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Some Mixed Metal Oxides of Perovskite Structure

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X-ray structural studies, mainly by powder techniques, have been made of a number of ABO_3-type mixed oxides. A cubic form of deformed perovskite structure, with eight formula units per cell, has been found in $BaThO_3$, $SrSnO_3$, and $SrZrO_3$. $BaCeO_3$ and $BaSnO_3$ have the ideal perovskite structure; orthorhombic distortions of this structure occur in $SrCeO_3$ and $CaSnO_3$, and rhombohedral distortions in KIO_3 and $TlIO_3$. Doubt is cast on the identification of a number of 'perovskites' reported previously. Structure changes with composition in several series of perovskite solid solutions are described.

1. Introduction

The perovskite structure and its various deformed modifications have been extensively studied since the discovery of ferroelectric behaviour in $BaTiO_3$ (Megaw, 1957). Brief description by Náray-Szabó (1947) of a variety of alleged ABO_3-type oxides, reported to have the perovskite structure, stimulated a further investigation of compounds of possible interest as dielectrics, particularly oxides of bivalent metals with quadrivalent cerium, thorium, and tin.

Binary and ternary solid solutions of some perovskite-type oxides have also been examined, in order to determine the structure changes that occur when substitutional solid-solutions are formed between a deformed and an undeformed perovskite structure.

2. Preparative and X-ray techniques

Most of the mixed oxides were prepared by high-temperature solid-state reaction between the oxide of the quadrivalent metal and the bivalent metal carbonate; the reagents used were of 'A.R.' or spectrographically pure grades. Accurately weighed quantities of the reactants, proportioned with due regard to moisture or carbonate contents (determined for each batch), were mixed by thorough grinding in an agate mortar. Firings were carried out in sintered alumina boats, in air. Firings at temperatures up to about 1500 °C. were conducted in an electric tube furnace wound with platinum–rhodium alloy; temperatures were measured by means of a platinum/platinum–rhodium thermojunction, and were maintained within ±10 °C. Firings at higher temperatures required a hydrogen-protected molybdenum-wound electric furnace and temperature measurement by means of a disappearing-filament optical pyrometer. Firing periods were normally about 15 hr. Firing temperatures (in °C.) used in preparing particular compounds are indicated below in parentheses; when a range is specified, it indicates the minimum and maximum temperatures at which a satisfactory product was obtained.

Binary solid-solutions were prepared by firing correctly proportioned mixtures of the component mixed oxides; ternary solutions were similarly obtained from an appropriate binary solution and the pure third component.

Single crystals of $CaSnO_3$ were grown by evaporation at 800–900 °C. of a calcium chloride melt in which the constituent oxides were dissolved (Ditte, 1883). $SrSnO_3$ crystals were similarly prepared from a melt of strontium chloride.

Powder photographs were obtained by means of 9 cm. or 19 cm. Unicam cameras. Lattice constants deduced from higher-angle lines were plotted against the function $\frac{1}{2}(\cos^2\theta/\sin\theta+\cos^2\theta/\theta)$ and extrapolated to $\theta=90°$. Unless other limits are stated, lattice-constant values in this paper are considered to be accurate to $\pm 0{\cdot}005$ Å. Single-crystal photographs were taken on a Leeds Weissenberg goniometer. Filtered copper (or, less frequently, chromium) radiation was employed.

3. The 'doubled' cubic perovskite cell

Powder photographs for $SrSnO_3$ (1000–1700 °C.), $BaThO_3$ (1500–1650 °C.), and $SrZrO_3$ (1000 °C.) showed a number of lines additional to those of a normal perovskite structure, all of which could be satisfactorily indexed by assuming a cubic unit cell having approximately twice the normal a value. The measured lattice constants were as follows:

$$SrSnO_3,\ a=8{\cdot}070\pm0{\cdot}002\ \text{Å};\ BaThO_3,\ a=8{\cdot}985\ \text{Å};\ SrZrO_3,\ a=8{\cdot}218\ \text{Å}\ .$$

Splitting of high-order reflexions, which would indicate lack of strictly cubic symmetry, was looked for but not observed with any of these compounds, though the doublet resolution obtained was very good for $SrSnO_3$ and good for $BaThO_3$. The doubling of the cell was confirmed by rotation and oscillation photographs from a single crystal of $SrSnO_3$; these also confirmed the primitive cubic cell, and systematic absence of ($h00$) reflexions with h odd indicated the space group to be $P2_13$–T^4 or $P4_232$–O^2.

The 'doubled' cell may develop by a coordinated tilting of the oxygen octahedra in eight adjacent cells of the normal perovskite structure, which then become 'octants' of the larger cell. The doubled cubic cell has not been reported previously in a simple stoichiometric perovskite, but Galasso, Katz & Ward (1959) have found it in defect structures containing an alkaline-earth cation with niobium or tantalum.

On exposure to the atmosphere, $BaThO_3$ is slowly decomposed by carbon dioxide to a mixture of barium carbonate and thorium dioxide; this confirms a report by Hoffmann (1935). The compound can be kept in a dry atmosphere free from carbon dioxide.

4. Compounds with the undeformed perovskite cell

$BaCeO_3$ (1000–1730 °C.) was found, from powder photographs, to have the simple perovskite structure, with $a=4{\cdot}397$ Å; Hoffmann (1934, 1935) reported a lower value, $a=4{\cdot}377\pm0{\cdot}003$ kX. ($4{\cdot}386\pm0{\cdot}003$ Å). The prediction of Náray-Szabó (1947) that this compound should have a monoclinic, doubled cell is therefore not fulfilled under the conditions now described.

$BaSnO_3$ (1000–1750 °C.) also proved to possess the simple cell, with $a=4{\cdot}117\pm0{\cdot}002$ Å; Megaw (1946) obtained $a=4{\cdot}1168\pm0{\cdot}0015$ Å. Calculated and observed line intensities in the powder photographs confirmed the perovskite structure; only one line (111) with an odd value of $h^2+k^2+l^2$ appeared in the films, owing to the comparable scattering factors of the metal ions, an effect also noticed with $BaCeO_3$. Wagner & Binder (1958, 1959) apparently found higher temperatures (1100 or 1200 °C.) necessary for the preparation of $BaSnO_3$; at 1000 °C. they obtained Ba_2SnO_4 with some unreacted stannic oxide.

5. Compounds with orthorhombic cells

$CaSnO_3$ (1250–1700 °C.) was found, from powder and single-crystal photographs, to have an orthorhombic structure, with

$$a=5{\cdot}519,\ b=7{\cdot}885,\ c=5{\cdot}668\ \text{Å}\ .$$

Megaw (1946) had obtained a larger orthorhombic cell involving doubling of the two smaller axial dimensions; more recently, Coughanour *et al.* (1955) have found the cell now confirmed here, with

$$a=5{\cdot}518,\ b=7{\cdot}884,\ c=5{\cdot}664\ \text{Å}\ .$$

The smaller cell was verified by preparing small single crystals of $CaSnO_3$, from which zero-layer normal-beam Weissenberg photographs and a first-layer equi-inclination photograph about the b-axis were obtained. These photographs gave no indication of doubling of a- and c-dimensions as assumed by Megaw. The general reflections showed no systematic absences; $h00$, $0k0$, and $00l$ reflexions were obtained only for even values of h, k, and l. It appeared at first that $hk0$ reflexions appeared only for even values of $h+k$, but closer inspection revealed very weak 450, 230, and 520 reflexions in appropriate photographs. The absences indicate the space group $P2_12_12_1$–D_2^4.

$SrCeO_3$ (1250–1650 °C.) gave a powder photograph very similar to that for $CaSnO_3$; the lattice constants derived from this were

$$a=6{\cdot}011,\ b=8{\cdot}588,\ c=6{\cdot}156\ \text{Å}\ ,$$

although in the absence of further data from single-crystal photographs a doubling of a or c cannot be excluded.

6. Rhombohedral cells; potassium and thallous iodates

Although mixed metal oxides were the primary objects of study, the reported perovskite-type structures of certain univalent metal iodates appeared to merit brief re-examination. Potassium iodate gave, on recrystallization from water, extensively twinned crystals; twinning was minimized by slow evaporation of a saturated solution in a vacuum desiccator held at a temperature just above 0 °C. Powder, rotation, oscillation, and zero-layer Weissenberg photographs on the resulting crystals showed a rhombohedral structure with $a=4{\cdot}410$ Å, $\alpha=89{\cdot}41°$. Single-crystal reflexions were obtained only with $h+k$ even. Náray-Szabó (1947) had described potassium iodate as monoclinic with a cubic pseudo-cell having $a=8{\cdot}92$ Å.

Untwinned single crystals of thallous iodate, initially prepared by precipitation from thallous nitrate and potassium iodate solutions, could not be obtained. Powder photographs, however, showed a rhombohedral unit-cell with $a=4{\cdot}510$ Å, $\alpha=89{\cdot}34°$; Rivoir & Abbad (1947) reported $a=4{\cdot}44$ Å, $\alpha=89{\cdot}10°$.

7. Unsuccessful attempts to prepare other perovskite structures

Attempts were made to prepare a number of compounds reported by Náray-Szabó (1943, 1947) and Coffeen (1953). The usual solid-state reactions, attempted over the reaction-temperature ranges given in parentheses, failed to give the reported perovskite structures in $CaCeO_3$ (850–1460 °C.) $CdCeO_3$ (800–1050 °C.), $PbCeO_3$ (1000 °C.), $MgCeO_3$ (1000–1650 °C.), $SrThO_3$ (1000–1650 °C.), $CaThO_3$ (1000–1460 °C.), $CdThO_3$ (800 °C.), $PbThO_3$ (800–1000 °C.), $MgThO_3$ (1000–1650 °C.), $NiSnO_3$ (1000–1400 °C.), and $CoSnO_3$ (300–1000 °C.). In all cases except the last no mixed-oxide product was obtained in which formation of the spindel Co_2SnO_4 was detected. Furthermore, the precipitation of a hydrated stannate followed by heating to give the anhydrous compound (Coffeen, 1953) did not give perovskite structures in $CdSnO_3$, $CoSnO_3$, $NiSnO_3$, $MnSnO_3$, and $CuSnO_3$.

Negative observations on these alleged structures do not, of course, prove that they do not exist, since there may be unsuspected differences between the starting materials or methods of preparation. It is noteworthy, however, that powder-photograph data presented by Náray-Szabó (1947) do not support his recorded conclusions; for example, the lines for '$MgCeO_3$', '$SrThO_3$', and '$PbThO_3$' correspond better with the patterns of the two component oxides, and a '$CaThO_3$' pattern proves to agree well with data for thorium dioxide and hydrated lime.

8. Solid solutions

Solid solutions of the types $(Ca, Sr)SnO_3$, $(Sr, Ba)SnO_3$, $(Ca, Ba)SnO_3$, $(Ca, Sr, Ba)SnO_3$, and $(Sr, Ba)CeO_3$ were prepared, and their lattice constants determined from powder diffraction patterns. The variation of lattice constants with composition is shown in Figs. 1–2. For further details see Smith (1956).

The series $(Ca, Sr)SnO_3$ (Fig. 1) and $(Sr, Ba)CeO_3$ (Fig. 2) show transitions from the orthorhombic structure to a cubic form, and the series $(Sr, Ba)SnO_3$ (Fig. 1) shows a transition from this cubic form to the 'ideal' structure. It thus appears that the route from the orthorhombic to the cubic perovskites is not necessarily through a rhombohedral form (Geller & Bala, 1956), nor even indirect (Kestigian, Dickinson & Ward, 1957; Wood, 1951). It would, of course, be unwise to predict direct thermal transitions from orthorhombic to cubic from the present data.

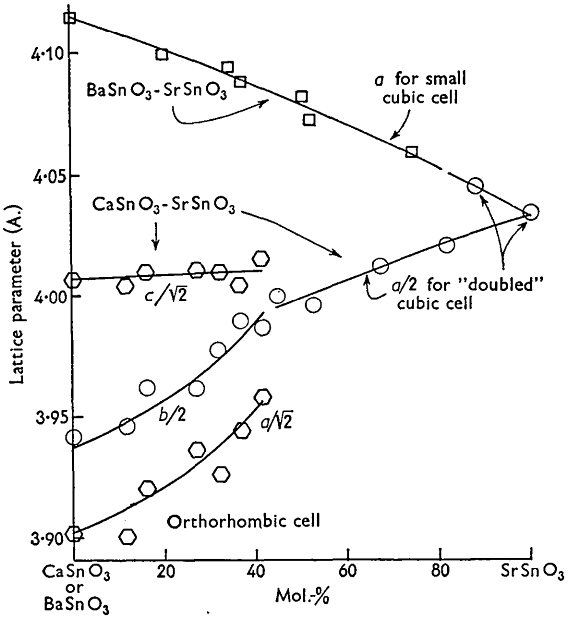

Fig. 1. Lattice-constant plots for the solid-solution series $(Ca, Sr)SnO_3$ and $(Sr, Ba)SnO_3$. The parameters plotted for the orthorhombic and 'doubled' cubic cells are those of pseudo-cells directly comparable with the normal perovskite (small cubic) cell.

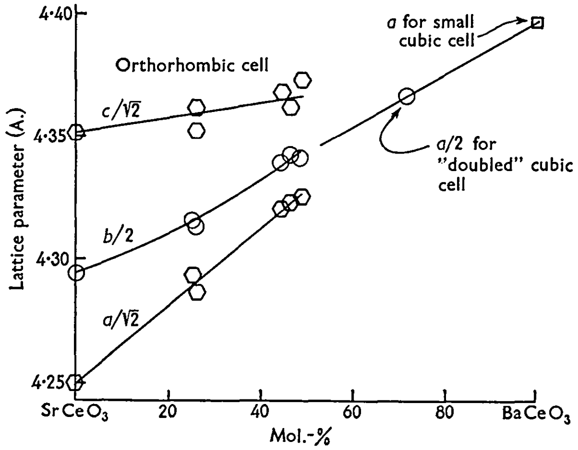

Fig. 2. Lattice-constant plots for the solid-solution series $(Sr, Ba)CeO_3$. The parameters plotted for the orthorhombic and 'doubled' cubic cells are those of pseudo-cells directly comparable with the normal perovskite (small cubic) cell.

Though no two-phase region was observed in these three series, $(Ca, Ba)SnO_3$ preparations showed a large miscibility gap. Solid solubility at the calcium end of the series was not detected, but the barium compound is capable of taking about 13 moles per cent of $CaSnO_3$ into solid solution.

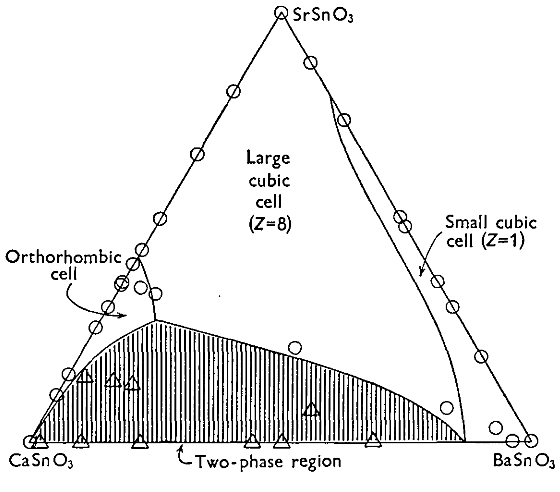

Fig. 3. Approximate ternary phase diagram for the system $(Ca, Sr, Ba)SnO_3$. The firing temperature for each of the plotted compositions was approximately 1450 °C. The composition axes are on a mol.% basis.

The ternary series $(Ca, Sr, Ba)SnO_3$ was studied only to the extent necessary for plotting of an approximate phase diagram (Fig. 3). The large area of existence of the large cubic-cell structure is noteworthy.

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The Crystal Structure of $SnCl_4 . 2\,SeOCl_2$

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The crystal structure of the addition compound $SnCl_4 . 2\,SeOCl_2$ has been determined and refined from three-dimensional X-ray data. The unit-cell dimensions are

$$a = 9{\cdot}24 \pm 0{\cdot}03,\ b = 9{\cdot}24 \pm 0{\cdot}03,\ c = 16{\cdot}26 \pm 0{\cdot}03\ \text{Å};\ \beta = 95°\ 34' \pm 10'.$$

There are four molecules per unit cell and the space group is $C2/c$. The crystal consists of discrete $SnCl_4 . 2\,SeOCl_2$ molecules. The tin atom is situated on a twofold axis, surrounded by a distorted octahedron of two oxygen atoms in *cis* position and four chlorine atoms. The oxygen atoms form bridges between the tin and the selenium atoms. The $SeOCl_2$-parts of the molecule are pyramid-shaped. The angle Sn–O–Se is 121·5°. A tendency to secondary acceptor-donor interaction within and between the adduct molecules can be recognized from the interatomic distances. A distorted octahedral coordination around the selenium atom is obtained, if all nearest neighbours are considered. In this compound selenium oxychloride acts as a donor as well as an acceptor molecule, although the donor action is predominant.

1. Introduction

It is well known that many oxychlorides give stable complexes. Several investigations have been made to establish the structure of such complexes in solution and the nature of the acceptor-donor reactions.

To give a more detailed study of the behaviour in solution a knowledge of the structure of the solvate is necessary. Groeneveld (1956) has suggested that the addition of an oxychloride to a Lewis acid gives a stable compound owing to the polar bond to oxygen. This has been confirmed by the X-ray study of $SbCl_5 . POCl_3$ (Lindqvist & Brändén, 1959). Furthermore Lindqvist (1958) has pointed out that the formation of an adduct molecule leads to an increase in coordination of the acceptor molecule, while the donor molecule is essentially unchanged. This proposal should be valid for a compound like $SnCl_4 . 2\,SeOCl_2$, and if the oxygens act as donor atoms, it is of interest to know whether they are in *cis*- or *trans*-positions.

2. Preparation of crystals

The compound $SnCl_4 . 2\,SeOCl_2$ was first isolated by Weber (1865), but the complete system $SnCl_4$–$SeOCl_2$ has been described by Agerman *et al.* (1958). The phase diagram shows a congruent melting point of 52–54 °C. at the composition $SnCl_4 . 2\,SeOCl_2$. Single crystals of the very hygroscopic compound were prepared in sealed capillary tubes by a method of zone melting. A capillary tube with an outer diameter of 0·11 mm. was used for the X-ray work. The crystal was stable during the time of exposure, judging from X-ray photographs.