

Formation of polyatomic ions during the sputtering of multicomponent oxides

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The mass-spectrometric composition and energy distributions of the secondary ions emitted from ceramics with the nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ and from $\text{CaO}\cdot\text{SrO}\cdot\text{BaO}$ oxide alloys bombarded Ar^+ ions with an energy of 5 keV are studied. The laws governing the variation of the yield of the secondary ions $\text{Ca}_m\text{Sr}_n\text{O}_x^+$, CaBiO_x^+ , and M_mCuO_x^+ ($\text{M}=\text{Ca}, \text{Cr}$) as a function of the molecular composition and the type of system provide evidence that the formation of each polyatomic ion is determined by a structure-sensitive process involving the direct ejection of a fragment from the lattice, the ionization probability, which is exponentially dependent on the combination of ionization potentials of the components of the molecule, and the stability of the sputtered cluster against decomposition, which, in turn, is determined by the dissociation energy of the interatomic metal–oxygen bonds. © 1995 American Institute of Physics.

1. INTRODUCTION

The formation of molecular and polyatomic secondary ions is one of the most complicated and still not fully understood processes in secondary-ion emission. The theoretical description of this process is presently confined to two principal models¹ based on the impulse theory of sputtering, which treats the emission of an atom or a group of atoms as a result of the development of a cascade of binary collisions. According to the statistical, or recombination, model,^{2,3} polyatomic ions form above a surface as a result of the agglomeration of atoms independently sputtered in one cascade from lattice sites, which are not necessarily adjacent. For the probability of this process to be significant, there must be a temporal and spatial correlation between the particles emitted, and the energy of the center of mass must be smaller than the dissociation energy of the molecules formed. Obviously, as the number of components in a polyatomic ion increases, the probability of its formation should decrease. The charge state of a cluster is determined in this model by the sum of the charge states of the components. One version of this model treats the formation of a molecular ion as a result of the “condensation” of sputtered neutrals on a charged center,^{3,4} which also determines the charge of the cluster. The correlation between the yield of polyatomic secondary ions and the yield of monatomic ions has been offered as proof of the recombination mechanism of their formation.⁵ The direct ejection model proposes the emission of a group of atoms as a whole without cleavage of the bonds existing between them in the crystal lattice.^{6,7} This mechanism is dominant when substances with polar bonds are sputtered. The formation of the charge of a cluster sputtered by direct ejection is very complicated for a theoretical treatment and is still not fully understood. Charge formation can occur in various stages of the sputtering process: either as a result of electron transfer between the surface and the departing cluster⁶ or as a result of the dissociation of polyatomic neutral molecules on the surface.⁸

The purpose of the present work was to obtain experi-

mental data which would make it possible to isolate the contributions of the individual factors to the intensity of the secondary-ion emission of polyatomic ions in order to elucidate the mechanism of their emission. Our experimental investigations of the secondary-ion emission of the high-temperature superconducting ceramic $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ (BSCCO) provided several interesting results, which shed light on the formation of polyatomic secondary ions.

2. EXPERIMENTAL METHOD

The experimental investigations of secondary-ion emission were performed on the apparatus described in Ref. 9. The samples were bombarded in a vacuum $\sim 10^{-6}$ Pa by a mass-separated beam of Ar^+ ions with an energy of 5 keV and a density of $100 \mu\text{A}/\text{cm}^2$ incident to the surface at a 45° angle. The system for analyzing the secondary particles included a hemispherical energy analyzer with particle-collection optics (the extracting potential was 80 V, and the energy resolution was 0.6%), and an ROMS-8 monopole mass spectrometer (the range of masses was 1–250, and the resolution was $\sim M$, where M is the mass of the ion). The mass spectra of the positively charged secondary ions were recorded in the optimal energy window ($E_{\text{av}} \approx 4$ eV, $\Delta E = 0.5$ eV). The mass spectra were interpreted using an interactive program on a personal computer. The essence of the interpretation process was as follows. A system of linear equations was composed on the basis of data on the natural abundance of the isotopes of the components of the samples and the proposed set of polyatomic ions. The possibility of breaking it up into several systems of smaller size, which would then be solved by the least-squares method, was analyzed. The quality of the interpretation was evaluated separately in terms of the magnitude of the deviation for the entire system, for the group of equations for each polyatomic ion, and for each peak in the mass spectrum. Because all the elements in the compound have several isotopes, we were able to interpret a complex secondary-ion emission spectrum with a total error $\sim 0.001\%$ and a maximum error for any of

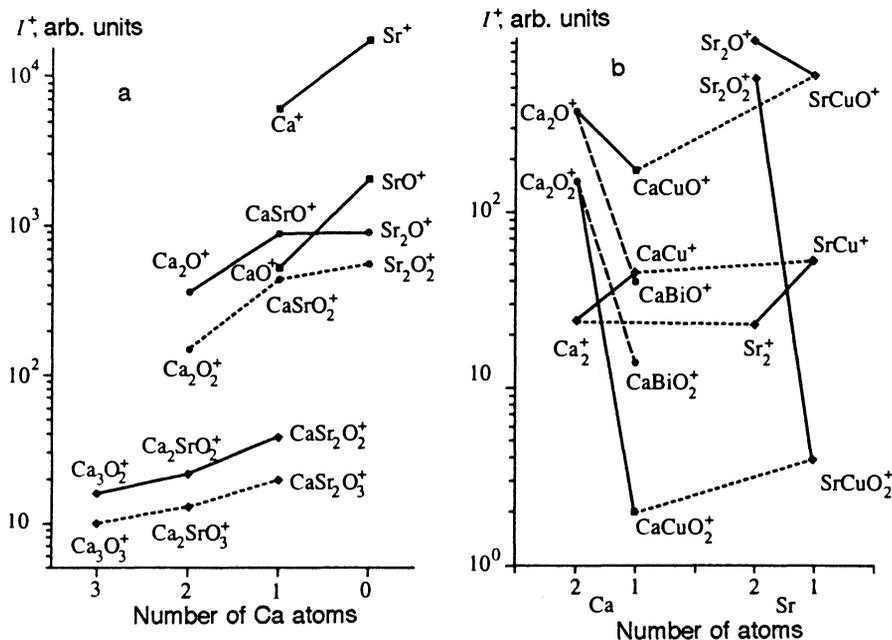


FIG. 1. Yield of the polyatomic ions $\text{Ca}_m\text{Sr}_n\text{O}_x^+$ (a) and $\text{M}_m\text{N}_n\text{O}_x^+$ ($\text{M}=\text{Ca}, \text{Sr}; \text{N}=\text{Cu}, \text{Bi}$) (b) emitted from the ceramic $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ as a function of the molecular composition.

the peaks smaller than 20%. The energy distributions were recorded for the most intensely emitted secondary ions passing at a constant rate through the entire analytical system.

Samples of a ceramic with the formula $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ were obtained by a solid-phase synthesis method.¹⁰ According to the data from an x-ray structural investigation, the samples were mixtures of several phases. All the lines in the x-ray diffraction pattern belonging to $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+6}$ phases, where $n=1, 2, 0$ (in order of decreasing intensity of the peaks). Since the 2212 phase was dominant, the transition to the superconducting state was protracted. Before these samples were placed in the analytical chamber, the surfaces were cleaved to remove the layer degraded during contact with the atmosphere. The surfaces were not treated chemically.

A CaO-SrO-BaO oxide alloy with an NaCl lattice, which was prepared using a technology for manufacturing cathodes for vacuum tubes and had the form of a porous tungsten matrix impregnated by an equimolar mixture of the alkaline-earth metal oxides, also served as a sample. The samples thus prepared, unlike the oxides of these elements themselves, have a high conductivity, which prevents charging of the surface during the measurement of the secondary-ion emission spectra. An equimolar mixture of the carbonates CaCO_3 , SrCO_3 , and BaCO_3 was added to powdered tungsten, mixed, compacted, and sintered at 1900°C . This temperature regime ensures melting of the oxides, the formation of solid solutions, and the absence of a reaction between the alkaline-earth metal oxides and the tungsten matrix. After cooling, the samples were placed in a vacuum. X-ray analysis showed that $(\text{BaSr})\text{O}$ and $(\text{SrCa})\text{O}$ solid solutions are present in the alloy; the presence of other phases could not be reliably determined. The vacuum flask was cut open immediately before the experiment, and the surfaces of the samples were mechanically polished. The surfaces were not treated chemically.

3. RESULTS

The mass spectra of the positively charged secondary ions emitted from the high- T_c superconductor BSCCO displayed peaks of the monatomic ions O^+ , Ca^+ , Sr^+ , Cu^+ , and Bi^+ ; the dimers Ca_2^+ and Sr_2^+ ; Ca_mO_x^+ and Sr_mO_x^+ molecular ions; the hydroxy ions CaOH^+ and SrOH^+ ; and a large number of polyatomic ions of diverse composition and intensity with the formulas $\text{Ca}_m\text{Sr}_n\text{O}_x^+$, $\text{Ca}_m\text{Sr}_n\text{Cu}_k\text{O}_x^+$, and $\text{Ca}_m\text{BiO}_x^+$. The energy spectra of the monatomic secondary ions had a maximum at approximately 4.5 eV and a half-width of about 9 eV. The energy spectra of the molecule and polyatomic ions had a maximum at 3–4 eV and a half-width from 2.8 to 4.5 eV. This variation of the parameters of the energy distributions in the transition from the monatomic ions to the larger species is consistent with other published data.¹¹

The emission of positive molecular ions from the high- T_c superconductor is qualitatively consistent with the valence model in Ref. 12, which describes the emission of ions of the form MO_x^+ from metal oxides. For example, in series of CaO_x^+ , CuO_x^+ , and SrO_x^+ ions differing only with respect to the number of oxygen atoms, the highest intensity in the mass spectrum was exhibited by the ions for which the total formal valence (G) of the components is equal to 1 or 2. In addition, we observed a similar dependence for ions containing more than one metal atom in the Ca_mO_x^+ , Sr_mO_x^+ , $\text{Ca}_m\text{Sr}_n\text{O}_x^+$, $\text{Ca}_m\text{Cu}_k\text{O}_x^+$, $\text{Sr}_m\text{Cu}_k\text{O}_x^+$, and $\text{Ca}_m\text{Sr}_n\text{Cu}_k\text{O}_x^+$ series for $1 < n+m+k \leq 3$. The ions containing trivalent Bi atoms did not conform to this rule. For example, the intensity of the CaBiO^+ peaks ($G=3$) was higher than that of the CaBiO_2^+ peaks ($G=1$), and BiO^+ ions were not detected at all.

The presence of diverse polyatomic ions in the mass spectrum of the high- T_c superconductor made it possible to trace how the emission intensity of ions of similar configura-

ions with a smaller number of atoms [the most striking examples are $I^+(\text{Sr}_2\text{O}_2^+) > I^+(\text{CaO}^+)$ and $I^+(\text{Ca}_{3-m}\text{Sr}_m\text{O}_3^+) > I^+(\text{CaCuO}_2^+)$, and the half-widths of the energy distributions ΔE of the triatomic molecular ions CaCuO^+ , Ca_2O^+ , and CaSrO^+ (3.2–3.6 eV) were greater than the values of ΔE for the diatomic SrCu^+ ions (2.8 eV), which, according to the theory in Refs. 2 and 3, should not be the case when sputtered atoms recombine.

From the crystal-structure standpoint, all the phases of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$, viz., the 2212, 2223, and 2201 phases, are similar and differ only with respect to the number of CuO_2 planes separated by Ca planes. It is also known that strict ordering of the metal atoms in the cationic crystal-lattice sites is not observed in these compounds. In our samples the 2212 phase was dominant. Therefore, the Ca atoms, which are excess atoms in the compounds with $n=0$ and $n=1$ are apparently placed in "foreign" cationic sites during synthesis. Redistribution of the intensities of the x-ray lines is known to occur in such cases (see, for example, Ref. 17) and was also observed in our case. Moreover, in the dynamic secondary-ion mass-spectrometric (SIMS) mode which we employed the structure of the surface layers, from which emission actually occurs, is disturbed by ion bombardment. We used a broad beam of primary ions and thus obtained averaged information from many crystallites of all the phases simultaneously. Therefore, the presence of polyatomic ions in the mass spectrum and the intensity of their emission are determined by the degree of disorder in the actual sample, rather than by the positions of the ions in the ideal crystal structure. For example, the CaBiO^+ and CaBiO_2^+ ions observed in the spectrum could not have formed by direct ejection of a cluster from an ideally ordered lattice, since the BiO atomic layers are separated from the Ca layers by SrO and CuO_2 layers; however, direct ejection of CaBiO and CaBiO_2 particles becomes possible when Sr atoms lying near Bi atoms in the lattice are replaced by Ca or when Bi atoms are replaced by Ca atoms.¹⁸

The following description can be proposed for the mechanism of the emission of positive polyatomic ions from materials with an ionic type of bonding. Ionic bombardment of polar compounds can eject ionized molecular fragments from the lattice, whose rate of emission is determined by the probability of the sputtering of each particular cluster S , its ionization probability P^+ , and the stability of the sputtered cluster against dissociation:

$$I^+(\text{MNO}) \propto I_0 S(C_i, W_i, n_i, m_i) P^+(\Omega, \varepsilon, v) R(D_{ij}), \quad (1)$$

where I_0 is a factor determined by the parameters of the primary beam. The factor S depends on the concentration C and the arrangement of the atoms of type i ($i = \text{M}, \text{N}, \text{O}$), i.e., on the type of lattice, the binding energies W_i of the components in the crystal, the number n_i and the mass m_i of the atoms of type i in the sputtered cluster. The value of P^+ clearly depends on the local electronic structure of the surface (Ω) of the sputtered cluster (ε) (the ionization potential I for the monatomic ions), and on the velocity v of the particles. The stability of the cluster R is determined by the

dissociation energy D_{ij} of its weakest bond, which apparently depends on the composition of the polyatomic ion and its electronic structure.¹⁹

The results obtained from studying the secondary-ion emission of the high- T_c superconductor BSCCO and the oxide alloy make it possible to isolate the contributions of the individual factors to the emission mechanism of the polyatomic ions. The observed differences between the ion-current ratios $I^+(\text{MO}^+)/I^+(\text{M}^+)$ and $I^+(\text{M}_2\text{O}_2^+)/I^+(\text{M}_2\text{O}^+)$ ($\text{M} = \text{Ca}, \text{Sr}$) for the high- T_c superconductor and the oxide are clearly caused by the influence of the structural factor S alone or, more specifically, by differences between the crystal structures, the character of the atomic environment, and, accordingly, the energies and lengths of the interatomic bonds in these compounds. According to Ref. 20, when the high- T_c superconductor $\text{RBa}_2\text{Cu}_3\text{O}_x$ and the corresponding oxides R_2O_3 (R is a rare-earth element) are bombarded, the value of $I^+(\text{RO}^+)/I^+(\text{R}^+)$ correlates with the $\text{R}-\text{O}$ bond length, clearly reflecting the energy inequivalence of the $\text{R}-\text{O}$ bonds in these structurally different compounds. Similarly, the larger lengths of the $\text{M}-\text{O}$ bonds in the high- T_c superconductor BSCCO (Ref. 18) in comparison with $\text{CaO} \cdot \text{SrO} \cdot \text{BaO}$ correspond to the observed higher values of the ion-current ratios. The higher rate of increase in the emission of ions when Ca atoms are replaced by Sr atoms in Ca_2O^+ [the $I^+(\text{CaSrO}^+)/I^+(\text{Ca}_2\text{O}^+)$ ratio] for the oxide than for the high- T_c superconductor (Figs. 1a and 2) is also stipulated by S , i.e., by the difference between their crystal structures and interatomic bond energies.

The influence of P^+ and R on the emission of $\text{Ca}_m\text{Sr}_n\text{O}_x^+$ is inferred from the fact that the concentrations of Ca and Sr in the high- T_c superconductor and of Ca, Sr, and Ba in the oxide are identical and, being isovalent elements from a single subgroup, they can occupy the same lattice sites, thereby ensuring the constancy of S . According to Ref. 21, the ion-current ratio has the form

$$I^+(\text{MO}^+)/I^+(\text{M}^+) \propto \exp[D(\text{M}^+ - \text{O})] \\ \equiv \exp[D(\text{M}_x\text{O}) + I(\text{M}) - I(\text{MO})], \quad (2)$$

where $D(\text{M}^+ - \text{O})$ and $D(\text{M}-\text{O})$ are the dissociation energies of the MO^+ ion and the neutral MO molecule, respectively. Since $I^+(\text{M}^+) \propto \exp[-I(\text{M})]$ (Fig. 3), it follows that $I^+(\text{MO}^+) \propto \exp[D(\text{M}-\text{O}) - I(\text{MO})]$. It can be postulated by analogy that

$$I^+(\text{M}_m\text{O}_m^+)/I^+(\text{M}_m\text{O}_{m-1}^+) \propto \exp[D(\text{M}_m - \text{O}_m) \\ - D(\text{M}_m - \text{O}_{m-1}) + I(\text{M}_m\text{O}_{m-1}) - I(\text{M}_m\text{O}_m)], \quad (3)$$

$$I^+(\text{M}_m\text{O}_m^+) \propto \exp[D(\text{M}_m - \text{O}_m) - I(\text{M}_m\text{O}_m)]. \quad (4)$$

The increase in the yield of molecular secondary ions from the high- T_c superconductor and the oxide when the Ca atoms in them are replaced by Sr and Ba atoms and Sr atoms are replaced by Ba atoms (Figs. 1a and 2) becomes understood, if it is assumed, first, that the dependence of P^+ on the electronic structure of the cluster ε can be represented by the dependence of P^+ on the ionization potential of the cluster I , second, that the ionization potential of the cluster is a mono-

tonic function of the ionization potentials of its components [as it is, for example, in $\text{CF}_{4-m}\text{Cl}_m$ ($m=0-4$) and other similar molecules²²] and, third, that the dissociation energy D of the cluster is monotonically dependent on the energies of the pairwise bonds between the components [this can be traced, for example, in the variation of D over the series of molecules CH_3X , where $\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$ (Ref. 22)]. Since the atomic ionization potential decreases along the Ca–Sr–Ba series,²² and since the bond energy $D(\text{M–O})$ increases monotonically through this series,²¹ $P^+(I)$, $R(D)$, and the emission intensity of the similar clusters $I^+(\text{MNO})$ should increase according to (4) when the metal atoms from this series in them are successively replaced.

We note that the successive replacement of the Ca atoms in Ca_mO_x by the heavier Sr and Ba atoms should result in a decrease in the velocity v of the corresponding polyatomic ions (all the ions were detected at the same energy) and, therefore, in a decrease in $P^+(v)$ (Refs. 13–15). The increase in emission along this series of ions (Figs. 1a and 2) provides evidence that the contribution of $P^+(I)$ and $R(D)$ dominates over the contribution of $P^+(v)$.

The replacement of the Ca atoms in Ca_2O_x by Cu or Bi atoms, unlike their replacement by the isoelectronic Sr and Ba atoms, significantly alters the electronic structure of the cluster. The bond dissociation energy $D(\text{Bi–O}) \approx 3.5$ eV is close to $D(\text{Ca–O}) \approx 3.95$ eV (Ref. 21; therefore, the decrease in the emission of CaBiO_x^+ ions compared with the emission of Ca_2O_x^+ ions (Fig. 1b) is caused [see (4)] mainly by the decrease in the ionization probability $P^+(I)$ due to the increase in the ionization potential of the molecule when Ca is replaced by Bi, since $I(\text{Bi})=7.27$ eV is far greater than $I(\text{Ca})=6.11$ eV (Ref. 21). The decrease in the yield of MCuO^+ in comparison to M_2O^+ , where $\text{M}=\text{Ca}$ or Sr (Fig. 1b) is also mainly due to the decrease in $P^+(I(\text{MNO}))$, since the ionization potential of Cu (7.72 eV) is also higher than that of Ca. Although the bond dissociation energy $D(\text{Cu–O})=2.7$ eV (Ref. 21) is very small, the stability $R(D)$ of a given cluster MCuO^+ , like that of M_2O^+ , is most likely provided by the M–O bond. On the other hand, the higher ionization potential and smaller energy of the bond with the oxygen atom in the case of Cu in comparison to the case of Bi should decrease the yield of CaCuO^+ ions more severely than that of CaBiO^+ . However, we observed the opposite picture (Fig. 1b): the yield of CaCuO^+ ions was higher than that of CaBiO^+ . Clearly, the structural factor S begins to play the decisive role in this case. In fact, the probability of the direct ejection of a CaBiO fragment is small and is determined by the degree of disorder in the lattice, i.e., by the possibility of the replacement of Sr or Bi atoms by Ca atoms, while the direct ejection of a CaCuO cluster can occur with a high probability owing to the placement of the Ca layers between the CuO_2 layers.¹⁸ We note that when Ca (Sr) is replaced by Cu in a molecule of M_2O_2 , the situation is drastically altered, and the low stability of the cluster due to the unavoidable appearance of a weak Cu–O bond begins to play the decisive role in the emission of MCuO_2^+ [see (4)]. As a result, the yield of MCuO_2^+ decreases considerably more strongly than the yield of CaBiO_2^+ (Fig. 1b).

Unlike the emission of the oxygen-containing molecules, the emission of dimers of the form M_2^+ and M_1M_2^+ ($\text{M}=\text{Ca}, \text{Sr}, \text{Cu}$) is low and is characterized by energy distributions with a very small half-width ($\Delta E=2.5-2.8$ eV), which is considerably less than ΔE not only for the diatomic CaO^+ and SrO^+ molecules (5.5 and 5.3 eV), but also for the triatomic M_2O^+ and $\text{M}_1\text{M}_2\text{O}^+$ molecules (3.2–3.6 eV). In addition, only for the Ca_2^+ , CaSr^+ , and Sr_2^+ dimers does the replacement of Ca (Sr) by Cu result in an increase in emission, rather than a decrease (Fig. 1b), the tendency for an increase in emission upon the replacement of Ca by isoelectronic Sr being maintained in the $\text{Ca}_2^+-\text{Sr}_2^+$ and $\text{CaCu}^+-\text{SrCu}^+$ series. These peculiarities are attributable to the fact that the M_2^+ and M_1M_2^+ dimers are formed by a recombination mechanism, although an appreciable contribution of direct ejection owing to the factor S (the Ca–Cu and Sr–Cu pairs, unlike the Ca–Ca and Sr–Sr pairs are nearest neighbors in the BSCCO lattice) has not been ruled out. This is responsible for their higher yield in comparison to M_2^+ .

The foregoing material also makes it possible to understand why the values of $I^+(\text{M}_m\text{O}_m^+)/I^+(\text{M}_m\text{O}_{m-1}^+)$ ($m=2, 3$) vary in a given manner and are close to one another when Ca is replaced by Sr or Bi, while they decrease sharply when Ca (Sr) is replaced by Cu. Since the changes in the ionization potentials of M_mO_m and M_mO_{m-1} caused by the replacements of M are apparently similar, then, according to (3), the ion-current ratios are determined mainly by the stability $R(D)$ of M_mO_m and M_mO_{m-1} . When Ca is replaced by Sr, the ratios increase somewhat due to the contribution of the stronger Sr–O bond [$D=4.27$ eV (Ref. 21)], and when Ca is replaced by Bi, the weaker Bi–O bond makes a contribution. The sharper decrease in the intensity ratios upon the replacement of Ca (Sr) by Cu is due to the appearance of the weak Cu–O bond in the molecules of CaCuO_2 and SrCuO_2 . Unlike $I^+(\text{MO}^+)/I^+(\text{M}^+)$, $I^+(\text{M}_2\text{O}_2^+)/I^+(\text{M}_2\text{O}^+)$, and $I^+(\text{M}_3\text{O}_3^+)/I^+(\text{M}_3\text{O}_2^+)$, $I^+(\text{M}_2\text{O}^+)/I^+(\text{M}_2^+)$ is far greater than unity, apparently due to the dominant contribution of the recombination processes to the emission of M_2^+ .

As for the charge of the sputtered polyatomic ions, the following mechanism for shaping it seems likely to us. When a cluster is emitted, several localized bonds between atoms of the cluster and the surface are cleaved practically simultaneously. The cleavage of each of these bonds can result in a separation of charges. However, when a stable charge forms on one of the atoms in the cluster (when it reaches a distance greater than the critical value), the levels of ionization of the remaining atoms in the cluster vary due to the Coulomb interaction in such a manner that the formation of a second charge of the same sign becomes impossible (in fact, multiply charged cluster-type secondary ions have never been observed), and the probability of charge compensation increases. The last bond cleaved possibly has the strongest influence on the shaping of the charge, since there is nothing to compensate the charge formed. Therefore, the ionization probability of a cluster is determined by a linear combination of the ionization probabilities of each of the atoms appearing in it or by their mean value, since the last bond cleaved belongs to any of the atoms in the cluster with equal probability. Such an interpretation is not, however, entirely cor-

rect, since the distance at which ionization occurs is comparable to the distance between atoms in the lattice and is therefore too large to neglect the influence of the other atoms in the cluster. On the other hand, a cluster cannot be treated as a single particle having a certain level of ionization, since the distance to the surface at the moment of ionization is so small that, for example, the pseudopotential of such a particle is negligible. However, in both limiting cases the ionization probability of a cluster is directly dependent on the ionization potentials of the atoms appearing in the cluster. Therefore, a similar monotonic dependence can be proposed for the intermediate case actually realized.

5. CONCLUSIONS

The yield of monatomic secondary ions of the components of the high- T_c superconductor $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ and $\text{CaO}\cdot\text{SrO}\cdot\text{BaO}$ are exponentially dependent on their ionization potentials. The relative yields of the polyatomic ions $\text{Ca}_m\text{Sr}_n\text{O}_x^+$ from BSCCO and $\text{CaO}\cdot\text{SrO}\cdot\text{BaO}$ depend on the structure of the object, which determines the energies of the interatomic bonds. The successive replacement of Ca atoms by Sr and Ba atoms in Ca_mO_x results in an increase in the emission of the corresponding polyatomic ions, and their replacement by Bi and Cu atoms results in a decrease in emission. The contributions of the structure-sensitive process of direct ejection of a fragment from the lattice, its ionization probability, which depends on the ionization potentials of the components of the molecule, and the stability of the sputtered cluster toward decomposition, which is determined by the dissociation energy of the metal–oxygen bonds, to the mechanism of the emission of polyatomic ions can be distinguished.

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