

Silver β'' -Alumina

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The "mean" structure of silver β'' -alumina, stabilized by MgO is refined with an R value of 0.037, on single crystals prepared by a self-crucible-heating method. Evidence is given for Ag^+ ion static disorder in a wide range of temperature.

Introduction

The so-called β'' -alumina is a metastable phase in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3$ system; it has strong structural relations with β -alumina, with which it coexists in a wide range of temperature (1). The fast ionic conduction observed in β'' -alumina is highly connected to the conducting ion localization and to its total amount in the structure.

However, crystallographic investigations cannot be performed on single crystals of the pure β'' phase since these are generally obtained in syntaxy with β -alumina (2), or they need to be stabilized by addition of Mg^{2+} ions. Indeed, the theoretical composition of the stabilized compound, $\text{Na}_2\text{O}-\text{MgO}-5\text{Al}_2\text{O}_3$, is never reached and the actual β'' -aluminate is M^+ deficient.

The Na^+ β'' structure was previously determined by X-ray (3) and neutron diffraction (4): it turned out to be a structure made of three spinel-like blocks separated by layers where the Na^+ ions have a high mobility.

We report here the structure refinement of stabilized silver β'' -aluminate, in which the heavy conducting ions are more easily

localized. Some complementary results are drawn from spectroscopic and X-ray diffuse scattering studies.

Experimental

Large single crystals of Na^+ β'' -alumina are prepared by a self-crucible-heating method with the following components: Al_2O_3 (75 wt%), MgO (5%), and Na_2O (20%). The excess of sodium ions is needed to avoid the presence of β -alumina and it also contributes to the formation of NaAlO_2 acting as a flux for the crystal growth. The system is heated and melted by high frequency at about 1800°C and cooled down in several hours. Na^+ β'' -aluminate crystals are separated from NaAlO_2 by dissolution of this last reagent in boiling HCl. They are obtained in the shape of easily cleavable platelets, of which the maximum size may reach 0.5 cm².

From such grown Na β'' -aluminate crystals we may obtain the series of corresponding Ag^+ , K^+ , Tl^+ , H_3O^+ , and NH_4^+ compounds. It is done by ionic exchange in the convenient molten salt.

The determination of remaining sodium

content is made by neutron activation analysis and it clearly shows that the exchange ratio is higher than 99%.

But there is a gradient of temperature within the melted bulk and we generally get crystals with various compositions: we have to check them carefully to be sure they are of β'' type.

Intensity measurements were performed on a platelet with well-defined faces and edges, of dimensions $0.4 \times 0.3 \times 0.05$ mm and mounted along the a axis. A Laue pattern confirmed that the cleavage plane exhibited the rhombohedral symmetry consistent with the space group $R\bar{3}m$ in which the structure was refined.

The rhombohedral unit cell determined on Weissenberg patterns has the constants $a = 11.61 \text{ \AA}$, $\alpha = 28^\circ 05'$ (with hexagonal axis $a' = 5.63 \text{ \AA}$, $c = 33.45 \text{ \AA}$), and contains three unit groups. Intensity data were collected for 395 independent reflections, using a CAD3 Nonius diffractometer equipped with $\text{MoK}\alpha$ radiation. They were corrected for Lorentz and polarization effects and for absorption.

The atomic positions of ideal Na β'' -alumina from Bettman and Peters were chosen as starting parameters for the least-

squares fitting. In the first step, the refinement on positional and isotropic thermal parameters, scale factor, and isotropic extinction led to an agreement factor R of 0.07. Anisotropic thermal parameters were then introduced and in the next step the silver atoms were allowed to move out of their theoretical $6c$ positions and the corresponding occupancy coefficient was refined. This gave out a final R value of 0.037. The corresponding structural parameters are listed in Table I.

Discussion

The final composition arising from the refinement is 1.64 silver atoms per unit group, located in the conducting plane (occupancy factor of 0.137 instead of 0.1667 which would correspond to 2 atoms per conducting plane).

They are shifted out of the $6c$ positions and do not exactly lie in the conducting planes ($z = 0.1695$ instead of 0.1667). Thermal parameters for Ag^+ are strongly anisotropic, as expected, with large values in the x - y plane, corresponding to the high mobility (or disorder) of Ag^+ ions in this plane.

Mg^{2+} ions cannot be differentiated from

TABLE I
SILVER β'' -ALUMINATE

	Positions	Number per unit cell	$x \cdot 10^4$	$z \cdot 10^4$	$U_{11} \cdot 10^4$	$U_{22} \cdot 10^4$	$U_{33} \cdot 10^4$	$U_{13} \cdot 10^4$	(\AA^2)
Al(1)	18h	18	1675(1)	9284(1)	68(5)	70(6)	53(6)	-1(2)	
Al(2)	6c	6	0	3504(1)	81(8)	U_{11}	63(10)		
Al(3)	6c	6	0	4503(1)	82(6)	U_{11}	23(10)		
Al(4)	3a	3	0	0	66(8)	U_{11}	30(10)		
O(1)	18h	18	1633(3)	2347(1)	89(8)	89(10)	100(10)	5(4)	
O(2)	18h	18	1536(3)	347(1)	100(10)	131(14)	60(11)	-6(7)	
O(3)	6c	6	0	985(1)	72(14)	U_{11}	64(18)		
O(4)	6c	6	0	2948(2)	78(15)	U_{11}	116(20)		
O(5)	3b	3	0	5000	910(75)	U_{11}	43(30)		
Ag	18h	4.93(4)	186(20)	-1695(1)	625(30)	782(80)	121(5)	59(11)	
	$R = 3.67\%$		$(a = 5.63 \text{ \AA}, c = 33.45 \text{ \AA})$						

TABLE II
INTERATOMIC DISTANCES IN SILVER β' -ALUMINATE

Al(1)-octahedron	O(1)	2×1.843	
	O(2)	2×1.996	
	O(3)	1.865	
	O(4)	1.958	
Al(4)-octahedron		6×1.896	
Al(2)-tetrahedron	O(2)	3×1.848	
	O(4)	1.861	
Al(3)-tetrahedron	O(1)	3×1.796	
	O(5)	1.663	
Ag-0.1	2×2.656		
	2.805		Oxygen of blocks
Ag-O(3)	2.380		
Ag-O(5)	2×3.17		
	3.426		Oxygen of planes

Al^{3+} by X-ray diffraction (same number of electrons as Al^{3+}). But from the interatomic distances listed in Table II, it comes out that Mg^{2+} ions are mainly located in the Al(2) tetrahedral site: Mg^{2+} is larger and less charged than Al^{3+} and this is related to these larger interatomic distances. This is consistent with neutron diffraction analysis (5).

As an X-ray investigation only provides a "mean structure" and mean atomic positions, it is not sufficient to study the real ionic disorder; X-ray diffuse scattering and Raman spectroscopy give more details on the local order. Though it is not quite evident from X-ray Ag^+ thermal factors which are reasonably high, the silver ions keep a high degree of disorder when the temperature is lowered; X-ray diffuse scattering patterns reveal this static disorder (6). In the temperature range 30–1000 K, the coherence length (related to the size of ordered domains) in the conducting plane, deduced from the width of diffuse spots (7)

is less than 20 Å; it is 70 Å in Na^+ β' -aluminate at 300 K.

An eventual order-disorder transition was looked for by Raman studies, down to 30 K, and it was not found. The Raman spectra exhibit a very wide and intense band ($\Delta\nu_{1/2} = 40 \text{ cm}^{-1}$ at 300 K), nearly hidden in the Rayleigh wing even at low temperature (60 K) (8). This band is attributed to the oscillation mode of Ag^+ ions in the conduction planes and it is characteristic of an important static disorder which seems to be more meaningful than that observed in Ag^+ β -alumina with close composition (1.6 ions per plane).

So the main point reported here is this predominant static disorder of silver ions (not thermally activated) which implies good ionic conductivity of Ag^+ β' -aluminate in a wide range of temperature (9).

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