **142**, 293 (1989).

[7] A. J. C. Wilson, Proc. Phys. Soc. London **80**, 286 (1962).

[8] T. Allen, *Particle Size Measurement* (Chapman and Hall, London, 1975), p. 358.

[9] H. G. Drickamer, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz, D. Turnbull, and H. Ehrenfest (Academic, New York, 1965), Vol. 17, p. 1.

[10] According to Fajan's Rules, the factors that favor covalency are (i) a smaller positive ion (Cu^{II} is smaller), (ii) a larger negative ion (no difference between $Cu^{II}O$ and $Cu^{I}_{2}O$), (iii) larger charges on either ion (Cu^{II} has the larger charge), (iv) the positive ion *not* having a noble-gas configuration (Cu^{II} does not have a noble-gas configuration, while Cu^{I} does). Hence $Cu^{II}O$ is expected to be more covalent than $Cu^{I}_{2}O$. For details, see, J. D. Lee, *Concise Inorganic Chemistry*, 4th ed. (Chapman and Hall, London, 1991).